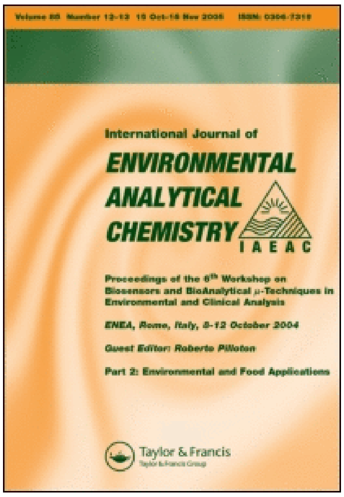

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Micelle mediated extraction of cadmium from water and tobacco samples with glyoxal-bis(2-hydroxyanil) and determination by electrothermal atomic absorption spectrometry

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Micelle mediated extraction of cadmium from water and tobacco samples with glyoxal-bis(2-hydroxyanil) and determination by electrothermal atomic absorption spectrometry

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The purpose of this article is to combine cloud point extraction (CPE) with electrothermal atomic absorption spectrometry (ETAAS) for determining cadmium in water and tobacco samples. This developed method is based on the colour reaction of cadmium with glyoxal-bis (2-hydroxyanil) (GBHA) in sodium hydroxide-sodium tetraborate buffer media and mixed micelle-mediated extraction of complex. The cadmium was extracted as Cd-GBHA complex, at pH 12.4 ± 0.2 mediated by micelles of the non-ionic surfactant Triton X-114 and anionic SDS. The incubation step is not necessary for the separation of the phases. The phase separation was observed at room temperature using TX-114/SDS/NaCl system. The optimal micellar extraction and reaction conditions (e.g., surfactant concentration, reagent concentration, effect of time) were studied and the analytical characteristics of the method (e.g., limit of detection, linear range and preconcentration factor) were obtained. Linearity was obeyed in the range of 0.02 to $0.4\,\mu\mathrm{g\,L^{-1}}$ of cadmium ion and the detection limit of Cd with ETAAS was $7\,\mathrm{ng\,L^{-1}}$. After optimising extraction conditions, a preconcentration factor of 22 was obtained for a sample of only 10 mL and the relative standard deviation ($n = 5$; $C = 0.2\,\mu\mathrm{g\,L^{-1}}$) was 2.3%. The interference effect of some anions and cations was also tested. The method was applied to the determination of Cd in tap (after standard addition), lake, seawater and tobacco samples, and validated by analysis of a geological sample.

Keywords: cadmium; cloud point extraction; preconcentration; electrothermal atomic absorption spectrometry; glyoxal bis(2-hydroxyanil); water analysis

1. Introduction

Cadmium is one of the most important heavy metal pollutants and has caused a major environmental catastrophe in history, the 'itai-itai' disease. Its wide technological uses in fertilizers, mining and pigments, and its emission from oil and coal burning and residue incineration, result in substantial anthropogenic contamination of the environment such as air, soil and water. Cadmium is known to be highly toxic for animals, plants and humans even at low concentrations and can be accumulated in several organs [1]. Therefore, the development of a sensitive and simple method for the determination of trace cadmium in

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environmental samples is significant. In the past few years, a number of techniques have been applied to the determination of Cd, including flame absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma-atomic optical emission spectrometry (ICP-OES), atomic fluorescence spectrometry (AFS), and cold vapour atomic absorption spectrometry (CVAAS) have been reviewed [2].

