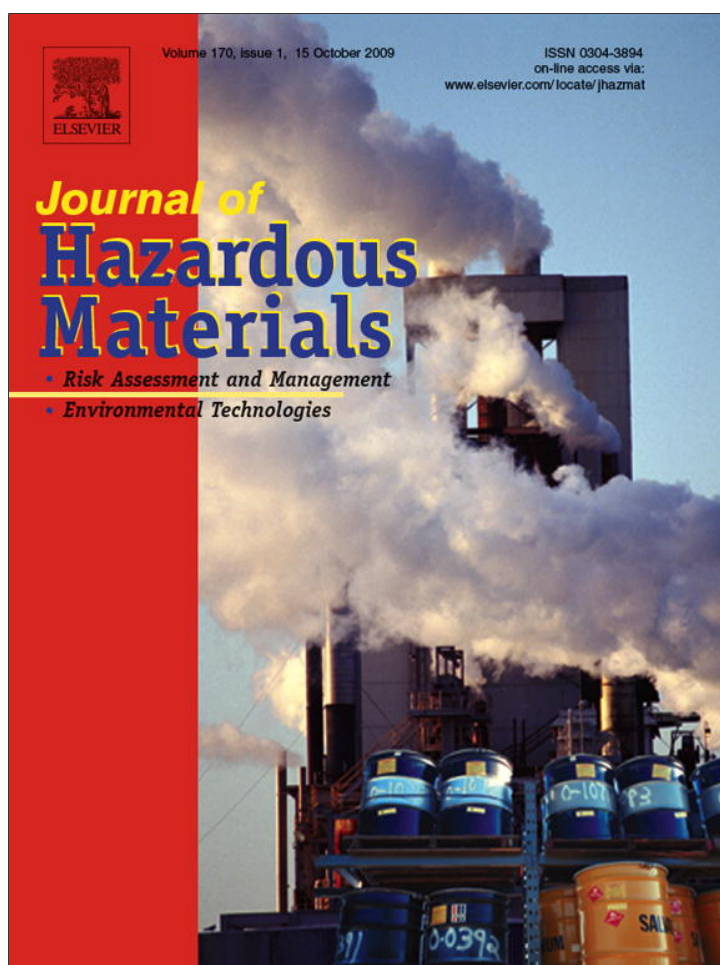


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Determination of cadmium at ultra-trace levels by CPE–molecular fluorescence combined methodology

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ABSTRACT

A highly sensitive micelle-mediated extraction methodology for the preconcentration and determination of trace levels of cadmium by molecular fluorescence has been developed. Metal was complexed with *o*-phenanthroline (*o*-phen) and eosin (eo) at pH 7.6 in buffer Tris medium and quantitatively extracted into a small volume of surfactant-rich phase of PONPE 7.5 after centrifugating. The chemical variables affecting cloud point extraction (CPE) were evaluated and optimized. The RSD for six replicates of cadmium determinations at 0.84 $\mu\text{g L}^{-1}$ level was 1.17%. The linearity range using the preconcentration system was between $2.79 \times 10^{-3} \mu\text{g L}^{-1}$ and $2.81 \mu\text{g L}^{-1}$ with a correlation coefficient of 0.99. Under the optimal conditions, it obtained a LOD of $8.38 \times 10^{-4} \mu\text{g L}^{-1}$ and LOQ of $2.79 \times 10^{-3} \mu\text{g L}^{-1}$. The method presented good sensitivity and selectivity and was applied to the determination of trace amounts of cadmium in commercially bottled mineral water, tap water and water well samples with satisfactory results. The proposed method is an innovative application of CPE-luminescence to metal analysis comparable in sensitivity and accuracy with atomic spectroscopies.

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1. Introduction

Heavy metal toxicity, or heavy metal poisoning, is everywhere in the world today. The accumulation of toxic heavy metals in the environment is increasing due to human activity [1]. Inadequate filtration and treatment of these waters for human consumption, particularly in poor countries, cause the exposition of many people in these affected regions.

Cadmium is highly toxic even at low concentrations, causing damages to organs such as kidneys, liver and lungs [2]. An interesting aspect of cadmium poisoning is that by replacing zinc in critical enzyme systems; cadmium can perform a homeostatic function. That is: many zinc-dependent enzymes can continue functioning to a certain extent with cadmium instead of zinc [3].

