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A greener and sensitive procedure for nickel determination by cloud point extraction and UV/Vis spectrophotometry

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ABSTRACT

A sensitive micelle-mediated extraction methodology for the preconcentration and determination of nickel by UV/Vis spectrophotometry is proposed. Metal ion was complexed with 1,5-bis(di-2-pyridylmethylene) thiocarbonohydrazide (DPTH) at pH 5.4 in buffer acetate medium and quantitatively extracted into a small volume of surfactant-rich phase of Triton X-114 after centrifugating. The optimal extraction conditions were studied and the analytical characteristics of the method were obtained. Linearity was obeyed in the range of 50-200 μg mL^{-1} of nickel. The detection limit of the method is 15 μg mL^{-1} of nickel (λ= 458 nm). The method was applied to the determination of nickel in different samples.

Keywords: Nickel; Cloud point extraction; UV-vis spectrophotometry; Spiked food samples, Waters.

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INTRODUCTION

Currently the interest in the preservation of the environment is increasing. The threshold concentrations for toxic species established by the environmental legislation have been continuously reduced and the detection limits of the analytical methodologies need to follow this trend. UV/Vis spectrophotometry is a mature analytical technique applied to many thousands of determinations owing to its simplicity, flexibility, low cost and convenience [1]. However, conventional UV/Vis spectrophotometry often presents detection limits incompatible to the requirements. Thus, alternatives have been investigated to increase sensitivity, such as formation of products with higher molar absorptivities [2], pre-concentration exploiting solid–liquid [3] or liquid–liquid [4] extraction, etc. Pre-concentration is the most usual approach, but it is time-consuming and often involves generation of toxic effluents such as organic solvents. At present, for to resolve these problems, a rich variety of greener methods have been developed to extract and concentrate analytes, such as ultrasound, microwave-assisted extraction, supercritical fluid extraction, superheated water extraction, membranes and cloud point extraction (CPE).

By means of CPE, the metals are extracted into micelles with a complexing agent in the presence of a surfactant. Above the critical micelle concentration, a separate phase is created [5]. This strategy has been used for sample clean up and mainly to concentrate the analyte or the reaction product before analysis, which can be carried out by several techniques, such as UV/Vis spectrophotometry, atomic spectrometry or capillary electrophoresis [6].

The CPE of metals, with spectrophotometric detection, was first reported by Watanabe and co-workers, who studied the preconcentration of Ni with 1-(2-thiazolylazo)-2-naphthol in Triton X-100 micellar solution [7], but this surfactant has a relatively high cloud point, around 70 ºC. Later, CPE was applied to other determinations of diverse ions, different of nickel, spectrophotometrically [8-25]. Table 1 shows some of these applications. Nickel is a moderately toxic element compared to other transition metals. Environmental pollution monitoring requires determination of nickel in trace levels in various samples. Recently, numerous methods have been published on the preconcentration of nickel, alone or in mixtures, by CPE method prior to its determination using spectrometric techniques [26-41]. Table 2 lists recent works concerning with nickel preconcentration by CPE and determination by spectrometric techniques.

This article presents the development of a procedure for the preconcentration of nickel from different samples and its determination by UV/Vis spectrophotometry. This procedure is based on CPE of this metal into micellar media of octylphenoxypolyethoxyethanol surfactant (Triton X-114) after complexing this metal with 1,5-bis(di-2-pyridylmethylene) thiocarbonohydrazide (DPTH).

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EXPERIMENTAL

Instrumentation and apparatus

A thermostated bath Model Selecta precisterm, maintained at the desired temperature, was used for the CPE experiments. Phase separation was achieved with a centrifuge Model Selecta Centromix in 10mL calibrated conical tubes.

A Thermo spectrophotometer Model Genesys 10uv was used for all measurements. Capacity cells of 3.5 mL and 700 μL were used in all instances.