However, the low level of cadmium in water samples is not compatible with the detection limit of ETAAS. Thus, separation and preconcentration steps are frequently required in order to improve the detection capability of this technique. Such preconcentration techniques have been used for In prior to GF-AAS [3] or for Co and Ni prior to FAAS [4] determinations for effective separation of analytes from interferent matrices. Separation and preconcentration techniques including solvent extraction (SE), solid phase extraction (SPE) and cloud point extraction (CPE) have been used for determination of Cd [2]. Separation and preconcentration based on cloud-point extraction (CPE) is becoming an important and practical application in the use of surfactants in analytical chemistry [5,6] because it does not require toxic organic solvents as used in SE. Many cloud point extraction procedures for cadmium determination have been developed, involving different kinds of analytical techniques and several chelating agents such as 1-(2-thiazolylazo)-2-naphthol (TAN) [7], dithizone (Dz) [8,9], O,O-diethyldithiophosphate (DDTP) [10–15], iodide [16], ammonium pyrrolidinedithiocarbamate (APDC) [17], 2-(5-brom-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP) [18], 1-(2-pyridylazo)-2-naphthol (PAN) [19], diethyldithiocarbamate (DDTC) [20], 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone [21], 8-hydroxyquinoline [22], capric acid/n-octylamine [23], 2-(2-thiazolylazo)-p-cresol (TAC) [24], and 2-[2′-(6-methyl-benzothiazolylazo)]-4-bromophenol (Me-BTABr) [4] have been used to determine and preconcentrate traces of cadmium from various samples. Most Cd-chelating ligands were of thiol-type, in accord with the theory of Hard and Soft Acids and Bases (HSAB). Additionally, cadmium was extracted efficiently without a complexing agent, using a non-ionic surfactant such as poly-oxyethylene-nonyl-phenyl-ether (PONPE 7.5) [25]. Giokas *et al.* developed a comparative application of CPE and low-temperature directed crystallisation (LTDC) in the analysis for trace elements in natural waters [26]. A comparison of the analytical features (specifically LOD) of the developed method with those of previously published spectrometric methods for Cd determination is given in Table 1.

The concentration of Cd in water samples is too low for direct determination. Therefore, a preconcentration step is necessary to bring the sample to the detectable limits of the existing instrumental method. To carry out the separation and preconcentration of the analyte, a mixed micelle-mediated extraction (mixed-MME) system was used in this study. MME is becoming an important and practical application of the use of surfactants in analytical chemistry [27] in accord with ‘green chemistry’ principles. The use of cationic or anionic surfactants in combination with non-ionic surfactant has been documented with an increase in the extraction efficiency of polar organic compounds [28,29]. In the present work we report the results obtained in a study of the cloud point preconcentration and separation of cadmium, after the formation of a complex with glyoxal-bis (2-hydroxyanil) (GBHA), and subsequent analysis by electrothermal atomic absorption spectrometry using Triton X-114/SDS mixture as surfactant. The use of GBHA in the spectrofluorometric estimation of cadmium was originally reported in reference [30].

Table 1. Comparison of the results of the published methods for the determination of Cd (in terms of LOD).

Reagent	Surfactant	Method	LOD (ng L^{-1})	Reference
1-(2-thiazolylazo)-2-naphthol (TAN)	TX-114	FAAS	99	7
Dithizone (Dz)	TX-114	FAAS	310	8
Dithizone (Dz)	TX-114	ICP-OES	LOQ:93	9
O,O-diethyl dithiophosphate (DDTP)	TX-114	FAAS	NR	10
DDTP	TX-114	ETAAS	6	11
DDTP	TX-114	FAAS	900	12
DDTP	TX-114	ETAAS	20	13
DDTP	TX-114	FAAS	620	14
DDTP	TX-114	GFAAS	2	15
Iodide	TX-114	FAAS	1000	16
Amonioum Pyrrolidinedithiocarbamate (APDC)	TX-114	TS-FAAS	40	17
2-(5-brom-2-pyridylazo)-5-(diethylamino)-phenol(5-Br-PADAP)	TX-114	GFAAS	40	18
1-(2-pyridylazo)-2-naphthol (PAN)	TX-114	GFAAS	5.9	19
Diethyldithiocarbamate (DDTC)	TX-114	GFAAS	2	20
1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP)	TX-114	FAAS	640	21
8-Hydroxyquinoline	TX-114	FAAS	150	22
Capric acid and n-octylamine	OP 10	FAAS	NR	23
2-(2-thiazolylazo)-p-cresol (TAC)	TX-114	SIMAAS	77	24
Without chelating agent	PONPE 7.5	CV-AAS	0.56	25
Low-temperature directed crystallization (LTDC)	TX-114	FAAS ICP-AES	NR NR	26
Glyoxal-bis (2-hydroxyanil) (GBHA)	TX-114 + SDS	ETAAS	20	This work

Notes: NR: Not reported; LOD: Limit of detection; LOQ: Limit of quantification.

The extraction was carried out at room temperature. The Cd chelate was trapped inside the micelles formed in a mixed surfactant medium consisting of an anionic sodium dodecyl sulfonate (SDS) and a non-ionic (Triton X-114) surfactant. The developed extraction method can be applied successfully to the CPE determination of cadmium in lake water, seawater and tobacco samples.

