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A permeation liquid membrane system for determination of nickel in seawater

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Abstract

The use of a permeation liquid membrane system for the preconcentration and separation of nickel in natural and sea waters and subsequent determination by atomic absorption spectroscopy is presented. 2-Hydroxybenzaldehyde *N*-ethylthiosemi-carbazone (2-HBET) in toluene is used as the active component of the liquid membrane. A study strategy based on a simplex design has been followed. Several chemical and physical parameters were optimized. Maximum permeation coefficient was obtained at a feed solution pH of 9.4, 0.3 mol l^{-1} of HNO_3 in the stripping solution and 1.66 mmol l^{-1} of 2-HBTE in toluene as carrier. The precision of the method was 4.7% at 95% significance level and a detection limit of 0.012 $\mu g\,l^{-1}$ of nickel was achieved. The preconcentration procedure showed a linear response within the studied concentration range from 3 to 500 $\mu g\,l^{-1}$ of Ni in the feed solution. The method was validated with different spiked synthetic seawater and certified reference water samples: TMDA-62 and LGC 6016, without matrix interferences and showing good concordance with the certified values, being the relative errors −5.9% and −2.2%, respectively. Under optimal conditions, the average preconcentration yield for real seawater samples was 98 ± 5%, with a nickel preconcentration factor of 20.83 and metal concentrations ranging between 2.8 and 5.4 $\mu g\,l^{-1}$.

Keywords: Bulk liquid membrane; Extraction–reextraction process; Seawater; Determination of nickel; 2-Hydroxybenzaldehyde *N*-ethylthiosemicarbazone

1. Introduction

Many heavy metals are toxic and cause environmental damage, such as nickel. This metal is released into the aquatic environment from dissolution of rocks and soil, atmospheric fallout and biological cycles. Also, the high consumption of nickel products in industrial activities and sewage waste-waters inevitably leads to environmental pollution.

Nickel is an essential metal to plants and some animals, being a component of the enzyme urease and of five other important enzymes [1]. It is moderately toxic element but can cause allergic reactions and certain nickel compounds are carcinogenic [2].

Natural water contains low concentration levels (0.5-1.5 $\mu g\,l^{-1}$), being background level of 0.3 $\mu g\,l^{-1}$ in river water [3] and 0.7 $\mu g\,l^{-1}$ in surface seawater [4]; but those are increased owing to pollution of water (i.e. nickel concentration in Mersey Estuary (UK) ranged from about 0.59 to 13.5 $\mu g\,l^{-1}$ (10–230 nmol l^{-1}) [5].

Considering the low content of nickel in environmental samples, sensitive analytical techniques are required. Nickel determination in water samples usually could be carried out directly by atomic spectrometry: inductively-coupled plasma optical emission (ICP-OES) or electrothermal and flame atomic absorption spectrometry (ETAAS and FAAS), although the detection limits is not sufficient when the concentrations are too low; moreover, seawater samples with high salinity require simplifying the matrix prior the analysis. So, preconcentration is an effective means for analyzing both complex matrices and samples with low levels of metal.

Many preconcentration techniques have been proposed. Various methods of preconcentration of analytes prior to determination with atomic spectrometry are based on solvent extraction [6–9], but sometimes these procedures cannot be combined with

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ICP-OES, ETAAS or FAAS, because of difficulties of introducing organic solvents into plasma, furnace or flame [10]. So, extraction-stripping methods have been used among others.

Permeation liquid membrane (PLM) techniques offer a potential attractive alternative to these conventional processes in that they combine the process of extraction and stripping in a single unit operation. Two aqueous phases are separated by an immiscible membrane liquid. Preconcentration and separation of analyte occurs automatically as soon as the permeation membrane, containing specific metal ion carrier (extracting agent), is in contact with the feed solution. The flux through the membrane is the key factor of interest [11]. Three basic PLM systems can be used: bulk (BLM), supported (SLM) and emulsion (ELM) liquid membranes; in this paper, a BLM system has been used because of simplicity to use [12].

