Talanta 85 (2011) 506–512

Contents lists available at ScienceDirect

Talanta

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

Direct simultaneous determination of Co, Cu, Fe, Ni and V in pore waters by means of adsorptive cathodic stripping voltammetry with mixed ligands

Juan Santos-Echeandía

INRB/IPIMAR, National Institute of Biological Resources. Avenida Brasília, 1446-006 Lisbon, Portugal

ARTICLE INFO

Article history:
Received 9 February 2011
Received in revised form 4 April 2011
Accepted 11 April 2011
Available online 16 April 2011

Keywords:
Metals
Direct
Simultaneous
Determination
Voltammetry
Porewaters

ABSTRACT

An analytical procedure is proposed for the direct simultaneous determination in a single scan of Co, Cu, Fe, Ni and V in sediment pore waters by means of adsorptive cathodic stripping voltammetry (ACSV) with mixed ligands (DMG and catechol). Optimum conditions for the determination of these five elements were studied. Detection limits of the technique depended upon the reproducibility of the procedure blank, and were found to be 0.04 nM Co, 0.09 nM Cu, 1.29 nM Fe, 0.46 nM Ni and 2,52 nM V making the method suitable for the direct simultaneous determination of these five metals in pore waters, estuarine waters and probably coastal waters.

1. Introduction

The use of the adsorptive cathodic stripping voltammetry (ACSV) and its application for dissolved trace metal determination in different matrixes (i.e. seawater, freshwater, rocks, blood, biological samples) is known since several years [1–5]. Years after years, new methods have been developed for the determination of almost each metal and nowadays, around 20 elements can be determined at trace levels in natural waters using adsorptive cathodic stripping voltammetry (ACSV)[6]. Although the pretreatment of the sample is simple (the determination is almost direct), it has low detection limits (picomolar to nanomolar) and needs a low volume of sample (around 10 mL), it takes a long time to analyze one sample in comparison with other techniques like inductively coupled plasma-mass spectroscopy (ICP-MS) or flow injection analysis (FIA). The multi-element detection capability is one of the main advantages of the ACSV technique, e.g., Ni and Co with dimethylglyoxime (DMG) or cyclohexane-1,2-dione dioxime (nioxime) [7,8]; Cu, Pb and Cd with 8-hydroxiquinoline (oxine) [9]; Mo, U, V and Sb with chloranilic acid [10], etc., significantly reducing the consuming of time and making it suitable for routine analysis. These multi-element detection capabilities have been exploited during the recent years using a mixture of ligands. Accordingly, for example Cu, Pb, Cd and Ni can be successfully determined using a mixture of DMG and oxine [9] or Cr and V using a mixture of propyl gallate (PG) and diethylenetriaminepentaacetic acid (DTPA) [11] in natural waters at trace levels.

In the last years, there has been an increasing interest about quantifying the fluxes of dissolved trace elements at the water-sediment boundaries of the coastal areas and oceans because they may be a significant part of the internal cycling of trace elements in the oceans [12]. Little is known about the net supply of trace elements from sediments that may alternately serve as a source or a sink, depending on local conditions. In order to estimate these fluxes, pore water concentrations of dissolved metals and its comparison with overlying water column levels should be done. Diagenetic transformation of continental detritus in coastal and hemipelagic sediments may similarly release trace elements into ocean margin waters. This is particularly true where chemically reducing conditions mobilise iron and manganese oxides formed on land, releasing oxide bound trace elements into solution [13]. Although the release of trace elements from ocean-margin sediments has been documented for some first-row transition metals [14,15] the extent to which this represents a net source, by diagenetic mobilization of continentally derived material versus the regeneration of biogenic and authigenic marine phases, remains undetermined.

Thus, one of the main goals of the Geotraces International programme [12] is to determine trace element fluxes between sediment and the water column.

Typical concentrations of Co, Cu, Ni, Fe and V in seawater have been successfully determined using ACSV with several ligands such as, among others, DMG and nioxime for Co [7,8] catechol,

---

E-mail addresses: jecheandia@ipimar.pt, jusae@iim.csic.es

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.04.035

salicylaldoxime (SA) or oxine for Cu [16–18], catechol, SA, 2-(2-thiazolylazo)-p-cresol (TAC) and 2,3-dihydroxynaphthalene (DHN) for Fe [19–22], DMG or nioxime for Ni [8,23] and catechol or chloranilic acid for V [24,25]. To date, however, the optimum conditions for their simultaneous determination in a single scan have not been proposed yet. In this article a methodology for a simultaneous determination of Co, Cu, Fe, Ni and V in sediment pore waters using a mixture of ligands DMG and catechol by ACSV is reported, reducing the analysis time and volume of sample needed.

2. Experimental

2.1. Equipment

The instrument used was a Metrohm VA-797 Computrace equipped with a hanging mercury dropping electrode (HMDE) as the working electrode (drop surface area 0.38 mm^2), an Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. The voltammetric cell and the stirring rod were made of PTFE. High-purity mercury – 99.9999% (Prolabo) was used. Samples were deoxygenated with N_2 (N-50 grade), presaturated with water vapor by passage through a gas scrubbing tube containing Milli-Q (Millipore) water. Sample pH was measured with a Multiline P4 WTW pH-meter. Analyses were carried out in a class – 10000 lab; manipulation of the sample (filtration, dilution, addition of reagents, digestion, etc.) was performed on a class-100 laminar flow bench housed inside the class – 10000 lab.

