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Article

Optimization of Experimental Parameters in the Determination of Zinc in Sea Water by Adsorptive Stripping Voltammetry

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Otimizamos um procedimento para a detreminação de zinco em água do mar usando voltametria de redissolução de onda quadrada (SWAdsV) com 8-hidroxiquinolina (oxina) como adsorvente e agente complexante. Inicialmente um estudo univariante da corrente máxima do complexo Zn-Ox em função do pH foi feito para obter os valores adequados de corrente. Posteriormente as condições experimentais foram selecionadas usando um planejamento multivariado experimental. Variaveis como pH, concentração de oxina (C_{ox}), tempo (t_{ads}) e potencial (E_{ads}) de adsorção foram otimizados. O primeiro passo de otmimização foi um planejamento fatorial de 2^4 com 16 medidas, usando valores altos e baixos e tres medidas no ponto central (10.0 µg L^{-1} Zn(II)). Analises de variança mostraram que o pH e a C_{ox} foram os fatores mais significantes, enquanto t_{ads} e E_{ads} não foram significativos, sendo mantidos constantes nos experimentos seguintes. Para encontrar então os valores ótimos de pH e C_{ox} um planejamento fatorial de 2^{2+*} foi usado. Os melhores paramentros experimentais foram pH 6,0; C_{ox} 25 µmol L^{-1}; t_{ads} = 10 s e E_{ads} = –0,70 V. Nessas condições o pico de corrente era proporcional a concentração de zinco, no intervalo 0,1-48,0 µg L^{-1}, com um limite de detecção de 0,05 µg L^{-1}. A reprodutibilidade para soluções de zinco de 5,0 µg L^{-1} foi de 1,9% (n = 16). O método foi validado usando-se água do mar sintética (ASTM D665) com adição de zinco, amostra de água do mar referenciada (CRM-SW, Zn 5 µg kg^{-1}) e amostra de água do mar refernciada com padrão interno (GBW08607, Zn 5 mg kg^{-1}) com resultados satisfatórios. O método pode ser aplicado para a determinação de zinco II em água do mar, sem tratamento prévio.

A procedure for the determination of zinc in sea water by square wave adsorptive stripping voltammetry (SWAdSV) using 8-hydroxyquinoline (oxine) as an adsorbing and complexing agent has been optimized. First, a univariate study of the Zn-Ox complex peak current as a function of pH was carried out choosing values at which adequate currents were obtained. Then, selection of the experimental conditions was made using a multivariate experimental design. Variables like pH, oxine concentration (C_{ox}), adsorption time (t_{ads}) and adsorption potential (E_{ads}) were optimized. The first optimization step was a 2^4 factorial design with 16 measurements made choosing high and low levels, and three measurements at the central point (Zn(II) 10.0 µg L^{-1}). Analysis of variance showed that pH and C_{ox} were the most significant factors, while t_{ads} and E_{ads} were not significant and were kept constant in later measurements. Next, to find the optimum values for pH and C_{ox} a 2^2 + star factorial design was used. The best experimental parameters were pH = 6.0; C_{ox} = 25 µmol L^{-1}; t_{ads} = 10 s and E_{ads} = -0.70 V. Under these conditions the peak current was proportional to the concentration of zinc over the 0.1-48.0 µg L^{-1} range, with a detection limit of 0.05 µg L^{-1}. Reproducibility for 5.0 µg mL^{-1} Zn(II) solution was 1.9 % (n = 16). The method was validated using spiked synthetic sea water (ASTM D665), sea water reference material (CRM-SW. Zn 5 µg kg^{-1}) and fortified water reference material (GBW08607. Zn 5 mg kg^{-1}) with satisfactory results. Finally, the method was successfully applied to the determination of Zn(II) in sea water samples without prior treatment.

Keywords: zinc, adsorptive voltammetry, sea water samples, multivariate experimental design

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Introduction

Zinc concentrations of in uncontaminated seawater are in the range of 0.03 to 10.0 µg L^{-1}.[1] However, coastal areas may receive anthropogenic pollutants from various sources located in the catchment area or in distant places. Industrial and farming activities, as well as urban effluents, are the major anthropogenic sources that supply important loads of toxic metals to the sea.

