J. Braz. Chem. Soc., Vol. 19, No. 3, 471-477, 2008.
Printed in Brazil - ©2008 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Sequential Cloud Point Extraction of Trace Elements from Biological Samples and Determination by Inductively Coupled Plasma Mass Spectrometry

Maria Fernanda Giné,,[a] Aparecida F. Patreze,[a] Edson L. Silva,[a] Jorge E. S. Sarkis[b] and Maurício H. Kakazu[b]*

[a]*Centro de Energia Nuclear na Agricultura CENA-USP, Universidade de São Paulo, Av. Centenário 303, 13400-970 Piracicaba-SP, Brazil*

[b]*Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN, Travessa rua 400, Cidade Universitária, 05508-000 São Paulo-SP, Brazil*

A extração no ponto nuvem (CPE) foi realizada em duas etapas seqüenciais para a determinação de elementos traço em soro humano, sangue animal e dieta alimentar por espectrometria de massas com fonte de plasma indutivamente acoplado. A primeira CPE foi realizada adicionando dietil-ditiofosfato, Triton® X-114 seguida de aquecimento a 40 °C, centrifugação e esfriamento a 0 °C. A fase rica em surfactante foi separada para determinar Cd, Pb e Cu pela técnica de quantificação por diluição isotópica. As medidas das razões isotópicas foram caracterizadas por RSD < 0.7%. O pH da solução empobrecida em surfactantante foi ajustado entre 4 e 5 antes da adição de 4-(2-pirilidazo)resorcinol, Triton® X-114 e seguiram-se os procedimentos para atingir o ponto nuvem. Na segunda fase rica em surfactante extraída foram quantificados Co e Ni pelo método de adições de padrão com RSD < 2%. Recuperações entre 85 a 96% foram obtidas para todos os elementos. A exatidão foi aferida pela análise de materiais de referência com valores recomendados e certificados.

A two-step sequential cloud point extraction (CPE) of trace elements from small sample volumes of human serum, animal blood, and food diet is proposed to gain analytical information in the analysis by inductively coupled plasma mass spectrometry. The first CPE was attained by adding *O,O*-diethyldithiophosphate, the non ionic surfactant Triton® X-114 followed by heating at 40 °C, centrifugation and cooling at 0 °C. The resulting surfactant-rich phase was separated to determine Cd, Pb and Cu by isotope dilution. Isotope ratio measurements presented RSD < 0.7%. The residual surfactant-poor phase solution had the pH adjusted in the range 4 to 5 before the chelating reagent, 4-(2-pyridylazo) resorcinol plus surfactant Triton® X-114 were added followed by the sequence to attain the CPE. Co and Ni were quantified in the second extracted surfactant-rich phases by standard additions method with RSD < 2%. Recoveries from 85 to 96% were obtained for all elements. Analyzing reference materials with certified and recommended values assessed accuracy.

Keywords: sequential cloud point extraction, CPE, inductively coupled plasma mass spectrometry, isotope dilution, biological samples, trace elements

Introduction

Surfactant mediated phase separation constitutes the basis for the approach known as cloud point extraction[1] which is a liquid-liquid extraction alternative to that of organic solvents. The main parameter to attain a surfactant monomer agglomeration in a micelle-rich phase is the surfactant concentration at the cloud point temperature. The temperature-concentration phase diagram is specific for each surfactant.[2] The effect of additives such as salts and other surfactants also has to be considered.[1,3] The first application of cloud point extraction for analytical purposes described the micelle aggregation of hydrophobic anionic metal complexes.[2] The ability of surfactant micelles to bind organic compounds separated by CPE was applied for pre-concentration of organic

*e-mail: mfgine@cena.usp.br

compounds prior to the separation of species by capillary electrophoresis[3] and chromatography.[4] The surfactants octylphenoxy polyethoxyethanol (Triton® X-114) and polyoxyethylene(7.5)nonylphenyl ether (PONPE® 7.5) with cloud point temperatures (CPT) below 40 °C and 20 °C, respectively, have been used preferentially for cloud point extraction of soluble metal ions complexes.[5] Both surfactants are characterized by forming a surfactant-rich phase denser than the aqueous solution which interacts with metallic species, mainly in the chelated form. This facilitates the phase separation by gravity or centrifugation at room temperature. Another advantage of surfactants attaining the critical micelle concentration (CMC) at low temperature is the minimum redissolution of micelles into the bulk aqueous solution occurring during phase separation.[1] Theoretical aspects and applications of phase separations using aqueous solutions of surfactants have been described.[5,6]