The applications of PLMs to analysis of natural waters show many potential advantages: high selectivity, reduced sample handling, easy automation and useful in field or in situ analysis. Also, these systems can provide free and other chemical forms of the test metals, being useful for speciation studies of environmental relevance [13]. Different reagents can be employed for sample enrichment and separation in trace analysis of metals in waters. One possibility is to use ion-pairing reagents (counter ion transport extraction) (di-2-ethylhexylphosphoric acid (DEPHA) [14], methyltrioctylammonium chloride (Aliquat 336) [15], laurate anion (LA) [11]). Another possibility is to use complexation equilibria, involving reagents such as crown ethers (1,10-didecyl-diaza-18-crown-6 (Kriptofix 22DD) [16], dibenzo-18-crown-6 [17]), calixarenes (5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-tri-methoxy calyx[6]arene-38,40,42-triol [18]), organophosphorous compounds (triisobutylphosphine sulphide (Cyanex 471X)[19]; tributylphosphate (TBP)[20]; phosphine oxide (Cyanex 923)[21,19], tri-*n*-octyl-phospine oxide (TOPO) [18]), benzoylthiourea derivates (*N*-benzoyl-*N*′,*N*-diheptadecylthiourea [22]), 8-hydroxyquinoline [23], ... Sometimes, a combination of these possibilities increases the efficacy of the system using synergic reagents. In most cases, the reported methods were applied to industrial waste water, synthetic water, river water or spiked seawater. There were only few applications to real seawater [17,18,24], but usually, the permeation fluxes were lower in seawater because the co-transport of other metals ions (principally, ions of seawater saline matrix) was an interference. So, the efficacies of the processes usually were not of 100% (40–95%). Papantoni et al. [23] have proposed a PLM system for the preconcentration of Ni using a combination of two extraction mechanisms (8-hydroxyquinoline in the donor solution and Aliquat-336 in the membrane liquid) with efficiency of 70%.

The use of ligands with imine group has been proposed previously for us as carrier in BLM [25]. This group of reagents shows interesting properties as complexing agent of transition metal ions: metallic complexes are quickly formed, usually as neutral chelates and the selectivity can be enhanced depending on pH values. A 100% preconcentration of Cu and Cd was obtained using 2-acetylpyridine benzoylhydrazone in real seawater, showing the potential applicability of these reagents [25].

In this paper, the preconcentration and separation of nickel in water using a new BLM system with an imine ligand is presented. A liquid membrane containing 2-hydroxybenzaldehyde *N*-ethylthiosemicarbazone (2-HBET) dissolved in toluene as carrier was used. 2-HBET is a multidentate ligand of transition metals with five potential coordination sites (3N, 1O and 1S atoms) [26]. After enrichment, metal was determined in the receiving acid solution by flame or furnace atomic absorption spectrometry, simple and conventional techniques. The effect of chemical and physical variables on the transport of nickel through the liquid membrane was studied using a modified simplex method [27]. The analysis of nickel in natural waters was possible, even in seawater samples. The method offers important advantages such as simplicity and economy and enables eliminating matrix interferences in waters.

2. Experimental

2.1. Instrumentation

The cell used for the transport experiments was a cylindrical glass cell (11.34 cm i.d.) with a concentric glass tube (2.56 cm i.d.) which contained separated two aqueous phases (described elsewhere [25]). The feed solution was placed into the external cylinder ($V_f = 250$ ml) and the stripping solution (receiving solution) was transferred into the inner cylinder ($V_s = 12$ ml). Liquid organic phase with carrier was added on the top of both aqueous solutions. The membrane area in contact with the two aqueous solutions was 95.85 cm^2. In these conditions the preconcentration factor was 20.83, provided by the ratio V_f/V_s. Solutions in the cell were stirred with two Teflon-coated magnetic bars by using a model Agimatic-S magnetic stirrer (Selecta, Spain). Transport experiments were carried out with temperature control using a thermostatic bath (TECTRON-100, 3473100, Selecta, Spain).

