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Synthesis of Bis(amino alcohol)oxalamides and Their Usage for the Preconcentration of Trace Metals by Cloud Point Extraction

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C_2-Symmetric two bis(amino alcohol)oxalamides (diamidediols) were synthesized and fully characterized. A new method was developed and successfully applied for the simultaneous preconcentration of both trace and toxic metals in water, by using C_2-symmetric compounds. Under the optimum experimental conditions (*i.e.* pH = 10.0 ± 0.2, 2.75×10^{-3} mol L^{-1} *N*,*N*′-bis[(1*R*)-1-ethyl-2-hydroxyethyl]ethanediamide (DAD1), 1.75×10^{-3} mol L^{-1} *N*,*N*′-bis[(1*S*)-1-benzyl-2-hydroxyethyl]-ethanediamide (DAD2), 0.10% w/v octylphenoxy-polyethoxyethanol (Triton X-114)), calibration graphs were linear in the range of 2.5 – 25.0 ng mL^{-1} for Cu and Cd, 5.0 – 25.0 ng mL^{-1} for Co and Ni. The enrichment factors were 18, 23, 18 and 20 for Cd, Cu, Co and Ni in the case of DAD1, respectively; 20, 22, 17 and 20 for Cd, Cu, Co and Ni in the case of DAD2. The limits of detection for DAD1 were found to be 0.45, 0.50, 1.25 and 0.60 ng mL^{-1} for Cd, Cu, Co and Ni, respectively, and for DAD2 were found to be 0.44, 0.25, 0.60 and 1.55 ng mL^{-1} for Cd, Cu, Co and Ni, respectively. The developed method was applied to the determination of Cu, Cd, Co and Ni in water samples and certified reference materials with satisfactory results.

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Introduction

Trace elements are of the great importance for the health of living organism. Their concentration levels in biological materials and water samples are fairly low. It is only partially known how trace elements play their essential roles, but their close relation with enzyme systems is considered to be their main biological function. Many metallo-enzymes occur where the metal is incorporated in an enzyme molecule, contributing to the stability and/or the reactivity of the molecule. Trace elements also play a role in oxidation/reduction processes, and in the synthesis and stabilization of proteins and nucleic acids.[1,2]

Due to the low concentration of trace elements and interfering effects of the major components of the initial sample matrix, a preconcentration/separation technique is generally necessary prior to atomic absorption spectrometry. For this purpose, various analytical methods have been used, such as adsorption on activated carbon,[3,4] co-precipitation,[5,6] column extraction,[7,8] ion-selective electrode[9,10] liquid–liquid extraction (LLE),[11] and cloud-point extraction (CPE).[12–27]

Cloud-point extraction (CPE), employed in analytical chemistry to separate and preconcentrate organic compounds and metal ions, has been well reviewed.[28–30] As a green liquid–liquid extraction method, compared with the traditional organic liquid–liquid extraction, cloud-point methodology requires a very small amount of non-flammable and non-volatile surfactants that are benign to the environment. Aqueous solutions of non-ionic surfactants may separate in two phases in a narrow temperature range, called the cloud-point temperature. By using appropriate conditions, such as the temperature, pressure and pH, the solution containing the surfactant becomes turbid and separates into surfactant-rich phases (in a very small volume) and the remaining larger volume (bulk solution) into the diluted aqueous solution with the surfactant concentration, which is approximately equal to its critical micelle concentration (CMC). The hydrophobic analytes of the solution are extracted into the surfactant-rich phase. Since the volume of the surfactant in the rich phase is very small compared to the initial volume, a high enrichment factor can be obtained.[31] From an analytical point of view, one of the most important properties of these organized structures is their good capacity to solubilize solutes of different character and nature. These solutes may interact electrostatically, hydrophobically or *via* a combination of both effects.[32]

