

Determination of cadmium in aqueous media by flow injection cold vapour atomic absorption spectrometry. Application to natural water samples

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A simple, sensitive and rapid flow injection system for Cd cold vapour generation coupled to atomic absorption spectrometry (FI-CV-AAS) was developed. A vesicular medium of didodecyldimethylammonium bromide (DDAB) was investigated in order to understand the possible mechanisms occurring in Cd cold vapour generation and the influence of this surfactant as a catalyst. Similar experiments in an aqueous medium were carried out with optimization of the physical and chemical parameters. Identical analytical characteristics such as linearity and precision, and similar detection limits (0.15 and $0.05 \mu\text{g l}^{-1}$ for DDAB and aqueous media, respectively), were found for both reaction media; hence, the use of surfactants was not necessary for Cd cold vapour generation. Validation of the method was carried out by determining the Cd content in several certified waters. The method was applied to the analysis of some natural waters by the standard additions calibration method.

Keywords: Cadmium; cold vapour; atomic absorption spectrometry; didodecyldimethylammonium bromide medium; aqueous medium; natural waters

Cadmium is a toxic element even at low concentrations and can be accumulated in several organs, producing carcinogenic effects. This element occurs naturally in rocks and soils, generally associated with Zn and its compounds. Anthropogenic sources include smelter emissions mainly related to the Zn industry, and application of fertilisers originating from incineration and purification stations,¹ and sewage sludge to the land. All these practices produce an accumulation of Cd in soils, allowing it to enter the food chain with the potential to cause serious health problems.^{2,3} Such reasons explain the need to monitor Cd in environmental samples.

Among the most important analytical techniques for monitoring this element are atomic absorption spectrometry (AAS), particularly electrothermal atomic absorption spectrometry (ETAAS), atomic fluorescence spectrometry (AFS) and inductively coupled plasma atomic emission spectrometry (ICP-AES).

The ultratrace levels of Cd usually present in the environment and the complexity of the matrices make it necessary to use preconcentration and separation procedures such as extraction methods,^{4,5} sorption on resins⁴ or ion exchange.^{6,7} However, this approach presents some disadvantages, such as the laborious nature of the procedure, the possible losses of the analyte or contamination of the sample. In addition, in many cases, the enhancement of sensitivity is not sufficient.

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 solution.

Several attempts have been made to determine Cd by the vapour generation technique. Many workers have recognized the convenience of using an organic reaction medium. Thus, Cacho *et al.*⁸ reported the generation of a volatile Cd species (presumed to be the hydride) in *N,N*-dimethylformamide and its determination by AAS with a detection limit of 200 ng l^{-1} . Based on the instability of this species, Sanz Medel and co-workers^{9,10} have proposed the use of surfactants, particularly didodecyldimethylammonium bromide (DDAB), which clearly enhance the efficiency of cold vapour generation and facilitate transport to the atomisation cell. A detection limit of 80 ng l^{-1} was obtained when the procedure was coupled to AAS. Other workers have developed a Cd cold vapour generation method using thiourea and cobalt as catalysts of the reaction, resulting in an increase in sensitivity. Detection limits obtained with this method were 20 ng l^{-1} by AAS,¹¹ 8 ng l^{-1} by AFS,¹² and 30 ng l^{-1} by ICP-MS.¹³ D'Ulivo and Chen¹⁴ and Ebdon *et al.*¹⁵ demonstrated that Cd can be determined in an aqueous medium based on its derivatization using tetraethylborate as ethylating agent. The volatile Cd compound, presumed to be diethylcadmium, was detected by AAS¹⁴ or AFS¹⁵ with detection limits of 200 and 20 ng l^{-1} , respectively. Finally, Bermejo-Barrera *et al.*¹⁶ have generated the Cd cold vapour compound in the absence of organic reaction media by adding metallic species as catalysts, resulting in a detection limit of 5 ng l^{-1} .

In the light of these experiences, this paper describes the possibility of the determination of Cd by cold vapour generation in a simple aqueous medium by applying a flow injection (FI) system, using NaBH_4 which is easier to handle than NaBH_4 . This method is simpler, faster and less prone to interferences than batch systems. All chemical, physical and instrumental parameters were optimised. An approach using an organic medium (DDAB) is also included in order better to understand the possible mechanisms occurring in Cd vapour generation.

