ELSEVIER

Talanta 58 (2002) 619–627

Talanta

www.elsevier.com/locate/talanta

Cloud point extraction of vanadium in parenteral solutions using a nonionic surfactant (PONPE 5.0) and determination by flow injection-inductively coupled plasma optical emission spectrometry

Gustavo M. Wuilloud [a], Jorgelina C.A. de Wuilloud [a], Rodolfo G. Wuilloud [a], María F. Silva [a], Roberto A. Olsina [a,b], Luis D. Martinez [a,b,*]

[a] *Faculty of Chemistry, Department of Analytical Chemistry, Biochemistry and Pharmacy, National University of San Luis, Chacabuco y Pedernera, P.O. Box 375, 5700 San Luis, Argentina*

[b] *Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Avda. Rivadavia 1917, CP C1033AAJ, Buenos Aires, Argentina*

Received 1 March 2002; received in revised form 14 May 2002; accepted 14 May 2002

Abstract

A preconcentration and determination methodology for vanadium at trace levels in parenteral solutions was developed. Cloud point extraction was successfully employed for the preconcentration of vanadium prior to inductively coupled plasma atomic optical emission spectrometry (ICP-OES) coupled to a flow injection (FI) system. The vanadium was extracted as vanadium-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [V-(5-Br-PADAP)] complex, at pH 3.7 mediated by micelles of the nonionic surfactant polyoxyethylene (5.0) nonylphenol (PONPE 5.0). The extracted surfactant-rich phase (100 μl) was mixed with 100 μl of ethanol and this final volume injected into ICP-OES for the vanadium determination. Under these conditions, the 50 ml sample solution preconcentration allowed raising an enrichment factor of 250-fold; however, it was possible to obtain a theoretical enrichment factor of 500-fold. The lower limit of detection (LOD) obtained under the optimal conditions was 16 ng l^{-1}. The precision for 10 replicate determinations at the 2.0 μg l^{-1} V level was 2.3% relative standard deviation (RSD), calculated with the peak heights. The calibration graph using the preconcentration system for vanadium was linear with a correlation coefficient of 0.9996 at levels near the detection limits up to at least 50 μg l^{-1}. The method was successfully applied to the determination of vanadium in parenteral solution samples.

Keywords: Vanadium determination; Parenteral solutions; ICP-OES; Cloud point extraction; 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol reagent

* Corresponding author. Present address: Faculty of Chemistry, Department of Analytical Chemistry, Biochemistry and Pharmacy, National University of San Luis, Chacabuco y Pedernera, P.O. Box 375, 5700 San Luis, Argentina. Fax: +54-2652-430224

E-mail address: ldm@unsl.edu.ar (L.D. Martinez).

0039-9140/02/$ - see front matter
PII: S0039-9140(02)00366-1

1. Introduction

Vanadium compounds can be highly toxic to man and animals [1] and their presence in the atmosphere is mainly due to the combustion of fossil fuels [2]. However, vanadium is an essential trace element, possessing specific physiological functions [1] and its determination is receiving increasing attention in pollution and nutritional studies [3].

Parenteral nutrition (PN) consists of administering intravenously all nutrients necessary to patients who cannot receive normal alimentation due to various pathologies [4,5]. Infusion solutions and solutions for PN have been identified as vanadium sources [6,7]. However, the quantitative requirements or the toxicity of trace elements in parenteral solutions are difficult to assess. The importance of trace elements in the nutritional management of patients receiving total parenteral nutrition (TPN) is now widely recognised [4–7] and long-term TPN patients can inadvertently receive significant amounts of vanadium present as contaminant in TPN.

Since vanadium concentrations in nonpolluted parenteral solutions are very low, powerful techniques are required and only few of them show enough sensitivity. Different analytical methods have been developed for the determination of vanadium at low concentrations, but the most commonly used ones are by neutron activation analysis (NAA) [8], inductively coupled plasma mass spectrometry (ICP-MS) [9], inductively coupled plasma optical emission spectrometry (ICP-OES) [10] and electrothermal atomisation atomic absorption spectrometry (ETAAS) [11].