2.2. Reagents

Milli-Q^{50} water (Millipore) was used for preparing standards and reagents. Co, Cu, Fe, Ni and V aqueous standard solutions were prepared by dilution of 1000 mg L^{-1} stock standards (Merck) and acidified at pH 2. A stock aqueous solution of 0.1 M DMG (dimethylglyoxime) (Riedel-de Haën) was prepared in 0.35 M NaOH (Riedel-de Haën). Stock aqueous solutions of 0.1 M catechol (1,2-dihydroxybenzene) (Fluka) were prepared fresh daily in deoxygenated Milli-Q^{50} water. 1 M HEPES (Sigma) buffer solution was prepared in 0.5 M NH_4OH (Merck Suprapur) giving a final ph around 7.0.

The H_2O_2 (Merck) used for digestion experiments was suprapur grade. The ammonium nitrate matrix modifier for iron analysis was prepared from NH_4OH 25% (Merck, suprapur) and HNO_3 65% (Merck Suprapur®).

2.3. Atomic absorption spectroscopy

Total dissolved Fe in pore waters was also determined by graphite furnace atomic absorption spectrometry (GF-AAS) using ammonium nitrate as matrix modifier. Concentrations were determined using the intrapolation method in a previously designed calibration curve [26]. Detection limit (defined as three times the standard deviation of a blank) was 2.6 nM for Fe. The reproducibility, measured as the RSD (Relative Standard Deviation) was always lower than 5%.

2.4. Pore water samples

Short sediment cores (approx. 10 cm) were sampled in 2005 onboard the *R/V* Mytilus (IIM-CSIC) in the main channel of the Vigo Ria (NW Iberian Peninsula). Acid-washed methacrylate tubes placed inside a *Rouvilloise* grab sampler were used to collect the cores. Once at the onshore lab, sediment cores were stored in plastic bags −18 °C.

In order to preserve the redox conditions, all sample treatment was undertaken inside a glove box filled with N_2 (815-PGB, Plas-Labs). Frozen cores were extruded from the tube and the overlying water was placed into acid-cleaned plastic bottles whereas the sediment was sliced at 2–3 cm layers and allow to thaw inside acid-cleaned polyethylene centrifuge tubes. In order to extract the pore water, sediments were centrifuged at 3000 rpm for 40 min, and the supernatant was passed through acid-washed 0.45 μm acetate cellulose syringe filters and collected in acid-washed 50 mL polyethylene bottles and acidified (pH 2) with concentrated HNO_3 (Merck Suprapur®). The overlying waters were filtered and acidified as above.

Optimization experiments were carried out using a composite sample of the above mentioned cores. This sample was diluted (×10) and UV-digested for 2 h in the presence of H_2O_2 (Merck Suprapur®) using a UV-Digestor equipped with a high-pressure mercury lamp of 200 W [27] in order to remove interfering organics and to breakdown organic complexing ligands. From the tests it was concluded that 2 h of irradiation time with a volume of 20 μL for each 20 mL sample are the optimal conditions. Pore water thus treated is hereafter termed “UVPW”. Dissolved metal concentrations in the sample were 0.92 nM (Co), 7.14 nM (Cu), 49,38 nM (Fe), 7.22 nM (Ni) and 11.3 nM (V).

2.5. Analytical procedures

Aliquots of 9 mL of UVPW were pipetted into 10 mL PFA tubes (Nalgene). The pH was adjusted near neutral with appropriate amounts of diluted ammonia solution (Merck Suprapur®) and HEPES buffer and ligands (catechol and DMG) were added. The sample was then transferred to the voltammetric cell and purged for 10 min. The stirrer rod was switched to 2000 rpm, three mercury drops were discarded and the deposition period, at the appropriate potential, was initiated after extrusion of the fourth. At the end of the adsorption period, the sample was allowed to rest for 15 s and the voltammogram was recorded as the potential was scanned in the negative direction to −1.15 V in the differential pulse mode. The scanning parameters used were a pulse amplitude of 50 mV, a pulse duration of 40 ms, a pulse frequency of 5 s^{-1} and a scan rate of 20 mV s^{-1}.

3. Results and discussion

3.1. Preliminary experiments

During routine measurements of dissolved copper, nickel and vanadium in estuarine sediment pore waters by ACSV [28], it was noticed that two additional defined peaks were obtained at −0.38 V (M_1) and −0.97 V (M_2) (Fig. 1a). In order to identify what element was behind the peaks, a bibliographic research [6] was conducted finding that metals like Co and Pd bind DMG while other metals like Fe, Ge, Sb and U bind catechol, giving measurable peaks by ACSV. Several experiments were conducted with standard additions of these metals in the pore water sample and finally it was discovered that M_1 corresponded with Fe while M_2 corresponded with Co (Fig. 1b). Thus, we considered that it would be interesting to set up a method for the simultaneous determination of the five metals (Co, Cu, Ni, Fe and V) in one scan.