EXPERIMENTAL

Apparatus

Sample and reagents were pumped with a peristaltic pump, and then injected through a six-way FI valve (Omnifit). The Cd cold vapour formed was separated from the solution in a gas-liquid separator and transported to a T quartz cell. Cadmium absorbance was measured with a Perkin-Elmer 3100 atomic absorption spectrometer provided with an electrically heated T quartz cell. A wavelength of 228.8 nm was used with a spectral bandpass of 0.7 nm . A Cd hollow cathode was used

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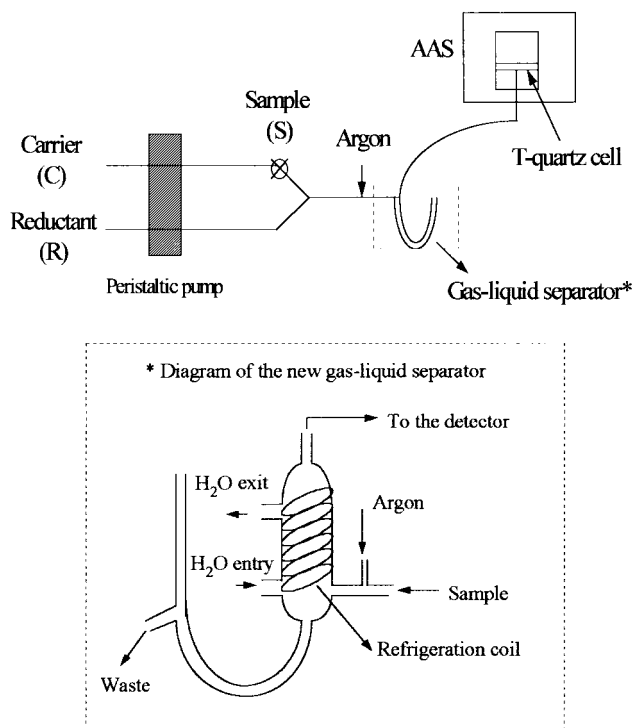


Fig. 1 Continuous and FI devices for Cd vapour generation. Continuous mode in DDAB vesicles: C = HCl + Cd + DDAB; R = NaBH₄ + DDAB. FI mode in DDAB vesicles: C = HCl; R = NaBH₄ + DDAB; S = Cd + DDAB. FI mode in aqueous medium: C = HCl; R = NaBH₄; S = Cd + HCl.

as the spectral source. Cooling of the reagents and the gas-liquid separator was carried out with a Tectron 200 thermostatically controlled water-bath (Selecta). A schematic diagram of the whole system in the different modes used is shown in Fig. 1.

Reagents

All reagents and solutions prepared were of analytical-reagent grade from Aldrich, Merck or Carlo Erba. Ultrapure water from a Milli-Q system (Millipore) was used throughout. Acid solutions were prepared daily with the appropriate dilutions. Solutions of NaBH₄ were prepared by dissolving the powder in ultrapure water and were stabilised with 0.1% NaOH. All solutions were filtered before use. A 1000 mg l⁻¹ atomic absorption standard solution of Cd^{II} (purchased from Sigma) was used to prepare a stock standard of 10 mg l⁻¹, and working solutions were freshly prepared by diluting appropriate aliquots of the stock solution.

For surfactant experiments, vesicles of DDAB (10⁻² mol l⁻¹) were prepared by dissolving the surfactant powder in water and sonicating at room temperature for about 25 min. An NaBH₄ solution in 0.1% NaOH, prepared as described above, was mixed with a solution of DDAB vesicles (10⁻² mol l⁻¹). The resulting solution, which was sonicated for 25 min, was prepared weekly and filtered before use.