An atomic absorption spectrometer (AAS) was used for the measurements of nickel in acid solutions using a Solaar M Series (Unicam, UK) (GFAAS, graphite furnace or FAAS, flame) with a hollow cathode lamp at a wavelength of 232 nm and a 0.1 nm spectral band. GFAAS determinations were performed using pyrolytically coated graphite tubes and Zeeman background corrector. Air-acetylene flame and deuterium background corrector were used for FAAS analysis. The instrumental parameters were those recommended by the manufacturer. A Metrohm model 757 VA Trace Analyzer processor with a Metrohm 747 VA Electrode Stand with automated hanging mercury drop electrode (HMDE) was used for the voltammetric measurements in saline samples, using a reference method for nickel with dimethylglyoxim by adsorptive cathodic stripping voltammetry (AdCSV) (VA Application Note No. V-69, Metrohm) [28]. A Unicam Helios Gamma&Delta (Unicam Limited, UK) spectrophotometer was used for UV–vis spectroscopic measurements with 1 cm quartz glass cells (1 cm × 1 cm × 4.5 cm).

Organic matter was removed for real water samples by UV irradiation with a Metrohm model 705 UV Digester in quartz tubes. A model 2001 pH-meter equipped with 52–02 combined glass-Ag/AgCl electrode (Crison, Spain) was used for pH measurements.

Sample handling and preparation of solutions were performed using polyethylene gloves and under a class 100 laminar flow hood cabinet Crusair model 9005-FL (Cruma, Spain).

Water used for experiments was purified by reverse osmosis with an Elix 3 system followed by deionization with an 18 $\mathrm{M\Omega\,cm^{-1}}$ deionised Milli-Q system (Millipore, USA).

All laboratory materials were acid cleaned (2 $\mathrm{mol\,l^{-1}}$ HNO_3), rinsed with Milli-Q water and stored in a laminar flow cabinet.

2.2. Chemicals

2-HBET was synthesized by reaction between 2-hydroxybenzaldehyde (2-HB) and ethylthiosemicarbazone (ET) (Sigma–Aldrich, Steinhein, Germany). Ethanolic solutions of 2-HB (1 ml in 20 ml) and ET (1.12 g in 20 ml) were mixed under reflux heating 15 min. Crystals were filtered off and subsequently crystallized from 1:1 ethanol/water. Actually, Sigma–Aldrich Company (2005 Catalog; CAS number: 76572-70-8) supplies this ligand ($C_{10}H_{13}N_3OS$; formula weight: 223.3). Solutions of 2-HBET (0.2–2.14 $\mathrm{mmol\,l^{-1}}$) in toluene were prepared weekly and kept at 4 °C in darkness when not use. They were used as liquid membrane. Aqueous stock metal standard solutions were prepared by dissolving AAS standard solutions of 1000 $\mathrm{mg\,l^{-1}}$(Merck, Darmstadt, Germany) in 0.05 $\mathrm{mol\,l^{-1}}$ HNO_3.

Britton buffer solutions were used to adjust the pH of feed solutions during the optimization process (pH 8–11) and prepared according to previously reported [29], using sodium hydroxide, o-boric acid, *o*-phosphoric acid, acetic acid and potassium chloride of Suprapur grade (Merck, Darmstadt, Germany).

The synthetic, certified and real samples were adjusted with 6 $\mathrm{mol\,l^{-1}}$ NH_4Cl/NH_3 buffer solution (pH 9.4), avoiding high dilution of samples.

All reagents were of analytical-reagent or Suprapur grade and all solutions were prepared using Milli-Q deionised water, absolute ethanol or toluene of pro analysis grade (Merck, Darmstadt, Germany).

2.3. Preconcentration and separation procedure

Transport experiments were carried out with the cell described above. The aqueous feed solution ($V_f = 250$ ml) contained ion nickel (500 $\mathrm{\mu g\,l^{-1}}$) and buffered with Britton-Robinson buffer (0.25 $\mathrm{mol\,l^{-1}}$ ionic strength in feed solution). The stripping solution ($V_s = 12$ ml) contained 0.1–1.5 $\mathrm{mol\,l^{-1}}$ HNO_3. The organic liquid membrane ($V_o = 80$ ml) containing 0.2–2.14 $\mathrm{mmol\,l^{-1}}$ 2-HBET in toluene was added over both aqueous solutions. Aqueous solutions were stirred by Teflon-coated magnetic bars at 750 rpm and the system temperature was controlled using a thermostatic bath.