Reagents and samples

High purity water (resistivity 18.2MΩcm^{-1}) obtained by a Milli-Q® water purification system (Millipore, Bedford, MA, USA) was used throughout this work. 1000 mg L^{-1} stock solutions of nickel (E. Merck, Darmstadt, Germany).Working standard solution was obtained daily by stepwise dilution of the standard stock solution. DPTH solution in DMF was prepared by dissolving solid reagent samples prepared and purified by the authors [42]. Non-ionic surfactant, Triton X-114 stock solution (4%, v/v) was prepared by dissolving 4 mL of concentrated solution (Merck, Darmstadt, Germany) in 100 mL hot deionised water. These reagents were all of analytical grade or better.

The proposed method was evaluated by analysis of nickel in several spiked food samples. The Ni concentrations in all the original samples were below the detection limit. For this purpose, standard solutions containing nickel were added to 0.2–0.5 g of diverse food and the resulting materials were mineralized by microwave digestion, adjusted pH and diluted at convenient volume.

Natural waters were collected in polypropylene bottles previously cleaned by soaking for 24 h in 10% (v/v) nitric acid and finally rinsed thoroughly with ultra-pure water before use.

Procedure

10 mL analyte solution containing nickel, 2 mL buffer solution pH 5.4, DPTH 2.5x10^{-3} % and 0.6 % (v/v) Triton X-114 was kept in a thermostated bath at 65 ºC for 30 min. Phase separation was accelerated by centrifuging the resultant solution at 3800 rpm for 5 min. The conical tubes were then immersed in an ice-water mixture for 20 min, allowing ease of removing the supernatant bulk aqueous phase. A small volume of surfactant rich phase remained at the bottom of the tube. To decrease the viscosity of the extract and to facilitate sampling, 1 mL or 2 mL of DMF was added to surfactant-rich phase when the cell capacity was 700 μL or 3.50 mL, respectively. The nickel content was determined by UV/Vis spectrophotometry at 410 and 458 nm against a blank solution. Calibration was carried using different standard solutions of nickel submitted to the same preconcentration and determination procedures. Blank solution was submitted to the same procedure and measured in parallel to the samples.

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RESULTS AND DISCUSSION

Optimization of the pre-concentration procedure

Due to advantages of CPE, it was used for preconcentration of nickel. Thus, for finding the optimum conditions, the influence of various parameters on extraction efficiency was investigated.

Effect of Triton X-114 concentration

We observed that Triton X-114 concentration as a non-ionic surfactant can be affect the extraction of complex and sensitivity of the method, therefore the effect of Triton X-114 concentration on the absorbance of the extracted phase was investigated. The absorbance of the surfactant-rich phase increased by increasing Triton X-114 concentration between 0.2 % and 0.6 % (v/v) and remained nearly constant at higher concentrations. Therefore, 0.6 % (v/v) Triton X-114 was used as optimum concentration.

Effect of ionic strength

The influence of ionic strength was examined by studying the extraction efficiency for NaCl concentration in the range 0.5-3 %. Ionic strength had no significant effect upon percent recovery and sensitivity up to 3%. So a concentration of 1% (w/v) as the optimum NaCl concentration was chosen in order to make secure the highest possible extraction efficiency.

Effect of pH

pH plays a unique role on metal-chelate formation and subsequent extraction. Nickel(II) reacts with DPTH to form intensely coloured complex and in a previous study, the characteristics of this chelate were described so nickel(II) forms a complex with DPTH in a wide range of pH [43]. The pH of the nickel solution was adjusted by the addition of 2 mL of buffer solution. The pH of buffer solution has been varied in the range of 3.6 –5.6. The results are shown in Fig. 1. It can be observed that the analytical signal is maxima at pH 5.4. Therefore, a pH 5.4 (acetate buffer) nickel solution was used in the following studies.

Effect of DPTH concentration

In order to determine the optimal reagent concentration, an experiment was carried out in which all other experimental variables, except reagent concentration, remained constant. The variation of the analytical signal as a function of the concentration of DPTH in the range of $1.5x10^{-3}$–$4x10^{-3}$% (w/v) was studied, and the experimental results in figure 2 demonstrated that the signal intensity of the analyte was practically constant by DPTH at concentrations up to about $4x10^{-3}$% (w/v). A $2.5x10^{-3}$% (w/v) DPTH was selected for further research.