3.2. Selection of the optimum DMG and catechol

The concentrations of DMG and catechol were varied in order to obtain the optimal conditions for the simultaneous determination of Co, Cu, Fe, Ni and V. Aware of the slow kinetics of complex formation between Co, Ni and DMG [9,23], a preliminary study was

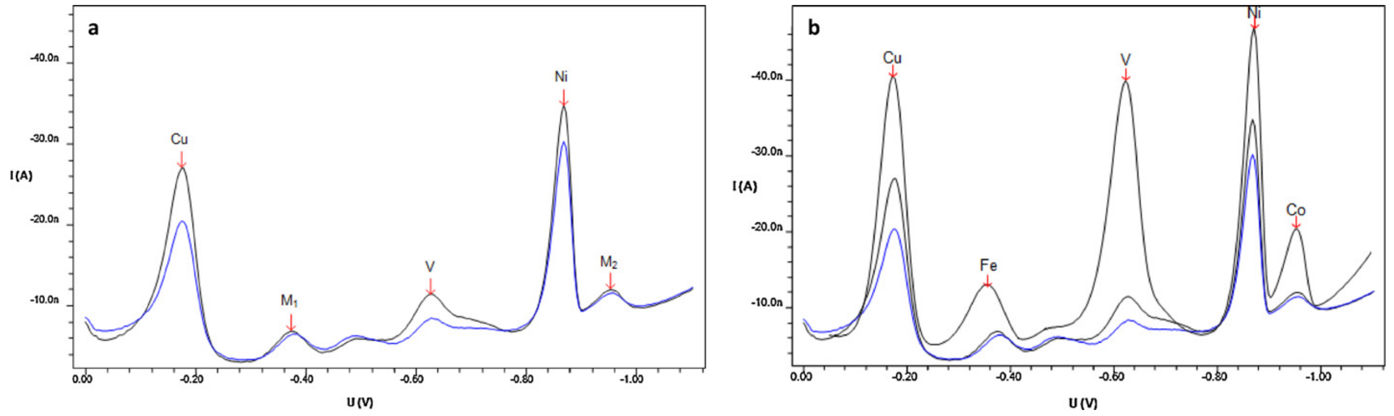

Fig. 1. Voltammograms for a porewater sample of the Vigo Ria. The one on the left (a) shows two unknown peaks (M_1 and M_2). The one on the right (b) shows an addition of 3 nM Co, 10 nM Cu, 50 nM Fe, 12 nM Ni and 60 nM V with a noticeable increase in all the five peaks.

undertaken in order to obtain the time needed to attain equilibrium. The Co and Ni peak heights were recorded as a function of time after the addition of 0.5 mM of DMG to the UVSW containing 0.01 M HEPES (pH ca. 7.0) and 0.8 mM catechol. The peak heights of Co and Ni became constant after 4 min; a further addition of 3 nM of Co and 14 nM of Ni also required 4 min to obtain a constant signal.

The dependence of Co and Ni sensitivity with DMG was checked varying the ligand concentration up to 0.9 mM (Fig. 2a) in the presence of 0.3 mM catechol; the Co and Ni cathodic peak currents increased with successive additions of DMG in this concentration range checked. Cu, Fe and V sensitivity (measured as peak height) was affected by the presence of DMG.

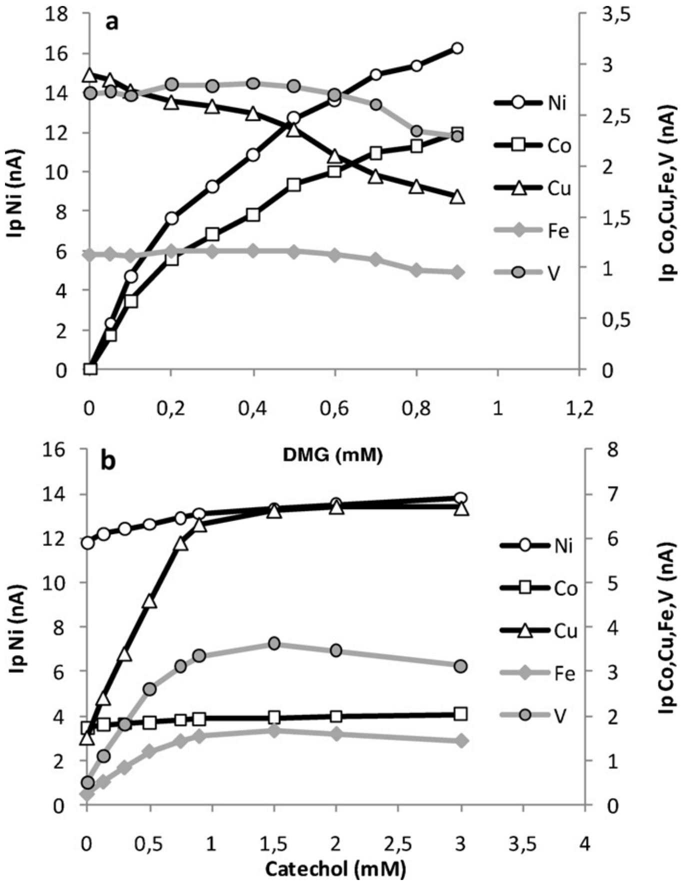

Fig. 2. Optimization of the ligand-catechol and DMG concentrations for the simultaneous determination of Co, Cu, Fe, Ni and V. (a) Optimization of DMG concentration in UVPW at pH 7.15 containing 0.01 M HEPES and 0.3 mM catechol; (b) Optimization of catechol concentration in UVPW at pH 7.15 containing 0.01 M HEPES and 0.6 mM DMG.

