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Multicommuted flow system for cadmium determination in natural water by cold vapour atomic absorption spectrometry

Laiana O. B. Silva[a,b], Lindomar A. Portugal[c], Edwin Palacio[c], Laura Ferrer[c], Víctor Cerdà[c], Sergio L.C. Ferreira[a,b]

The present paper proposes the use of a multisyringe flow injection analysis (MSFIA) system for determination of Cd in natural waters by cold vapour atomic absorption spectrometry (CV-AAS). The chemical and physical conditions for vapour generation were investigated and optimized using multivariate optimization methodology. Some complexing reagents were tested as additives to increase the analytical signal. Thiourea showed a positive effect, whereas L-cysteine reduced the signal of Cd. The method allows the direct determination of Cd, i.e. without sample pre-concentration, with limits of detection and quantification of 5.8 and 19.3 ng L^{-1}, respectively and employing external calibration technique. The precision expressed as relative standard deviation varied between 1.4 and 2.9 % for two levels of cadmium (0.25 and 2.5 µg L^{-1}). An injection throughput of 87 h^{-1} was achieved employing 2 mL of sample volume. The accuracy was confirmed by analysis of a certified reference material of seawater (CASS-4) furnished by National Research Council of Canada and addition/recovery tests, obtaining recoveries between 94 and 101%. The method was satisfactorily applied for determination of Cd in seawater and ground water samples from Mallorca, Spain.

1. Introduction

The Cd has great carcinogen effect on the human and its contamination in the environment is a global concern. The main anthropogenic sources of Cd contamination are from fossil fuel combustion, phosphate fertilizers, iron and other iron-matrices production, cement production and related activities, nonferrous metals production, and municipal solid waste incineration. The Cd contamination in natural aqueous systems comes from principally of smelting activities of nonferrous metal ores and of the use of phosphate fertilizers by agriculture.

The first study of determination of Cd using vapour generation was proposed by D'Ulivo and Chen in 1989. These authors observed that Cd forms a volatile compound by reaction with sodium tetraethylborate at room temperature. The method proposed was applied for quantification of cadmium in sea and tap water using non-dispersive atomic fluorescence spectrometry with Ar hydrogen mini-flame atomization [1]. In the same period, Cacho et al. used the generation of a volatile Cd compound in an organic medium (N,N-dimethylformamide) for the determination of this metal by AAS with a detection limit of 200 ng L^{-1} [2]. Then, several interesting papers have been published involving vapour generation of this metal, including strategies based on flow systems such as flow injection analysis (FIA) and continuous flow (CF) systems [3-11]. Liu and Xu used the vapour generation reaction of Cd in a FIA system for quantification of this element in water, urine, blood, human hair, geochemical soil and polluted soil standard reference samples. In this work, thiourea was employed as complexing agent in order to increase the sensibility [3]. Cámara et al. also proposed a FIA system for the determination of Cd in natural water samples using CV-AAS, employing the analyte addition technique for calibration [4]. This same system was also used for determination of Cd in wastewater and sewage sludge samples. Nevertheless, the use of potassium cyanide as masking agent for elimination of interferences allows the determination by external calibration technique [5]. Fitzgerald et al. proposed a multimode sample introduction device in a FIA system for the determination of Cd employing CVAAS. The system allowed the use of high concentrations of reagents required for efficient production of volatile Cd avoiding the significant bubbling, frothing, and associated liquid transport problems common to conventional gas-liquid separators while maintaining a low volume [6]. Others FIA systems were developed for the determination of Cd by cold vapour (CV) in a diversity of samples, exploiting a strong anion exchange resin in the tetrahydroborate(III) form [7] or using a pre-concentration system by a quartz trap, which allowed the determination of Cd with a low limit of detection (1.8 ng L^{-1}) [8]. Recently a FIA system was also developed for quantification of Cd in high salt content matrices [9]. Besides FIA, the chemical vapour generation was as well performed by CF [10].The combination of pre-concentration by cloud point extraction and continuous vapour generation allowed the development of a method for the determination of ultratrace amounts of Cd [11].

[a] Universidade Federal da Bahia, Instituto de Química, CEP 40170-270, Salvador-Bahia, Brazil.

[b] Instituto Nacional de Ciência e Tecnologia, INCT, de Energia e Ambiente, Universidade Federal da Bahia, 40170-290 Salvador-BA, Brazil.

[c] Group of Analytical Chemistry, Automation and Environment, Department of Chemistry, University of the Balearic Islands, E-07122, Palma de Mallorca, Spain.