Dialkyl phosphorodithiotic acids and the sodium salt diethyldithiophosphate were ligands proposed for solvent extraction of several metals.[7,8] *S*everal applications of the complexation with DDTP in acidified solutions and cloud point concentration (CPE) have been described in the literature.[9-13]

The formation of micelles at low temperature using PONPE® 7.5 allowed the high-efficiency extraction of Pb(II) ions from saliva samples without any complexant.[14] The cloud point extraction of water-soluble metal complexes with 4-(2-pyridylazo) resorcinol (PAR) has been described before.[15,16] A surfactant media is necessary to dissolve chelating reagents such as 1-(2-thiazolylazo)-2-naphtol (TAN),[17] dithizone[18] and 1-(2-pyridylazo)2-naphtol (PAN).[1]

Cloud point extraction has been extensively described as a separation and pre-concentration procedure for metals prior to their determination by atomic spectrometric techniques.[19] Specific applications of CPE with Triton® X-114 to determine traces of Bi-dithizonate in urine and human hair by electrothermal atomic absorption spectrometry (ET AAS) have been reported.[18] The CPE with DDTP and Triton® X-114 was applied to determine Cd in tobacco and water samples with flame atomic absorption spectrometry (F AAS) detection[10] and Cd, Pb and Pd in blood by ET AAS.[11] The same reagents were employed for the simultaneous determination of noble metals in urine by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS)[12] and Ag, As, Au, Cd, Cu, Pb and Se in water samples using ultrasonic nebulization ICP-MS.[13] The micellar phases are very viscous, and commonly they require dilution. Methanol or ethanol plus nitric acid have been described to facilitate the introduction of micellar phases into F AAS,[10] ET AAS,[11] ETV-ICP-MS[12] and ICP-MS.[13] Tetrahydrofuran has been used for introduction into ETAAS,[18] or just water has been applied for dilution.[15,20] The combination of electrothermal devices using appropriately programmed vaporization temperatures avoided matrix interferences in the atomic spectrometry detection of micellar phases.[11,12,18] The flow injection of small sample volumes (100 μL) by using an ultrasonic nebulizer with a dessolvation unit avoided the main drawbacks of introducing micelles dissolved in methanol into an ICP-MS. Seven trace elements were determined by ICP-MS in the transient signals.[13] Precision characterized by RSD ≤ 6% was reported. To overcome matrix effects the extracted analytes by CPE has been quantified by isotope dilution,[20] and standard additions.[14] The application of isotope dilution (ID) is convenient to determine trace elements in problematic samples, especially when recoveries are variable or matrix dependent. Nevertheless, quantification by ID requires precise isotope ratio measurements to avoid error magnification on results.[21] Typical RSD's from 0.1 to 0.5% for isotope ratio measurements by quadrupole ICP-MS and from 0.05 to 0.2% using sector-field mass spectrometers ICP-SFMS have been reported.[22] Corrections for mass bias and detector dead time are required to attain accurate results when applying ID.

In this research, a two-step cloud point extractions are planned that produces two surfactant-rich phases in sequence. The micelle extracts are then subjected to oxidative digestion before analysis to facilitate sample introduction and to improve precision on isotope ratio measurements. Quantification by applying either isotope dilution or standard additions is proposed.

Experimental

Instrumentation

An inductively coupled plasma mass spectrometer, Element 1 (Finnigan MAT, Bremen, Germany), was used in low-resolution mode with a low-flow (0.6 mL min^{-1}) concentric nebulizer (Meinhard, Santa Ana, CA, USA) and a Scott-type spray chamber cooled to 10 °C. The ICP-MS operating conditions are summarized in Table 1. The medium and high resolution modes were not practiced for presenting worsen sensitivity and precision.[23] Samples were digested in a microwave oven (Ethos 1600, Milestone, Italy) installed in a class-100 clean room. A heating block (Tecnal, Piracicaba, Brazil) and a centrifuge (Cientec model 55, Piracicaba, Brazil) were used to accelerate the phase separation. Conical Pyrex centrifuge tubes (15 mL)

(Corning, New York, USA) were used. Spikes were applied from solutions at 20 °C by using a 20.0 ± 0.04 to 200.0 ± 0.03 µL micropipette (model NPX-200, Nichipet EX, Tokio, Japan).