Most analytical chemists have been studying in the field of preconcentration and detection of trace metals. In these studies, organic compounds purchased from chemical production companies are used as complexation reagents. They include functional groups that can form strong complexes with metals. In recent literature, some ligands, such as ammonium pyrrolidinedithiocarbamate (APDC),[33] 1-(2-pyridylazo)-2-naphthol (PAN),[34] 1-(2-thiazolyazo)-2-naphthol (TAN),[35] *O*,*O*-diethyldithiophosphate (DDTP),[36] 2-amino-cyclopentene-1-dithiocarboxylic acid (ACDA),[37] diethyldithiocarbamate (DDTC),[38] 8-hydroxyquinoline (oxine),[39] dithizone,[40] and 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (Br-PADAP)[41] have been especially used for the preconcentration of different metals. The complexes form with ligands in individual pH values for one or two element with their active centers. The synthesized ligands in this study, having C_2-symmetry and complexation reactions of the C_2-symmetric compounds, were different from non-symmetric ones. We thought that the symmetry of the ligands might play an important role in multi-element preconcentration due to the formation of a chiral

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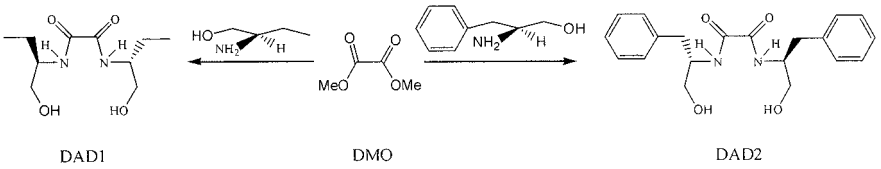

Fig. 1 Synthesis of diamidediols.

environment and the catalytic effect of the symmetric ligands to bond the metals. The synthesized ligands may behave as a tetradentate that is able to coordinate to a metal center through the hydroxyl and amido groups. The design and synthesis of new molecules able to act as chiral symmetric ligands in catalytic asymmetric reactions is one of the most important goals in modern organic chemistry.[42] The conformationally constrained metal chelate and the presence of stereocenters close to the nitrogen donor atoms assure a well-ordered chiral environment at the catalytic site.[43]

Here, we report the synthesis of two chiral bis(amino alcohol)oxalamides from aminoalcohols derived from natural aminoacids, and their application to the preconcentration of Cu, Cd, Co and Ni by using cloud-point extraction methodology prior to atomic-absorption determination. The Triton X-114 was found to be the best surfactant. The parameters, such as pH, concentration of ligands, concentration of surfactant, equilibration temperature and centrifugation time, affecting the complexation and phase separation were optimized.

Experimental

Reagents and chemicals

The non-ionic surfactant Triton X-114 (Sigma) was used without further purification. Stock standard solutions of Cu, Cd, Co and Ni at a concentration of 1000 μg mL^{-1} were prepared by dissolving their nitrate salts in 1.0 mol L^{-1} nitric acid. Working standard solutions were obtained by appropriate dilutions of the stock standard solutions; 2.75×10^{-3} mol L^{-1} solutions of diamidediols were prepared by dissolving appropriate amounts of these reagents in ethanol (Merck), and kept in a refrigerator (4°C) until use. Acetic acid, phosphoric acid and boric acid (0.04 mol L^{-1} each of weak acids) were used to prepare Britton–Robinson buffers by adding the required amount of sodium hydroxide. L-Phenylalanine, pyridine, (*R*)-2-amino-1-butanol and oxalyl chloride were purchased from Fluka and used without further purification.

All other reagents were of analytical reagent grade, and during all analytical work, double-distilled water was used. The pipettes and vessels used for the analysis were kept in dilute nitric acid at least over night, and subsequently washed with distilled water.