Effects of equilibration temperature and time

To achieve easy phase separation and preconcentration as efficient as possible, optimal incubation time and temperature are necessary to complete reactions. The effect of the equilibration temperature was investigated from 40 to 80 ºC. It was found that the CPE efficiency reach maximum in the range of 60–80 ºC. So, an equilibration temperature of 65 ºC was used. Studies on the effect of the incubation time between 10-40 min showed that the maximum extraction efficiency was observed from 30 min. For the rest experiments, an incubation time of 30 min was used.

Effect of Centrifugation Time

An insignificant increase in the preconcentration factor was observed, when the centrifugation time at 3800 rpm was increased from 2 up to 10 min. A centrifugation time of 5 min was selected as the optimum, since complete separation occurred during this time and no appreciable improvements were observed for a longer interval.

Analytical properties of merit

The analytical properties of merit were obtained by preconcentrating 10 mL of analytical solution in aforementioned experimental conditions. The proposed extraction procedure provided linear calibration curves according to the following equations in the 50-200 µg/L range:

By using 3.50 mL capacity cell

$A = 0.0031[Ni^{2+}] + 0.079$, with $R^2 = 0.9938$, at $\lambda = 410$ nm;
$A = 0.0024[Ni^{2+}] + 0.0625$, with $R^2 = 0.9942$, at $\lambda = 458$ nm;

By using 700 µL capacity cell

$A = 0.0023[Ni^{2+}] - 0.032$, with $R^2 = 0.9875$, at $\lambda = 410$ nm;
$A = 0.0028[Ni^{2+}] + 0.002$, with $R^2 = 0.9728$, at $\lambda = 458$ nm;

Where A is the absorbance and R^2 is the squared correlation coefficient.

Table 3 contains other figures of merit obtained by the preconcentration procedure. The precision of the method was evaluated for a solution containing 100 µg/L of nickel (n = 7). The limit of detection was defined as the analyte concentration which resulted in a response equivalent to intercept plus three times the statistical parameter $s_{y/x}$. The preconcentration factor was defined as the slope ratio of the calibration graph of the CPE method to that of the calibration graph without preconcentration and/or the ratio of analytical signal of the preconcentrated sample to that obtained without preconcentration. Phase volume ratio, calculated as the ratio between the volume of the aqueous phase and the final volume of the surfactant-rich phase, was 10 and 5 times for the two cells type, 750 µL and 3.50 mL, respectively.

Interferences

The potential interferences in the CPE–UV/Vis spectrophotometry system were investigated using a solution containing 100 µg L^{-1} of nickel in the selected conditions. An ion was considered to interfere when its presence produced a variation of more than 5% in the absorbance of the sample. In general, the most interference are caused by ions form chelates with the reagent (Fe^{3+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+}) with a tolerance ratio of 2. Tolerance ratio for other ions tested as Ca^{2+}, Ba^{2+}, Mg^{2+}, Pb^{2+}, Bi^{3+}, SO_4^{2-} , NO_3^- were >10.

Determination of nickel in water and food samples

The proposed CPE– UV/Vis spectrophotometry methodology was applied to the determination of nickel in several water samples (i.e., tap water, well water and seawater). In order to validate the proposed method, recovery experiments were carried out by spiking the water samples with nickel before any pretreatment. The solutions were analyzed using the standard additions calibration and the percentage recoveries were calculated. Table 4 shows the obtained results.

On the other hand, the proposed procedure was applied to determination of Ni from different samples spiked with this ion. All samples were arbitrarily selected and acquired from a local superstore. For this purpose, standard solutions containing different quantities of nickel were added to samples and the resulting material was prepared as described under Experimental. Standard additions method was used in all instances and the results were obtained by extrapolation. The results of these analyses are summarised in Table 4, and indicated good recoveries in all instances.

CONCLUSIONS

CPE preconcentration is an easy, safe and inexpensive methodology for separation and preconcentration of trace metals in aqueous solutions. In this way, a very simple cloud point extraction methodology has been developed and optimized for the preconcentration of nickel before its determination by UV/Vis spectrometry. The proposed method gives a simple, sensitive and low-cost spectrophotometric procedure for the determination of nickel. The combined advantages of the cloud point methodology and the use of DPTH as a ligand for nickel were utilized for determination of Ni in water and food samples with satisfactory results.

