Talanta 103 (2013) 161–165

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A bulk liquid membrane–flow injection (BLM–FI) coupled system for the preconcentration and determination of vanadium in saline waters

Juan J. Pinto*, Manuel García-Vargas, Carlos Moreno

Department of Analytical Chemistry, Faculty of Marine and Environmental Sciences, University of Cadiz, 11510 Puerto Real, Spain

ARTICLE INFO

Article history:
Received 5 June 2012
Received in revised form
4 October 2012
Accepted 7 October 2012
Available online 12 October 2012

Keywords:
Flow injection analysis
Vanadium
Bulk liquid membrane
Seawater
Di-2-pyridyl ketone benzoylhydrazone
Spectrophotometry

ABSTRACT

A bulk liquid membrane–flow injection (BLM–FI) system has been developed for the preconcentration and spectrophotometric determination of vanadium in saline waters. The preconcentration step was based on a bulk liquid membrane containing Aliquat 336 (acting as a carrier) dissolved in dodecane/dodecanol. Vanadium species were chemically pumped due to the pH gradient between the sample (pH 3.2) and the receiving solution (pH 9.8). Vanadium transport through the membrane was monitored by a new and sensitive spectrophotometric method based on its reaction with di-2-pyridyl ketone benzoylhydrazone (dPKBH) in an acidic medium. As a consequence of membrane transport, vanadium was recovered in an ammonium solution, where total vanadium concentration was spectrophotometrically determined at 375 nm, as the pentavalent species, by using a flow injection analysis (FIA) system. Under optimal conditions, this FIA system provided a detection limit of 4.7 μg L^{-1} ($3s_{\mathrm{blank}}/m$) and RSD 2.72%, for vanadium determination in saline samples. Both preconcentration and determination steps were previously optimized by modified simplex methodologies.

The proposed coupled method was successfully applied to the determination of vanadium in a certified reference material (TMDA-62) and in two seawater samples.

1. Introduction

Vanadium is a trace element that plays an important role in many biochemicals, environmental, biological and industrial processes. When present in trace concentrations (μg L^{-1}) is an essential element for cell growth, but can be toxic at higher concentrations [1]. Although in aqueous solutions it may occur in oxidation states from (II) to (V), forms (IV) and (V) are the most stable, with V(V) being more toxic than V(IV) [2].

Because of its toxic and essential nature in biological systems, the development of analytical methodology to determine vanadium in environmental samples has received considerable interest by many authors. Several analytical techniques have been used for this purpose, spectroscopy [3–6] and voltammetry [7] being amongst the most frequently employed. Besides the well-known advantages of these instrumental techniques, all of them present a series of disadvantages (difficulty for *in situ* application, high investment cost, complexity or specific electrodes). Therefore, simple, reliable and low-cost analytical methods are also convenient.

In this sense, spectrophotometric methods have been extensively used for the determination of vanadium in environmental and biological samples. They may be based on complex formation, redox, ion-association, catalytic reactions, etc. [8]. Many examples of different spectrophotometric reagents applied to the determination of vanadium in environmental samples may be found in the bibliography [8–11]. Although it may be subject to interferences, 4-(2-pyridylazo) resorcinol (PAR) is probably one of the most extensively applied, and a detection limit of 2.8 μg L^{-1} has been reported [12]. This reagent has also been applied to the flow-injection determination of vanadium, with a limit of determination of 0.05 g L^{-1} [13]. Thus, since spectrophotometry provides higher limits of detection than other advanced techniques, new and more sensitive reagents as well as easy-to-use preconcentration methodologies are needed too.

Several preconcentration procedures have been reported for vanadium determination, which mainly use solvent extraction [14–16] and ion exchange [17–19]. Although they normally provide good preconcentration factors, many of them generally suffer excessive sample and/or reagents manipulation, involving a high risk of contamination during sample treatment.