All these facts, which cause alarm in the public health, demand accurate analytical procedures for the quantification of this element at, trace levels [4]. The American Environmental Protection Agency (U.S. EPA) establishes a maximum contaminant level with cadmium of $10 \mu\text{g L}^{-1}$ in drinking water [5]. The official regulations have shown a world-wide tendency to lower the maximum permissible

levels of cadmium. This analyte low concentration level requires the introduction of a preconcentration step previous to instrumental detection. Micelle-mediated extraction procedures have found wide applications in different areas of analytical chemistry [6,7]. The cloud point procedure offers convenience and simplicity when compared with conventional liquid–liquid extraction, including higher extraction and preconcentration factors. Additionally, it fits well to the principles of the “green chemistry” because of the use of diluted solutions of surfactants, resulting in the economy of reagents and generation of few laboratory residues [8].

Even the use of CPE process for extraction of metal ions, biological and clinical species and environmental clean-up methods have been reported; several workers agree that these complex systems require a great deal of fundamental research. Any species that originally present associations to these micellar aggregates can be extracted from the initial solution and preconcentrated in a small volume of the surfactant-rich phase. The clouding phenomenon can be induced by changing the temperature, the additive content, or the pressure through which results the separation of a single isotropic micellar phase into two isotropic phases: (i) a small volume surfactant-rich phase composed mainly of surfactant, and (ii) an aqueous phase containing surfactant with the concentration level near to critical micellar concentration [9].

Analytical methodologies commonly used nowadays to determine heavy metals in water samples are based on atomic techniques such as atomic absorption spectrometry, inductively coupled

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plasma (ICP)-atomic emission spectrometry and ICP-mass spectrometry [10–13]. However, there is an increasing need for simple, low cost techniques for their monitoring. Spectrofluorometric methods of cadmium are generally based on the formation of the metal complexes with organic dyes [14–16]. Spectrofluorimetric determination of cadmium has analytical advantages such as high sensitivity, proper selectivity and wide dynamic range. For other side, CPE gives high efficacy of extraction, operative simplicity and safety produced by using of nontoxic solvents when it is compared to other traditional extraction procedures [17–26].

In this paper, a new combined methodology of CPE and fluorimetric determination of cadmium based in the formation of a ternary association complex with *o*-phen and eo has been developed. The results obtained showed that this methodology was very satisfactory for determining the concentrations of cadmium in real samples of commercial bottled mineral water, tap water and water well. Taking into account its sensitivity and accuracy, the present methodology represents a valid alternative to atomic spectroscopies for cadmium determination.

2. Materials and methods

2.1. Reagents

$1 \times 10^{-6} \text{ mol L}^{-1}$ of Cd(II) stock solutions were prepared by diluting of $100 \mu\text{g mL}^{-1}$ standard solution plasma – pure (Leeman Labs, Inc., Hudson, USA).

Extractant solution of the nonionic surfactant PONPE 7.5 0.01% (polyethyleneglycolmono-*p*-nonylphenylether, Tokyo Kasei Industries, Chuo-Ku, Tokyo, Japan) was prepared as follows: 10 ml PONPE 7.5 and 40 mL distilled ethanol were poured into a 100 mL volumetric flask and made up to volume with ultrapure water.

$1 \times 10^{-2} \text{ mol L}^{-1}$ Tris (Mallinckrodt Chemical Works, New York, Los Angeles, St. Louis, USA) solution was prepared. This solution was adjusted to the desired pH, with aqueous HClO_4 (Merck, Darmstadt, Germany) or NaOH (Mallinckrodt Chemical Works) using a pH meter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) Model EA 940.

The nonionic surfactant Triton X-100 (TX-100) was purchased from (Merck) and was used without further purification.

A $1 \times 10^{-6} \text{ mol L}^{-1}$ stock eosin solution (H.E – Daniel Ltd., England) and a $1 \times 10^{-5} \text{ mol L}^{-1}$ stock *o*-phenanthroline solution (Merck) were weekly prepared by dissolving the appropriate amount of each in ultrapure water. The stability of solutions was checked by spectrophotometric measurements.

All used reagent were analytical grade.