The NAA method is time consuming, and routine analysis of numerous samples is laborious. ICP-MS is used for the determination of vanadium because of its high sensitivity, high selectivity and high sample throughput; however, the cost of instrumentation may be prohibitive to many laboratories.

Although ICP-OES or ETAAS are the most used techniques in the determination of traces of vanadium, the low level of vanadium concentration in parenteral solutions is not compatible with the detection limit of these techniques. In order to achieve accurate, reliable and sensitive results, preconcentrations and separations are needed when the concentrations of analyte elements in the sample are too low to be determined directly by ICP-OES.

Cloud point extraction (CPE) is an impressive alternative to conventional solvent extraction because it produces high extraction efficiencies and preconcentration factors, and uses inexpensive, non-toxic reagents. The use of CPE process for extraction of metal chelates, biological and clinical samples and environmental clean-up procedure have been reported [12–26]. In view of the possibility of vanadium chelation with the pyridylazo reagent 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) [27], and from our previous experience [28,29] on CPE using pyridylazo chelating reagents, the aim of this paper was to develop an extraction–preconcentration scheme for V in parenteral solutions mediated by micelles of PONPE 5.0. It has to be pointed out that until now this extraction methodology has never been used for vanadium.

In this work, a CPE preconcentration methodology has been developed and optimised for the determination of vanadium in parenteral solutions. Vanadium was chelated with 5-Br-PADAP reagent, and later preconcentrated mediated by PONPE 5.0. The determination of vanadium was performed using a flow injection (FI) system coupled to ICP-OES.

2. Experimental

2.1. Reagents

Vanadium(V) stock standard solution, 1000 μg l^{-1} prepared by dissolving 2.2966 g of ammonium metavanadate (99.99%, Merck) in 1000 ml of ultrapure water.

A 1×10^{-2} mol l^{-1} solution of 5-Br-PADAP (Aldrich, Milwaukee, WI) was prepared by dissolution in ethanol. Lower concentrations were prepared by serial dilution.

As it is not possible to obtain a real aqueous solution of the surfactant polyoxyethylene (5.0) nonylphenol (PONPE 5.0, Tokyo Kasei Indus-

tries, Chuo-Ku, Tokyo, Japan) (cloud point below room temperature), it was experimentally convenient to prepare a standard solution as follows: 20 ml of PONPE 5.0 and 40 ml of distilled ethanol (Merck, Darmstadt, Germany) were mixed and made up to 100 ml with ultrapure water.

The buffer solution (2 mol l^{-1} acetic acid–0.25 mol l^{-1} sodium acetate, pH 3.7) was prepared by mixing 45.6 ml of 8.8 mol l^{-1} acetic acid and 50 ml of 1.0 mol l^{-1} sodium acetate solution with dilution to 200 ml with ultrapure water.

A $NaClO_4$ (Merck) solution was used in order to adjust ionic strength.

Ultrapure water (18.3 MΩ cm) was obtained from Barnstead EASY pure RF water system (IA). All the reagents were of analytical reagent grade and the presence of vanadium was not detected within the working range.

2.2. Apparatus

The measurements were performed with a sequential inductively coupled plasma spectrometer (Baird, Bedford, MA) ICP 2070. The 1 m Czerny–Turner monochromator had a holographic grating with 1800 grooves mm^{-1}. The ICP operating conditions are listed in Table 1. The FI system used is shown in Fig. 1. A Minipuls 3 peristaltic pump (Gilson, Villiers-Le-Bell, France) was used. A sample loop of 100 μl and a Rheodyne (Cotati, CA) Model 50, four-way rotary valve were used for the sample injection. Tygon-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL) was employed to propel the sample, reagent and eluent.