General procedures

Continuous and FI cold vapour generation of Cd species from DDAB vesicles was carried out using the laboratory-built flow system shown in Fig. 1. Cadmium sample (acidified with 0.4 mol l⁻¹ HCl) and NaBH₄ solutions were prepared in DDAB vesicles (10⁻² mol l⁻¹) and sonicated for 25 min in order to ensure vesicle formation. The solutions were pumped through a peristaltic pump in the continuous mode at a flow

rate of 1.5 ml min⁻¹, merging in a T-piece and forming the Cd cold vapour which was transported by an argon carrier to the quartz cell of the atomiser. In the FI mode, the Cd sample (containing 10⁻² mol l⁻¹ DDAB and acidified with 0.4 mol l⁻¹ HCl) was injected into a FI valve. A 0.4 mol l⁻¹ HCl carrier solution dragged the sample out of the sample loop (200 µl) when the valve was turned to the inject position. The solution was merged with NaBH₄ + DDAB solution and the volatile Cd species was transported to the atomisation cell as described above.

FI Cd cold vapour formation in aqueous medium was carried out by using the same flow system shown in Fig. 1. In this case, the carrier, 1 mol l⁻¹ HCl, was continuously pumped through one of the channels of the peristaltic pump at a flow rate of 1.5 ml min⁻¹. The carrier stream dragged the Cd sample, dissolved in 1 mol l⁻¹ HCl, out of the sample loop and then merged with a stream of 4% NaBH₄ at the same flow rate. The volatile species formed was transported to the atomisation cell in the same way as for the DDAB experiments.

RESULTS AND DISCUSSION

Volatile Cd species formation in DDAB vesicles medium

Sanz Medel and co-workers^{9,10} have described the cold vapour generation of Cd using tetrahydroborate in an organised medium in combination with ICP-AES or AAS. They found that the vesicles had the ability to organise reductants at the molecular level, thereby improving the kinetics of reactions for the generation of Cd cold vapour, assumed to be the hydride. Based on the high instability of this hydride, the organised medium provided by the DDAB vesicles was able to manipulate favourably the hydride formation reaction in solution.¹⁰ According to these experiences, a series of experiments were performed in a DDAB vesicles medium in order to compare the continuous and FI introduction modes.

Optimisation of reagent concentrations

First, reagent concentrations, *viz.*, HCl as carrier, NaBH₄ as reductant and DDAB as organic medium, were optimised. The reaction vessel temperature greatly affected the reaction kinetics and the efficiency of Cd cold vapour generation. Thus, reagents and samples were maintained at a temperature around 5 °C with a thermostatically controlled water-bath. The results are plotted in Fig. 2. The Cd signal is represented *versus* concentration of chemical reagents for comparison of the two sample introduction modes. A slightly higher signal was obtained in all cases by using the FI system rather than the continuous system.

In both continuous and FI systems, acid concentration had a significant effect on the efficiency of Cd vapour generation [Fig. 2(a)]. It was a critical parameter in the continuous mode, resulting in significant absorbance shifts with a small variation in the acidity of the medium; in contrast, the FI introduction mode showed a gradual signal increase between 0.3 and 0.7 mol l⁻¹ HCl. Higher acid concentrations produced a sharp decrease in the analytical signal. For further experiments, 0.4 mol l⁻¹ HCl was selected. However, the same behaviour was observed for continuous and FI introduction modes in relation to NaBH₄ concentration [Fig. 2(b)]. A concentration of 2% or higher of NaBH₄ gave the maximum absorbance, and a concentration of 4% was eventually chosen. Finally, the effect of DDAB concentration on the Cd signal is shown in Fig. 2(c). Addition of DDAB vesicles at a concentration of 10⁻² mol l⁻¹ or higher produced a 3-fold enhancement with respect to the Cd signal in aqueous medium. The optimum values obtained here are in good agreement with the experimental conditions reported in previous work.^{9,10} A second observation was the formation of foam due to the surfactant