2.2. Apparatus

All spectrofluorimetric measurements were made using a Shimadzu RF-5301 PC spectrofluorophotometer equipped with a 150 W Xenon lamp and 1.00 cm quartz cells. Instrument excitation and emission slits both were adjusted to 3 nm. A centrifuge was used to accelerate the phase separation process.

2.3. General procedure. CPE and molecular fluorescence determination

An adequate aliquot of sample or metal ion solution ($2.80 \times 10^{-3} \mu\text{g L}^{-1}$ to $2.80 \mu\text{g L}^{-1}$), $100 \mu\text{L}$ buffer Tris solution $1 \times 10^{-2} \text{ mol L}^{-1}$ (pH 7.6), $250 \mu\text{L}$ *o*-phen ($1 \times 10^{-5} \text{ mol L}^{-1}$), $500 \mu\text{L}$ eo ($1 \times 10^{-6} \text{ mol L}^{-1}$) and 0.5 mL of extractant solution, were placed in a 10 mL graduated centrifuge tube. The whole mixture was diluted to 10 mL with ultrapure water. The solution prepared was kept at 313 K for 15 min in a thermostatic bath for equilibrating and then centrifuged for 5 min at 3500 rpm at approximately

$1000 \times g$. After being cooled at 255 K during 5 min the surfactant-rich phase became a viscous gel and the aqueous phase could be poured off. The surfactant phase in the tube was then made up to 3 mL by adding $300 \mu\text{L}$ of buffer Tris pH 7.6, 1 mL of absolute ethanol and ultrapure water. Fluorescent emission was measured at $\lambda_{\text{em}} = 545 \text{ nm}$ ($\lambda_{\text{exc}} = 525 \text{ nm}$).

2.4. Sampling procedure

Tap water and water well were allowed to run for 10 min and approximately 1000 mL of each, were collected. The water samples were filtered through 0.45 mm pore size membrane filters immediately after sampling. Drinking water was processed without previous treatment. All the glass instruments used were previously washed with a 10% (v/v) HNO_3 water solution and then with ultrapure water. Samples were processed immediately after collection as described in Section 2.3.

3. Results and discussion

3.1. Fluorescent spectra

Previous researches have shown the feasibility of formation of ternary complexes with metallic ions [27] using *o*-phen and eo. The fluorescence of *o*-phen–Cd(II) system was initially explored using CPE of the complex formed in aqueous medium. The effect of eo addition on *o*-phen–Cd(II) system was researched. The ternary association formed in aqueous solution showed poor stability making difficult the metal quantification and the study of the stoichiometric ratio. The implementation of CPE step by addition of the nonionic surfactant PONPE 7.5 promoted the quantitative extraction of the formed ternary complex, which in this medium presented adequate stability. This step has the double advantage of separating potential matrix interferences and preconcentrating analyte.

The obtained results showed an important enhancement of the fluorescent signal; this fact supports the formation of a ternary association complex between Cd(II), *o*-phen and eo, with an extra advantage respect to the sensibility of the luminescent response as can be seen in Fig. 1.

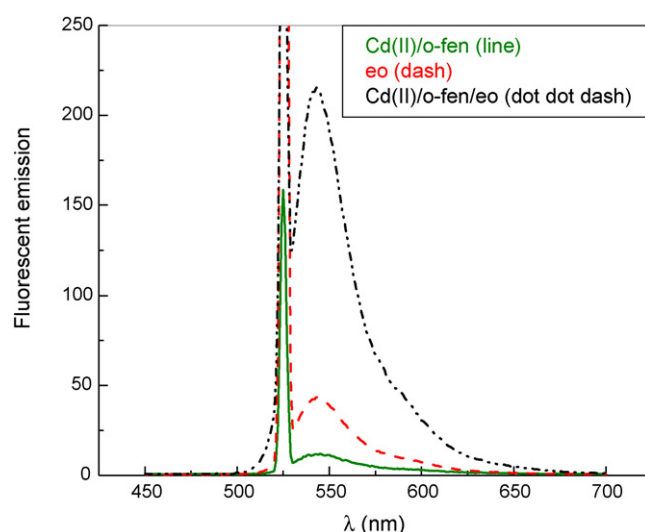


Fig. 1. Fluorescent spectra of Cd(II)–*o*-phen, eo and Cd(II)–*o*-phen–eo systems previous CPE. Conditions: $1.7 \mu\text{g L}^{-1}$ Cd(II), $8.3 \times 10^{-7} \text{ mol L}^{-1}$ *o*-phen, $1.6 \times 10^{-7} \text{ mol L}^{-1}$ eo, pH 7.6 buffer Tris and $1.6 \times 10^{-3} \%$ (v/v) PONPE 7.5. Other experimental conditions are described under procedures.