Apparatus

An ATI UNICAM Model 929 flame atomic absorption spectrophotometer (FAAS) equipped with ATI UNICAM hollow cathode lamps as radiation sources were used for the determinations of Cu, Cd, Co and Ni. The optimum conditions for AAS are given in Table 1. The pH of the solutions was measured with a Mettler Toledo pH meter. A thermostated bath maintained at the desired temperature in the experiments was used for cloud-point preconcentration experiments, and phase separation was assisted using a centrifuge in 50 mL calibrated centrifuge tubes.

Table 1 Operating parameters for AAS

Parameter	Cu	Cd	Co	Ni
Wavelength/nm	324.8	228.8	240.7	232.0
Hollow cathode lamp current/mA	2.5	7.5	7.5	7.5
Acetylene flow rate/L min^{-1}	0.5	0.5	0.5	0.5
Slit width/nm	4.0	4.0	4.0	4.0
Air flow rate/L min^{-1}	0.5	0.5	0.5	0.2

The melting points were determined with a Gallenkamp Model apparatus with open capillaries. Infrared spectra were recorded on an MIDAC-FTIR Model 1700 spectrophotometer. Elemental analysis was obtained with a Carlo-Erba 1108 Model apparatus. Optical rotations were taken on a Perkin Elmer 341 Model polarimeter. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker DPX-400 high-performance digital FT-NMR spectrometer. Refraction indices were measured by using an Atago Abbe refractometer.

Synthesis procedure

The synthesis of diamidediols is shown in Fig. 1.

Synthesis of aminoalcohols. The synthesis of L-phenylalanilol was accomplished in one step from L-phenylalanine, according to procedures described in the literature.[44]

Synthesis of dimethyloxalate (DMO). Methanol (38.4 g, 1.2 mol) was added dropwise to pyridine (47.4 g, 0.6 mol). A solution of oxalyl chloride (38.0 g, 0.3 mol) in benzene (250.0 mL) was added to the mixture in 3 h under dry N_2 atmosphere at room temperature. The mixture was then refluxed for 3 h, and kept at room temperature for one day. The solvent was evaporated under reduced pressure. The white solid compound was extracted with cold ethers, and dried over Na_2SO_4. The product was recrystallized from ether to yield 32.0 g (92%), Mp. 54 – 54.5°C. Mw. 118.0 g (required C, 40.68; H, 5.09; found C, 40.62; H, 5.11). ^1H NMR (400 MHz, $CDCl_3$): δ 3.58 (6H, s).

Synthesis of N,N′-bis[(1R)-1-ethyl-2-hydroxyethyl]ethanediamide (DAD1). A solution of (*R*)-2-amino-1-butanol (2.76 g, 31 mmol) in methanol (10.0 mL) was added dropwise to a solution of dimethyloxalate (1.83 g, 15.5 mmol) in methanol (30.0 mL) at room temperature for 0.5 h. After addition, solid product was precipitated and then filtered, and washed with ether to give 7.1 g (99%) of white compound, DAD1. Mp. 210 – 212°C; $[\alpha]_D^{25}$ + 25.3 (c, 1.0 DMSO); IR (KBr) ν 3365, 3280, 2967, 2935, 2854, 1665, 1530, 1048 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 0.85 (6H, t, *J* = 7.4 Hz), 1.42 (2H, m), 1.55 (2H, m), 3.3 (4H, m), 3.7 (2H, m), 4.7 (2H, bs), 8.2 (2H, d, *J* = 9.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ 11.4, 24.4, 54.2, 63.7, 161.7.