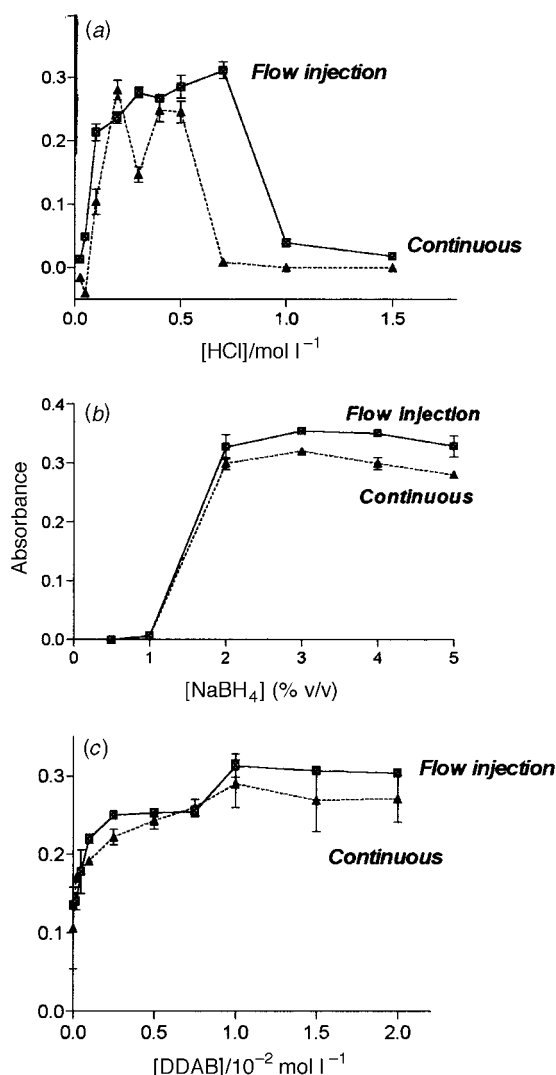


Fig. 2 Effect of the concentration of (a) HCl, (b) NaBH₄ and (c) DDAB vesicles on Cd signal by using both continuous and FI introduction modes. [Cd²⁺] = 5 µg l⁻¹. ■, Flow injection mode. ▲, Continuous mode.

medium, leading to some instability of the signal. It can be seen from Fig. 2(c) that FI offered a better precision in the measurements than the continuous mode; the reduction of this foaming by using an FI system might be responsible for both the precision and sensitivity improvements. In addition, analysis time was reduced by using the FI system. In the continuous

mode, it was necessary to wait between two analyses in order to reduce foam formation in the gas-liquid separator. The FI introduction mode was therefore adopted in further experiments.

The optimum conditions for volatile Cd cold vapour generation in a DDAB vesicles medium with a FI system are summarised in Table 1.

Influence of the reaction temperature

As stated above, the efficiency of Cd cold vapour formation is greatly affected by temperature. Some deposition of metallic Cd occurred if the connecting tube was too long. The relationship between reagents and sample temperature, and the length of the tube connecting the gas-liquid separator to the atomiser cell, was studied. The temperature of the reagents and sample was maintained within the range 2–10 °C by means of a thermostatically controlled water-bath. An increase in the signal, around 4-fold, was observed by decreasing the temperature with respect to that obtained at room temperature. Lower temperatures were not feasible as solutions were partially frozen, whereas higher temperatures caused significant loss of the Cd signal owing to decomposition of the volatile compound, presumed to be CdH₂, into Cd⁰ and H₂. It seemed that, around 5 °C (selected for subsequent work), hydride generation was improved, as was the efficiency and transport of volatile Cd, and consequently a higher Cd signal was obtained. In order to prevent the deposition of metallic Cd⁰ by decomposition (as mentioned above), the connection between the hydride generator and the atomisation cell was kept as short as possible, the optimum length being approximately 7 cm.

Influence of the vesicles preparation mode

The efficiency of an organised medium in the formation of Cd cold vapour is demonstrated in Fig. 2(c). It is known that in a vesicles medium, substrate organisation leads to altered reaction rates, paths and stereochemistries owing to the ability of vesicles to act as a catalyst.¹⁷ In order to determine the role of vesicles in this reaction, and based on the experiments of Valdés Hevia y Temprano *et al.*,⁹ preparation of three different solutions was undertaken: firstly, the DDAB and Cd²⁺ solutions were mixed and simultaneously sonicated for 20 min; in the second set of experiments, a DDAB solution was prepared and sonicated for 20 min and then Cd²⁺ was added to the DDAB vesicles already formed; the last case involved the preparation of the DDAB solution, which was sonicated for a similar time, addition of Cd²⁺ to the vesicles and sonication of the mixture again (this process is termed ultrasonication in

Table 1 Optimum conditions for Cd hydride generation by AAS in DDAB or aqueous medium