3.2. Study of experimental conditions

The efficiency of the CPE process depends on the hydrophobicity of the ligand and the produced complex, the apparent equilibrium constants, and kinetics of complex formation and transference of phases. In order to find the optimum experimental conditions, any parameter affecting the complexing reaction and CPE (pH, nature and concentration of surfactant, concentrations of chelating reagents, diluting solvent, temperature and equilibration time) was investigated.

The pH was the first parameter examined because it plays a unique role on metal-chelate formation and subsequent extraction. The results illustrated in Fig. 2, show that at pHs above 7, a plateau in the extraction of Cd(II) was obtained. Due to this behavior, the pH value of 7.6 was selected as the working value for the following experiments.

The effects of different buffers on the extraction efficiency were tested. The most enhanced fluorescent emission and shortest separation time was obtained with buffer Tris. The system was studied within Tris concentration range 5×10^{-3} to 4×10^{-2} mol L⁻¹. The best performance, highest extraction percentage, optimal stability, lowest equilibration time and easiest phase separation, was achieved for a Tris concentration of 1.1×10^{-2} mol L⁻¹.

The addition of NaClO₄ neither showed any benefic effect on the extraction efficiency, nor an improvement in phases separation, with the consequent loss of sensitivity, similarly to other studied systems [28]. Thus, this electrolyte was not used in the subsequent assays.

The concentration effect of the chelating reagent *o*-phen and the dye eo on the extraction of cadmium were subsequently studied and the results are presented in Figs. 3 and 4, respectively. As can be seen, the excess of *o*-phen and/or eo probably acts as inner filter effect, causing a severe attenuation of fluorescent emission. For this reason, an *o*-phen concentration of 8.3×10^{-7} mol L⁻¹ and eo of 1.6×10^{-7} mol L⁻¹ were chosen as optimal for following assays.

The surfactant type, the chemical structure of the reagents and the reaction mechanism are some of the parameters that control the enhancement factor. A successful CPE should maximize the extraction efficiency by minimization of the phase volume ratio.

TX-100 nonionic surfactant was tested as potential extractant agent. Two complications were presented: the first was the high cloud point temperature (above 340 K) necessary for the quantita-

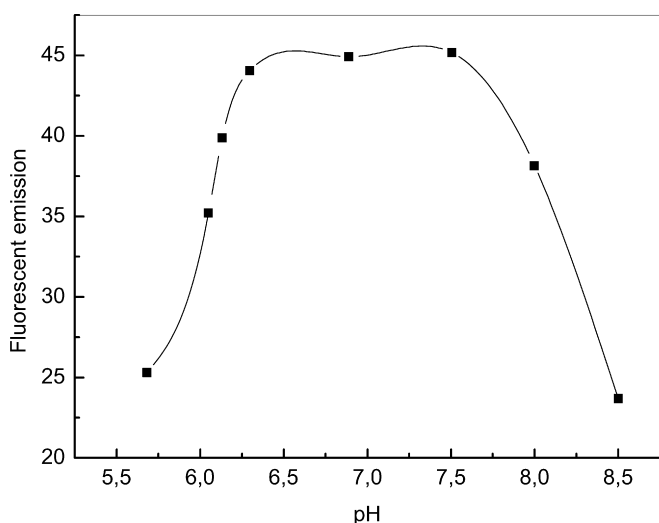


Fig. 2. Influence of pH on the extraction of cadmium association complex with *o*-phen and eo. Conditions: $1.7 \mu\text{g L}^{-1}$ Cd(II), 8.3×10^{-7} mol L⁻¹ *o*-phen, 1.6×10^{-7} mol L⁻¹ eo and $1.6 \times 10^{-3}\%$ (v/v) PONPE 7.5. Other experimental conditions are described under procedures.