2. Experimental

2.1 *Apparatus*

Spectrophotometric studies were performed on a Cary-1E UV-visible spectrophotometer. The absorption spectrum or the absorbance of the complex at 569 nm was recorded in a 1 cm quartz cell. The measurements for cadmium determination were performed with a Perkin Elmer 600 atomic absorption spectrometer equipped with a Zeeman background corrector, an AAnalyst 600-electrothermal atomizer and an AS-800 autosampler. Wall atomization with standard high-density graphite tubes was used. A cadmium hollow-cathode lamp was employed as radiation source. The hollow cathode lamp for Cd

(Perkin Elmer) was operated at 4 mA, with a spectral bandwidth of 0.7 nm. The selected analytical wavelength was 228.8 nm for Cd. Aliquots of 20 µL for all sample and calibration solutions were injected directly into the graphite tube. The graphite furnace temperature programme for analyte is shown in Table 2.

2.2 *Reagents*

All chemicals used were of analytical reagent grade, and supplied from E. Merck (Darmstadt), unless otherwise stated; de-ionised distilled water was used for the preparation of all solutions. A stock standard solution of cadmium (1.0×10^{-3} mol L^{-1}) was prepared by dissolving $CdCl_2 \cdot 2H_2O$ in 100 mL of 0.1 mol L^{-1} HCl. Further dilutions with distilled water were made for appropriate concentrations. The colour developing solution (borax buffer) was prepared by dissolving 2.0 g NaOH and 2.0 g $Na_2B_4O_7 \cdot 10\ H_2O$ in 100 mL distilled water ($pH = 12.4 \pm 0.2$). The stock colour reagent of GBHA solution was prepared by dissolving 0.15 g of the reagent in 50 mL of ethanol. A 1% (w/v) solution of SDS (anionic surfactant) was prepared in distilled water. Sodium chloride was used for promoting phase separation.

2.3 *Sample preparation*

Lake water samples were collected from around the coastal area of Istanbul (Turkey). The water samples were stored in 500-mL polypropylene bottles in a refrigerator and filtered through a 0.45-mm pore size membrane filter. The water samples were also analysed. Tobacco samples were also acquired from a local market. Triplicate samples of about 0.5 g were weighed and digestion was carried out using concentrated sulfuric acid (0.1 mL) and perchloric acid (5.0 mL). After digestion, the samples were heated on a hot plate to near dryness, filtered through quantitative filter paper and diluted to 50 mL with deionised water. An aliquot (3 mL) of this analyte was taken and assayed according to the recommended procedure.

The proposed method was applied to the determination of total cadmium in a reference geological sample (IAEA-405). The wet digest of the sample was made in the following manner: the geological sample was dried at 105°C and powdered. A 1.0 g of powdered geological sample was treated in a PTFE beaker with 10 mL concentrated nitric acid, and heated in a sand bath (120°C) for the oxidation of organic substances and the solution was carefully evaporated to dense white fumes to drive off the nitrogen oxides and then cooled. It was treated with 10 mL of the mixture containing concentrated HF and $HClO_4$ acids

Table 2. Operating conditions for ETAAS.

Stage	Temperature (°C)	Ramp/s	Hold/s	Ar Flow rate (mL min^{-1})
Drying I	110	5	10	250
Drying II	130	15	20	250
Pyrolysis	1300	10	10	250
Atomisation	2350	0	3	0
Cleaning	2500	1	5	250

(1 : 1, v/v), and heated in a sand bath until dryness. The residue was then treated with 10 mL 1 M HCl, under gentle warming to achieve complete dissolution. The volume was made up to 50 mL with distilled water, and this solution was used in the preconcentration step. In a suitable aliquot of this solution, where the pH was adjusted to ~3.0 by adding aqueous ammonia solution by drop (if needed), iron was precipitated in the conventional manner as ferric hydroxide $Fe(OH)_3$. After settling, $Fe(OH)_3$ could be separated from Cd (without letting the amorphous precipitate to mature in the mother solution), and the total Cd was determined by the recommended procedure.