Synthesis of N,N′-bis[(1S)-1-benzyl-2-hydroxyethyl]ethanediamide (DAD2). Following an analogous procedure that has been described for DAD2, from L-phenylalanilol (4.75 g, 31.5 mmol) were obtained almost quantitative (5.56 g, 99%). Mp. 252 – 253°C; $[\alpha]_D^{25}$ –43.8 (c 0.03, MeOH), IR (KBr) ν, 3416, 3300, 3063, 3037, 3247,1658, 1523, 1047 cm^{-1}; ^1H NMR (400 MHz,

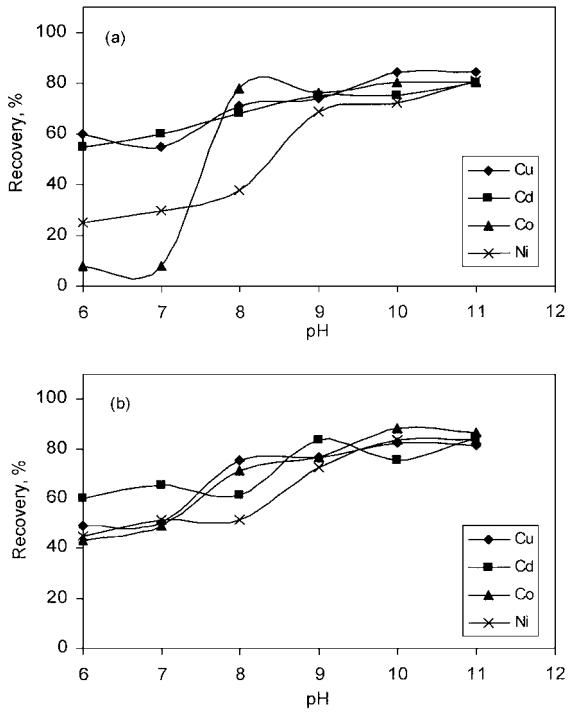

Fig. 2 Influence of the pH on the recovery of extraction for Cu, Cd, Co and Ni. Conditions: 25.0 ng mL^{-1} each metal; 40.0 mL cold aqueous solution; 2.75 × 10^{-3} mol L^{-1} each of ligand; 0.25% w/v Triton X-114; 45°C. (a) DAD1, (b) DAD2.

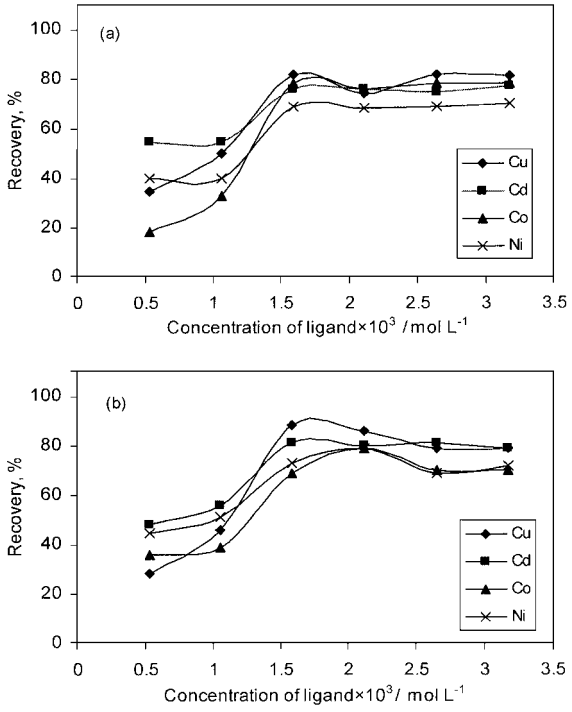

Fig. 3 Effect of the ligand concentration on the recovery of extraction for Cu, Cd, Co and Ni. Conditions: 25.0 ng mL^{-1} each metal; pH, 10.0 ± 0.2; 40.0 mL cold aqueous solution; 0.25% w/v Triton X-114; 45°C. (a) DAD1, (b) DAD2.

DMSO-d_6): δ 2.77 (2H, dd, J = 13.5, J = n5.4 Hz), 2.91 (2H, dd, 13.5, 5.4 Hz), 3.43 (4H, m), 3.95 (2H, m), 4.93 (2H, t, J = 5.6 Hz), 7.3 - 7.1 (10 H, m), 8.4 (2H, d, J = 9.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ 36.6, 53.4, 62.7, 126.4, 128.6, 129.4, 139.3, 159.9.