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All these previous works have been performed exploiting FIA technique and CF, both using peristaltic pumps as liquid driver. Even if FIA is the most widely flow-based approach because of its easy and low cost implementation, both FIA and CF presents some disadvantages when compared to multicommuted techniques, based on their own modes of injection, i.e. continuous or discontinuous, respectively. In the case of FIA and CF, the continuous flow leaded to the detector or to the waste, consumes a large amount of sample and reagents at the same time that generates a lot of waste. Multicommuted techniques, such as multisyringe flow injection analysis (MSFIA) based on multi-commutation operation have shown great potential in minimizing reagents consumption and waste production providing more environmentally friendly methods, since liquids are only propelled to the system when required and returned to their reservoirs when not. Besides, the use of tubes of peristaltic pumps requires the periodic re-calibration of the flow rate due to the aging of the flexible tubes. Finally, the use of software to control the complete multicommuted system ensures high reproducibility in the analytical signal [12].

Thus, a direct, rapid and automated system based on a MSFIA multicommuted technique was developed. The proposed method is founded on the cold vapour generation by reaction with sodium tetrahydroborate in acidic media to determine Cd in natural waters employing AAS, without pre-concentration step and using thiourea as a chelating reagent with sensibility enhancement effect. The optimization of variables by multivariate design is discussed in detail.

2. Experimental

2.1 Instrumentation for the determination of cadmium by MSFIA system coupled to CV-AAS

A Perkin-Elmer Model AAnalyst 400 atomic absorption spectrophotometer (Connecticut, USA) fitted with a cadmium hollow cathode lamp was employed as detector. A wavelength of 228.8 nm was used and Cd concentrations were determined by analyzing the peak height.

Into the MSFIA system the main device is a multisyringe burette module with programmable flow rates (Crison Instruments, Barcelona, Spain), which can be equipped with up four syringes, each one with a three-way solenoid valve (NResearch, West Caldwell, NJ, USA) coupled to them. In the proposed system four glass syringes (Hamilton, Switzerland) were used: syringe 1 (S1) of 2.5 mL, syringe 2 (S2) of 5 mL and syringes 3 and 4 (S3 and S4) of 10 mL. An additional independent solenoid valve (SV, Takasago Electric, Nagoya, Japan) was employed in the system and a three-way connector (TWC) was used to connect flows of Ar and $NaBH_4$. The proposed MSFIA system is shown in Figure 1.
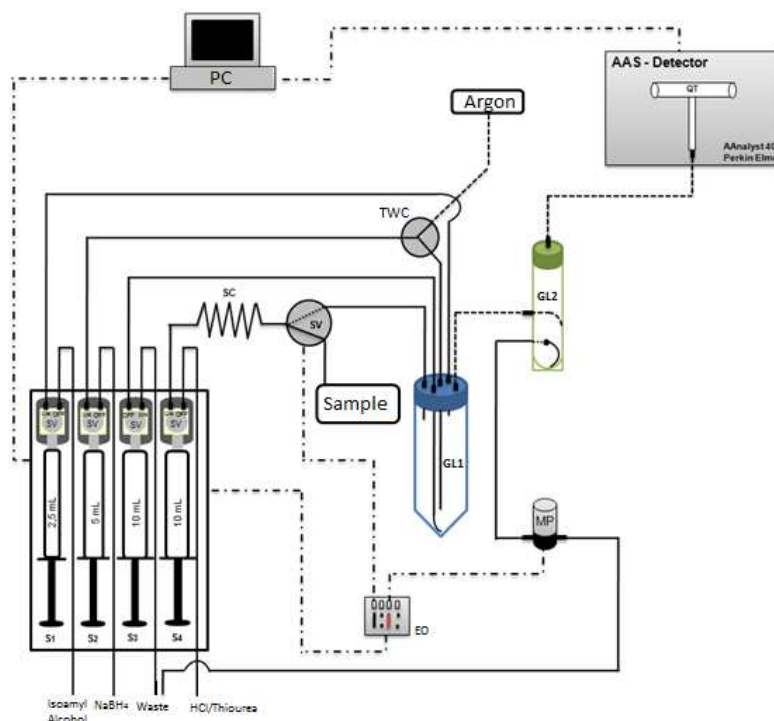

Fig.1 MSFIA system setup. EO: external output, GL: gas-liquid separator, MP: micropump, QT: quartz tube, SC: sample coil, SV: solenoid valve, TWC: tree-way connector.

Two gas-liquid separators (GL1 and GL2), which were made by adapting the 50 and 15 mL centrifuge tubes, were used. GL1 separator was employed as reaction cell, to which all the reagents were channelized. While GL2 separator located between GL1 and the quartz cell, was used to prevent liquid from being carried into the detection system. In addition, a micropump (MP, Biochem Valve Inc., Boonton, NJ, USA) connected through an external output, which is a pulse generator (EO, Sciware Systems, Bunyola, Spain) to the multisyringe module, was used to help drain the cumulative liquid in the GL2 separator. A PTFE tubing (20 cm length and 0.8 mm i.d.) was used to connect GL2 separator and the quartz cell.