2.4 *Recommended procedure*

For the cloud point extraction, aliquots of 10 mL of a solution containing the analyte, 1 mL of 4% (w/v) TX-114, 0.5 mL of 1% (w/v) SDS and 0.5 mL of 0.3% (w/v) GBHA as complexing reagent was adjusted to the appropriate pH value ($pH = 12.4 \pm 0.2$) with borax buffer solution. The colour did not develop instantaneously at room temperature, and after leaving for 5 min, an almost constant absorbance was obtained. To this, 0.5 mL of 20% NaCl solution was added, and the final volume was completed to the mark with distilled water. The order of addition of reagents is important. Separation of the phases was achieved by centrifugation for 5 min at 3500 rpm. On cooling in a freezer (5 min), the surfactant-rich phase became viscous. Then, the aqueous phase was removed. The remaining micellar phase was diluted with ethanol (~0.5 mL) until a final volume of 1 mL was reached. Finally, the absorbance of the resulting solution was measured at $\lambda = 569$ nm against reagent blank. A calibration curve for spectrophotometric determination was prepared in the concentration range of 4×10^{-6}–1.4×10^{-5} M of Cd.

For the ETAAS method, in order to decrease the viscosity and facilitate sample handling prior to the assay, 0.3 mL of an acidified ethanol solution containing 0.1 mol L^{-1} HNO_3 was added to the surfactant rich phase. The acidified ethanolic aqueous samples were introduced into the graphite furnace by autosampler.

3. Results and discussion

Since the proposed procedure involves the formation of a metal-ligand chelate and its micellar extraction using a surfactant, the critical parameters like ligand and surfactant concentration combined with pH were optimised with the aid of spectrophotometry, as practiced in other work concerning extractive preconcentration prior to atomic spectrometric determination [31]. Thus the concentrations of the analyte (Cd) used in parametric optimisation were naturally higher than those analysed by GF-AAS after micellar extraction.

3.1 *Effect of pH*

The pH was the first parameter examined for its effect on the micellar extraction of cadmium. The complex forming reaction between Cd (1×10^{-5} mol L^{-1}) and GBHA is pH dependent. The results illustrated in Figure 1 reveal that at pH ~ 12.0 maximum extraction efficiency was attained. Cd was completely extracted with GBHA in the surfactant rich phase at pH 12.4 ± 0.2. This value was therefore selected as the working pH. At lower pH values, formation of complexes is not quantitative due to protonation of phenolic-OH

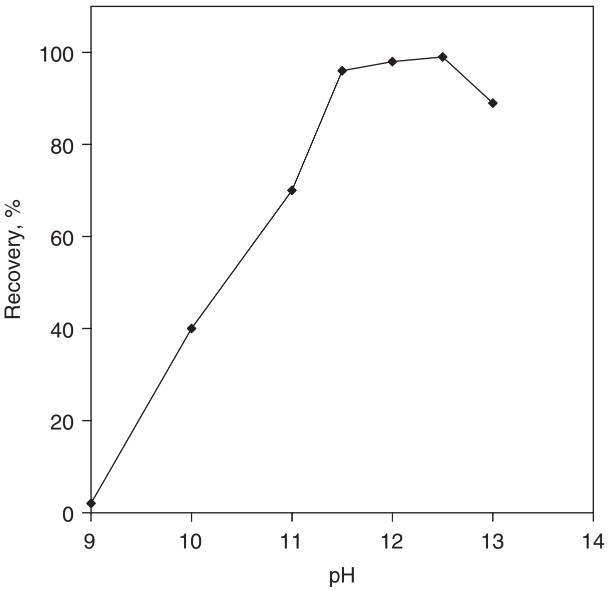

Figure 1. The extractability of Cd-GBHA with TX-114/SDS mixture as a fuction of pH. ('Recovery, %' is the percentage of stabilised maximal absorbance at a given concentration of the coloured chelate).

groups of the ligand [30], and at higher pH values, hydrolysis of the Cd-complex occurs. Figure 1 shows the effect of pH on the micellar extraction of cadmium complex.

3.2 *Effect of GBHA concentration*

Effect of GBHA concentration on the CPE yield of cadmium was investigated in the range 0.01–0.03% (w/v). Different excesses of GBHA were added to fixed Cd ($1 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) concentration and absorbance was measured according to the general procedure. The absorbance for the sample increased by increasing GBHA concentration up to 0.015% and remained nearly constant at higher concentrations. As shown in Figure 2, the highest molecular absorbance due to the extracted Cd-ligand complex was obtained at 0.015% (w/v) GBHA concentration. Thus, a concentration of 0.015% (w/v) of GBHA was chosen as optimum.