Table 1. ICP-MS operating conditions

Cool gas flow rate	16 L min^{-1}
Auxiliary gas flow rate	0.9 L min^{-1}
Sample gas	1mL min^{-1}
RF power	1300 W
Sample Flow rate	0.6 mL $min.^{-1}$
Measurements *per* peak	30
Sample time	0.010 s
Segment duration	0.150 s
Mass Window	50
Detection mode	Pulse Counting
Spray chamber	Scott type

Materials and solutions

Purified water (18.2 MΩ cm) was produced by a Milli-Q system (Millipore Co., Bedford, MA, USA); sub-boiling distilled HNO_3 and HCl acids (Merck, Darmstadt, Germany) and H_2O_2 30% (m/v) (Suprapur Merck), were used throughout. A quality control standard QCS-21 prepared by High Purity Standards (Charleston, NC, USA) containing 21 elements was used in preliminary tests. Reference standards were prepared from stock solutions of Cd, Cu, Pb, Co and Ni (1,000.0 mg L^{-1}) (SPEX, Edison, NJ, USA). Spikes of Co and Ni were obtained from a 1.00 mg L^{-1} solution. Isotopic spikes were performed from 1.00 mg L^{-1} solutions enriched in ^{112}Cd (97.02 at. %), ^{65}Cu (99.68 at. %) and ^{206}Pb (99.74 at. %) (CIL Cambridge Isotope Laboratories, Andover, MA, USA). A 0.100 mg L^{-1} solution of the NIST SRM 982 certified for Pb isotopic composition was prepared. Acetate buffer solution pH 4.5 was used (Merck). A solution of 10% m/v DDTP (Sigma, St Louis, MO, USA) in water, (purified as described elsewhere[13]) and another containing 10 mmol L^{-1} PAR (Merck, for synthesis) were used. A 10% m/v stock solution of Triton® X-114 [4-$(C_8H_{17})C_6H_4(OCH_2CH_2)_nOH$] (Sigma) surfactant was employed.

Samples and sample preparation

Certified reference materials including IRMM Human Serum IMEP-17 (Institute for Reference Materials and Measurements) and HPS Mixed Food Diet (High Purity Standards) were analyzed. Blood samples (0.1 mL) collected from rats contaminated with Cd were analyzed.

Samples solutions in triplicate received the spiked amounts presented in Table 2 calculated for each sample by the reverse isotope dilution equation. Standards containing 0.5 and 1.0 mg L^{-1} of Co and Ni were used for spiking the samples to perform the standard additions method. The samples and blanks received 3 mL of nitric acid and 2 mL of H_2O_2 in sequence before digestion in microwave oven in closed PTFE vessels. Three heating steps of 2, 4, and 10 min at temperatures of 60 °C, 85 °C and 120 °C, respectively were used.

Preliminary experiments of cloud point extraction using DDTP and PAR

The application of cloud point extraction to a 200 µg L^{-1} of QCS-21 in 0.1 mol L^{-1} HCl solution was performed. The digested micelles were analyzed by ICP-MS in

Table 2. Spiked amounts and experimental isotope ratios and precision (n = 3)

Samples	Estimated mass (ng)	Spiked mass (ng)	Measured Ratio	% RSD
Mixed Food Diet HPS				
$^{112}Cd/^{114}Cd$	60	80.0 ± 0.3	10.5	0.41
$^{65}Cu/^{63}Cu$	400	150.0 ± 0.2	1.04	0.14
Samples of animal blood				
$^{112}Cd/^{114}Cd$	70	65.0 ± 0.2	8.02	0.39
$^{65}Cu/^{63}Cu$	20	10.0 ± 0.5	1.05	0.48
$^{206}Pb/^{208}Pb$	4	5.0 ± 0.5	2.82	0.62
Human Serum				
IRMM-IMEP-17				
$^{112}Cd/^{114}Cd$	300	800.0 ± 0.1	10.05	0.46
$^{65}Cu/^{63}Cu$	3,000	1,300.0 ± 0.1	1.05	0.11
$^{206}Pb/^{208}Pb$	40	300.0 ± 0.2	15.8	0.48

semiquantitative mode. The feasibility of promoting CPE for Co by chelating with several pyridine and thiazole azo compounds was reported before.[16,17] PAR forms anionic HR^- water-soluble complexes with Co and Ni at pH from 4.2 to 7.[17] However, the capability for simultaneous cloud point extractions using PAR was not established before. Experiments were carried out to characterize the CPE of PAR chelates from a 200 μg L^{-1} QCS-21 solution. Different concentrations of PAR mixed with Triton® X-114 (0.2% m/v) were tested. The micelle-rich phases were digested and analyzed directly by ICP-MS as well as the residual surfactant-poor phase to determine the percentage of recovery for each element.