Table 1
CPE and ICP-OES work conditions

ICP-OES parameters	
RF generator power (kW)	1.0
Frequency of RF generator (MHz)	40.68
Plasma gas flow rate (l min^{-1})	9.0 l
Auxiliary gas flow rate (l min^{-1})	1.0
Carrier gas flow rate (l min^{-1})	0.5
Observation height (above load coil) (mm)	15
Analytical line: V (nm)	309.311
CPE parameters	
Equilibration temperature (°C)	70
Equilibration time (before and after centrifugation) (min)	3
Centrifugation time (min)	5
Cooling time (min)	5
Working pH	3.7
Buffer solution (concentration)	Acetic acid–acetate solution 1×10^{-3} mol l^{-1}
Chelating reactive (mol l^{-1})	1×10^{-4}
Ionic strength (mol l^{-1})	< 0.8
Surfactant (%, v/v)	0.04
%E[a]	99.9

[a] Percentage extracted by the successive extraction method.

2.3. Cloud point preconcentration procedure

0.100 ml of surfactant solution, 0.5 ml of 1×10^{-2} mol l^{-1} chelating solution, 0.25 ml of 2.0×10^{-4} mol l^{-1} metal–ion solution and 0.025 ml of buffer solution (pH 3.7) were placed in a centrifuge tube. The mixture was diluted to 50 ml with ultrapure water. The resultant solution was equilibrated at 70 °C (temperature well above cloud point temperature of the system, which is 17 °C) for 3 min. In order to separate the phases, the turbid solution was centrifuged (5 min at 3500 rpm ($1852.2 \times g$)), and then cooled in an ice–NaCl bath for 5 min. The removal of the aqueous phase was carried out by means of a peristaltic pump.

In the case of preconcentration of 50 ml of parenteral solution sample, the CPE procedure was performed in the same way.

2.4. Measurements with the FI-ICP-OES system

0.1 ml of ethanol was added to the surfactant-rich phase (100 μl). A 100 μl loop was loaded with this solution and the vanadium concentration was determined by FI-ICP-OES system. The optimised conditions for this system are given in Table 1. A schematic diagram of the CPE procedure, including spectral detection, is shown in Fig. 1.

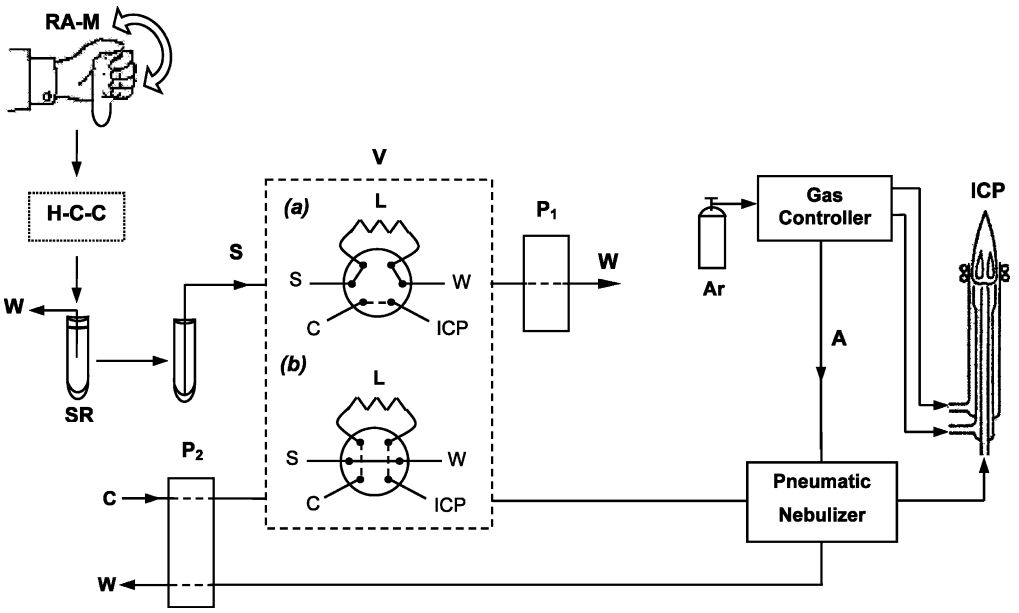

Fig. 1. Schematic diagram of the instrumental setup. RA-M: reagent adding and mixing; H–C–C: heating, centrifugation and cooling; SE: supernatant removing; S: sample (surfactant-rich phase (100 μl)+100 μl de ethanol); L: sample loop (100 μl); P_1, P_2: peristaltic pumps; V: injection valve; valve positions: (a) sample loading, (b) injection; C: carrier solution; A: Ar (flow rate: 0.5 l min^{-1}); W: waste.