3.3 *Effect of diluent*

High viscosity of the surfactant-rich phase is drastically decreased using diluting agents. For measurements of the absorption spectra, the surfactant rich phase was diluted with ethanol (~0.5 mL). For the ETAAS method, the addition of a diluent into a surfactant-rich phase is often needed to obtain a homogeneous solution with compatible viscosity to attain a good sample introduction into the graphite furnace. The condensed surfactant phase is introduced into the graphite furnace by autosampler after its treatment with an acidified alcoholic solution. Hence 0.3 mL of ethanol and 0.1 mL of $1\,\mathrm{mol\,L^{-1}}$ HNO_3 were added to 0.15 mL of the surfactant rich-phase.

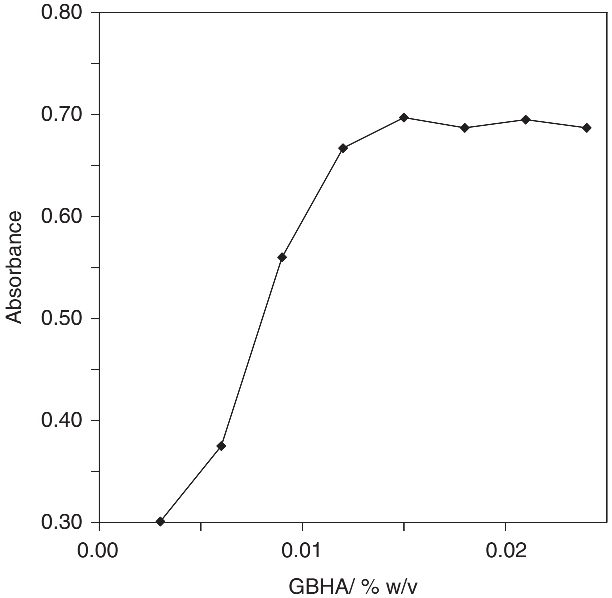

Figure 2. Influence of GBHA concentration on CPE ($[Cd] = 1.0 \times 10^{-5}$ M).

3.4 *Effect of surfactant concentration*

In this work, a surfactant mixture of TX-114/SDS was selected for the formation of the surfactant-rich phase because of its very low cloud temperature which facilitates phase separation at normal temperature. When the cloud point was lower than room temperature, the solution was directly centrifuged, and the phase ratio determined. Mixed micelle formation depends on the anionic and nonionic surfactant concentrations. Therefore, the variation of the Cd extraction efficiency was studied within the TX-114 and SDS concentration range from 0.1–1% (w/v). A combination of 0.4% TX-114 and 0.1% SDS was chosen in order to achieve quantitative extraction (Figure 3). The analyte recoveries were almost quantitative even by using single-step extraction. The use of a mixed micellar extractant for CPE/preconcentration of Cd to provide low temperatures of separation was also an improvement introduced by this method.

3.5 *Preconcentration factor*

The theoretical preconcentration factor was ~67, as the original volume was 10 mL and final volume was 0.15 mL of the surfactant-rich phase. Because of dilution of surfactant-rich phase (final vol = 0.45 mL), the experimental preconcentration factor was found to be 22-fold for the ETAAS determination.

3.6 *Effect of NaCl*

To reduce the cloud point to room temperature, the addition of both electrolyte and an anionic surfactant was necessary. In this work, the addition of high concentrations of

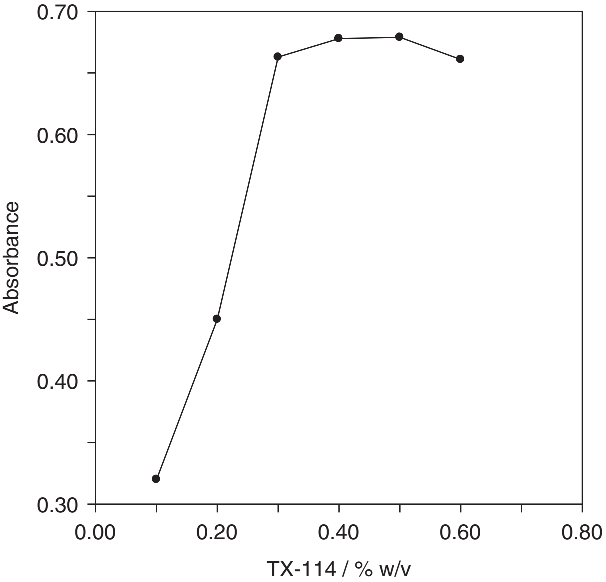

Figure 3. Influence of TX-114 concentration on CPE in the presence of 0.1% SDS; $[Cd] = 1.0 \times 10^{-5}$ M.