Nowadays, liquid membranes are simple and effective means for the separation and preconcentration of trace metals in environmental samples [20], and they have proved their applicability to trace element determination even in complex samples such as seawater [21,22]. The transport of the chemical species through an organic solution is based on the simultaneity of the extraction and back extraction processes, reducing sample

---

* Corresponding author. Tel.: +34 956 016431; fax: +34 956 016262.
E-mail address: juanjose.pinto@uca.es (J.J. Pinto).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.10.026

manipulation and then, decreasing the risk of contamination. Usually, an improvement in the transport process is achieved by adding a reagent in the liquid membrane, which acts as a chemical carrier. Tricaprylylmethylammonium chloride (Aliquat 336®) [23,24], tri-n-octyl amine (TOA) [25] or di-2-ethylhexyl phosphoric acid (D2EHPA) [26,27] have been described as carriers for vanadium transport in liquid membranes. Although the transport conditions have been optimised for different media, to the best of our knowledge no application for the preconcentration and determination of vanadium in real samples has been reported.

In this work, we have developed a BLM–FI coupled system for the preconcentration and spectrophotometric determination of vanadium in natural and seawater samples. It is based on the spectrophotometric reaction of vanadium with dPKBH, which has demonstrated its applicability in the determination of trace metals in natural waters [28], after its preconcentration by a liquid membrane system containing Aliquat 336 in dodecane/dodecanol. Once optimized, the new system was successfully applied to the determination of vanadium in a certified reference material (TMDA-62) and in two real seawater samples.

2. Experimental

2.1. Reagents and solutions

Commercial standard solutions of 1000 mg L^{-1} V(V) were purchased from Merck (Darmstadt, Germany). All the chemicals used were of analytical-reagent grade and were purchased from Merck or Flucka (Buchs, Switzerland). All the solutions were prepared with MilliQ water (Millipore, USA). The spectrophotometric reagent dPKBH was synthesized according to the procedure outlined by García-Vargas et al. [28].

The FIA reagent consisted of a 7.0×10^{-4} mol L^{-1} dPKBH (5% *v/v* ethanol) solution at pH 4.7, kept in a 0.1 mol L^{-1} acetate buffer solution.

For liquid membrane experiments, Aliquat 336 (A336) was dissolved in dodecane with 3.5% *v/v* 1-dodecanol. Stripping solutions consisted of 0.1 mol L^{-1} NH_4OH in 0.6 mol L^{-1} $NaNO_3$ solution (in order to compensate the ionic strength). Feed solutions were prepared with 1 mg L^{-1} V in a 35 g L^{-1} NaCl solution and adjusting pH by addition of HNO_3 or NaOH when necessary.

2.2. Instruments

The coupled BLM–FI system used in this study is shown in Fig. 1. The flow injection manifold consisted of a Perimax 12 four-path peristaltic pump (Spetec, Germany) equipped with Tygon tubing, which was used to manipulate the flows of three channels (reagent, carrier and sample solutions), a Model 1106 injection valve (Omnifit, UK), and PU 8750 UV–Vis spectrophotometer (Philips, The Netherlands) equipped with a quartz flow cell with a 10 mm pathlength (Hellma, Germany). Transport lines and reaction coils were made using 0.8 mm i.d. PTFE tubing (Omnifit, UK). Connections were made of polypropylene (Omnifit, UK). The bulk liquid membrane consisted of a glass homemade beaker-in-a-beaker type cell with 39 mL and 24 mL being the volumes of the external and internal beakers, respectively. Solutions in the cell were stirred with Teflon-coated magnetic bars by using a model Agimatic-N magnetic stirrer (Selecta, Spain).

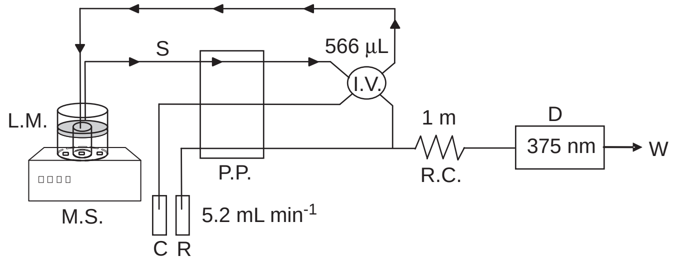

Fig. 1. BLM–FI manifold. L.M.: liquid membrane cell; M.S.: magnetic stirrer; I.V.: injection valve; S, C, R: sample, carrier and reagent channels,respectively P.P.: peristaltic pump; R.C.: reaction coil; D.: detector; W.: waste.