Organic DDAB vesicles medium	[HCl]	0.4 mol l ⁻¹
	[NaBH ₄]	4% m/v in 1% m/v NaOH + 10 ⁻² mol l ⁻¹ DDAB
	[DDAB]	10 ⁻² mol l ⁻¹
Aqueous medium	[HCl]	1 mol l ⁻¹
	[NaBH ₄]	4% m/v in 1% m/v NaOH
AAS conditions—		
	Wavelength/nm	228.9
	Lamp current/mA	7
	Slit/nm	0.7
	Argon flow rate/ml min ⁻¹	400
	Reagent flow rate/ml min ⁻¹	1.5
	Sample loop/µl	200
	Atomisation temperature/°C	Room temperature
	Reaction temperature/°C	3–5 °C
	Connecting tube length/cm	7 cm

Table 2 Effect of sample preparation on the Cd signal. $[\text{Cd}^{2+}] = 5 \mu\text{g l}^{-1}$

Preparation mode	Cd signal (absorbance)
Cd in aqueous solution	0.180
Cd and DDAB simultaneously sonicated	0.275
Cd added to DDAB vesicles already sonicated	0.235
Cd and DDAB ultrasonicated	0.357

this work). Finally, a reference Cd^{2+} aqueous solution was prepared for comparative purposes. Absorbance values for each experiment are summarised in Table 2. A higher signal was obtained when the DDAB and Cd^{2+} solutions were mixed and sonicated rather than when Cd^{2+} was added to DDAB vesicles already formed. The same results were obtained by Valdés Hevia y Temprano *et al.*⁹ They explained this effect by arguing that at least 50% of Cd remained inside the vesicles if Cd^{2+} and DDAB were sonicated simultaneously, whereas no Cd^{2+} was able to enter the DDAB vesicles already formed by sonication. This assessment was based on micellar ultrafiltration studies designed to verify if Cd^{2+} was present in the DDAB vesicles. In order better to understand the processes occurring in the organisation of the media and the effect of sonication, we attempted the ultrasonication experiment. This preparation mode led to a 50% enhancement of the signal, representing the best result (Table 2). This enhancement might be explained by the supposition that vesicles are capable of organising a large number of molecules in their compartments and small charged ions can be electrostatically attached to the oppositely charged vesicle surface.¹⁷ In such a case, ultrasonication will accelerate the passage of Cd to bilayers of the vesicles. Based on this evidence, the influence of ultrasonication time was evaluated in the range 0–40 min. An enhancement of the signal of about 50% was observed for sonication times between 20 and 25 min compared with that obtained without ultrasonication. A value of 20 min was chosen as the optimum ultrasonication time for subsequent experiments.

The absorbance of an aqueous Cd^{2+} solution, without a DDAB vesicles reaction medium, is also given in Table 2. This value is in disagreement with the results of Valdés Hevia y Temprano *et al.*⁹ as these workers did not obtain any signal for Cd in an aqueous medium. This difference led us to investigate in more detail this simple reaction medium.

Volatile Cd species formation in aqueous medium

Different parameters, such as acid and reductant concentrations, and reaction and atomisation temperatures, were optimised by using a simple aqueous medium. An FI system was used for all the experiments, and the reagents and samples were cooled in the same way as in the surfactant medium.

Optimisation of reagent concentrations

The influence of the concentrations of HCl and NaBH_4 on the Cd signal is shown in Fig. 3(a) and (b). From Fig. 3(a), a displacement of the optimum concentration of HCl to higher values, *viz.*, 0.8–1.2 mol l^{-1} , with respect to the optimum obtained with DDAB vesicles [Fig. 2(a)], can be observed. As explained above, cold vapour generation was favoured in a DDAB medium owing to its ability to organise and accelerate the reaction. However, in an aqueous medium a higher HCl concentration (1 mol l^{-1}) is needed. This higher concentration of H^+ will favour the formation of H^* ('nascent' hydrogen)