Sequential cloud point extraction procedure

The proposed sequential CPE scheme is presented on the right side diagram shown in Figure 1. The first extraction was performed from spiked, digested samples at pH < 1 by adding 0.5 mL of the 10% m/v DDTP and 0.1 mL of the 10% surfactant Triton® X-114 to attain 0.2% m/v in the final solution.

Tubes containing the solutions were immersed in a thermostatic bath heated at 40 °C for 15 min. Immediately after heating, the warm solutions exhibiting turbidity were centrifuged at 4800 rpm for 10 min, and finally the flasks were immersed in an ice bath for 5 min. Two phases were clearly observed: a transparent solution and a white or pale yellow depleted residue. Inverting the tubes separated the supernatant solution corresponding to the surfactant-poor phase. The pH of the surfactant-poor solutions was adjusted to a pH range of 4 to 5 with acetate buffer. The PAR mixed with Triton® X-114 solution was added as the chelating reagent to perform another cloud point extraction. A second micelle-rich phase was formed just by heating to 40 °C for 15 min, followed by centrifugation and cooling in an ice bath. The depleted organic phase exhibited an orange color. After separation, the micelle-rich surfaces and the tube walls were washed twice with 0.5 mL of water to remove external residues. The separated micelles were easily dissolved by adding 500 μL of HNO_3 plus 200 μL of H_2O_2 and heated at 120 °C for 15 min in a digestion block to obtain a clear final solution. The micelle containing the DDTP complexes was analyzed by isotope dilution without

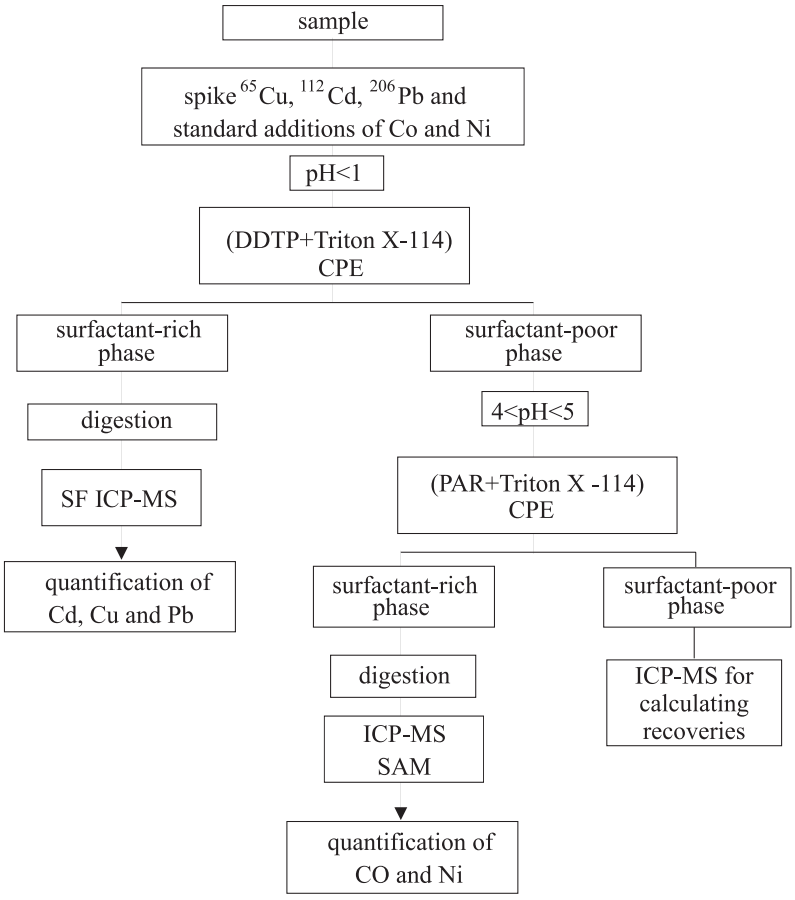

Figure 1. Schematic representation of the sequential cloud point extraction and the quantification procedures. Isotope dilution performed to quantify analytes on the first CPE by measuring isotope ratios (IR) and the standard additions method (SAM) for Co and Ni quantification in the second CPE.

a volumetric adjustment. After digestion of the second micelle, the volume was made up to 3 mL. The elements in the sample solutions were quantified by standard additions with the addition of 0.0; 50.0 and 100.0 μg L^{-1} Co and Ni. The surfactant-poor phase separated from the second CPE was also analyzed to calculate recoveries.