3. Results and discussion

3.1. Optimisation of the CPE preconcentration variables

The effect of pH upon complex formation of V-5-Br-PADAP was studied within the pH range 1.0–5.5. The results are shown in Fig. 2a. As can be seen, the complex extraction begins at pH 2.0 and starts to decrease at pH 4.5, showing a plateau for the pH range 3.0–4.5. This phenomenon is understandable, since better complexation occurs within this range. Considering these results, the selected pH was 3.7. Working at this pH value had the advantage of selectively complexing and preconcentrating vanadium, since most metal ions which can form complexes with 5-Br-PADAP, do so at higher pH values [30,31].

In order to achieve the total complexing and preconcentration of vanadium, an experiment was carried out in which the other experimental variables, except reagent concentration, remained constant. The results are shown in Fig. 2b. A minimum 5-Br-PADAP concentration of 1×10^{-4} mol l^{-1}, permitted to raise the total formation of the V-5-Br-PADAP complex. The signal remained constant from a concentration value of 10^{-5} mol l^{-1} up to at least 2×10^{-4} mol l^{-1} for a vanadium concentration of 50 μg l^{-1}.

Numerous trials were carried out in order to study the effect of ethanol concentration prior to CPE. There was not any variation on both enrichment factor (EF) and kinetics of phase separation within the ethanol concentration range 0.5–13% (v/v). Higher ethanol concentrations led to non-reproducible results due to inefficient phase separation. A minimum ethanol concentration of 0.7% (v/v) was needed in order to achieve a convenient cloud point temperature (Fig. 3) and an increase of phase separation rate with respect to the situation in the absence of organic solvent in the extraction system. Fig. 3 shows the variation on cloud point temperature with ethanol concentration for the system, PONPE 5.0–ethanol–water.

The acetic acid–acetate system was used as buffer solution. The system was studied within the buffer concentration range 10^{-4}–10^{-2} mol

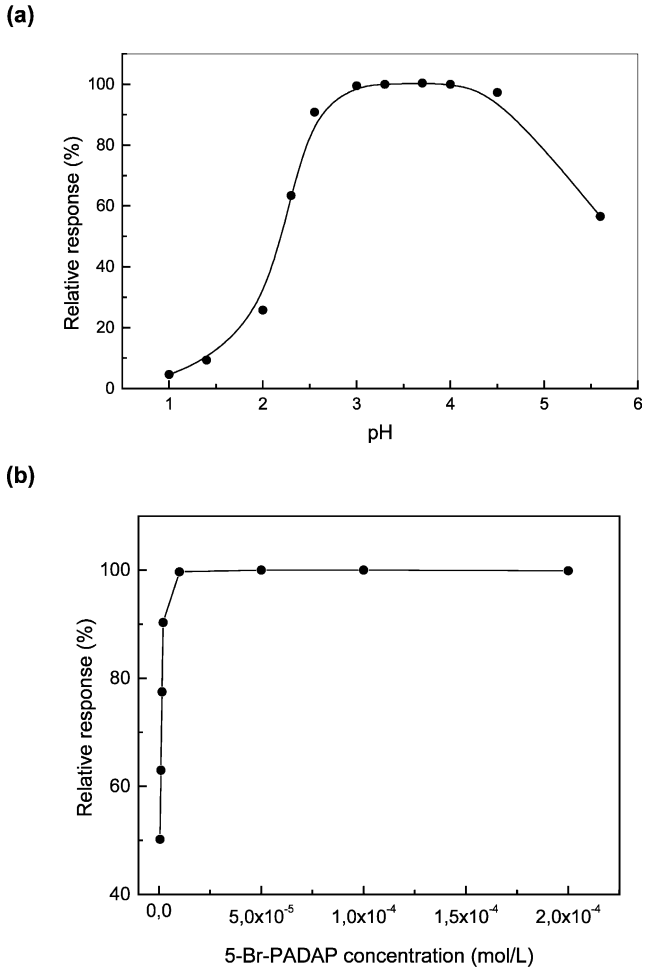

Fig. 2. Effect of (a) pH, (b) chelating reagent excess. Other conditions are given in Table 1.