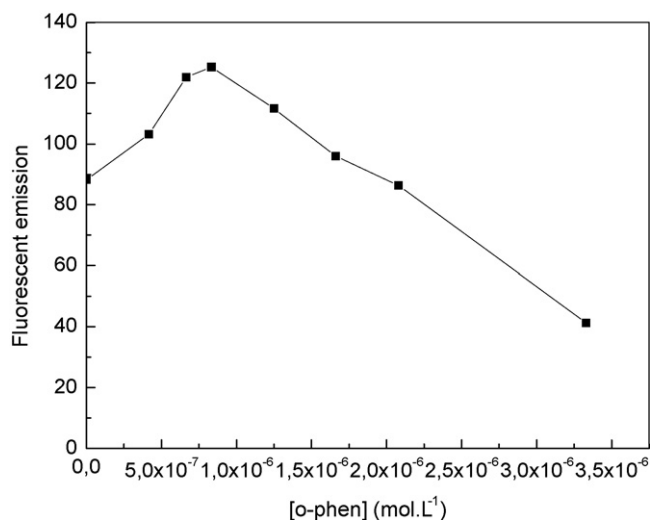


Fig. 3. Effect of *o*-phenanthroline concentration on the extraction of cadmium. Conditions: $1.7 \mu\text{g L}^{-1}$ Cd(II), 1.6×10^{-7} mol L⁻¹ eo, pH 7.6 buffer Tris and $1.6 \times 10^{-3}\%$ (v/v) PONPE 7.5. Other experimental conditions are described under procedures.

tive complex extraction. This fact involves the risk of decomposition of organic reagents. The second complication was with respect to the spectral interference caused by the broad fluorescent signal of TX-100 present in high concentration in the surfactant-rich phase. Other experimental difficulty to overcome when working with extracting agents of high cloud point temperature is the consequent loss of extraction efficiency during the centrifugation step by decrease of the temperature of the system.

When working with nonionic surfactant PONPE 7.5, extraction efficiency higher than 99.9% was obtained using a single-step extraction. The cloud point of the studied system with this surfactant was near room temperature, offering experimental advantages, and being especially adequate for metallic complexes and organic species extracting [29–31]. It is also desirable to employ the shortest equilibration time and the lowest equilibration temperature, which compromise the completion of reaction and efficient separation of the phases. The phase volume ratio decreases as the equilibration temperature increases.

The greatest analyte preconcentration factors can be obtained when the CPE is conducted at the temperatures well above the

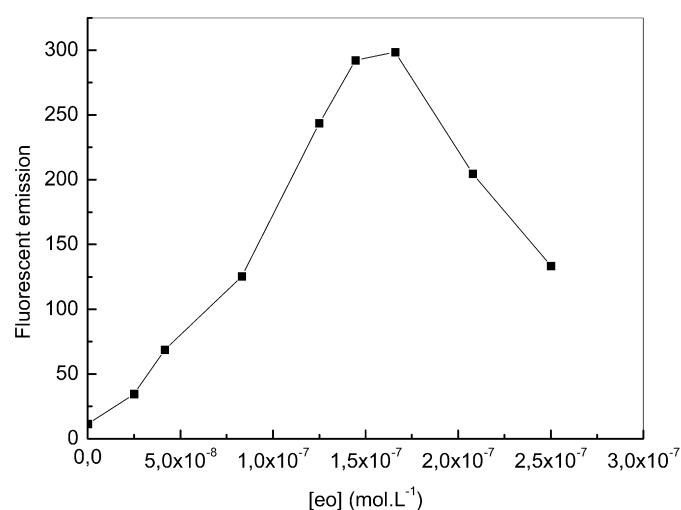


Fig. 4. Effect of eosin concentration on the extraction of cadmium. Conditions: $1.7 \mu\text{g L}^{-1}$ Cd(II), 8.3×10^{-7} mol L⁻¹ *o*-phen, pH 7.6 buffer Tris and $1.6 \times 10^{-3}\%$ (v/v) PONPE 7.5. Other experimental conditions are described under procedures.

Table 1

Analytical methodologies applied to cadmium traces determination present in water samples after CPE.