During transport experiment, different 2 ml aliquots of the stripping solution were taken periodically to measure nickel concentration, while 2 ml of nitric acid with the same concentration used and saturated in toluene were added to keep the volume of the receiving solution constant. The acid extracts were measurement by atomic absorption spectroscopy and the nickel concentrations obtained were corrected taking into account these dilutions. Saline samples were measurement by stripping voltammetry: 10 ml of sample was transferred into the voltammetric cell and the pH adjusted by pH 9.5 ammonium buffer solution (0.5 ml of 6 $\mathrm{mol\,l^{-1}}$); 0.1 ml of 0.053 $\mathrm{mol\,l^{-1}}$ DMG in ethanol was added and AdCSV measurements of the Ni-DMG complex were carried out.

UV digestion of real waters with organic matter content was carried out when was necessary, in order to avoid metal organic complexes with high stability to avoid interference in the metal transport experiments or for voltammetric measurements.

The experimental variables were optimized in order to achieve the highest efficiency in the transport of nickel complex across the membrane. Therefore, the permeability P ($\mathrm{cm\,min^{-1}}$) of nickel across the membrane was used as response variable, using the following linear curve:

$$-\ln[\mathrm{Ni}]_\mathrm{f} = \frac{Q}{V_\mathrm{f}} Pt - \ln[\mathrm{Ni}]_{\mathrm{f},0}$$

The P-value was determined from data sets in the form of nickel concentration versus time, where A was the effective membrane area and V_f was the volume of feed solution. $[\mathrm{Ni}]_{\mathrm{f},0}$ and $[\mathrm{Ni}]_\mathrm{f}$ were the nickel concentrations in the feed solution at time 0 and t, respectively. Also, nickel recovery (%) in the stripping solution was used.

3. Results and discussion

2-HBET is a thiosemicarbazone multidentate ligand. Usually, it can be bonded to different transition metals, producing very stable heteropolynuclear complexes [26]. This ligand has been applied in this paper for the first time as carrier of nickel in a liquid membrane, forming an uncharged chelate. This neutral complex is extracted by the organic phase and destroyed by the acid phase, producing the metal transport through the membrane. The pH gradient between feed and stripping solutions is the driving force for this transport. The absence of organic reagent did not produce transport of the metal ion.

The continuous variation method (Job's method) was applied in order to establish the stoichiometry of the complex used in this study. About 8:2 aqueous-ethanolic solutions of nickel chelate buffered at pH 9.4 were prepared and their absorbances were measured at 420 nm with visible spectrophotometer. The nickel/ligand ratio obtained was 1:1.

3.1. Optimization of the preconcentration procedure

A set of preliminary experiments was performed to establish the significant variables on the metal transport, which were subsequently analyzed by using a modified simplex design.

The previous physical and chemical parameters studied were pH and components of the feed and strip solutions, type and volume of organic solvent, 2-HBET concentration in organic liquid membrane and stirring rate of solutions. These experiments were carried out with temperature control at 28 ± 0.5 °C.

Table 1
Simplex design with significant variables and values for the *P* (permeability) response (toluene volume: 80 ml; feed solution: 500 μg l^{-1} of Ni; stirring rate: 750 rpm; temperature: 28 ± 0.5 °C; extraction time: 4.5 h)

Vertex	pH of feed solution	Strip solution: [HNO_3] (mol l^{-1})	[2-HBET] (mmol l^{-1})	Permeability ($\times 10^3$ cm min^{-1})	Type
1	7	1.5	0.20	0.026	I
2	7	0.5	1.00	4.69	I
3	9	0.5	0.20	7.82	I
4	9	1.5	1.00	2.34	I
5	9.7	0.2	1.27	14.61	R
6	11	−0.5	1.80	Not possible	E
7	8.1	−0.7	0.65	Not possible	R
8	8.8	0.9	0.91	6.26	C^-
9	11.3	0.6	0.59	2.09	R
10	8.1	0.5	0.90	10.17	C^-
11	9.1	−0.1	0.67	Not possible	R
12	8.9	0.6	0.85	12.78	C^-
13	8.8	0.4	1.81	10.69	R
14	10.2	0.3	1.72	15.64	R
15	11.2	0.2	2.13	3.65	E
16	10.4	0.3	0.75	15.64	R
5RE1	9.7	0.2	1.27	19.56	R
17	11.3	−0.1	1.64	Not possible	R
18	9.5	0.4	1.05	16.43	C^-
19	9.2	0.3	1.94	17.21	R
20	8.7	0.3	1.12	12.51	R
21	9.8	0.3	1.57	19.30	C^-
22	9.6	0.1	2.14	15.91	R
23	9.5	0.3	1.32	21.13	C^-
24	10.1	0.2	0.83	17.21	R
25	9.4	0.3	1.66	21.38	C^-

I: initial simplex; R: reflexion; E: expansion; C^+: positive contraction; C^- negative contraction.