Isotope dilution

In preliminary tests the possibility of quantifying Cd, Pb and Cu by isotope dilution in the micelle produced by DDTP and Triton® X-114 was evaluated.

The instrumental conditions were adjusted to measure isotope ratios $^{112}Cd/^{114}Cd$ and $^{65}Cu/^{63}Cu$ in standard solutions accurately. Due to the Pb isotopic variability a solution of the Pb isotopic standard NIST SRM 982 was analyzed to determine the instrumental mass bias factor. Detector dead time of 20 ms was experimentally determined for the *m/z* of interest.

Results and Discussion

Preliminary results

Preliminary results of the cloud point extraction of Co and Ni complexes using PAR are presented in Figure 2. The efficiency of PAR to form chelates with Co could be affected by high concentrations of concomitants, mainly for samples with high concentrations of transition metals in the +2 oxidation state.[24] In effect, PAR in acetate medium at pH 4-6 is also efficient for Zn, Cd, Ni, Cr, V, Ti, Cu and other metals.

The serial scheme was defined for extracting first several transition elements with DDTP. After separating the micelle, the CPE performed on the surfactant-poor solution in acetate media adding PAR previously mixed with Triton® X-114. Higher stability of PAR in the organized media was observed. An excess of (1 mmol L^{-1}) of PAR was used to overcome effects of concomitants guarantying for Co and Ni recoveries higher than 95%.

Results of preliminary tests of cloud point extraction performed on standard solutions and blanks demonstrated that more than 90% of As, Cd, Fe and Pb and 60% of Cu were extracted with DDTP and close to 100% of Co, Ni, V, Ti, Cr and Zn with PAR. No effect from the main matrix constituents in biological samples, such as Na, K, Ca and Mg was noticed. However, the cloud point extraction of blanks and spiked blanks yielded contamination levels of 0.1 ng mL^{-1} for Cd, Ni and Co of 3.0 ng mL^{-1} for Cu and Pb. Those levels were related to the reagents impurities. To decrease Cu and Pb contaminations the purification of DDTP was provided. Impurities from ^{206}Pb-certificated material (CIL PBLM-3662) of Cd < 0.05% and Cu < 0.01% becomes important for isotope dilution quantification.

Preliminary tests of sequential cloud point extraction performed in 3 mL of biological samples allowed estimating the analytes concentration in the residual solution of both micelles.

Quantitative results

The spiked samples were submitted to the sequential CPE scheme represented in Figure 1. The mole fraction ratio[25] was used for calculating the spikes. The simplest case was for ^{65}Cu with natural ratio $^{65}Cu/^{63}Cu$ (0.44563) and highly enriched spike material with isotope ratio R_s > 300, allows projecting a final isotope ratio closed to 1. In the case of ^{112}Cd, the natural isotopic ratio is $^{112}Cd/^{114}Cd$ (0.84009) and the R_s ~100; then the choice for ratios close to 10 was preferred to obtain highly precise results. For Cd and Pb the isotope ratios were variable, increasing when the sample mass was over estimated and a higher mass was spiked. In all situations precise isotope ratio measurements were attained (RSD < 0.7%) indicating the effectiveness of micelles digestion procedure. The precision of isotopic ratio measurements on CPE micelles just diluted with nitric acid plus methanol reported elsewhere[13] was characterized by RSD from 3-8 %, thus not appropriate for applying isotope dilution quantification. This behavior was attributed to poor aerosol formation and plasma instabilities resulting from the high organic content. The C content of the digested micelle solutions was less than 0.3%. Uncertainties of isotope ratio measurements on Table 2 were calculated by the counting statistic equation proposed elsewhere[25] that considers the square root of the sum of the inverse of counts s^{-1} on both isotopes. Detection limits of 0.10 μg L^{-1} for $^{65}Cu/^{63}Cu$, 0.06 μg L^{-1} for $^{112}Cd/^{114}Cd$ and 0.05 μg L^{-1} for $^{206}Pb/^{208}Pb$