Instrumental methodology	Experimental details	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	LOL ($\mu\text{g L}^{-1}$)	RSD% ^a	Reference
FAAS	DDTP in an acidic medium using Triton X-114	0.9	2.9	3–400	–	[12]
FAAS	DTZ using Triton X-114. Diluent agent THF	0.31	–	1–100	2.4 (10.0)	[13]
FAAS	TAN using TX-114; pH 8.6	0.099	–	0.099–50	3.1	[17]
CV-AAS	PONPE 7.5 without adding chelating agent	0.56×10^{-3}	–	4×10^{-3} to 0.1	3.2 (0.02)	[35]
TS-FF-AAS	APDC solution and a Triton X-114	0.04	–	0.1–5	2.9 (1.0)	[36]
ETAAS	5-Br-PADAP	0.008	0.027	Close to LOD–1	3.5 (0.2)	[37]
ETAAS	GBHA in NaOH-Borax buffer and Triton X-114 SDS/NaCl	0.007	–	0.02–0.4	2.3 (0.2)	[38]
Mol. Fluorescence	<i>o</i> -phen; eo and PONPE 7.5	0.84×10^{-3}	2.79×10^{-3}	2.80×10^{-3} to 2.80	1.17 (0.84)	This work

FAAS: Flame atomic absorption spectroscopy; CV-AAS: cold vapor-atomic absorption spectroscopy; TS-FF-AAS: thermospray flame furnace atomic absorption spectroscopy; ETAAS: electrothermal atomic absorption spectroscopy. DDTP: diethyldithiocarbamate; DTZ: ditione; TAN: 1-(2-thiazolylazo)-2-naphthol; THF: tetrahydrofuran; APDC: ammonium pyrrolidinedithiocarbamate; 5-Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol; GBHA: glyoxal-bis (2-hydroxyanil).

^a Level of Cd(II) ($\mu\text{g L}^{-1}$) for which the RSD% was calculated.

cloud point temperature of the surfactant [30]. An equilibration time up to 10 min has been suggested as sufficient for the completion of the physicochemical process and quantitative extraction of the organic species into micellar aggregations [13,32,33]. The dependence of extraction efficiency upon equilibration time was studied within a range of 5–30 min and temperature range of 293–323 K. It was found that the equilibration time affects scarcely the extraction efficiency. Furthermore, this parameter was kept in 15 min in all cases. Employing temperatures above 318 K the fluorescence intensity decreases, which indicates that decomposition of complex had initiated. So, a temperature of 313 K was chosen as optimal.

In general, centrifugation time hardly affects micelle formation but accelerates phase separation, in the same sense as in conventional separations of a precipitate from its original aqueous environment. The effect of centrifugation time upon extraction efficiency was studied for the range: 1–20 min. The complete phase separation was achieved for times longer than 3 min. Centrifugation times of 5 min were chosen as optimal, with good efficiency for separating both phases and experimental convenience.

Although the very high viscosity of the surfactant-rich phase (20 cP approximately) loaded on the bottom of the centrifuge tube, facilitate the phase separation; the manipulation for measuring step is complicated. Besides, the small volume of this phase after centrifuging was insufficient to allow the fluorescence measurement, being necessary an adequate dilution. Different solvents for diluting the surfactant-rich phase were tried so as to select the one producing the optimal results regarding sensitivity and decreasing the viscosity. The best results were achieved with ethanol/buffer Tris mixture, permitting its appropriate manipulation for the fluorescence measurement.

4. Analytical parameters

4.1. Calibration parameters

Calibration curve for Cd(II) concentration range between $2.79 \times 10^{-3} \mu\text{g L}^{-1}$ and $2.81 \mu\text{g L}^{-1}$ was attempted. Table 1 summarizes the main characteristics of the calibration plot and experimental conditions, which support the validation of the proposed methodology for quantifying Cd(II); likewise, other analytical published methodologies for trace cadmium determination in water samples after CPE, have been included.

The limits of detection (LOD) and quantification (LOQ) were calculated in accordance to the formulas given by the official compendia methods [34], using the relation $k(\text{SD})/m$ where $k=3$ for LOD and 10 for LOQ. SD is the standard deviation from 15 responses of blank replicates and m is the slope of the calibration curve.

Table 2Tolerance limits of interfering species in the determination of $1.70 \mu\text{g L}^{-1}$ of Cd(II).