The most adequate conditions were found to be basic pH values for feed solution, dilute nitric acid as strip solution, toluene as organic solvent, minimum volume of organic solution that could permit a good contact among the phases (V_o = 80 ml) and maximum stirring rate (750 rpm) avoiding the mix of different phases. Also, the transport was facilitated with an increase of the 2-HBET:Ni concentration ratio. In any cases, the significant variables were pH of the feed and strip solution and 2-HBET concentration as carrier.

Therefore, several variables were kept fixed, whilst a modified simplex with the significant variables was carried out in order to obtain the optimal conditions (Table 1) by using the software Multisimplex 2.0.4 [27]. The response of simplex was the permeability coefficient. The initial simplex with four vertices (three variables) was performed using previous adequate conditions for no significant variables. The simplex was stopped after 26 transport experiments. The criterion selected for stopping the simplex was based on the comparison of the variance of the proposed method (variance of experiment number 5 = 1.46×10^{-6}, for $n = 4$) with the variance of each simplex. This comparison was carried out using the corresponding *F*-values. Optimum conditions were obtained for trial 25 producing a permeability of 21.38×10^{-3} cm min^{-1} with the following values of chemical variables: pH 9.4 in the feed solution, 0.3 mol l^{-1} HNO_3 in the stripping solution, 1.66 mmol l^{-1} 2-HBET in the liquid membrane.

At optimum conditions, the dependence of the transport of metal with the temperature was studied within the range of 25–50 °C. Higher values diminished the permeability probably due to the hydrolysis of 2-HBET. Fig. 1 shows the temporal variation of preconcentration yield of nickel at different temperature. Hundred percent efficiency was possible to achieve from 4 to 5.5 h depending on this parameter.

3.2. *Effect of saline matrix in the source phase*

The effect of saline concentration in the source phase on the efficiency of nickel transport was studied using NaCl addition in the usual range of natural water: 0, 10, 20, 30 and 40 g l^{-1}, at 50 °C, containing 500 μg l^{-1} of Ni. It was found a low decrease in the percentage of metal transport, being successively the preconcentration yield diminished a value of 3.3 ± 0.3% for each studied salinity value. It was necessary to increase the shaking time, from 4 to 6.5–7 h with higher saline samples in order to

Table 2
Preconcentration of nickel from different concentrations of spiked synthetic seawater (temperature: 50 °C; preconcentration time: 7 h; $n = 2$)

Ni spiked (μg l^{-1})[a]	Ni found by proposed method (μg l^{-1})[b]	Error (%)
50 ± 2	48 ± 5	−4.0
17 ± 2	18 ± 1	+5.9
5.30 ± 0.01	5.45 ± 0.08	+2.83

[a] Determination by AdCSV [28].
[b] Proposed preconcentration method + detection by AAS.

Table 3
Determination of nickel in certified reference waters and seawater samples using the proposed new method (temperature: 50 °C; preconcentration time:7 h)

Sample	Ni concentration ($\mu g\, l^{-1}$)	Ni found by proposed method ($\mu g\, l^{-1}$)[a]	Relative error (%)
LGC 6016	186 ± 3[b]	182 ± 4	−2.2
TMDA-62	98 ± 9[b]	92 ± 1	−5.9
Seawater 1[c]	5.4 ± 0.5[d]	5.1 ± 0.1	−5.6
Seawater 2[c]	3.9 ± 0.2[d]	3.81 ± 0.09	−2.3
Seawater 3[c]	2.8 ± 0.2[d]	2.86 ± 0.06	+2.1

[a] Proposed preconcentration method + detection by AAS ($n = 2$).
[b] Certified value.
[c] Seawater samples were collected in different sectors of Huelva Coast, Spain.
[d] Determination by AdCSV ($n = 6$) [28].

obtain complete efficient preconcentration (100 ± 3% at 6.5 h and 10–40 $g\, l^{-1}$ of NaCl).