Acidity was measured with a Model 2001pH meter provided with a combined glass–Ag/AgCl electrode (Crison, Spain).

2.3. Procedure

To ensure the highest sensitivity of the determination method, the optimization of the FI manifold was performed in two steps: firstly, a univariate pre-optimization procedure was carried out by varying the sample injection volume (66–750 µL), reaction coil length (1–4 m), and reagent flow rate (1.6–6.6 mLmin^{-1}). Then, a second optimization process was performed to find out optimum conditions by applying a modified simplex methodology. The experimental conditions for each experiment were obtained by using software MultiSimplex 98 (MultiSimplex AB, Sweden) [29].

Once the FI system was optimized, it was coupled to the preconcentration cell and then, the chemical conditions of the preconcentration system (pH of feed and stripping solutions and A336 concentration) were optimized by applying a modified simplex methodology. The amount of metal passing through the BLM was monitored spectrophotometrically at scheduled time intervals, and the concentration values obtained were corrected by taking into account the amount of metal in the aliquots of the receiving solution previously removed. In order to control the flux of V through the liquid membrane, we used the Permeability coefficient, P (cm min^{-1}), obtained according to the expression

$$-\ln[\mathbf{V}] = \frac{Q}{V_s} Pt - \ln[\mathrm{V}]_0$$

where $[\mathrm{V}]_0$ and [V] are sample vanadium concentrations at time 0 and t, respectively, Q is the effective membrane area and V_s is the sample volume.

For each experiment, the increment of absorbance (sample minus blank) was calculated as an average of, at least, three replicates. Once optimized, the proposed method was applied to the determination of vanadium in real samples. The results were statistically compared with those obtained when the samples were spiked with vanadium and directly analysed by FAAS.

3. Results and discussion

3.1. Optimization of FI system

3.1.1. Univariate methodology

The spectrophotometric signal increased with sample volume up to 566 µL, with a plateau being reached for larger volumes injected. Therefore, 566 µL sample injection volume was chosen as the optimum value. On the other hand, when reaction coil length was varied, a decrease was observed in the signal with an increase of the coil length. This behaviour is related with an increase in the dispersion of the sample into the reagent stream, reducing the peak height. Thus, a reaction coil length of 1 m was used henceforth. Finally, signal increased with reagent flow rate up to 5.2 mL min^{-1}, which was selected as the optimum.

The optimum values reported above were chosen mainly by the highest signal and taking into account reproducibility, time and reagent consumption.

Table 1
Simplex optimization for FIA variables. Sample: 1 mg L^{-1} V(V). Reagent: $7.0 \cdot 10^{-4}$ mol · L^{-1} dPKBH; 0.1 mol · L^{-1} acetate buffer (pH 4.72) 5% v/v ethanol. Carrier: MilliQ water.

Vertex	I.V.[a] (μL)	R.C.[b] (m)	F.R. [c] (mL min^{-1})	*A*
1	141	1.86	1.04	0.034
2	141	2.11	2.26	0.027
3	191	1.86	2.26	0.043
4	191	2.11	1.04	0.043
…	…	…	…	…
22	1045	1.15	8.32	0.081
…	…	…	…	…
28	1207	1.41	9.87	0.077

[a] Injection volume.
[b] Reaction coil length.
[c] Flow rate.