Cloud point extraction procedure

For cloud-point extraction, aliquots of cold solutions (40 mL) containing each analyte at 25.0 ng mL^{-1}, Triton X-114 (0.25% w/v), diamidediols (2.75 × 10^{-3} mol L^{-1}), buffered at a suitable pH with Britton–Robinson buffers, were kept for 15 min in thermostatic bath at 45°C. Separation of the phases was accelerated by centrifuging at 4000 rpm for 10 min. After cooling in an ice-bath, the surfactant-rich phases became viscous. Then, the aqueous phase could be separated by using a syringe. Subsequently, to decrease the viscosity of the surfactant-rich phase, 1.0 mol L^{-1} HNO_3 in methanol was added in order to make the final volume for 2.0 mL. The preconcentrated solutions were introduced into the flame by conventional aspiration.

Results and Discussion

Effect of the pH

The preconcentration of metal ions by the cloud-point method involves the prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of the surfactant-rich phase, thus obtaining the desired preconcentration. The extraction efficiency depends on the pH at which complex formation is carried out. pH plays a unique role in metal-chelate formation and subsequent extraction. The effects of the pH on the extraction of metals were investigated, and the results are shown in Fig. 2. The maximum extraction efficiencies were obtained at pH 10.0 ± 0.2. It is well known that the use of the borate buffer is more appropriate in the basic region. Therefore, the borate buffer solution at an approximate pH value of 10.0 ± 0.2 was used instead of the Britton–Robinson buffer solution, in the following experiments.

It is well known that most metals precipitate as their hydroxides in the basic regions. In the present study, the pH of the solutions was adjusted to approximately pH 10.0 ± 0.2 and buffered. Then, the solutions of diamidediols and Triton X-114 were added to the solution. No precipitation related to metal hydroxides was seen during the experiments. Therefore, we thought that the MOH^+, which was soluble in the surfactant medium, could have been formed instead of the metal hydroxide [$M(OH)_2$]. Then, MOH^+ was reacted with a ligand to form a hydrophobic complex.

Effect of diamidediols concentration

The extraction recoveries of the metals depend on the concentrations of the complexation reagents. In order to select the optimum concentrations of the diamidediols, the effects of the concentrations of the chelating reagents on the recovery were investigated; the results are shown in Fig. 3. The maximum signals were obtained at 2.75 × 10^{-3} mol L^{-1} for DAD1 and 1.75 × 10^{-3} mol L^{-1} for DAD2. Therefore, these concentrations were selected as the optimum concentrations of the chelating reagents.

Effect of the Triton X-114 concentration

Triton X-114 provides a high-density of a surfactant-rich phase as well as its appropriate cloud-point temperature (25°C), as compared with other surfactants.[18] The variations in the extraction recovery as a function of the concentration of Triton