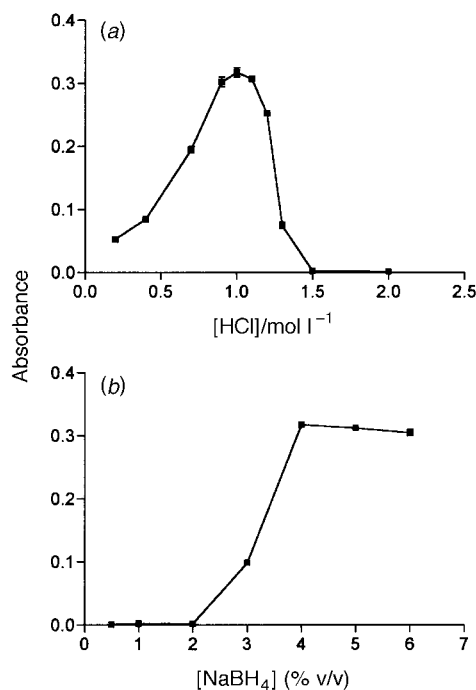
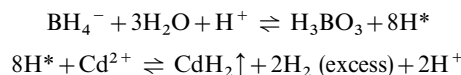


Fig. 3 Influence of the concentration of (a) HCl and (b) NaBH_4 on Cd signal in aqueous medium by using FI. $[\text{Cd}^{2+}] = 5 \mu\text{g l}^{-1}$.

and hence CdH_2 according to:



Likewise, the concentration of NaBH_4 necessary for the maximum efficiency of Cd hydride generation is also higher than 3.5% and similar to that for the DDAB media. Indeed, the profile of the curve clearly shows that the same NaBH_4 concentration that was used in the DDAB medium (4%) can be applied in an aqueous medium.

The higher acid concentration needed in an aqueous medium (1 mol l^{-1} HCl) produced a more vigorous reaction and some water vapour reached the quartz cell along with the Cd vapour. The presence of water led to very poor repeatability of the measurements. The design of a gas-liquid separator with an incorporated cooling system solved this problem. The cooling system consisted of an internal coil cooled by a cold water circulation device (see Fig. 1). The water was maintained at about 5 °C with a thermostatically controlled water-bath. The use of this device provided two main benefits: firstly, the elimination of water vapour by condensation; and secondly, the prevention of Cd hydride decomposition owing to its high thermal instability as explained above. In this case, there was no need to cool the reagents and samples.

Influence of the atomisation temperature

The influence of temperature on hydride generation was studied earlier and decomposition of the assumed CdH_2 at high temperature was demonstrated. In a further effort to ascertain the effect of temperature in the atomisation cell, an electrothermal quartz furnace with a fine temperature control system was used. The results obtained are plotted in Fig. 4 and clearly show that the maximum number of Cd atoms is present in the atomisation cell at room temperature. The signal remained stable up to 70 °C after which a progressive decrease in the intensity was observed with increasing temperature. For a temperature higher than 200 °C no signal was detected. This effect might be attributed to (a) possible dilution of the analyte owing to the greater expansion of the H_2 produced during the

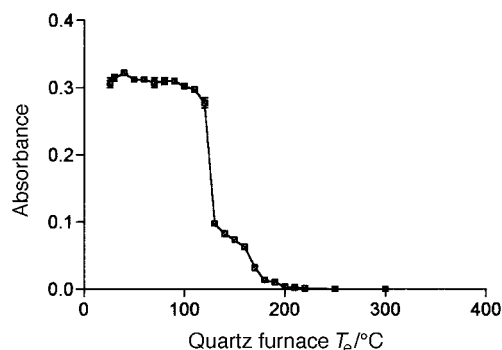


Fig. 4 Effect of the atomisation temperature on Cd hydride generation. $[\text{Cd}^{2+}] = 5 \mu\text{g l}^{-1}$.

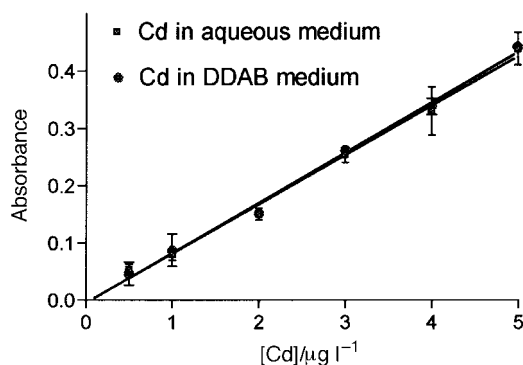


Fig. 5 Comparative study of the calibration graphs obtained for Cd in DDAB vesicles with $[\text{DDAB}] = 10^{-2} \text{ mol l}^{-1}$, $[\text{HCl}] = 0.4 \text{ mol l}^{-1}$, $[\text{NaBH}_4] = 4\%$, or in aqueous medium with $[\text{HCl}] = 1 \text{ mol l}^{-1}$, $[\text{NaBH}_4] = 4\%$. Detection limits: Cd in aqueous medium, $0.05 \mu\text{g l}^{-1}$; Cd in DDAB medium, $0.15 \mu\text{g l}^{-1}$.

reaction, (b) possible deposition of Cd^0 , arising from the decomposition of the highly unstable CdH_2 ,¹⁰ in the entrance of the T quartz cell, out of the optical path.