3.1.2. *Modified simplex methodology*

In this second procedure, sample volume, reaction coil length and reagent flow rate were varied simultaneously. In order to select the initial conditions of the simplex (shown in Table 1) we took into account the results obtained from the previous univariate pre-optimization. As can be seen in Table 1, 28 experiments were required to reach the optimum conditions. They were chosen by using the criterion based on the measurement of response variation due to the simplex. This variation was estimated by means of sample variance of all the responses of each simplex. A small response variation means that differences between response values at the vertexes are only due to random error. This estimation was carried out by calculating the *F*-values for the ratio of simplex variance to a variance of the method, which was experimentally calculated [30]. As shown in Table 1, trial 22 gave the highest response value, the optimum conditions being reaction coil length 1.15 m, sample injection volume 1045 μL, and reagent flow rate 8.32 mL min^{-1}.

Although simplex optimization allows a better selection of experimental conditions, in our study the improvement in the analytical response if compared with that of the univariate procedure was only about 12%. As a consequence, in further liquid membranes experiments, we decided to use optimum conditions obtained by the univariate methodology in order to reduce sample (566 μL instead of 1045 μL) and reagents (5.2 mL min^{-1} instead 8.32 mL min^{-1}) consumption.

3.2. *Optimization of the BLM system*

3.2.1. *Preliminary experiments*

Palet et al. described the membrane transport of vanadium (V) with A336, from non-saline aqueous solutions within the pH range 5–7 to a basic solution [23]. Since these authors described the co-transport of Cr(VI), Se(IV) and Mo(VI) through the membrane, we studied the potential interferences of these ions by the spectrophotometric determination of V(V), and no effect was observed until a 1:10 Molar ratio for all the elements.

In this work, we studied the influence of saline matrix in the liquid–liquid extraction of vanadium (V) by varying NaCl concentration in the feed aqueous solution between 0 and 35 g L^{-1}. The results obtained showed that extraction of V was practically independent of the saline content. On the other hand, to verify the back-extraction process, we employed a 0.1 mol L^{-1} NH_3/NH_4^+ solution in 0.6 mol L^{-1} $NaNO_3$ as the stripping solution, and its pH varied in the range 9–12. The results obtained highlighted a maximum vanadium transport at pH 11.

Once extraction and back-extraction processes were verified, they were tested simultaneously to determine whether transport of vanadium took place across the BLM. Table 2 shows the composition of feed, stripping and membrane solutions employed. The three phases were placed in the membrane cell and stirred at 900 rpm. Aliquots of stripping solution were measured spectrophotometrically every 30 min for 120 min. Fig. 2 shows the average variation of −ln[V] vs. time for the four replicate experiments performed, confirming the vanadium transport across the membrane. The permeability coefficient ($P = 0.0097 \pm 0.0028$ cm min^{-1}) was calculated as the mean of the four replicate experiments.

Table 2
Initial conditions for vanadium transport across the BLM. FIA variables: reaction coil length, 1 m; sample injection volume, 566 μL; reagent flow rate, 5.2 mL min^{-1}.

Feed solution	Membrane	Stripping solution
V=39 mL	*V*=7 mL	*V*=24 mL
0.5 mg L^{-1}V(V)	0.15 mol · L^{-1} A336	0.1 mol L^{-1} NH_3/NH_4^+
35g L^{-1} NaCl	3.5% v/v dodecanol	0.6 mol L^{-1} $NaNO_3$
pH 5	Dodecane	pH 11