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Table 1. CPE applications with spectrophotometric detection

Ions	Reagent/surfactant	Wavelength (nm)	Matrix	Ref.
Al	CAS–BDTAC/PONPE 7.5	554	Parenteral solutions	8
Be	CAS-CPC/Triton X-114	585	Water samples	9
Be	Anthralin-CPC/Triton X-114	-	Water samples	10
Bi	BPR/Triton X-114	542	Human urine	11
Cu	Dithizone/Triton X-114	-	Liver samples	12
Cu	HEPTS/Triton X-114	790	Water and saturated saline samples	13
Cu	4-BPDC/Triton X-114	435	Water samples	14
Er	3,5-diClDMPAP/PONPE 7.5	584	Synthetic samples	15
Gd	3,5-diClDMPAP/PONPE 7.5	592	Urine	16
Hg	Dithizone/Triton X-100	500	Natural water samples	17
Hg	Iodide/Triton X-114	300	Water samples	18
Hg	DDTC/Triton X-100	-	-	19
Mo	BPR/CTAB-KI	576	Steels and water samples	20
Pd	TMK/Triton X-114	508	Water samples	21
U	PAN/Triton X-114	665	Tap and river waters	22
U	DMB/Triton X-114	400	Water samples	23
U	Br-PADAP/Triton X-114	577	Water samples	24
U	PCV-KI/Triton X-114/CTAB	690	Water samples	25

Table 2. Nickel preconcentration by CPE

Matrix	Reagent/surfactant	Pre-concentration factor	Technique	Ref.
Waters	ACDA/ Triton X-114	-	UV/Vis spectrophotometry	26
Saline oil-refinery effluents	Br-PADAP/Triton X-114	74	FAAS	27
Waters	Dithizone/ Triton X-114	39	FAAS	28
Waters	PMBP/Triton X-100	27	GFAAS	29
Waters	H_2mdo/Triton X-114	59	FAAS	30
Water and urine	PAN/Triton X-114	20	UV/Vis spectrophotometry	31
Tap, river and dispenser water (for drinking), saline serum and dextrose (for injection) and synthetic samples	PAN/Triton X-114	199	FO-LADS	32
Water and CRM, NIST 1570a spinach leaves	Me-BTABr/Triton X-114	23	FAAS	33
Foods	BDAP/ Triton X-114	25	FAAS	34
Biological water, natural water and wastewater, soil and blood	Methyl-2-pyridyl-ketone oxime/Triton X-114	58	FAAS	35
River, brook, mineral and synthetic sea water samples	Diethyldithiocarbamate/Triton X-114		GFAAS	36
High-salinity waters	DDTC/Triton X-114	20.6	ICP-OES	37
Environmental samples	IYPMI/Triton X-114	30	FAAS	38
Environmental samples	PHBI/Triton X-114	45	FAAS	39
Waters	PAR/Triton X-114	9,79	ICP-OES	40
Water and food samples	Magneson/Triton X-114	17	FAAS	41

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Table 3. Analytical characteristics of the method

Analytical parameters	700 µL cell type	3.50 mL cell type
Detection limit (µg L^{-1})		
λ= 410 nm	26	19
λ= 458 nm	40	15
Relative standard deviation (R.S.D. %) (*n*=7)	5.5	5.7
Preconcentration factor[a]	7.3	8
Preconcentration factor[b]	10	5

a Calculated by dividing the slope of the calibration curve after preconcentration by that obtained without preconcentration

b Calculated as the ratio of concentration of the analyte in the final surfactant-rich phase to that in the initial solution