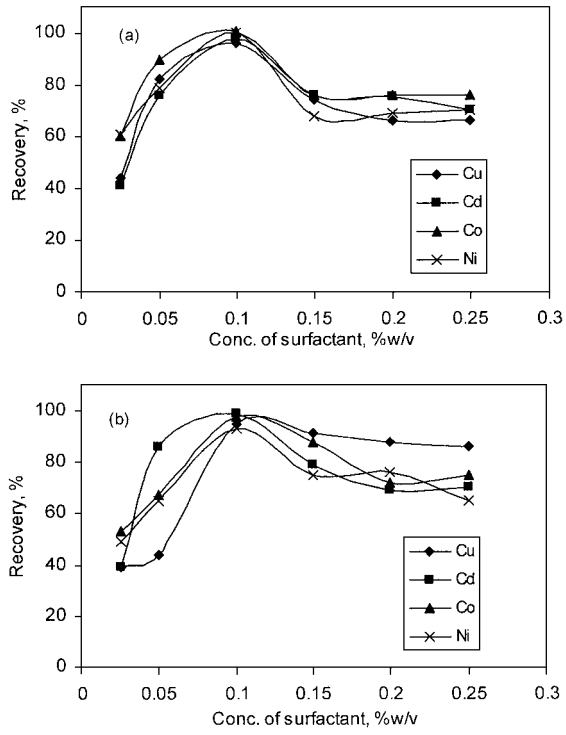

Fig. 4 Effect of the surfactant concentration on the recovery of extraction for Cu, Cd, Co and Ni. Conditions: 25.0 ng mL^{-1} each metals; pH, 10.0 ± 0.2; 40.0 mL cold aqueous solution; 2.75×10^{-3} mol L^{-1} for DAD1 and 1.75×10^{-3} mol L^{-1} for DAD2. (a) DAD1, (b) DAD2.

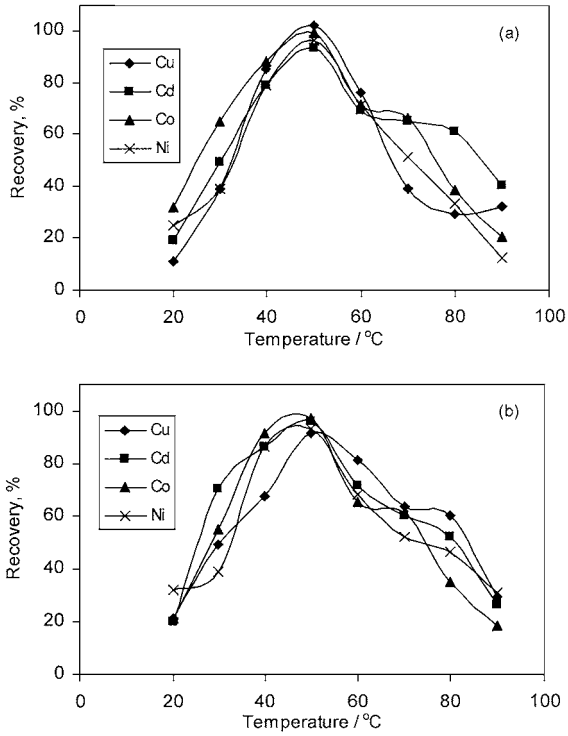

Fig. 5 Effect of the temperature on the recovery of extraction for Cu, Cd, Co and Ni. Conditions: 25.0 ng mL^{-1} each metals; 0.1% w/v Triton X-114; pH, 10.0 ± 0.2; 40.0 mL cold aqueous solution; 2.75×10^{-3} mol L^{-1} for DAD1; 1.75×10^{-3} mol L^{-1} for DAD2. (a) DAD1, (b) DAD2.

Table 2 Analytical characteristics of the method (n = 3)

Metal	Condition	Concentration range/ng mL^{-1}	Slope	Intercept	r^2	RSD[a], %	LOD/ng mL^{-1}	LOQ/ng mL^{-1}
Cd	Without preconc.	100 - 1000	1×10^{-4}	3×10^{-3}	0.9972	3.2 (250)	20.0	60.0
	Preconc. with DAD1	2.5 - 25.0	1.8×10^{-3}	1.1×10^{-3}	0.9980	2.6 (20.0)	0.45	1.4
	Preconc. with DAD2	2.5 - 25.0	2.0×10^{-3}	2.2×10^{-3}	0.9924	2.8 (20.0)	0.44	1.4
Cu	Without preconc.	100 - 1000	1×10^{-4}	5×10^{-4}	0.9954	4.6 (250)	15.0	45.0
	Preconc. with DAD1	2.5 - 25.0	2.2×10^{-3}	1.4×10^{-4}	0.9947	5.1 (20.0)	0.50	1.50
	Preconc. with DAD2	2.5 - 25.0	2.3×10^{-3}	6×10^{-4}	0.9930	3.6 (20.0)	0.25	0.75
Co	Without preconc.	100 - 1000	6×10^{-5}	3×10^{-3}	0.9980	4.6 (250)	20.0	60.0
	Preconc. with DAD1	5.0 - 25.0	1.1×10^{-3}	6×10^{-4}	0.9962	2.6 (20.0)	1.25	3.7
	Preconc. with DAD2	5.0 - 25.0	1×10^{-3}	8×10^{-4}	0.9889	2.6 (20.0)	0.60	1.7
Ni	Without preconc.	100 - 1000	6×10^{-5}	2×10^{-2}	0.9959	5.6 (250)	22.0	65.0
	Preconc. with DAD1	5.0 - 25.0	1.2×10^{-3}	6×10^{-4}	0.9953	5.5 (20.0)	0.60	1.80
	Preconc. with DAD2	5.0 - 25.0	1.2×10^{-3}	8×10^{-4}	0.9929	3.9 (20.0)	1.55	4.7