l^{-1} and ionic strength within the range 0–1 mol l^{-1}, adjusted with $NaClO_4$. The best performance (higher extraction percentage; optimal stability; lower equilibration time and ease of phase separation) was achieved for a buffer concentration of 10^{-3} mol l^{-1} and ionic strength of 0–0.8 mol l^{-1}. For ionic strength higher than 0.8 mol l^{-1}, a quantitative phase separation was not possible.

The critical micelle concentration (cmc) for the nonionic surfactant PONPE 5.0 was determined in the usual manner via surface tension measurements. A series of solutions of increasing nonionic surfactant concentration was prepared and the surface tension of each measured. The cmc value obtained for PONPE 5.0 at a temperature of 24.0 °C was 6.4×10^{-5} mol l^{-1}.

The variation of extraction efficiency upon the surfactant concentration was examined within the range: CPONPE 5.0 = 0.025–1.2% (v/v). The results are shown in Fig. 4. Quantitative extraction was observed for a surfactant concentration higher than 0.04% (v/v). In order to achieve a good EF, 0.04% (v/v) was chosen as optimal. This surfactant concentration permits to obtain a final volume of 100 μl of surfactant-rich phase.

The ratio of the volumes of the surfactant-rich phase to the aqueous phase (V_s/V_w) for the extraction system was obtained measuring the

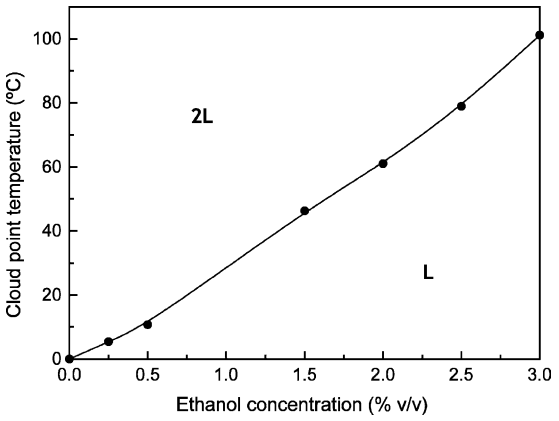

Fig. 3. Effect of the ethanol concentration on cloud point temperature for the system, PONPE 5.0–ethanol–water. L = one isotopic phase, 2L = other isotopic phase; the cloud point is determined by observing the onset of turbidity upon heating. Condition: [PONPE 5.0] = 0.04% (v/v).

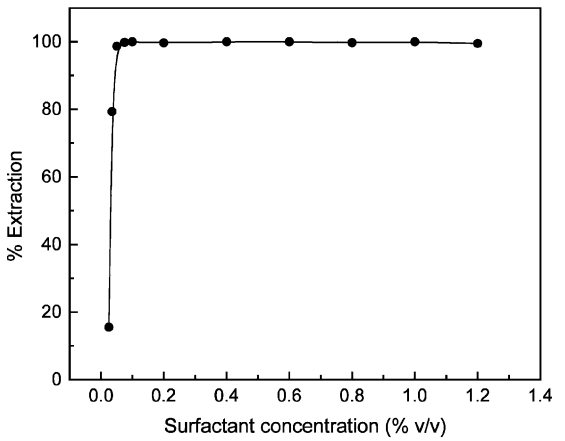

Fig. 4. Effect of surfactant concentration on the performance of the extraction system. Other conditions are given in Table 1.

initial sample volume (50 ml) and the final surfactant-rich phase volume (0.1 ml). The phase ratio value obtained in the present work was 0.002.

3.2. Influence of equilibration temperature and time

EF is affected by equilibration time and temperature. Therefore, these parameters were studied within the ranges 25–90 °C and 1–30 min, respectively. The cloud point temperature of the system under study is 17 °C. 70 °C was selected in order to achieve the minimum equilibration time (3 min) to avoid complex decomposition and to reach the optimal EF.