The execution of the analytical protocol was computerized by using the AutoAnalysis 5.0 software package (Sciware Systems). The WinLab32 for AA software (Perkin-Elmer, Connecticut, USA) was used to register the analytical signal.

2.2 Reagents and solutions

Analytical grade reagents were used in all experiments and all solutions were prepared using ultrapure water obtained from a Milli-Q water purification system from Millipore (Bedford, MA, USA). The working standard solutions were prepared by the serial dilution of a Cd stock solution (1000 mg L^{-1}) from Merck (Germany) in 2 mol L^{-1} hydrochloric acid. The blanks used in this study were 2 mol L^{-1} HCl solution prepared via appropriate dilutions from concentrated hydrochloric acid (Scharlau, Barcelona, Spain). Reducing reagent solution of 6 % (w/v) sodium tetrahydroborate was prepared daily by dissolving solid NaBH$_4$ from Scharlau in a 0.5 % (w/v) NaOH (Scharlau). The carrier solution, thiourea 0.75% (w/v) in 0.05 mol L^{-1} HCl solution, was prepared by dissolving of appropriate amount of thiourea from Panreac (Barcelona, Spain) in 0.05 mol L^{-1} HCl solution. Isoamyl alcohol from Sigma Aldrich (Germany) was employed as antifoam agent in this work. A certified reference material of seawater (CASS-4), which was provided by the National Research Council Canada (Ottawa, Canada), was used to evaluate the method accuracy. All glassware and plastic material were cleaned by acidification in HNO$_3$ (10% v/v) for 48 h, and thoroughly rinsed with Milli-Q water before used.

2.3 Samples of natural waters

Twelve samples of ground water were collected in Mallorca (Balearic Islands, Spain) between the cities of Santa Margalida, Arta, Manacor and Bunyola and five samples of coastal surface seawater were collected in Palma city (Mallorca). The samples were collected in period between February and April of 2014. Amber glass bottles previously decontaminated with nitric acid 10% (v/v) for 24 h, and washed with ultrapure water to remove at the maximum of contaminants, especially Cd, were used to collect samples. In the laboratory, water samples were filtered through 0.45 µm nylon membrane filter to separate any particulate matter present. The samples were analyzed after being acidified with hydrochloric acid to achieve a final concentration of 2 mol L^{-1}.

2.4 General procedure

The proposed MSFIA system comprises four syringes (S1-S4) with their corresponding solenoid commutation valves. S1 contains isoamyl alcohol; S2 was used to dispense the reducing solution (NaBH$_4$); S3 was employed for cleaning step; and S4 was used for loading the sample coil and dispensing the sample using HCl/thiourea as carrier.

Four syringes operating simultaneously drive the liquids depending on the position of each solenoid valve. In the proposed system for syringes S1, S2 and S4, "On" position dispense to the flow network and "Off" position return the liquids to the solution reservoirs. While, for syringe S3, fluids were pick-up in "On" position and residues were collected from GL1 separator in "Off" position, during the cleaning step.

Before each sample analysis, a conditioning and cleaning of the system was performed. For this, 1 mL of the new sample was aspirated by S4 to the sample coil (SC) by activation of a three-way solenoid valve (SV), thereupon, the solenoid valve was turned to "Off" position and S4 dispensed 2 mL to GL1 separator. After this step, S3 was activated to "Off" position in order to empty GL1 separator.

The conditioning and cleaning step was followed by a sample injection and measuring step. In this step, 2 mL acidified sample volume was aspirated by S4 to SC. Then, S4 was activated and the SV was turned "Off" position in order to dispense 2.8 mL (2 mL sample and 0.8 mL HCl/thiourea carrier solution) to GL1 separator. S1 then dispensed 70 µL in GL1 separator. After that, S2 dispensed 4 mL of reducing reagent NaBH$_4$, which were directly introduced into the liquid within the GL1 separator via a 3-way connector blended with Ar (flow rate: 150 mL min^{-1}). The chemical Cd vapour generated by this reaction was carried to GL2 separator and to quartz cell by the aid of Ar where was made the Cd detection. After a waiting time of 30 seconds, a cleaning protocol was performed, including two aspiration steps and one step for dispensing the liquid, in order to remove all residues from GL1 separator. Finally, a micro-pump (MP) connected to the GL2 separator was activated to empty the liquid, before starting a new analytical cycle. All syringes were operated at 7.5 mL min^{-1} flow rate in all steps.