Other parameters, such as liquid flow rate, carrier gas flow rate and sample loop volume, were also optimised. The optimum conditions are summarised in Table 1.

Analytical performance

Calibration graphs obtained in DDAB and in aqueous media, using the optimum experimental conditions, are plotted in Fig. 5 for comparative purposes. Superposition of the two graphs was observed; the equations of the linear graphs are: $y = 0.0877x - 0.0057$, and $y = 0.0861x - 0.0048$ for DDAB and aqueous media, respectively. In practice the slope is the same for the two procedures, and the detection limits obtained were very similar (see Fig. 5), being lower in an aqueous medium owing to a better signal-to-background ratio. A linear range of $0.5\text{--}6 \mu\text{g l}^{-1}$, a detection limit of $0.05 \mu\text{g l}^{-1}$ and a quantification limit of $0.16 \mu\text{g l}^{-1}$ were obtained by optimising all parameters in ultrapure water. The precision obtained for five measurements of Cd solutions at $5 \mu\text{g l}^{-1}$ was 3–4%. It is important to emphasise here the simplicity and rapidity of this method. Thus, these results present the first evidence of the use of a simple aqueous medium for Cd cold vapour generation by using FI. This procedure will simplify sample preparation and provide sufficient sensitivity for the analysis of real water samples.

Sample analysis

Validation of the method was carried out by determining the content of Cd in four different certified waters, three of which

Table 3 Determination of Cd in certified and natural water samples

Sample	Measured value/ $\mu\text{g l}^{-1}$	Reported value/ $\mu\text{g l}^{-1}$
113*	3.04 ± 0.14	3.52 ± 0.76
SRM 1643†	5.92 ± 0.42	6.47 ± 0.37
7878‡	47.19 ± 2.80	48.40 ± 4.61
7879‡	245.1 ± 9.9	248.05 ± 12.06
Sea-water	0.20 ± 0.01	
Tap water	0.20 ± 0.03	

* Intercomparison exercise organised by WRC aquacheck (UK).

† Commercial Standard Reference Material (SRM) from NIST (USA).

‡ Standard certified for trace metals content by APG, Analytical Products Group (USA).

have been certified for Cd content and the fourth has been used in an interlaboratory comparison exercise. Results are presented in Table 3, showing the good agreement between the value found with the proposed method and the reported value. Finally, the proposed method was applied to the determination of Cd in tap water and sea-water; the results are also presented in Table 3. A matrix effect was observed with a significant shift of the calibration slope. This change in the slope can be assigned to the presence of various interferences. In tap water, large amounts of lead may be present owing to the use of lead pipes in the supply system. This element can produce a significant depression of the Cd signal.^{11,12} Also, the high NaCl content in sea-water will change the ionic strength, again resulting in a calibration slope change. In order to prevent these error sources, the determination of Cd was undertaken by the standard additions calibration method.

The contents of Cd found in these real samples are below the maximum permitted value for Cd ($5 \mu\text{g l}^{-1}$) allowed by international regulations.^{18,19}

CONCLUSIONS

The determination of ultratrace amounts of Cd can be performed in an aqueous medium by using FI cold vapour generation coupled to AAS. A comparison between an organic reaction medium (DDAB surfactant) and an aqueous medium has shown a similar Cd response by optimising the most important experimental parameters. The HCl concentration appeared to be an important parameter as was the temperature of the reaction medium and also ultrasonication in the DDAB experiments. Calibration graphs obtained in the two different media led us to discard the use of surfactants for Cd determination by this technique. Finally, the proposed method was validated and then successfully applied to the determination of Cd in sea-water and tap water samples by using the standard additions method.

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