The cathodic peaks of Cu, Fe and V sharply increased (Fig. 2b) with the addition of catechol to a sample containing 0.6 mM DMG, reaching the highest sensitivity at ligand concentrations of ca. 0.9 mM (Fe) and 1.5 mM (Cu and V). Further additions of catechol provoked a decrease in the peak height, probably due to saturation of the mercury drop. On the other hand, the addition of catechol to the sample also caused a slight increase of Co and Ni sensitivities (Fig. 2b). From the results obtained, optimum ligands concentrations of 0.6 mM DMG and 0.9 mM catechol were found for the direct simultaneous determination of Co, Cu, Fe, Ni and V.

3.3. *Selection of the optimum pH*

The optimum pH ranges for the metals in a single ligand solution were 7.4–10 for the Co-DMG complexes, 6–9 for the Cu-catechol complexes, 6.8–8 for the Fe-catechol complexes, 7–10 for Ni-DMG and 6.6–7.2 for V-catechol [6]. Therefore, the optimum pH for the simultaneous determination of Co, Cu, Fe, Ni and V was studied varying the pH from 6.8 to 8.3 in the UVPW containing 0.01 M HEPES, 0.6 mM DMG and 0.9 mM catechol, at a deposition potential of −0.4 V. As observed in Fig. 3a, the highest sensitivity for Co, Ni and V was around 6.8–7.0. In the case of Cu, higher sensitivities were found below 7 units of pH while Fe sensitivity increased considerably towards higher pH values reaching a maximum at pH 8.3. It seems that the great increase in sensitivity for iron makes the mercury drop to saturate, decreasing the sensitivities for the rest of the elements. Therefore, an optimum pH of 6.8–7.1 was chosen. The peak potential became more negative with increasing pH, indicating that metal–ligand complexes were stronger and less easily reduced, which is indicative of the lower competition of protons for DMG and catechol at higher pH [8].

3.4. *Selection of the optimum adsorption potential*

The adsorption of Co, Cu, Fe, Ni and V on the HMDE was studied by varying the deposition potential in the 0.0 to −1.0 V range (Fig. 3b); UVPW contained 0.01 M HEPES (pH ca. 7.15), 0.5 mM DMG and 0.8 mM Catechol. After deposition, the solution was allowed to rest for 20 s at a potential of −0.05 V, from where the cathodic scan was initiated and terminated at −1.2 V. The peak height of Co, Cu, Ni and Fe showed a sigmoidal shape with deposition potential,

Table 1
ACSV determination of Co, Cu, Fe, Ni and V in seawater reference material CASS-4 (nearshore seawater). Mean concentrations and standard deviations were calculated from seven replicates.

			Cu	Fe	Ni	V
Observed	$x \pm \sigma(nM)$	0.56 ± 0.08	8.5 ± 0.8	14 ± 3	5.9 ± 0.5	19 ± 2
Certified	$x \pm \sigma(nM)$	0.44 ± 0.05	9.3 ± 0.9	13 ± 1	5.4 ± 0.5	23 ± 3

markedly increasing at potentials more negative than −0.2 V (Ni), −0.3 V (Co, Cu and Fe), from where a plateau was observed. For V, however, the peak height begins to increase at potentials more positive than −0.6 V, reaching the maximum values at around −0.3 V. Therefore, a deposition potential of −0.35 V was found to be optimal for the simultaneous determination of these five metals.