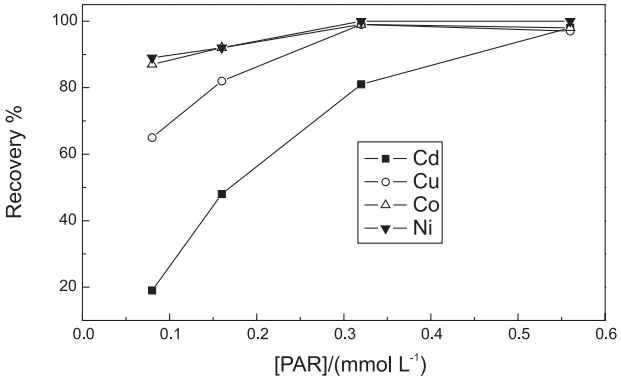

Figure 2. Recoveries attained for different elements in a 200 μg L^{-1} solution chelated with PAR and extracted by Cloud Point Extraction with Triton® X-114 (0.2% m/v).

Table 3. Results found in samples, in triplicate, and their reported/certified values

Samples	Element	Found values mg L^{-1}	Reported/Certified values mg L^{-1}
Mixed Food Diet (HPS)	Cd	0.012 ± 0.005	0.008
	Cu	0.073 ± 0.008	0.06
	Co	0.0011 ± 0.0002	0.0008
	Ni	0.025 ± 0.003	0.02
Animal Blood	Cd	0.651 ± 0.028	
	Cu	0.238 ± 0.015	
	Pb	0.040 ± 0.005	
	Co	0.186 ± 0.009	
		µmol L^{-1}	µmol L^{-1}
Human Serum (IRMM-IMEP-17)	Cd	0.898 ± 0.030	NC
	Cu	17.45 ± 0.50	17.57 ± 0.1
	Pb	0.058 ± 0.006	0.08*

* average value NC not certified.

were calculated.[26,27] The high isotopic enrichment of the spikes led to lowering detection limits of isotope dilution once the spiked blanks presented isotopic ratios closed to the spike solution.[26] The interferences of Ar Na^+ on ^{63}Cu were avoided by washing twice the rich-surfactant surface and the tube walls.

The quantification of Co and Ni was performed in micelle-rich produced by CPE using PAR plus Triton® X-114 in the original samples and spiked samples. The LOD for Co and Ni were 0.04 and 0.06 µg L^{-1}, respectively. Table 3 lists the average concentrations and uncertainties obtained analyzing three independent sub-samples of different materials. The sample of mixed food diet presented very low concentrations for Co (1.1 µg L^{-1}) and Cd (12 µg L^{-1}) with precision deteriorated probably by blank corrections. In the case of Cd uncertainties could also due to mass fraction effects and spiking accuracy.[28]

The sequential CPE procedure generates two surfactant-rich extracts containing specific trace elements and a residual solution containing most of the matrix elements.

The analysis of the extracted solutions was performed with no matrix effects since alkaline and alkaline earth elements are not complexed by DDTP or PAR.[29] The CPE procedure applied to the CRM´s, presented recoveries for Cd, Pb, Co and Ni in the range from 85 to 96% of the total content.

Conclusions

The sequential CPE procedure is convenient for trace elements determination in low-volume samples, which elements are separated in small volumes of extracted solutions containing specific analytes. The cloud point extraction performed in biological fluids with Triton® X-114 allowed producing two rich surfactant phases: the first extracting DDTP complexes with Cd, Cu, Pb and the second containing PAR chelates of Co and Ni. The advantage of the two-step CPE separation procedure over sample mineralization and direct analysis results from the possibility of doubling the volume without diluting the analytes and also performing the analysis with less matrix and interferences effects. The high analytes recoveries reveal the right choice of selective ligands and extraction efficiencies. The subsequent digestion of micelles produced by CPE resulted in highly precise isotope ratio measurements making feasible the quantification by isotope dilution ICP-MS.

Acknowledgments

The authors thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support.