a. Values in parentheses are the concentrations of metal for which the relative standard deviations was obtained.

X-114 in the range of 0.025 - 0.25% (w/v) were investigated. Quantitative extractions were observed at nearly 0.05% (w/v) Triton X-114 concentration. Figure 4 highlights the differences observed in the extraction recoveries at different concentrations of the surfactant. At lower surfactant concentrations, the extraction efficiencies of the complexes were low, probably due to an inadequacy of the assemblies to entrap the hydrophobic complex quantitatively. At higher concentrations of Triton X-114, the signals decreased because of the increment of the volumes and the viscosity of the surfactant-rich phase. Therefore, the greatest extraction recoveries were achieved at 0.1% (w/v) Triton X-114.

Effect of the equilibration temperature and the centrifugation time

In order to optimize the method, it was necessary to examine the effect of the temperature on cloud-point extraction. It was desirable to employ the lowest possible equilibration temperature and the shortest incubation time, as a comprise between completion of extraction and efficient separation of the phases. The results illustrated in Fig. 5 show excellent recovery for equilibration temperatures from 40 to 60°C. Therefore, 45°C was chosen for the equilibration temperature.

The effect of the centrifugation time on the extraction efficiency was studied in the time range of 5.0 - 25.0 min at from 3000 to 6000 rpm. A centrifugation time of 10.0 min at

Table 3 Determination of Cu, Cd, Co and Ni in a tap-water sample (ng mL^{-1})

Metal	DAD1			DAD2		
	Added	Found[a]	R[b]	Added	Found[a]	R[b]
Cd	—	< LOQ[c]	—	—	< LOQ	—
	5	4.8 ± 0.1	96.4	5	4.8 ± 0.2	97.3
	10	10.5 ± 0.2	105.5	10	10.2 ± 0.8	101.9
Cu	—	< LOQ	—	—	< LOQ	—
	5	4.7 ± 0.2	94.8	5	5.2 ± 0.4	103.0
	10	10.2 ± 0.4	101.7	10	10.6 ± 0.3	106.0
Co	—	< LOQ	—	—	< LOQ	—
	10	10.1 ± 0.4	101.1	10	9.9 ± 0.3	99.3
	15	14.5 ± 0.4	96.5	15	15.5 ± 0.6	103.1
Ni	—	< LOQ	—	—	< LOQ	—
	10	10.2 ± 0.3	102.0	10	9.4 ± 0.6	94.2
	15	14.5 ± 0.3	96.5	15	14.4 ± 0.3	96.1

n = 3.
a. Average of three determinations ± standard deviations.
b. Recovery, %.
c. Lower than the limit of quantification.

3500 rpm was fixed for the entire procedure, since the analyte extractions in this time were almost quantitative.