Table 4. Application of CPE procedure in spiked samples

Water samples	Added (µg L^{-1})	Found* (µg L^{-1})	Recovery (%)
Tap water	50	51.1 ± 4.6	102.2
Well water	50	46.4 ± 2.85	92.8
Sea water	50	52.9 ± 3.5	105.8
Food samples	Added (µg g^{-1})	Found* (µg g^{-1})	Recovery (%)
Rice	12.3	13.2 ± 0.9	107.3
Lentil	25.8	26.0 ± 1.4	100.8
Chickpea	11.2	10.0 ± 1.0	89.3
Apple	15.3	14.2 ± 1.1	92.8
Lettuce	27.4	26.1 ± 1.0	95.3
Liver	36.5	32.1 ± 1.5	87.9
Fish	13.1	12.1 ± 0.8	92.4

* mean ± standard deviation, n=3

Figure 1. Effect of pH on cloud point extraction of nickel

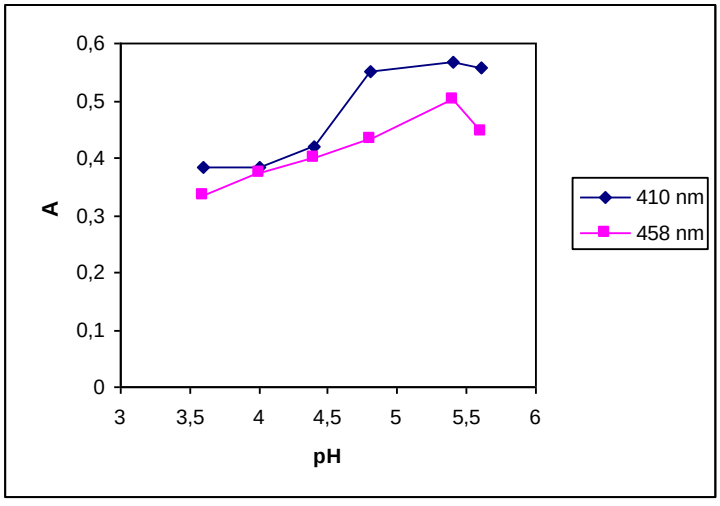

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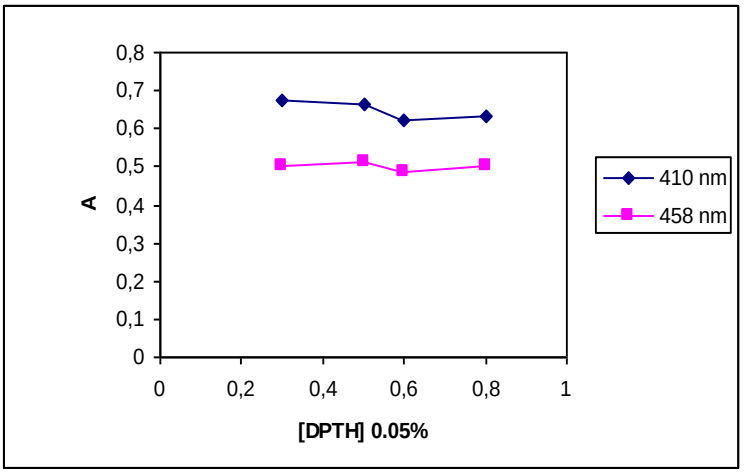
Figure 2. Effect of DPTH concentration on CPE of nickel