3.3. Evaluation of centrifugation time

A centrifugation time of 5 min at 3500 rpm was selected as optimum, since complete separation occurred for this time and no appreciable improvements were observed for longer times.

3.4. Efficiency and EFs for CPE

An extraction percentage higher than 99.9% was achieved when the procedure was carried out under the optimal experimental conditions (Table 1). The theoretical EF was approximately 500, as the original volume was 50 ml and the final volume was 0.1 ml of the surfactant-rich phase.

3.5. Pre-conditioning of the surfactant-rich phase

Due to the high viscosity of the surfactant-rich phase, the micellar phase had to be conditioned before its introduction into the FI system. Hence, 100 μl ethanol was added to the 100 μl of the surfactant-rich phase. The resultant solution and the sample loop were thermostatised at 70 °C.

3.6. Interference species

The effects of representative potential interfering species were tested. Thus, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{3+} could be tolerated up to at least 2000 μg l^{-1}. Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes and are not CPE extracted. On the other hand, anions such as CO_3^{2-}, F^-, SO_4^{2-}, Cl^- and PO_4^{3-} could be tolerated up to at least 500,000 μg l^{-1}.

The recoveries were not influenced by the presence of these ions because they are not complexed with 5-Br-PADAP reagent at the working pH value of 3.7. Thus, they are not extracted allowing for highly selective determination of V in the presence of other ions. The value of the reagent

blank signal was not modified by the presence of the potentially interfering ions assayed.

3.7. Figures of merit and analytical performance

The relative standard deviation (RSD) resulted from the CPE-FI-ICP-OES analysis of 10 replicates of 50 ml solution containing 2.0 μg l^{-1} V was 2.3%. EF was obtained as the ratio of the slopes of the calibration curves with and without the preconcentration step. It must be pointed out that the calibration curve without the preconcentration step was obtained by determining the analyte in the presence of an equal quantity of surfactant as used for the calibration curve with preconcentration. The only difference between these situations was the presence of the 5-Br-PADAP reagent, which did not produce any effect on the analytical signal. Consequently, by means of CPE preconcentration an EF of 250-fold was achieved with respect to ICP-OES using pneumatic nebulisation. The calibration graph was linear with a correlation coefficient of 0.9996 at levels near the detection limits up to at least 50 μg l^{-1}. The detection limit (DL) was 16 ng l^{-1}, calculated as the amount of vanadium required to yield a net peak was calculated considering three times the standard deviation of the background signal (3σ).

The overall time required for loop loading, injection and FI signal development was about 30 s. Thus, the number of determinations per hour was about 120.

Table 3
Concentrations of vanadium in parenteral solutions (95% confidence interval; $n = 6$)

Sample	V concentration (μg l^{-1})
1[a]	0.76 ± 0.08
2[b]	8.82 ± 0.09
3[c]	5.64 ± 0.07
4[d]	4.87 ± 0.10
5[e]	0.45 ± 0.09

[a] Ringer physiological solution.
[b] NaCl physiological solution.
[c] Isotonic dextrose 5% physiological solution.
[d] Dextrose 10% physiological solution.
[e] Sterile distilled water.

3.8. Method of validation

In order to validate this method, 500 ml of parenteral solution sample were collected and divided into 10 portions of 50 ml each. The proposed method was applied to six portions and the average quantity of vanadium obtained was taken as a base value. Then, increasing quantities of vanadium were added to the other aliquots, and vanadium was determined following the recommended procedure (Table 2).

3.9. Determination of vanadium in parenteral solutions

The results of the method applied to vanadium determination in parenteral solutions are shown in Table 3. The concentrations were in the range 0.45–8.82 μg l^{-1} of vanadium. The results ob-

Table 2
Method validation

Aliquots	Base value (μg l^{-1})	Quantity of V added (μg l^{-1})	Quantity of V found (μg l^{-1})	Recovery (%)[a]
1	–	0.00	0.76 ± 0.08	–
2	0.76	0.20	0.95	97.9
3	0.76	0.60	1.36	100.1
4	0.76	1.00	1.75	98.9
5	0.76	2.00	2.76	100.4

[a] 100 × ((Found − base)/added).

tained are in good agreement with those of Pluhator-Murton et al. [6]. The mean value of vanadium concentrations reported in parenteral solutions by these authors is 5.5 μg l^{-1}.