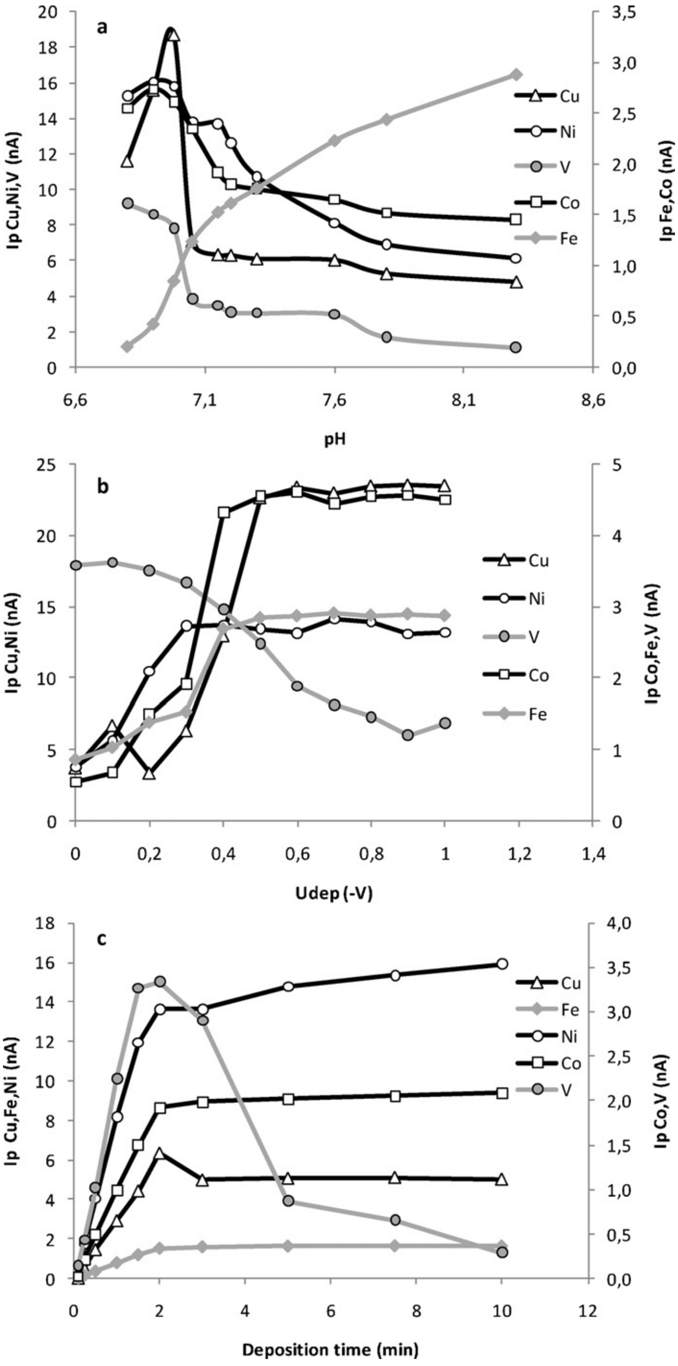

Fig. 3. Optimization of the pH (a), adsorption potential (b), and deposition time (c) for the simultaneous determination of Co, Cu, Ni, Fe and V in porewaters. Samples contained 0.5 mM DMG and 0.8 mM catechol in UVPW.

3.5. *Effect of the adsorption time, working range and mutual interferences*

The sensitivity of Co, Cu, Fe, Ni and V peaks was studied as a function of adsorption time using UVPW containing 0.01 M HEPES (pH ca. 7.0), 0.6 mM DMG and 0.9 mM catechol (Fig. 3c) Under these conditions, the cathodic peak heights varied linearly with adsorption time from 0 to 2 min for Co, Cu, Fe and Ni, and from 0 to 1.5 min for V. From these results, a deposition time of 60 s was chosen as the most suitable for the determination of these five metals at typical concentrations of interstitial waters. For other samples with substantially lower or higher concentrations, the appropriate adsorption time can be easily modified using a higher or lower deposition time. The working range was examined using the above mentioned conditions. The cathodic stripping peak was linear with metal concentrations up to 60 nM for Co ($R^2 = 0.997$), 80 nM for Cu ($R^2 = 0.998$), 300 nM for Fe ($R^2 = 0.999$), >200 nM for Ni ($R^2 = 0.998$) and >300 nM for V ($R^2 > 0.999$). If concentrations were higher, a dilution of the sample with Milli-Q[50] water or even a reduction of the deposition time may solve the problem of un-linearity. On the other hand, experiments were carried out in order to check the mutual interferences, finding that metal peaks were not affected by the addition of the other metals at low concentrations.

3.6. *Accuracy, precision and detection limits*

Detection limits of the technique depended upon the reproducibility of the procedural blank, composed of Milli-Q water with the same reagents and treatment procedure as a regular sample, rather than the instrumental noise. Blank concentrations of Cu, Fe and Ni, using a deposition time of 300 s, were 0.49 ± 0.03 nM ($n = 11$), 1.3 ± 0.4 nM ($n = 11$), and 1.5 ± 0.2 nM ($n = 11$) respectively; for Co and V, using a 900 s deposition time, blank concentration was found to be 0.04 ± 0.01 nM ($n = 8$) and 1.9 ± 0.8 nM ($n = 9$) respectively. This gives detection limits (3σ) of 0.04 nM Co, 0.09 nM Cu, 1.29 nM Fe, 0.46 nM Ni and 2,52 nM V making the method suitable for the direct simultaneous determination of these five metals in sediment pore waters. Although this method has been applied to the determination of dissolved metals in pore waters, looking at the detection limits and blanks obtained, it would be probably also applied to estuarine and coastal waters. The accuracy of the analytical procedure was checked using the CASS-4 (nearshore seawater) certified reference material, finding good agreement (±5) with the certified values (Table 1). Standard deviations expressed in Table 1 correspond to between-run analysis – different aliquots of the sample subject to all the analytical procedure, including digestion – and range from 7% for Ni to 19% for Fe. The in-run precision – subsamples of the same UV-digested aliquot – of pore water samples varied from ($n = 5$) 3% for Ni and V, 6% for Cu and Fe and 10% for Co.

Voltammograms obtained during an analysis of an aliquot of an interstitial water sample from the Vigo Ria can be observed in Fig. 4, showing that Co, Cu, Ni, Fe and V can be simultaneously determined in pore waters by means of ACSV under the conditions proposed.