REFERENCES

[1] Thomas M, Ultraviolet and visible spectroscopy, in: Analytical Chemistry by Open Learning, 2nd edition, Wiley, New York, 1996.
[2] Prenesti E, Daniele PG, Toso S. Anal Chim Acta 2002; 459: 323.
[3] M Knochen, J Giglio. Talanta 2004; 64: 1226.
[4] N Teshima, N Fukui, T Sakai. Talanta 2005; 68: 253.
[5] Paleologos EK, Giokas DL, Karayannis MI. Trends Anal Chem 2005; 24: 426.
[6] Bosch Ojeda C, Sánchez Rojas F. Anal Bioanal Chem 2009; 394: 759.
[7] Watanabe H, Saitoh T, Kamidate T, Haraguchi K, Mikrochim. Acta 1992; 106: 83.
[8] Sombra L, Luconi M, Silva MF, Olsina RA, Fernandez LP. Analyst 2001; 126: 1172.
[9] Beiraghi A, Zarei AR, Babaee S. Anal Sci 2007; 2: 527.
[10] Beiraghi A, Babaee S. Asian J Chem 2008; 20:1999.
[11] Afkhami A, Madrakian T, Siampour H, J Braz Chem Soc 2006; 17: 797.
[12] Manzoori LJ, Karim-Nezhad G. Iran J Chem Chem Eng 2005: 2; 47.
[13] Hassanien MM, Abdel-Rhman MH, El-Asmy AA. Trans Metal Chem 2007; 32:1025.
[14] Shemirani F, Jamali MR, Kozani RR. Chem Analityczna 2007; 5: 327.
[15] Silva MF, LP Fernandez, RA Olsina and D Stacchiola. Anal Chim Acta 1997;342:229.
[16] MF Silva, Fernandez LP, Olsina RA. Analyst 1998; 123:1803.
[17] Garrido M, Di Nezio MS, Lista AG, Palomeque M, Fernández Band BS. Anal Chim Acta 2004; 502: 173.
[18] Afkhami A, Madrakian T, Siampour H. Int J Environ Anal Chem 2006; 86: 1165.
[19] Sohrabi MR, Farokhi E, Adnani A, Ziaian M. J Appl Sci 2007; 7: 3123.
[20] Madrakian T, Ghazizadeh F. J Hazard Mater 2008; 153:695.
[21] Shemirani F, Kozani RR, Jamali MR, Assadi Y, Hosseini MRM. Int J Environ Anal Chem 2006; 86: 1105.
[22] Laespada MEF, Pavon JLP, Cordero BM. Analyst 1993; 118: 209.
[23] Shemirani F, Kozani RR, Jamali MR, Assadi Y, Milani SMR. Sep Sci Technol 2005; 40: 2527.

[24] Ferreira HS, Bezerra MDA, Costa Ferreira SL, Microchim Acta 2006; 154: 163.
[25] Madrakian T, Afkhami A, Mousavi A. Talanta 2007; 71: 610.
[26] Safavi A, Abdollahi H, Nezhad MRH, Kamali R. Spectrochim Acta A 2004; 60: 2897.
[27] Bezerra MA, Conceição ALB, Ferreira SLC. Anal Bioanal Chem 2004; 378: 798.
[28] Manzoori JL, Karim-Nezhad G. Anal Chim Acta 2004; 521: 173.
[29] Sun Z, Liang P, Ding Q, Cao J. J Hazard Mater 2006; 137:943.
[30] Shemirani F, Jamali MR, Kozani RR, Salavati-Niasari M. Sep Sci Technol 2006; 41: 3065.
[31] Afkhami A, Bahram M. Microchim Acta 2006; 155: 403.
[32] Shokoufi N, Shemirani F, Memarzadeh F. Anal Chim Acta 2007; 601: 204.
[33] Lemos VA, França RS, Moreira BO. Sep Purif Technol 2007;54:349.
[34] Lemos VA, Santos MS, David GT, Maciel MV, Bezerra MDA. J Hazard Mater 2008; 159: 245.
[35] Ghaedi M, Shokrollahi A, Ahmadi F, Rajabi HR, Soylak M. J Hazard Mater 2008; 150: 533.
[36] Amais RS, Tarley CRT. Canadian J Anal Sci Spectrosc 2008; 53:130.
[37] Escaleira LA, Saltelli RE, Oliveira EP, Carvalho MFB, Becerra MA. Intern J Environ Anal Chem 2009; 89:515.
[38] Ghaedi M, Shokrollahi A, Niknam K, Niknam E, Soylak M. Cent Eur J Chem 2009; 7: 148.
[39] Ghaedi M, Shokrollahi A, Niknam K, Soylak M. Sep Sci Technol 2009; 44: 773.
[40] Silva EL, Roldan PS, Giné MF. J Hazard Mater 2009; 171:1133.
[41] Sahin CA, Efecinar M, Satiroglu N. J Hazard Mater 2010; 176:672.
[42] Bonilla Abascal J, Garcia de Torres A, Cano Pavon JM. Microchem J 1983; 28: 132.
[43] Cano Pavon JM. Garcia de Torres A, Bosch Ojeda C. Analyst 1985; 110: 1137.