3. Results and discussions

3.1 Optimization of the experimental conditions for vapour generation

Firstly, a two-level full factorial design was performed involving the followings variables: hydrochloric acid concentration in working standard solution [HCl], sodium tetrahydroborate concentration [NaBH$_4$], isoamylic alcohol volume (alcohol-Vol) and sodium tetrahydroborate volume (NaBH$_4$-Vol). Table 1 shows the experimental dominions for the variables (as coded and real values) and also the responses found in this experiment.

Table 1 Full two-level factorial design - optimization of the experimental conditions for Cd vapour generation

Experiment	NaBH$_4$-Vol (mL)	Alcohol-Vol (µL)	[NaBH$_4$] (w/v)	[HC] (mol L^{-1})	Absorbance
1	- 1 (2)	- 1 (0)	- 1 (2%)	- 1 (0.5)	0.0322
2	1 (4)	- 1 (0)	- 1 (2%)	- 1 (0.5)	0.0233
3	- 1 (2)	1 (200)	- 1 (2%)	- 1 (0.5)	0.0549
4	1 (4)	1 (200)	- 1 (2%)	- 1 (0.5)	0.0175
5	- 1 (2)	- 1 (0)	1 (4%)	- 1 (0.5)	0.2139
6	1 (4)	- 1 (0)	1 (4%)	- 1 (0.5)	0.1066
7	- 1 (2)	1 (200)	1 (4%)	- 1 (0.5)	0.0843
8	1 (4)	1 (200)	1 (4%)	- 1 (0.5)	0.1367
9	- 1 (2)	- 1 (0)	- 1 (2%)	1 (2.5)	0.0036
10	1 (4)	- 1 (0)	- 1 (2%)	1 (2.5)	0.0060
11	- 1 (2)	1 (200)	- 1 (2%)	1 (2.5)	0.0056
12	1 (4)	1 (200)	- 1 (2%)	1 (2.5)	0.0043
13	- 1 (2)	- 1 (0)	1 (4%)	1 (2.5)	0.0396
14	1 (4)	- 1 (0)	1 (4%)	1 (2.5)	0.1837
15	- 1 (2)	1 (200)	1 (4%)	1 (2.5)	0.0211
16	1 (4)	1 (200)	1 (4%)	1 (2.5)	0.2472
17 (CP)	0 (3)	0 (100)	0 (3%)	0 (1.5)	0.0511
18 (CP)	0 (3)	0 (100)	0 (3%)	0 (1.5)	0.0543
19 (CP)	0 (3)	0 (100)	0 (3%)	0 (1.5)	0.0479
20 (CP)	0 (3)	0 (100)	0 (3%)	0 (1.5)	0.0529

(CP) - Central Point

The data obtained were evaluated using a statistical program and the results expressed as Pareto chart are presented in Figure 2.
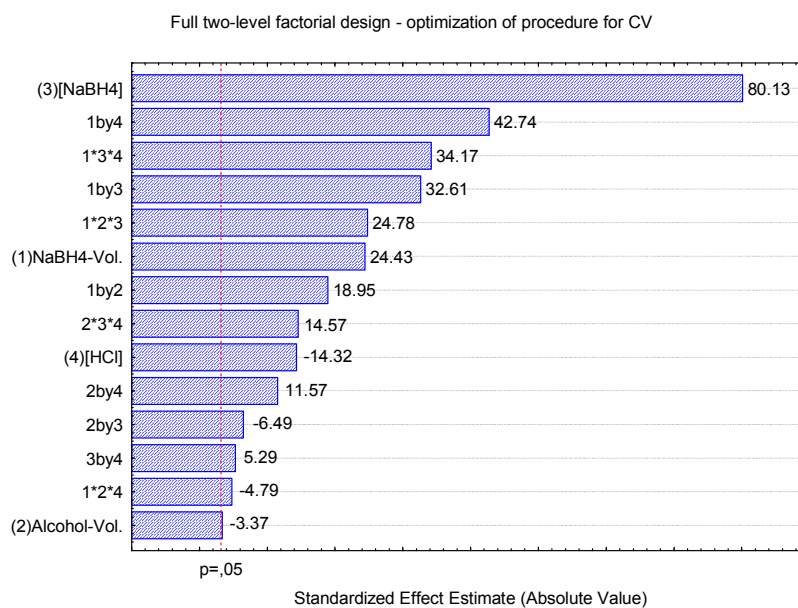

Fig. 2 Pareto Chart for the factorial design.