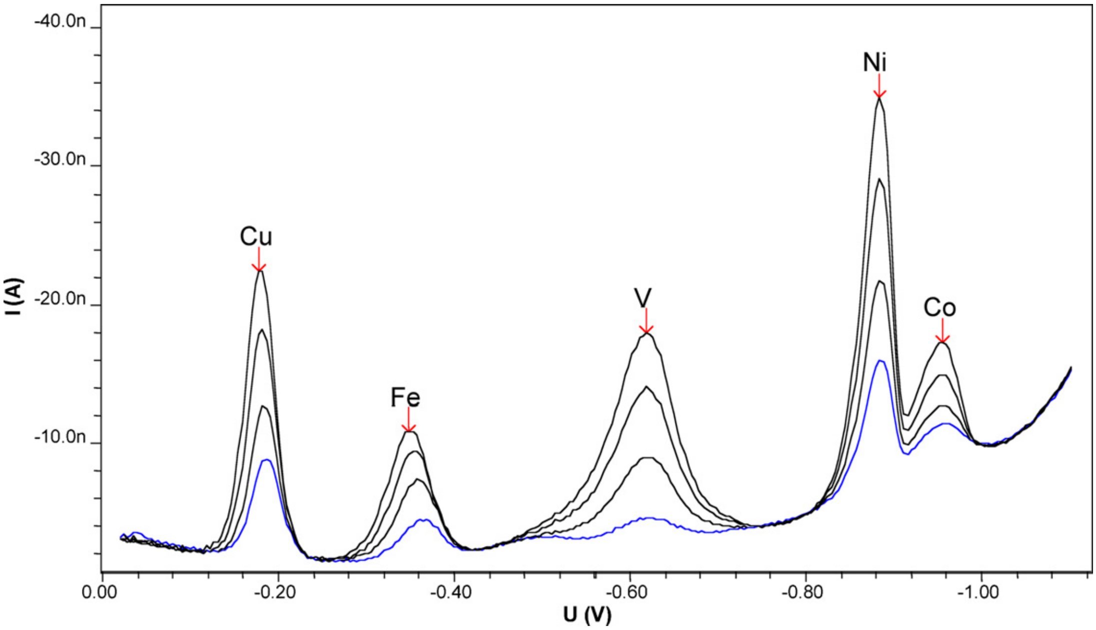

Fig. 4. ACSV voltammograms for the pore water sample of the Vigo Ria. Scan 1: UV-irradiated sample at pH 7.15 containing 0.6 mM DMG, 0.9 mM catechol and 0.01 M HEPES, 60 seconds of adsorption at −0.35 V. Scan 2: +0.5 nM Co, +5.0 nM Cu, +53.7 nM Fe, +5.5 nM Ni, +39.3 nM V. Scan 3: +1.0 nM Co, +10.0 nM Cu, +107.4 nM Fe, +11.0 nM Ni, +78.5 nM V. Scan 4: +1.5 nM Co, +15.0 nM Cu, +161.2 nM Fe, +16.5 nM Ni, +117.8 nM V.

3.7. *Measurement of unusually high concentrations of Fe by voltammetry*

The concentrations of dissolved Fe usually measured by means of stripping voltametry with different types of ligands are in the picomolar to low nanomolar range [20–22]. In our case, these concentrations are in the range of high nanomolar to low micromolar. Although the method has demonstrated to work when analyzing certificate reference material of nearshore water (CASS-4) as we have shown in Section 3.6, it was a challenge for use to test if the method really worked at higher iron concentrations. To do so, two profiles of Vigo Ria pore waters were measured for dissolved iron by means of adsorptive cathodic stripping voltammetry (the method developed in this paper) and by means of graphite furnace atomic absorption spectroscopy [26]. From Figure S1 we can assure that our method was really working with high dissolved iron concentrations as both methods generated similar results.

3.8. *Application to pore water samples*

The present methodology was applied for the determination of dissolved Co, Cu, Fe, Ni and V in pore waters of two different estuaries from the Atlantic margin of the Iberian Peninsula: the Vigo Ria (Spain) and the Tagus Estuary (Portugal).

3.8.1. *Redox conditions classification*

Vertical profiles of dissolved trace metal concentrations in the pore waters of the Vigo Ria sediments and Tagus estuary salt marshes are shown in Fig. 5. Several authors have addressed the suitability of Fe as a tracer to distinguish the various sediment redox layers [29]. Suboxic environments are well characterized by a peak of dissolved Fe which is reduced in the absence of oxygen and thus mobilized to the dissolved phase. In the anoxic zone, a decrease of dissolved Fe concentrations occurs due to the formation of insoluble iron sulphides [30].

In the case of Vigo Ria sediments (Fig. 5a), the thickness of the oxic layer was <1 cm because dissolved iron is already present in the upper layers (≈400 nM). Below this layer, the suboxic region is marked by a dissolved iron wide peak (1–8 cm depth) that reaches values around 6 μM. The anoxic layer should begin at a deeper layer and is not appreciated in the figure as dissolved iron is still observed at 9 cm depth.

Dissolved copper shows a surface maximum (60 nM) that is coherent with the oxic layer. This could be explained by the association with organic matter [31,32] that can be oxidized by the microbial community present in the sediments with the subsequent release of Cu as dissolved species. Below the oxic layer, levels are relative constant and lower (≈10 nM) than the ones measured in the upper layer, probably due to the formation of insoluble sulphides [33]. Regarding the V profiles, this metal shows a surface peak (≈95 nM) associated to the oxidation of organic matter, as was the case for Cu [31]. Dissolved V concentrations tend to decrease at mid-depths, probably due to the adsorption of the reduced form (vanadyl) to the sediments. A net increase in deeper layers is observed reaching values around 330 nM. The complexation of V with organic matter or “yellow substances”, observed in other studies could explain this behavior [32]. Dissolved Ni profile shows a surface maximum (≈150 nM) and below this oxic layer, values are similar and decreasing with depth (to 50 nM). The redox behavior of Co was similar to that of Ni.