References

1. Watanabe, H.; Tanaka, H.; *Talanta* **1978**, *25*, 585.
2. Carabias-Martinez, R.; Rodriguez-Gonzalo, E.; Dominguez-Alvarez, J.; Hernandez-Mendez, J.; *Anal. Chem.* **1999**, *71*, 2468.
3. Watanabe H.; In *Solution Behavior of Surfactants*; Mitral, K. L.; Fendler, E. J., eds.; Plenum Press: New York, 1982, 1305.
4. Fang, Q.; Yeung, H. W.; Leung, H. W.; Huie, C. W.; *J. Chromatogr. A* **2000**, *904*, 47.
5. Quina, F. H.; Hinze, W. L.; *Ind. Eng. Chem. Res.* **1999**, *38*, 4150.
6. Hinze, W. L.; Pramauro, E.; *Crit. Rev. Anal. Chem*. **1993**, *24*, 133.

7. Handley, T. H.; Dean, J. A.; *Anal. Chem.* **1962**, *34*, 1312.
8. Bode, H.; Arnswald, W.; *Fresenius Anal. Chem.* **1962**, *185*, 179.
9. Silva, M. A. M.; Frescura, V. L. A.; Aguilera, F. J. N.; Curtius, A. J.; *J. Anal. At. Spectrom.* **1998**, *13*, 1369.
10. Coelho, L. M.; Arruda, M. A. Z.; *Spectrochim. Acta, Part B* **2005**, *60*, 743.
11. Borges, D. L. G.; Veiga, M. A. M. S.; Frescura, V. L. A.; Welz, B.; Curtius, A. J.; *J. Anal. At. Spectrom.* **2003**, *18*, 501.
12. Silva, M. A. M.; Frescura, V. L. A.; Curtius, A. J.; *Spectrochim. Acta, Part B* **2001**, *56*, 1941.
13. Silva, M. A. M.; Frescura, V. L. A.; Curtius, A. J.; *Spectrochim. Acta, Part B* **2000**, *55*, 803.
14. Luconi, M. O.; Silva, M. F.; Olsina, R. A.; Fernandez, L. P.; *Talanta* **2000,** *51*, 123.
15. Doroschuk, V. O.; Lelyushok, S. O.; Ishchenko, V. B.; Kulichenko, S. A.; *Talanta* **2005**, *64*, 853.
16. Nascentes, C. C.; Arruda, M. A. Z.; *Talanta* **2003**, *61*, 759.
17. Chen, J.; Teo, K. C.; *Anal. Chim. Acta* **2001**, *434*, 325.
18. Shemirani, F.; Baghdadi, M.; Ramezani, M.; Jamali, M. R.; *Anal. Chim. Acta* **2005**, *534*, 163.
19. Bezerra, M. A.; Arruda, M. A. Z.; Ferreira, S. L. C.; *Appl. Spectrosc. Rev*. **2005**, *40*, 269.
20. Bellato, A. C. S.; Gervasio, A. P. G.; Giné, M. F.; *J. Anal. At. Spectrom*. **2005**, *20* 535.
21. Adriaens, A. G.; Kelly, W. R.; Adams, F. C.; *Anal. Chem.* **1993**, *65*, 660.
22. Heumann, K. G.; Gallus, S. M.; Radlinger, G.; Vogl, J.; *J. Anal. At. Spectrom.* **1998**, *13*, 1001.
23. Yu, L. L.; Vocke, R. D.; Murphy, K. E.; Beck II, C.M.; *Fresenius J. Anal. Chem.* **2001**, *370*, 834.
24. Nonova, D.; Evtimova B.; *Anal. Chim. Acta* **1972**, *62*, 456.
25. Hayes, J. M.; Schoeller, D. A.; *Anal. Chem.* **1977**, *49*, 306.
26. Yu, L. L.; Fasset, J. D.; Guthrie, W. F.; *Anal. Chem*. **2002**, *74*, 3887.
27. Saint'Pierre, T. D.; Frescura, V. L. A.; Curtius, A. J.; *Talanta* **2006**, *68*, 957.
28. Murphy, K. E.; Long, S. E.; Vocke, R. D.; *Anal. Bioanal. Chem*. **2007**, *387*, 2453.
29. Marczenko, Z.; *Separation and spectrophotometric determination of elements*, 2nd ed., Ellis Horwood: Chichester, 1986.

Received: July 26, 2007
Web Release Date: February 29, 2008

FAPESP helped in meeting the publication costs of this article.