3.3. Analytical performance of the method

In transport experiments, the reproducibility of the preconcentration yield was studied by performing four replicate transport experiments with 500 $\mu g\, l^{-1}$ of Ni under the optimized conditions at 50 °C. The precision of the method was 4.7% for significance level at 95% ($n = 4$) with 500 $\mu g\, l^{-1}$ of Ni, Ni recovery being 99 ± 3% at 4 h.

Four replicates of blank were measured using optimal conditions and deionised water. The obtained value was 0.036 ± 0.004 $\mu g\, l^{-1}$. The limit of detection, defined as the concentration of analyte giving response equivalent to three times the standard deviation of the blank, were 0.012 $\mu g\, l^{-1}$ of Ni. Blank samples were measured by GFAAS, because detection limit of FAAS was not enough.

The preconcentration procedure showed a linear response within the tested concentration range from 3 to 500 $\mu g\, l^{-1}$ in the feed solution.

In order to determine the application of the method to seawater, synthetic seawater [30] solutions containing Ni were prepared and analyzed by the proposed method and compared with those obtained by AdCSV [28]. Studies with different concentration of metal showed that seawater synthetic matrix did not interference in nickel determination after the preconcentration procedure (Table 2).

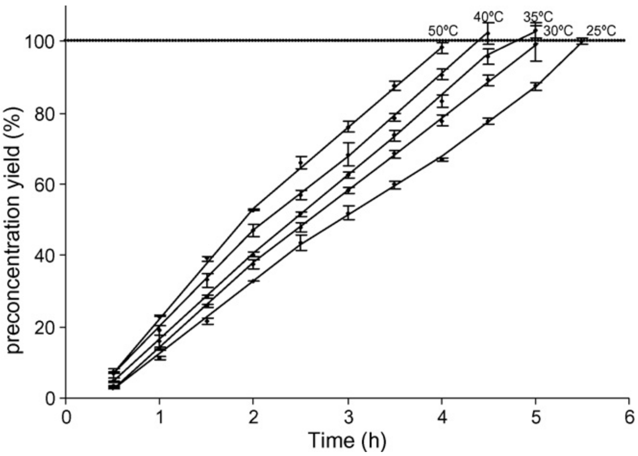

Fig. 1. Temporal variation of preconcentration yield at different temperature (feed solution: 500 $\mu g\, l^{-1}$ of Ni at pH 9.4; stripping solution: 0.3 $mol\, l^{-1}$ HNO_3; BLM ($V_o = 80$ ml): 1.66 $mmol\, l^{-1}$ 2-HBET in toluene; stirring rate: 750 rpm).

3.4. Accuracy of the method

The accuracy of the method for nickel was assessed by analyses of two reference certified water: fortified water from Lake Ontario (TMDA-62) and estuarine water (LGC 6016). Two replicates of each reference material were preconcentrated and analyzed after UV digestion with hydrogen peroxide 30% Suprapur (Merck, Darmstadt, Germany), being UV digestion not necessary for TMDA-62. Efficient preconcentration was achieved after 7 h, being the relative errors −5.9% and −2.2%, respectively (Table 3).

3.5. Determination of nickel in seawater samples

The method was applied to different samples of seawater from coast of Huelva (Spain) for the determination of nickel. Samples were filtered through 0.45 μm pore size filters, acidified with HNO_3 and stored until the application of the method. Nickel was measured after UV digested with H_2O_2 using the proposed method. The results in Table 3 were in good agreement with the values obtained using AdCSV method for seawater [28] and no significant differences at 95% confidence interval were found between them. The average preconcentration yield for real samples was 98 ± 5%.

4. Conclusions

Nickel can be effectively transported, through a liquid membrane of toluene containing 2-HBET. The efficiency of the process is 100% at 4–7 h, depending on the ionic strength of the sample and the temperature of the process. The method has a nickel preconcentration factor of 20.83.

This system permits the separation, preconcentration and quantitative determination of nickel in natural water, where low levels of metal concentration are found. Also, the proposed method can be applied satisfactorily to the analysis of seawater with complex saline matrix, allowing measurements by AAS, a common and simple technique but in which saline ions interfere with analysis direct.

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References

[1] R.K. Thauer, Science 293 (5533) (2001) 1264.