NaCl to the TX-114/SDS system drastically reduces the cloud point, thus allowing phase separation at room temperature. A NaCl concentration of $1\,mol\,L^{-1}$ was selected as optimum to induce phase separation and improve extraction efficiency. When small amounts of inorganic salts were added to the system, a decrease in the cloud point was noted. The presence of a high concentration of NaCl not only induced phase separation in the mixed micellar system at ambient temperature [12,32] but also ensured the analysis capability of seawater samples. The lower cloud point achieved with NaCl is attributed to the effect of electrolytes to promote dehydration of polyoxyethylene chains and to increasing interattraction between micelles as a result of salting-out effects [12]. NaCl may be considered to reduce the repulsive forces between anionic micelles, thereby enabling the achievement of higher phase ratios (i.e., concentrating the surfactant-rich phase in a smaller volume [32].

3.7 *Other conditions*

Several other conditions which could affect the efficiency of the CPE procedure, for example, equilibration and centrifugation time for CPE, were subsequently investigated. The equilibration achieved at a temperature of 25°C is adequate for Cd analysis. This method does not require the use of heat. The centrifugation time influences the phase separation step directly. The effect of centrifugation time upon extraction efficiency was studied for the range: 1–10 min. A centrifugation time of 5 min was selected for the entire procedure, since analyte extraction during this time period is almost quantitative. The results obtained were chosen as the optimal because they yielded the greatest precision. All other CPE variables and their optimal values are listed in Table 3.

Table 3. Optimisation of cloud point extraction variables.

Variable	Working range	Selected value
GBHA (% w/v)	0.01–0.03	0.015
Triton X-114 (% w/v)	0.1–1	0.4
SDS (% w/v)	0.1–1	0.1
NaCl concentration (%)	1–4	1
Centrifugation time (min)	2–10	5
Incubation temperature (°C)	15–30	25
Cooling time (min)	3–10	5

3.8 *Precision and accuracy of the proposed method*

The method was applied to the determination of total cadmium in a reference geological sample (IAEA-405) for investigating the accuracy and precision of the proposed assay. The reference material was collected in 1998 from the intertidal mudflats of the Tagun estuary (Portugal). The certified concentration of cadmium of the standard geological sample is $0.73 \pm 0.05\,\mathrm{mg\,kg^{-1}}$. Three determinations on the reference geological sample yielded a mean Cd value of 0.78 ± 0.08 and $0.70 \pm 0.05\,\mathrm{mg\,kg^{-1}}$ for the spectrophotometric and ETAAS methods, respectively. Statistical evaluation of these results revealed the 'null hypothesis' stating that the means and variances of these two sample populations were alike were accepted at 98% and 95% confidence levels, respectively. Thus, these results are in agreement with the certified value.

3.9 *Interferences*

In order to test the selectivity of the method, solutions containing cadmium ($0.05\,\mathrm{\mu g\,L^{-1}}$) and other ions were prepared and analysed by the proposed procedure. The effects of representative potential interfering species were tested. The results (Table 4) proved that cadmium recoveries were almost quantitative in the presence of excessive amount of potentially interfering cations. The optimal pH was high enough to favour the formation of extractable Cd-ligand complex while preventing the recovery of most other metal ions by precipitation removal. The tolerance limits of various foreign ions resulted in a relative error of less than ±6%, and are shown in Table 4.

3.10 *Figures of merit*

A calibration graph was obtained by pre-concentrating 10 mL of a sample containing known amounts of analyte under experimental conditions. The graph was constructed in the usual way according to the recommended procedure. The regression equation for spectrophotometry was reasonably linear, and can be expressed by the following equation: $A_{569} = 0.65 \times 10^5\,\mathrm{C}\ (\mathrm{mol\,L^{-1}}) + 0.03\ (r = 0.9982)$ where A is the absorbance at 569 nm and C is the molar concentration of Cd in the final solution. The absorbance was linear for $4 \times 10^{-6} - 1.4 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ of Cd. The limit of detection (LOD) achieved for Cd with spectrophotometry, estimated by $3s_B/m$, was $16\,\mathrm{\mu g\,L^{-1}}$ and the RSD was 4.3% ($n = 5$; $C = 1 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$).

Table 4. Effect of foreign ions on the preconcentration and determination of Cd (50 ng L^{-1}) ($n = 3$).