An evaluation of this figure shows that:

a) The main factors that have significant effects for the Cd vapour generation are: sodium tetrahydroborate concentration (effect: 0.1107 ± 0.0044) and sodium tetrahydroborate volume (effect: 0.0338 ± 0.0044). These have positive effects and it indicates that the increased of the concentration or volume of this substance increases the Cd vapour generation. This fact is expected, since the sodium tetrahydroborate is an integral part of the cold vapor Cd generation reaction.

b) The hydrochloric acid concentration has a negative effect (- 0.0198 ± 0.0044), which indicates that increasing this factor decreased the analytical signal. This result can be explained considering that the hydrolysis reaction of tetrahydroborate in aqueous media increases with the increased of acid concentration, which leads to the largest production of hydrogen gas, according to equation 1 [13] . The hydrogen gas dilutes the analyte (elemental cadmium) in the quartz tube during the analytical measurement, decreasing the absorbance.

$$\left[BH_4\right]^- + H_3O^+ + 2\,H_2O \rightarrow H_3BO_3 + 4\,H_2$$
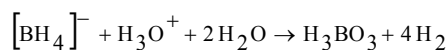
c) The isoamyl alcohol volume tested as antifoaming agent has an effect slightly negative (- 0.0047 ± 0.0044). It indicates that in the worked experimental domain, larger volumes of this alcohol (200 µL) decrease the analytical signal (absorbance). This result suggests that lower volumes should be tested, since adequate amounts prevent foam formation, which increases the efficiency of the release of reduced elemental Cd from the liquid phase to the gaseous phase.

Considering the results found in two-level full factorial design, a Box Behnken matrix was performed to determine the critical conditions of the studied experimental factors. The Table 2 shows the coded and real values of the experimental dominions of these factors and the chemometric response (analytical signal of cadmium).

The obtained results were evaluated using a statistical program, being that these generated a quadratic model (without lack of fit). Thus, a maximum condition of analytical signal of cadmium is shown when the factors are in experimental conditions (expressed as real values) of: 2 mol L^{-1} hydrochloric acid (final concentration in working standard solution or sample), 6% (w/v) sodium tetrahydroborate, 70 µL of isoamyl alcohol and 4 mL of sodium tetrahydroborate volume.

Table 2 Box-Behnken design - optimization of the experimental conditions for Cd vapour generation

Experiment	[HCl] (mol L^{-1})	[NaBH$_4$] (w/v)	Alcohol-Vol (µL)	NaBH$_4$-Vol (mL)	Absorbance
1	- 1 (1)	- 1 (4%)	0 (150)	0 (4)	0.1869
2	1 (3)	- 1 (4%)	0 (150)	0 (4)	0.0611
3	- 1 (1)	1 (6%)	0 (150)	0 (4)	0.2410
4	1 (3)	1 (6%)	0 (150)	0 (4)	0.4001
5	0 (2)	0 (5%)	- 1 (50)	- 1 (3)	0.3478
6	0 (2)	0 (5%)	1 (250)	- 1 (3)	0.2987
7	0 (2)	0 (5%)	- 1 (50)	1 (5)	0.3561
8	0 (2)	0 (5%)	1 (250)	1 (5)	0.3532
9 (CP)	0 (2)	0 (5%)	0 (150)	0 (4)	0.4407
10	- 1 (1)	0 (5%)	0 (150)	- 1 (3)	0.2037
11	1 (3)	0 (5%)	0 (150)	- 1 (3)	0.0619
12	- 1 (1)	0 (5%)	0 (150)	1 (5)	0.2101
13	1 (3)	0 (5%)	0 (150)	1 (5)	0.3432
14	0 (2)	- 1 (4%)	- 1 (50)	0 (4)	0.3168
15	0 (2)	1 (6%)	- 1 (50)	0 (4)	0.4107
16	0 (2)	- 1 (4%)	1 (250)	0 (4)	0.3627
17	0 (2)	1 (6%)	1 (250)	0 (4)	0.3874
18 (CP)	0 (2)	0 (5%)	0 (150)	0 (4)	0.4236
19	- 1 (1)	0 (5%)	- 1 (50)	0 (4)	0.3288
20	1 (3)	0 (5%)	- 1 (50)	0 (4)	0.1902
21	-1 (1)	0 (5%)	1 (250)	0 (4)	0.2273
22	1 (3)	0 (5%)	1 (250)	0 (4)	0.2123
23	0 (2)	- 1 (4%)	0 (150)	- 1 (3)	0.0973
24	0 (2)	1 (6%)	0 (150)	- 1 (3)	0.3712

5

25	0 (2)	- 1 (4%)	0 (150)	1 (5)	0.3330
26	0 (2)	1 (6%)	0 (150)	1 (5)	0.3526
27 (CP)	0 (2)	0 (5%)	0 (150)	0 (4)	0.4089

(CP) - Central Point

In another step, the factors sodium tetrahydroborate flow rate and Ar flow rate were also optimized using a two-level full factorial design. The experiments were performed using 2.0 mL of 5.0 $\mu g\ L^{-1}$ cadmium solution in 2 mol L^{-1} hydrochloric acid and the other factors as described previously. The Table 3 shows the experimental conditions for the two factors and the chemometric response.