Regarding the Tagus estuary salt marsh sediments (Fig. 5b), the oxic layer is not present because high concentrations of Fe (≈1.5 μM) are already observed in the upper layer. The anoxic layer goes from the surface to around 18 cm depth with a pronounced reduction peak of 23 μM at 12 cm depth. Iron concentrations decrease dramatically from 17 to 23 cm depth. Dissolved copper profile is quite constant with depth showing a maximum coincident with iron reduction peak (12 cm). Vanadium behavior is similar to the one presented in the Vigo Ria sediments with a surface maximum (≈60 nM) decreasing the values towards deeper layers with a new increase at around 15 cm depth (≈100 nM). In the case of Ni and Co two surface or subsurface maxima are observed decreasing towards the bottom of the core.

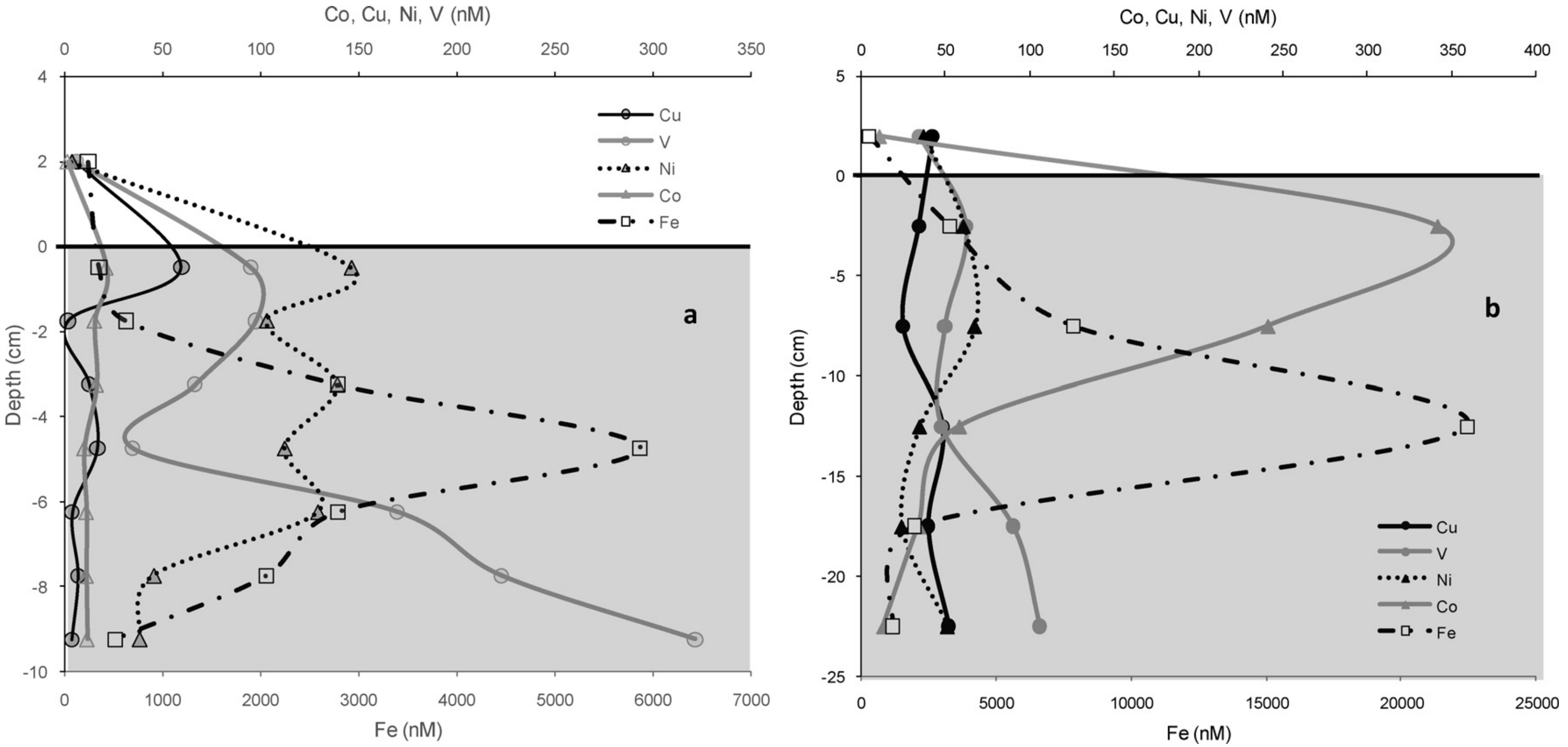

Fig. 5. Dissolved trace metal profiles in the overlying (white area) and pore waters (grey area) of (a) Vigo Ria sediments, (b) Tagus estuary salt marsh sediments.