Foreign ions	Concentration (μg L^{-1})	Recovery (%)
Mn^{2+}	200	99
Cu^{2+}	50	101
Co^{2+}	50	101
Ni^{2+}	50	97
Zn^{2+}	200	99
Mg^{2+}	200	99
Sr^{2+}	100	101
Al^{3+}	100	97
Ba^{2+}	200	100
Ca^{2+}	200	97
PO_4^{3-}	200	98
SO_4^{2-}	750	99

Table 5. Figures of merit of two different assays using cloud point extraction for Cd preconcentration.

	Spectrophotometry	ETAAS
λ (nm)	569	228.8
Linear range (μg L^{-1})	448–1568	0.02–0.4
LOD (μg L^{-1})	16	0.007
Equation	$Y = 0.65 \times 10^5\ C^a + 0.03$	$Y = 0.042\ C^b + 0.006$
RSD (%)	4.3	2.3
R	0.9982	0.9990

Notes: ^{a} mol L^{-1}; ^{b} μg L^{-1}.

For the ETAAS method, under selected conditions the calibration curve was rectilinear with a dynamic range from 0.02 to 0.4 μg L^{-1} for Cd determination by ETAAS. Since the seawater concentration of Cd is around 0.05 μg L^{-1} [33], Cd determinations in seawater can be performed with this method. The regression equation was $A = 0.042\,C$ (μg L^{-1}) + 0.006. The correlation coefficient was 0.9995. Preconcentration of only 10 mL of the sample in the presence of 0.4% TX-114 and 0.1% SDS permitted the detection of 7 ng L^{-1} of Cd, and the RSD was 2.3% ($n = 5$; $C = 0.2$ μg L^{-1}). Figures of merit of the two assays are shown in Table 5. It should be stressed here that spectrophotometry is not a competitively sensitive alternate procedure for ETAAS, but was only used for parametric optimisation.

3.11 *Application of the method*

The proposed method was applied to the determination of Cd in tap, lake and seawater samples collected from Istanbul, Turkey. Different tobacco samples were tested in the developed system. The water samples were analysed, and none was found to contain

Table 6. Analysis of Cd in spiked samples ($n = 5$).

Sample	Cd, ng L^{-1} Added	Found (ng L^{-1})	Recovery (%)
Tap water	–	Nd[a]	
	20	19.8 ± 0.2	98
	–	15 ± 1[b]	
Lake water	10	24.6 ± 0.4	96
	20	35.0 ± 0.3	100
	–	34 ± 0.4	
Seawater	10	44.0 ± 0.3	100
	20	53.8 ± 0.2	99

Notes: Nd: not detected; [a] Below the LOD, defined as three times the signal-to-noise ratio; [b] Value between LOD and LOQ, determined with lower precision

Table 7. Cadmium determination in tobacco samples ($n = 3$) by ETAAS.

Sample	Found (μg g^{-1})	Added (μg g^{-1})	Found (μg g^{-1})	Recovery (%)
Tobacco 1	0.250 ± 0.03	0.200	0.448	99
Tobacco 2	0.210 ± 0.02	0.200	0.411	101
Tobacco 3	0.150 ± 0.05	0.200	0.351	101

cadmium in tap water. The results in Table 6 show that the Cd spikes could be quantitatively recovered. The amount of spike plus originally contained Cd could be precisely found in seawater samples (Table 6). The method was used for the analysis of commercial tobacco samples. The tobacco samples contained Cd at a concentration detectable with the proposed technique. Table 7 shows the obtained results. In addition, recovery experiments for different amounts of Cd were carried out. Recoveries for Cd were found to lie in the range 95–101%, indicating that the method enables the determination of Cd in the analysed samples (Tables 6 and 7).

4. Conclusions

The use of micellar systems as an alternative to other techniques of separation and preconcentration offers several advantages including low cost, safety and high capacity to preconcentrate various elements with high recoveries and enrichment factors (EF). The results for this work demonstrate the possibility of using the Cd-GBHA/TX-114/SDS system for the preconcentration of cadmium, since the Cd-GBHA complex was quantitatively extracted, and an EF of 22-fold was obtained. Extraction and preconcentration of Cd using cloud point methodology was studied for the first time in highly alkaline solution at $pH \geq 12$, thereby enabling precipitation removal of possible interferent metal cations. The preconcentration method allows determination of ultra low levels of Cd by ETAAS. The significant advantages of this work comprise the low temperature (25°C) required for forming the two phases, and the capability to determine Cd even in seawater of very high salinity.

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