[2] H.A. Mckenzie, L.E. Smythe, Quantitative Trace Analysis of Biological Materials, Elsevier, Amsterdam, 1988.

[3] B. Salbu, E. Steinnes, Trace Elements in Natural Waters, CRC Press, Boca Raton, 1995.

[4] U. Forstner, G.T.W. Wittmann, Metal Pollution in the Aquatic Environment, 2nd revised ed., Springer-Verlag, Berlín, 1983.

[5] M. Martino, A. Turner, M. Nimmo, Mar. Chem. 88 (2004) 161.

[6] K.W. Bruland, R.P. Franks, G.A. Knauer, J.H. Martin, Anal. Chim. Acta 105 (1979) 233.

[7] L.G. Danielsson, B. Magnusson, S. Westerlund, K. Zhang, Anal. Chim. Acta 144 (1982) 57.

[8] A.M. De Kersabiec, G. Blanc, M. Pinta, Fresenius'Z. Anal. Chem. 322 (1985) 731.

[9] S. Sachsenberg, T. Klenke, W.E. Kumbein, E. Zeeck, Fresenius'J. Anal. Chem. 342 (1992) 163.

[10] J.W. Olesik, A.W. Moore, Anal. Chem. 62 (1990) 840.

[11] J. Buffle, N. Parthasarathy, N.K. Djane, L. Matthiasson, in: J. Buffle, G. Horvai (Eds.), In Situ Monitoring of Aquatic Systems: Chemical Analysis and Speciation. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, John Wiley and Sons Ltd, Sussex, England, 2000, pp. 408–493.

[12] R.R. Bartch, J.D. Way, ACS Symposium Series 716, Washington, DC, 1996, 422 p.

[13] N. Parthasarathy, M. Pelletier, J. Buffle, J. Phys. IV France 107 (2003) 1021.

[14] K. Ndungú, N.K. Djane, L. Mathiasson, J. Chromatogr. A 826 (1998) 103.

[15] N. Djane, K. Ndungú, C. Johnsson, H. Sartz, T. Tornstrom, L. Mathiasson, Talanta 48 (5) (1999) 1121.

[16] N. Parthasarathy, M. Pelletier, J. Buffle, J. Chromatogr. A 1025 (1) (2004) 33.

[17] Y.K. Agrawal, S. Sudhakar, Sep. Pur. Technol. 27 (2002) 111–119.

[18] J. Ramkumar, S.K. Nayak, B. Maiti, J. Membr. Sci. 196 (2002) 203.

[19] F.J. Alguacil, H. Tayibi, Desalination 180 (2005) 181.

[20] H.G. Nowier, N. El-said, H.F. Aly, J. Membr. Sci. 177 (2000) 41.

[21] F.J. Alguacil, A.G. Coedo, M.T. Dorado, Hydrometallurgy 57 (2000) 51.

[22] C. Fontás, M. Hidalgo, V. Salvadó, E. Anticó, Anal. Chim. Acta 547 (2005) 255.

[23] M. Papantoni, N. Djane, K. Ndung'u, J.A. Jonson, L. Mathiasson, Analyst 120 (1995) 1471.

[24] C. Mendiguchía, C. Moreno, M. García-Vargas, Anal. Chim. Acta 460 (2002) 35.

[25] M.D. Granado-Castro, M.D. Galindo-Riaño, M. García-Vargas, Spectrochem. Acta Part B 59 (2004) 577.

[26] D. Kovala-Demertzi, P.N. Yadav, M.A. Demertzis, J.P. Jasiski, F.J. Andreadaki, I.D. Kostas, Tetrahedron Lett. 45 (2004) 2923.

[27] MultiSimplex, version 2.0.4, MultiSimplex AB (publ), Karlskrona, Sweden, 1998.

[28] Methrom, Determination of nickel and cobalt in seawater, VA Application Note No. V-69, 2004, http://www.metrohm.com/infocenter/applications/notes/index.php4.

[29] C. Mongay, V. Cerda, Ann. Chim. 64 (1974) 409.

[30] K. Grasshoff, M. Ehrhardt, K. Kremling, Methods of Seawater Analysis, 2nd ed., Verlag-Chemie GmbH, Weinheim, Germany, 1983, p. 365.