4. Conclusions

In this work, the preconcentration of vanadium in parenteral solutions was possible with a simple FI system, which was easily coupled to ICP-OES with pneumatic nebulisation. The use of micellar systems as an alternative to other techniques of separation and preconcentration offers several advantages including low cost, safety and high capacity to preconcentrate various elements with high recoveries and very good EFs. The results for this work demonstrate the possibility of using the 5-Br-PADAP–PONPE 5.0 system for the preconcentration of vanadium, since the V-5-Br-PADAP complex was quantitative extracted, and an EF of 250-fold was obtained. The preconcentration method allows vanadium determinations in parenteral solutions samples at levels of V as low as ng l^{-1} with good accuracy and good reproducibility.

Acknowledgements

This work was supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET); FOMEC program and Universidad Nacional de San Luis, Argentina.

References

[1] H. Seiler, A. Sigel, H. Sigel, Handbook on Metals in Clinical and Analytical Chemistry, Marcel Decker, New York, 1994.
[2] D.H.K. Lee, Metallic Contaminants and Human Health, Academic Press, New York, 1972.
[3] Md. Jamaluddin Ahmed, A.K. Banerjee, Non-extractive spectrophotometric determination of vanadium(V) in alloys and environmental, biological and soil samples using 5,7-dibromo-8-hydroxyquinoline, Analyst 120 (1995) 2019–2023.
[4] Y. Berner, T. Shuler, F. Nielsen, C. Flombaun, S. Farkouh, M. Shike, Selected ultratrace elements in total parenteral nutrition solutions, Am. J. Clin. Nutr. 50 (1989) 1079–1083.
[5] B. Harraki, P. Guiraud, M.H. Rochat, J. Alary, A. Favier, Interactions related to trace elements in parenteral nutrition, Pharm. Acta Helv. 70 (1995) 269–278.
[6] M.M. Pluhator-Murton, R.N. Fedorak, R.J. Audette, B.J. Marriage, R.W. Yatscoff, L.M. Gramlich, Trace element contamination of total parenteral nutrition, JPEN 23 (1999) 222–227.
[7] F.Y. Leung, Trace elements in parenteral micronutrition, Clin. Biochem. 28 (1995) 561–566.
[8] R.S.S. Murthy, D.E. Ryan, Determination of arsenic, molybdenum, uranium and vanadium in sea-water by colloid flotation, Anal. Chem. 55 (1983) 682–684.
[9] E. Sabbioni, J. Kuèera, R. Pietra, O. Vesterberg, A critical review on normal concentrations of vanadium in human blood, serum, and urine, Sci. Total Environ. 188 (1996) 49–58.
[10] S. Hirata, Y. Umezaki, M. Ikeda, Determination of chromium(III), titanium, vanadium, iron(III) and aluminium by inductively coupled plasma atomic emission spectrometry with an on-line preconcentration ion-exchange column, Anal. Chem. 58 (1986) 2602–2606.
[11] K. Fujiwara, T. Morikawa, K. Fuwa, Determination of molybdenum and vanadium in sea-water by carbon furnace atomic absorption spectrometry with metal chelate coprecipitation, Bunseki Kagaku 35 (1986) 361–367.
[12] H. Watanabe, T. Saitoh, T. Kamidate, H. Haraguchi, Distribution of metal chelates between aqueous and surfactant phases separated from a micellar solution of a nonionic surfactant, Microchim. Acta 106 (1992) 83–85.
[13] E. Pramauro, E. Pelizzetti, Surfactant in Analytical Chemistry, Elsevier, New York, 1996.
[14] E. Pelizzetti, E. Pramauro, Analytical applications of organized molecular assemblies, Anal. Chim. Acta 169 (1985) 1–29.
[15] M.J. Rosen, Surfactants and Interfacial Phenomena, Wiley, New York, 1978.
[16] M.O. Luconi, M.F. Silva, R.A. Olsina, L.P. Fernández, Cloud point extraction of lead in saliva via use of nonionic PONPE 7.5 without added chelating agents, Talanta 51 (2000) 123–129.
[17] H. Watanabe, H. Tanaka, A non-ionic surfactant as a new solvent for liquid extraction of Zinc(II) with 1-(2-pyridylazo)-2-naphthol, Talanta 25 (1978) 585–589.
[18] P. Frankewich, W.L. Hinze, Evaluation and optimization of the factors affecting nonionic surfactant-mediated phase separations, Anal. Chem. 66 (1994) 944–954.
[19] M.A. Mesquita da Silva, V.L. Azzolin Frescura, A.J. Curtius, Determination of trace elements in water samples by ultrasonic nebulization inductively coupled plasma mass spectrometry after cloud point extraction, Spectrochim. Acta B 55 (2000) 803–813.
[20] G. Stangl, R. Niessner, Micellar extraction—a new step for enrichment in the analysis of napropamide, Int. J. Environ. Anal. Chem. 58 (1995) 15–22.