Table 3 Factorial design optimization of the experimental conditions of sodium tetrahydroborate flow rate and Ar flow rate.

Experiment	NaBH$_4$ flow rate (mL min^{-1})	Ar flow rate (mL min^{-1})	Absorbance
01	- 1 (3.5)	- 1 (70)	0.2347
02	- 1 (3.5)	1 (150)	0.3595
03	1 (7.5)	- 1 (70)	0.3958
04	1 (7.5)	1 (150)	0.5148
05 (CP)	0 (5.5)	0 (110)	0.4111
06 (CP)	0 (5.5)	0 (110)	0.3994
07 (CP)	0 (5.5)	0 (110)	0.4394

(CP) - Central Point

The factorial design demonstrated that both factors have positive effects on the cadmium vapour generation, being that the effects values are: (0.1582 ± 0.0885) and (0.1219 ± 0.0885) for sodium tetrahydroborate flow rate and Ar flow rate, respectively. The interaction between these two factors is not significant (- 0.0029 ± 0.0883). Although, the sodium tetrahydroborate flow rate factor have presented a positive effect, this factor was fixed at 7.5 mL min^{-1} (superior level established in the factorial design) due to an instrumental limitation, which do not allow use of a flow rate higher than this.

Then, Ar flow rate was optimized by univariate methodology. Figure 3 shows the results obtained in this experiment. As can be seen, the higher analytical signals were obtained using a flow rate of 210 mL min^{-1}. However, at this flow rate the system presents high turbulence and the precision is damaged. This way, the Ar flow rate established for the system was 150 mL min^{-1}. This condition is smaller (up to 3 times lower) than the flow rate commonly employed in CV-AAS methods reported in the literature. Probably because the flow rate of hydrogen from the decomposition of NaBH$_4$ was relatively high (without compromising the analytical signal), which effectively helped the transport of analyte for the detection system, thus requiring a smaller flow rate of Ar.
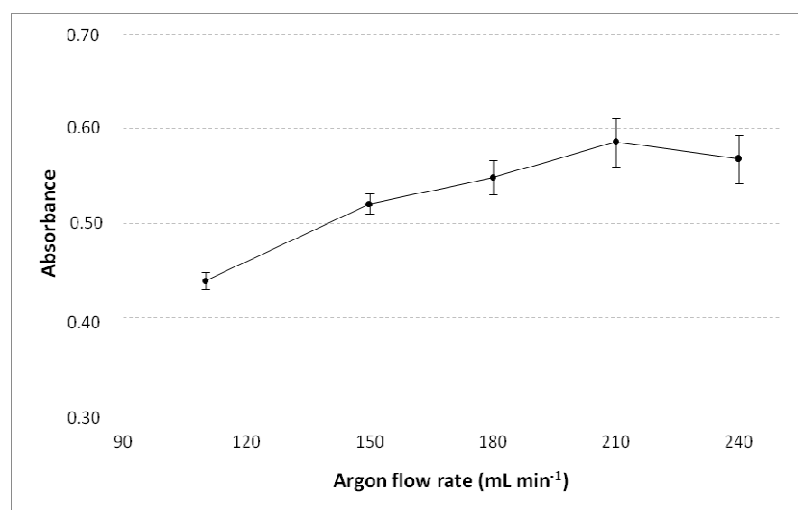

Fig. 3 Effect of the Ar flow rate (mL min^{-1}) on analytical signal (absorbance) of Cd 5 $\mu g\ L^{-1}$.

Also some complexing reagents were tested with the objective to increase the sensitivity of the analytical method. Thus, thiourea, sulfanilamide and L-cysteine, all at a concentration of 0.50% (w/v) were investigated using a Cd solution of 0.50 µg L^{-1}. The analytical signals obtained (expressed as confidence interval at 95% level) were: (0.1395 ± 0.0104) for thiourea; (0.1190 ± 0.0125) for sulfanilamide and (0.0025 ± 0.0015) for L-cysteine, while in absence of complexing it was (0.0851 ± 0.0215). Considering these results, another experiment was developed, where the effect of the thiourea concentration on the vapour generation was investigated. In it, the thiourea concentration varied from 0 to 2%, and the data obtained are showed in Figure 4.
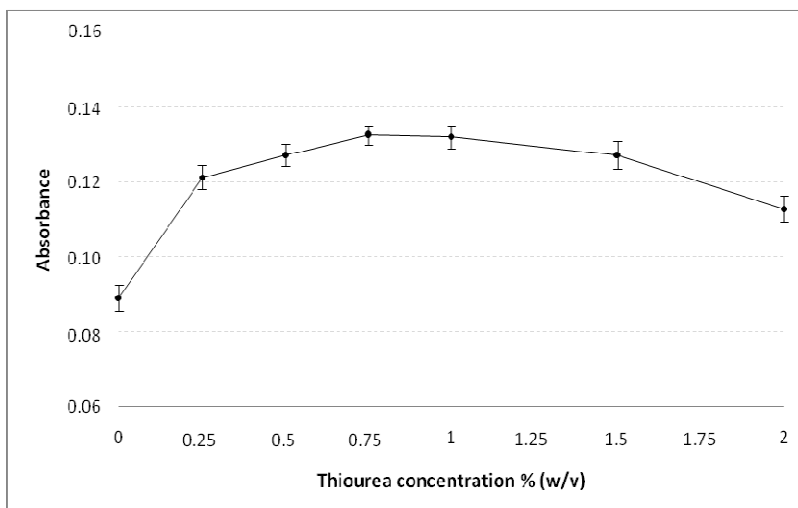