Interferent/Cd(II) mole ratio	Interferent specie
10000:1	Li^+ , Na^+ , K^+ , Cl^-
1000:1	Ca^{2+} , Mg^{2+} , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , CO_3^{2-} , SO_4^{2-}
100:1	Fe^{2+} , Ba^{2+} , Sr^{2+} , Zn^{2+} , Cu^{2+} , Cr^{3+} , Bi^{3+} , PO_4^{3-}

4.2. Interferences study

The effect of foreign ions on the recovery of Cd(II) was tested. Different amounts of common cations in water samples were added to the test solution containing $1.70 \mu\text{g L}^{-1}$ of Cd(II) and the developed methodology was applied. An ion was considered as interferent, when it caused a variation in the fluorescent signal

Table 3

Recovery study in drinking water samples.

Sample	Cd(II) added ($\mu\text{g L}^{-1}$)	Cd(II) found ($\mu\text{g L}^{-1}$)	Recovery (%; $n=6$)
1	–	0.47 ± 0.02	–
	0.55	1.02 ± 0.07	100.00
	1.10	1.58 ± 0.06	100.90
	2.25	2.74 ± 0.09	100.88
2	–	0.68 ± 0.06	–
	1.10	1.80 ± 0.22	101.82
	1.70	2.41 ± 0.30	101.76
	2.25	2.99 ± 0.10	102.66
3	–	1.40 ± 0.07	–
	2.25	3.66 ± 0.08	100.44
	3.35	4.75 ± 0.15	100.00
	4.50	5.99 ± 0.03	102.00
4	–	0.87 ± 0.04	–
	0.55	1.42 ± 0.04	100.00
	1.10	2.01 ± 0.04	103.63
	3.35	4.37 ± 0.20	104.47
5	–	1.45 ± 0.03	–
	1.10	2.55 ± 0.02	100.45
	1.70	3.19 ± 0.08	102.64
	3.35	4.82 ± 0.05	100.74
6	–	0.92 ± 0.02	–
	1.10	2.55 ± 0.07	99.08
	2.25	3.19 ± 0.05	100.00
	3.35	4.82 ± 0.04	102.08
7	–	0.84 ± 0.04	–
	0.55	1.40 ± 0.02	101.81
	1.10	1.98 ± 0.06	103.63
	4.50	5.29 ± 0.07	100.00

1: Comercial bottled mineral water manufactured in Mendoza (Argentina). 2: Comercial bottled mineral water manufactured in San Luis (Argentina). 3: Tap water (Campus Universidad Nacional de San Luis). 4: Water well (Potrero de Funes). 5: Tap water (Potrero de Funes). 6: Water well (Leandro N. Alem). 7: Tap water (San Luis city).

of the sample greater than $\pm 5\%$. The tolerance limits of various foreign ions are given in Table 2. These results demonstrated that large excess amounts of some common cations and anions did not interfere on the determination of trace level of Cd(II). The cations Co(II), Pb(II) and Al(III) interfered in the determination when they were presented in a ratio of 1:1 (foreign ion/Cd(II)); if this was the case, some additional separation step must be included to solve this problem [39–42].

Phosphate specie interferes seriously in the Cd(II) determination; Ca(II) excess was employed as masking to resolve this interference.

4.3. Applications

In order to study the usefulness of the proposed methodology, it was applied to the determination of Cd(II) in different types of drinking water samples: commercial bottled mineral water, tap water and **water well. The accuracy of the methodology was performed using the standard addition method. 5 mL sample aliquots were spiked with increasing amounts of Cd(II) ($0.55\text{--}4.50\ \mu\text{g L}^{-1}$). The reproducibility of the method was evaluated repeating the proposed methodology, six times for each sample. The recoveries of Cd(II) in each type of sample based on the average of replicate of measurements are illustrated in Table 3; the obtained results show that the proposed method is suitable for determination of Cd(II) in such water samples.

5. Conclusions

Although atomic spectroscopies are the most important techniques for metal trace analysis, they require specialized and very expensive instruments. The increasing importance of cadmium and its toxicity in environmental health has demanded the development of simple and rapid analytical methods for its determination. The proposed method represents a promising approach in the area of environmental monitoring with low operation cost, simplicity of instrumentation and non-polluting solvents. The method was validated with real samples with good tolerance to regular foreign water constituents.

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