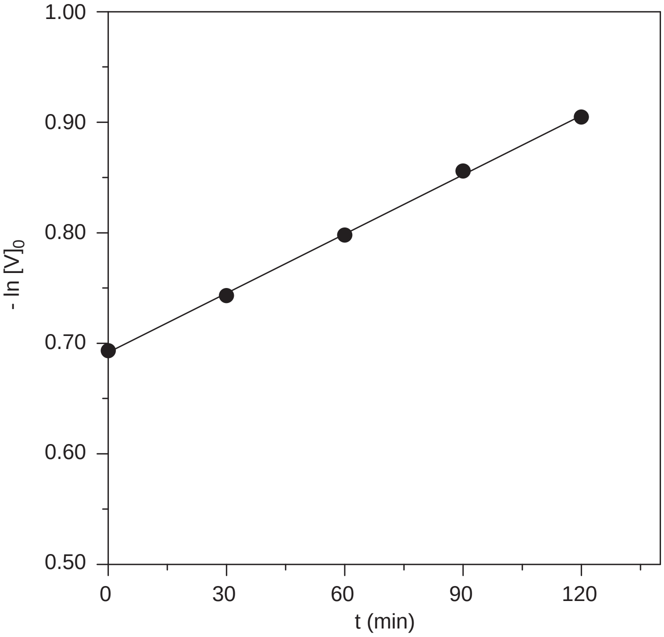

Fig. 2. Variation of vanadium concentration vs. time. Conditions as in Table 2.

3.2.2. *Optimization of the transport process*

In order to accomplish the optimization of the system, pH of feed and stripping solutions and A336 concentration were varied simultaneously by applying simplex methodology. The conditions for the first simplex (shown in Table 3) were selected taking into account the results obtained from the previous liquid–liquid extraction experiments. The parameter chosen to evaluate the response of each run was the Permeability coefficient. A total of 15 different experiments were required to decide the optimum conditions. This time, the criterion chosen for stopping the search was based on minimum distance between vertexes [30]. Accordingly, when the system progresses towards optimum conditions, the coordinates of the successive vertexes will be closer. In the present study, we selected 10% as the variation between successive vertexes. This variation was observed in runs 14 and 15, with the simplex made up of experiments 4, 5, 13 and 14. Therefore, optimum conditions were selected for the experiment (number 5) showing the highest permeability coefficient ($P = 0.04688$ cm min^{-1}).

Table 3
Simplex optimization of chemical variables for vanadium transport. FIA variables in Table 2.

Vertex	pH_{feed}	$pH_{stripping}$	[A336] (mol L^{-1})	*P* (cm min^{-1})
1	3.5	9.5	0.30	0.00915
2	3.5	8.5	0.50	0.02630
3	4.5	8.5	0.30	0.00201
4	4.5	9.5	0.50	0.03129
5	3.2	9.8	0.57	0.04688
6	2.5	10.5	0.70	0.01610
…	…	…	…	…
14	3.9	9.4	0.63	0.02622
15	3.9	9.8	0.61	0.01683

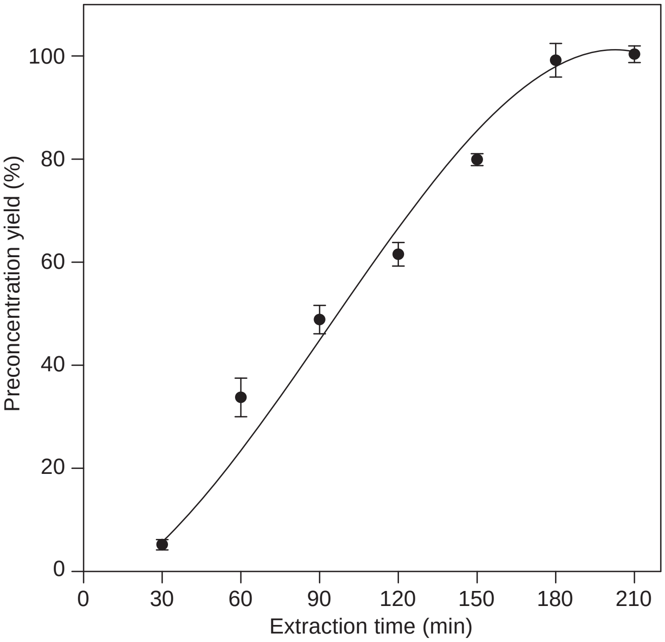

Fig. 3. Effect of time on the preconcentration yield. Sample: 0.1 mg L^{-1} V(V) in 35 g L^{-1} NaCl, pH 3.2. Membrane: 0.57 mol L^{-1} A336 in dodecane and dodecanol (3.5% *v*/*v*). Stripping: 0.1 mol L^{-1} NH_4OH in 0.6 mol L^{-1} $NaNO_3$, pH 9.8.