Fig. 4 Effect of the thiourea concentration on the vapour generation using a 0.50 µg L^{-1} Cd solution.

As can be seen in Figure 4, the higher signal for Cd was observed when the thiourea concentration was 0.75%. This way, a 0.75% (w/v) thiourea solution prepared in 0.05 mol L^{-1} hydrochloric acid solution was established as carrier.

3.2 Analytical parameters

Several analytical parameters were determined from the experimental conditions established in the optimization step, i.e. detection and quantification limits, sensitivity, linearity and precision.

The limits of detection (LOD) and quantification (LOQ) were determined following the IUPAC recommendation, considering the measurement of 15 blank solutions. The values found were 5.8 and 19.3 ng L^{-1}, respectively. The LOD obtained by the proposed method is similar to those obtained by methods with a pre-concentration step [8,14], and up to one order of magnitude lower than those obtained with FIA-CV-AAS systems, e.g. 54 ng L^{-1} and 32 ng L^{-1} [5,7].

The calibration curve was linear in the range from 19.3 ng L^{-1} to 5.0 µg L^{-1}, showing a slope of 0.2689±0.0086 (n=10). Experiments involving the analyte addition technique for ground water and seawater samples were developed and the slopes obtained of the calibration curves were: (0.2615±0.0090) for seawater and (0.2666±0.0050) for ground water. These results show that the external calibration technique can be used with proposed method to determine the Cd in ground water and seawater.

The precision expressed as relative standard deviation (RSD) was determined for three levels of Cd concentration (0.025, 0.25 and 2.5 µg L^{-1}), obtaining 7.2%, 2.9% and 1.4% RSD, respectively.

An injection throughput of 87 h^{-1} was achieved employing 2 mL of sample volume, being the proposed method a fast tool for Cd monitoring.

The accuracy of the proposed method was confirmed by analysis of a certified reference material of seawater (coastal) furnished by National Research Council of Canada. The Cd content achieved by this method was (0.0241 ± 0.0031) µg L^{-1} while the value certified is (0.0260 ± 0.0027) µg L^{-1}.

Addition/recovery tests were also performed in seawater and a ground water samples. The results showed in Table 4 demonstrated recoveries between 94 and 101%, indicating that the proposed method can be applied to complex water samples.

Table 4 Addition/recovery tests performed in seawater and ground water sample (n=3).

| Samples | Cd concentration (µg L^{-1}) | | Recovery(%) |
	Added	Found	
Seawater	0	$0.027 \pm 0,002$	-
	0.025	0.052 ± 0.011	98.9
	0.25	0.280 ± 0.060	101.2
Ground water	0	$0.032 \pm 0,005$	-
	0.025	0.056 ± 0.009	94.0
	0.25	0.282 ± 0.042	99.8

Comparing the reagent consumption, mainly the sodium tetrahydroborate, with others flow analysis systems, it can be seen a real saving when using multicommuted system like MSFIA. Thus, while a FIA or CF systems can use between 0.06 and 0.13 g min^{-1} sodium tetrahydroborate, depending on its concentration and flow rate, in a continuous flow way, the proposed MSFIA system uses 0.24 g per analysis only when is required.

3.3 Application to natural water samples

The proposed method was employed for the determination of Cd in 12 ground water samples and 5 coastal seawater samples collected from Mallorca Island (Spain). The results are showed in Table 6.

Table 6 Determination of Cd in ground water and seawater samples collected in Mallorca Island, Spain (n = 3).