[21] C. García Pinto, J.L.P. Pavón, B.M. Cordero, E. Romero Beato, S. García Sanchez, Cloud point preconcentration and flame atomic absorption spectrometry: application to the determination of cadmium, J. Anal. Atom. Spectrom. 11 (1996) 37–41.
[22] A.E. Böyükbayram, M. Volkan, Cloud point preconcentration of germanium and determination by hydride generation atomic absorption spectrometry, Spectrochim. Acta B 55 (2000) 1073–1080.
[23] M.A. Mesquita da Silva, V.L. Azzolin Frescura, F.J. Nome Aguilera, A.J. Curtius, Determination of Ag and Au in geological samples by flame atomic absorption spectrometry after cloud point extraction, J. Anal. Atom. Spectrom. 13 (1998) 1369–1373.
[24] W.L. Hinze, E. Pramauro, A critical review of surfactant-mediated phase separations (cloud point extractions): theory and applications, Anal. Chem. 24 (1993) 133–177.
[25] A. Sanz-Medel, M.R. Fernandez de la Campana, E. Blanco Gonzales, M.L. Fernandez-Sanchez, Organised surfactant assemblies in analytical atomic spectrometry, Spectrochim. Acta B 54 (1999) 251–287.
[26] F.H. Quina, W.L. Hinze, Surfactant-mediated cloud point extractions: an environmentally benign alternative separation approach, Ind. Eng. Chem. Res. 38 (1999) 4150–4569.
[27] R.G. Wuilloud, J.A. Salonia, R.A. Olsina, L.D. Martinez, Determination of vanadium(V) in drinking water by flow injection and pre-concentration in a knotted reactor by inductively coupled plasma optical emission spectrometry with ultrasonic nebulization, Spectrochim. Acta B 55 (2000) 671–680.
[28] M.F. Silva, L. Fernández, R.A. Olsina, D. Stacchiola, Cloud point extraction, preconcentration and spectrophotometric determination of erbium(III)-2-(3,5 dichloro-2-pyridylazo)-5-dimethylaminophenol, Anal. Chim. Acta 342 (1997) 229–238.
[29] M.F. Silva, L. Fernández, R.A. Olsina, Monitoring the elimination of gadolinium-based pharmaceuticals: cloud point preconcentration and spectrophotometric determination of Gd(III)-2-(3,5 dichloro-2-pyridylazo)-5-dimethylaminophenol in urine, Analyst 123 (1998) 1803–1807.
[30] L.D. Martinez, J.A. Gasquez, R.A. Olsina, E. Marchevsky, Spectrophotometric determination of neodymium in high sensitivity conditions in rocks with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP), Chem. Anal. (Warsaw) 41 (1996) 275–282.
[31] L.D. Martinez, E. Perino, E. Marchevsky, R.A. Olsina, Spectrophotometric determination of gadolinium(III) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP), Talanta 40 (1993) 385–390.