4. Conclusions

The method proposed here is useful and suitable for the direct simultaneous determination of Co, Cu, Fe, Ni and V in pore water samples (and probably estuarine and coastal waters) by means of adsorptive cathodic stripping voltammetry (ACSV). After UV digestion of the samples for 2 h in the presence of 20 $\mu L\,mL^{-1}$ of H_2O_2, maximum sensitivity was obtained by using a DMG and catechol concentrations of 0.6 mM and 0.9 mM, respectively, a pH solution of 7.0 and an adsorption potential of -0.35 V.

Since pore waters contain significant amounts of several trace elements due to diagenetic postdepositional processes that can be exported to the water column, this method is suitable for determining pore water concentrations and estimating benthic fluxes in sediment water boundaries.

Acknowledgements

The author would like to thank the crew of the R/V Mytilus for their kind cooperation during sampling in the Vigo Ria, Dr. Miguel Caetano (IPIMAR–Lisbon) for his help during sampling in the Tagus estuary and with Fe analyses by means of GF-AAS, and finally, the Basque Government for financial support (BFI09.73 post-doctoral grant).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.04.035.

References

[1] K. Yokoi, C.M.G. van den Berg, Anal. Chim. Acta 245 (1991) 167–176.
[2] K. Yokoi, A. Yamaguchi, M. Mizumachi, T. Koide, Anal. Chim. Acta 316 (1995) 363–369.
[3] N. Verma, K.S. Pitre, Analyst 118 (1993) 65–69.
[4] E.A. Hutton, B. Ogorevc, S.B. Hocevar, M.R. Smyth, Anal. Chim. Acta 557 (2006) 57–63.
[5] L. Chiang, B.D. James, R.J. Magee, Microchim. Acta 98 (1989) 149–156.
[6] C.M.G. van den Berg, Anal. Chim. Acta 250 (1991) 265–276.
[7] A. Meyer, R. Neeb, Fresenius. Z. Anal. Chem. 315 (1983) 118–120.
[8] J.R. Donat, K.W. Bruland, Anal. Chem. 60 (1988) 240–244.
[9] C. Colombo, C.M.G. van den Berg, Anal. Chim. Acta 337 (1997) 29–40.
[10] S. Sander, Anal. Chim. Acta 394 (1999) 81–89.
[11] J. Wang, J. Lu, J. Wang, D. Luo, B. Tian, Anal. Chim. Acta 354 (1997) 275–281.
[12] GEOTRACES Planning Group, GEOTRACES Science Plan, Scientific Committee on Oceanic Research, Baltimore, Maryland, 2006, ISSN1932-7943, www.geotraces.org.
[13] B.A. Haley, G.P. Klinkhammer, Geochim. Cosmochim. Acta 68 (2004) 1265–1267.
[14] V.A. Elrod, W.M. Berelson, K.H. Coale, K.S. Johnson, Geophys. Res. Lett. 31 (2004) L12307.
[15] K.S. Johnson, V.A. Elrod, S.E. Fitzwater, J.N. Plant, F.P. Chavez, S.J. Tanner, R.M. Gordon, D.L. Westphal, K.D. Perry, J.F. Wu, D.M. Karl, Global Biogeochem. Cycles 17 (2003) 1063.
[16] C.M.G. van den Berg, Anal. Chim. Acta 164 (1984) 195–207.
[17] M.L.A.M. Campos, C.M.G. van den Berg, Anal. Chim. Acta 284 (1994) 481–496.
[18] C.M.G. van den Berg, J. Electroanal. Chem. 215 (1986) 111–121.
[19] C.M.G. van den Berg, Z.Q. Huang, J. Electroanal. Chem. 177 (1984) 269–280.
[20] E.L. Rue, K.W. Bruland, Mar. Chem. 50 (1995) 117–138.
[21] P.L. Croot, M. Johansson, Electroanalysis 12 (2000) 565–576.
[22] H. Obata, C.M.G. van den Berg, Anal. Chem. 73 (2001) 2522–2528.
[23] B. Pihlar, P. Valenta, H.W. Nürnberg, Z. Fresenius, Anal. Chem. 307 (1981) 337–346.
[24] C.M.G. van den Berg, Z.Q. Huang, Anal. Chem. 56 (1984) 2383–2386.
[25] S. Sander, G. Henze, Fresenius J. Anal. Chem. 356 (1996) 259–262.
[26] J.R. Montgomery, G.N. Peterson, Anal. Chim. Acta 117 (1980) 397–401.
[27] E.P. Achterberg, C.M.G. van den Berg, Anal. Chim. Acta 291 (1994) 213–232.
[28] A. Cobelo-Garcia, J. Santos-Echeandia, R. Prego, O. Nieto, Electroanalysis 17 (2005) 906–911.
[29] H.J. Brumsack, J.M. Gieskes, Mar. Chem. 14 (1983) 89–106.
[30] I. Rivera-Duarte, A.R. Flegal, Croat. Chem. Acta 70 (1997) 389–417.
[31] G. Klinkhammer, D.T. Heggie, D.W. Graham, Earth Planet. Sci. Lett. 61 (1982) 211–219.
[32] T.J. Shaw, J.M. Gieskes, R.A. Jahnke, Geochim. Cosmochim. Acta 54 (1990) 1233–1246.
[33] G. Klinkhammer, Earth Planet. Sci. Lett. 49 (1980) 81–101.