Ground water sample	Cd found (ng L^{-1})
GW 1	27.5 ± 8.3
GW 2	32.1 ± 5.2
GW 3	< 19.3 (LOQ)
GW 4	30.3 ± 7.1
GW 5	30.2 ± 9.8
GW 6	53.5 ± 9.0
GW 7	38.2 ± 8.6
GW 8	39.1 ± 6.5
GW 9	27.0 ± 6.7
GW 10	< 19.3 (LOQ)
GW 11	< 19.3 (LOQ)
GW 12	26.7 ± 7.0
Seawater sample	**Cd found (ng L^{-1})**
SW 1	38.1 ± 6.5
SW 2	< 19.3 (LOQ)
SW 3	25.5 ± 5.4
SW 4	27.1 ± 2.0
SW 5	29.1 ± 4.2

The Cd content in the ground water sample analyzed varied of < 19.3 (LOQ) to 53.5 ng L^{-1} and for seawater samples from < 19.3 (LOQ) to 38.1 ng L^{-1}. These results are agreeing with data reported by literature for ground and seawater water samples.

4. Conclusions

The proposed system proved to allow accurate, sensitive, selective and reliable determination of Cd in ground water samples as well as seawater, with suitable quantification limits for the low concentrations often found in these matrices and comparable to methods based in sample pre-concentration or using ICP-MS as detector.

The multivariate optimization techniques herein employed, proved effective in research and optimization of variables that influencing the determination of Cd by CV-AAS and MSFIA system.

The coupling of the MSFIA system with CV-AAS allowed the lower consumption of samples and reagents (mainly sodium tetrahydroborate and Ar) and less generation of waste when compared to FIA or CF systems, excellent robustness and high reproducibility.

The Cd concentrations found in ground water and seawater samples analyzed are in agreement with the results achieved by other authors.

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Graphical abstract
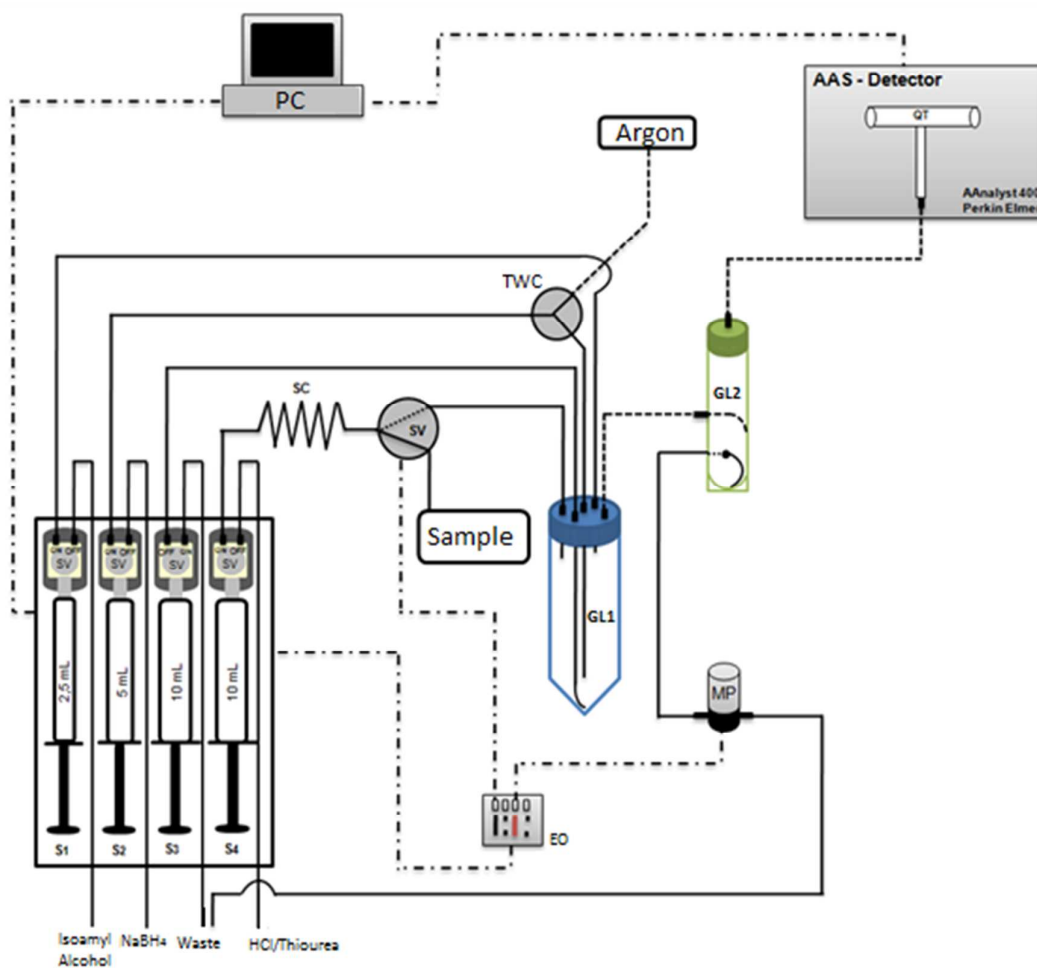
MSFIA-CV-AAS system setup for cadmium determination