3.2.3. *Influence of stirring rate*

Duplicate experiments were carried out in the optimal conditions previously selected and the stirring rate was varied within the range 500–900 rpm (for higher rates, mixing of different phases occurred). The Permeability coefficients were calculated and showed to be directly related with the stirring rate, with maximum responses obtained at 900 rpm.

Thus, optimum preconcentration conditions were obtained with pH 3.2 in feed solution, pH 9.8 in stripping solution, 0.57 mol L^{-1} A336 in dodecane and dodecanol (3.5% v/v) as the liquid membrane, and a mixing rate of 900 rpm.

3.2.4. *Time dependence of vanadium transport*

The vanadium transport through the liquid membrane was investigated under optimal conditions. The efficiency–time profile of metal transport is shown in Fig. 3 and after 3 h the concentration of vanadium in the stripping solution was independent of the time and the transport was completed with a preconcentration yield of 100%.

3.2.5. *Analytical performance*

Linear calibration graphs were obtained in order to evaluate Beer's law range, detection limit and quantification limit. Under optimal conditions a linear relationship between absorbance and vanadium concentration was obtained within the range 0–3 mg L^{-1}($A=0.0229$ (± 0.0005)$+0.0341$ (± 0.0003)[V], $r^2=0.99996$). At the low level vanadium concentration, the detection limit of the method (4.7 μg L^{-1}) and quantification limit (15.8 μg L^{-1}) were calculated as $3s_b/m$ and $10\,s_b/m$, where s_b and m were the standard deviation of blank and the slope of the linear regression, respectively.

Table 4
Analysis of seawater samples.

Sample	FAAS	This method	*t*(95%)
Cadiz	32 ± 3	27 ± 2	2.51
Huelva	51 ± 4	44 ± 3	2.49

The accuracy of the method was studied by analyzing a certified reference material (TMDA-62) with a certified concentration for vanadium of 108 ± 8.19 μg L^{-1}. This sample was analyzed in triplicate under optimal conditions and the obtained results (108.7 ± 10.2 μg L^{-1}) are in good agreement with those certified. Finally, the precision of the method was evaluated by measuring 11 samples containing 1 mg L^{-1} V in 0.1 mol L^{-1} NH_4OH and a 0.6 mol L^{-1} $NaNO_3$ under optimal conditions. A value of 2.72% was obtained for R.S.D., indicating good repeatability of the system.

3.2.6. *Application*

The proposed coupled method was applied to the preconcentration and determination of vanadium in two real seawater samples collected from the bay of Cadiz and Huelva estuary. They were stirred for 3 h in the preconcentration cell and then, the received solutions were spectrophotometrically determined at 375 nm. The results obtained, shown in Table 4, were statistically evaluated in terms of Student's *t*-test with those obtained by direct determination by FAAS (spiked with 100 μg L^{-1} V) at the 95% confidence level. The *t*-values obtained were below the theoretical one (2.78; $n=4$), thus indicating the accuracy of the proposed method.

4. Conclusions

A BLM-FI coupled system has been developed for the preconcentration and on-line determination of vanadium in natural and seawater samples. It is concluded that the proposed method is simple and reliable, and reduces sample manipulation, avoiding possible risks of contamination. Moreover, it fits with some of the basic principles of green analytical chemistry, in which reduction of reagents consumption (only 7 mL of organic solvent is employed in the preconcentration cell) and minimization of wastes (this is inherent of flow-based systems) are recommended. On the other hand, a preconcentration factor of 1.62 has been obtained, which could be easily increased by changing cell dimensions. The time necessary to reach maximum efficiency in the transport (3 h) was reasonable. Statistical analysis of the results indicates that the method allows obtaining both precise and accurate results in the determination of vanadium in real natural and seawater samples.