Characteristics of the method

Calibration curves were constructed by preconcentrating 40.0 mL of the sample solutions in the presence of 0.1% (w/v) Triton X-114 in a medium buffered at pH = 10.0 ± 0.2 with borate buffer. After the required amount of 1.0 mol L^{-1} HNO_3 in methanol was added to the surfactant, a rich phase of the cloud-point extraction process of the sample to obtain 2.0 mL of final volume was introduced into the flame by the conventional aspiration. In this case, linear relationships between the absorbance measured and the concentrations of the metals in solutions were obtained. Table 2 gives the parameters of the calibration curves and the relative standard deviations (RSDs) obtained for 3 replicates subjected to the complete procedure. The limit of detection (LOD) and quantification (LOQ) were calculated according to IUPAC recommendation.[45] Table 2 also gives the calibrations obtained with standard solutions of the metals not subjected to the preconcentration step. The enrichment factors, calculated as the ratio of the slope of the preconcentrated samples that were obtained without preconcentration, were 18, 23, 18 and 20 for Cd, Cu, Co and Ni in the case of DAD1, respectively; 20, 22, 17 and 20 for Cd, Cu, Co and Ni in the case of DAD2.

Application of the method to water samples

In order to evaluate the analytical applicability of the proposed method, it was applied for the determination of Cu, Cd, Co and Ni in a tap-water sample, certified waste water (CWW-TM-D) and spiked fortified water (NWTM-15) by atomic absorption spectrometry. The water sample was filtered to remove the suspended solids with 0.45 μm Teflon filters. A 4.0-mL portion of certified waste water was taken and diluted to 40.0 ml with distilled water. A fortified water sample was directly applied to cloud-point extraction; 40.0 mL of each sample was preconcentrated with 0.1% (w/v) Triton X-114, a DAD1 concentration of 2.75×10^{-3} mol L^{-1} and a DAD2 concentration of 1.75×10^{-3} mol L^{-1}, following the proposed procedure. Each sample was analyzed three times. The standard-addition method was also used for the tap-water sample. The analytical results and recoveries are presented in Tables 3 and 4. The analytical contents of Cu, Cd, Co and Ni in environmental reference materials were in good agreement with the certified value.

Table 4 Determination of Cu, Cd, Co and Ni in certified reference materials by AAS (ng mL^{-1})

	CWW-TM-D			NWTM-15		
	Certified	Found		Certified	Found	
		DAD1	DAD2		DAD1	DAD2
Cd	250	236 ± 4	240 ± 8	13.2	12.1 ± 0.3	12.6 ± 0.7
Cu	1000	988 ± 13	990 ± 21	18.3	18.0 ± 1.1	17.9 ± 0.9
Co	1000	987 ± 20	965 ± 14	15.1	14.8 ± 0.6	14.1 ± 0.8
Ni	1000	980 ± 23	985 ± 14	18.1	17.3 ± 0.3	17.3 ± 0.5

Conclusion

The C_2-symmetric chiral ligands, including ethyl and benzyl derivates, provided multielement preconcentration in the cloud-point methodology. According to our results, both derivates reacted with Cu, Cd, Co and Ni to form stable complexes. The major advantage and novelty of the present study is the use of the C_2-symmetric chiral ligands. It can be stated that these C_2-symmetric ligands did not have any selectivity to any metals. However, tested trace and toxic metals were recovered quantitatively. The simultaneous preconcentration of trace metals is very important because it can reduce the analysis time, providing an economic analysis. The method based on cloud-point extraction and the use of C_2-symmetric chiral ligands is rapid, easy, safe and inexpensive for the preconcentration and separation of trace metals in aqueous solutions. The use of diamidediols as a complexation reagent for Cu, Cd, Co and Ni was utilized for the determination of trace metals in tap water. The developed method was provided to determine the concentration of the studied metals at ng mL^{-1} levels, and hence represented a promising approach for the monitoring of toxic metals in water at low cost, simplicity and efficiency. The proposed CPE method gave, a low LOD, good RSD and solvent-free extraction of toxic metals from its initial matrix.

Acknowledgements

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