References

[1] H.G. Seiler, H. Sigel, Handbook on Toxicity of Inorganic Compounds, in: Marcel Dekker (Ed.), Basel, New York, 1988, pp. 651–663.
[2] B. Patel, G.E. Henderson, R. Haswell, R. Grzeskowiak, Analyst 115 (1990) 1063–1066.
[3] H. Filik, Z. Yanaz, R. Apak, Anal. Chim. Acta 620 (2008) 27–33.
[4] P. Berton, E.M. Martinis, R.G. Wuilloud, J. Hazard. Mater. 176 (2010) 721–728.

[5] R.G. Wuilloud, J.A. Salonia, R.A. Olsina, L.D. Martínez, Spectrochim. Acta, Part B 55 (2000) 671–680.
[6] Z. Cheng, Y. Zheng, R. Mortlock, A. van Geen, Anal. Bioanal. Chem. 379 (2004) 512–518.
[7] A.A. Ensafi, B. Naderi, Fresenius' J. Anal. Chem. 358 (1997) 480–483.
[8] K. Pyrzyńska, Microchim. Acta 149 (2005) 159–164.
[9] Q.Z. Zhai, X. Zhang, H. Chong, Spectrochim. Acta Part A 69 (2008) 911–916.
[10] S. Nakano, Y. Matumoto, Y. Fukumoto, M. Hayashi, Microchim. Acta 164 (2009) 211–216.
[11] N.G.S. Al-Tayar, P. Nagaraja, R.A. Vasantha, A.K. Shresta, Environ. Monit. Assess. 148 (2012) 181–191.
[12] X. He, M. Tubino, A.V. Rossi, Anal. Chim. Acta 389 (1999) 275–280.
[13] M.J.C. Taylor, G.D. Marshall, S.J.S. Williams, J.F. van Staden, C. Saling, Anal. Chim. Acta 329 (1996) 275–284.
[14] K.B. Gavazov, V.D. Lekova, A.N. Dimitrov, G.I. Patronov, Cent. Eur. J. Chem. 5 (2007) 257–270.
[15] A.S. Amin, A.L. Saber, T.Y. Mohammed, Spectrochim. Acta A 73 (2009) 195–200.
[16] P.V. Racheva, K.B. Gavazov, V.D. Lekova, A.N. Dimitrov, Talanta 58 (2010) 21–25.
[17] C. Ekinci, Ü. Köklü, Spectrochim. Acta B 55 (2000) 1491–1495.
[18] Q. Li, X. Zhao, K. Jiang, G. Liu, Microchim. Acta 158 (2007) 123–130.
[19] L. Rostampour, M.A. Taher, Talanta 75 (2008) 1279–1283.
[20] J.A. López-López, C. Mendiguchía, J.J. Pinto, C. Moreno, Trends Anal. Chem. 29 (2010) 645–653.
[21] C. Mendiguchía, C. Moreno, M. García-Vargas, Anal. Chim. Acta 460 (2002) 35–40.
[22] L. Irigoyen, C. Moreno, C. Mendiguchía, M. García-Vargas, J. Membr. Sci. 274 (2006) 169–172.
[23] C. Palet, M. Muñoz, M. Hidalgo, M. Valiente, J. Membr. Sci. 98 (1995) 241–248.
[24] A. Rosell, C. Palet, M. Valiente, Anal. Chim. Acta 349 (1997) 171–178.
[25] M.A. Chaudry, N. Bukhari, M. Mazhar, F. Tazeen, Sep. Purif. Technol. 54 (2007) 227–233.
[26] S.V. Yadav, V.V. Mahajani, Sep. Sci. Technol. 42 (2007) 1283–1303.
[27] M. Hor, A. Riad, A. Benjjar, L. Lebrun, M. Hlaïbi, Desalination 255 (2010) 188–195.
[28] M. García-Vargas, M. Belizón, M.P. Hernández-Artiga, C. Martínez, J.A. Pérez-Bustamante, Appl. Spectrosc. 40 (1986) 1058–1062.
[29] Multisimplex (1998), Multisimplex 98, Multisimplex, Karlskrona.
[30] C.K. Bayne, I.B. Rubin, Practical Experiments Design and Optimization Methods for Chemist, VCH Publishers Inc., Florida, 1986.