Stripping analysis has been widely recognised as a powerful tool for trace metal analysis. Its remarkable sensitivity is attributed to the combination of an effective preconcentration step coupled with pulse measurements that generates an extremely favourable signal-to-background ratio. Using anodic stripping voltammetry (ASV), the metals are cathodically preconcentrated on a working electrode such as a mercury electrode by amalgam formation and then stripped out of the electrode by applying an anodic potential scan (e.g., Cd, Pb and Zn). In some cases in which the metals form intermetallic compounds, react irreversibly, or cannot form an amalgam (e.g., Co and Ni), the adsorptive cathodic stripping (AdSV) method is employed. AdSV involves the formation, adsorptive accumulation and then reduction of a surface-active complex of the metal. The ligands used must be good complexing agents, in addition to contain –OH, –SH or other groups with unpaired electrons to interact with the working electrode and adequate charge. The principles and applications of AdSV had been well documented by Kalvoda,[2-6] Economou and Fielden,[7] Panelli and Voulgaropoulos,[8] Wang,[9] Zuhri and Voelter,[10] Honeychurch and Rechnitz,[11] Abollino *et al.*,[12] and Van den Berg.[13]

8-Hydroxyquinoline (oxine) and its derivatives occupy a uniquely important place in analytical chemistry, perhaps second only to EDTA and its analogues. Indeed, few analytical reagents have deserved multivolume monographs devoted only to them, and new applications of oxine and its derivatives in modern analytical chemistry are continually being developed.[14] This compound has been used as solid phase for trace elements determination,[15] in liquid chromatographic separation with fluorescence detection,[16] spectroscopic studies,[17] and lately in fluorimetric determination in micellar medium.[18,19] Oxine and most of its analogues form water insoluble complexes.

Oxine has been used as complexing reagent in adsorptive stripping voltammetry for many metal ions like Mo(VI),[20-24] Cu(II),[25-29] Cd(II),[26,17,30,31] Pb(II),[27] Zn(II),[32] U(VI),[33-36] Sn(IV),[37] Te(IV),[38] In(III)[39] etc. Even though Zn is ubiquitous in real samples and with this technique interference due to intermetal compounds is not significant, there are not many reports on the application of AdSV for the determination of zinc. They have used morin,[40] 2-quinolinethiol,[41] aluminon,[42] tetramethylenedithiocarbamate[43] and catechol violet[44] as complexing agents. The lowest reported limit of detection was achieved using morin as ligand for zinc.[40] It was 0.06 µg L^{-1} with an adsorptive time of 60 s, while the detection limits for 2-quinolinethiol[41] and aluminon[42] as ligand were 65 and 30 µg L^{-1}, respectively. The paper on zinc with tetramethylenedithiocarbamate[43] studied the effect of potential scan speed until 100 V s^{-1} using adsorptive cathodic stripping voltammetry. The authors determined zinc in sea water at levels of 0.13 µg L^{-1} (adsorptive time of 60 s). On the other hand, catechol violet was used as ligand[44] to determine zinc in human hair samples in which levels are higher than in sea water, combining the use of UV irradiation and the polarographic adsorptive technique. Detection limits were not reported.

In the present work a sensitive and selective voltammetric procedure for the determination of zinc is described, based on the accumulation of Zn(II) on a mercury electrode. Optimization of the influential variables on peak current, such as potential, deposition time, pH, and concentration of the complexing agent were chosen first by the univariate method and then by a two-level factorial design, high and low, and replicating values at a centre point. The proposed method provides a low detection limit (0.05 µg L^{-1}) for a short preconcentration time of 10 s with good selectivity. Satisfactory results have been obtained using this method for determination of zinc in sea water without prior treatment. This method is reproducible and fast and it is being used in laboratory practice in an Analytical Chemistry course.

Experimental

Apparatus

Voltammetric measurements were carried out using a Metrohm 757 VA Computrace with a multimode electrode (MME) operating in the HMDE mode. An Ag/AgCl (3 mol L^{-1} KCl) reference electrode and a platinum wire auxiliary electrode were used. Dissolved oxygen was removed with argon. For pH measurements an Orion 430 pH meter was used. All potentials are given relative to the Ag/AgCl electrode. UV-irradiation of water samples was carried out in quartz tubes using a Metrohm 705 UV-digester.

Reagents and solutions

All solutions were prepared with Milli-Q water (18.2 MΩ). Standard stock solutions containing 0.1 and 1.0 mg L^{-1} of zinc were prepared from a standard

1000 mg L^{-1} zinc solution (Merck, Darmstadt, Germany). The solution of oxine (8-hydroxyquinoline. Merck) in methanol was prepared freshly every day. Britton-Robinson buffer[45] was prepared by mixing equal volumes of 0.4 mol L^{-1} orthophosphoric acid, acetic acid and boric acid, adjusting to the required pH with 0.2 mol L^{-1} NaOH solution, and diluting 10 times with water. Synthetic sea water (ASTM D665, Aldrich), contaminated ICP multi-element standard solution IV (Merck), sea water reference material (CRM-SW, Zn 5 µg kg^{-1} ± 0.5%, 2% HNO_3, High purity standards, Charleston, SC, USA) and water reference material (GBW08607, Zn 5.00 mg kg^{-1}) were used for measurement validation.

Sea water samples

Sea water samples were obtained from 4 beaches close to several industries and near to a populated area with much tourism. Las Salinas beach faces an area where several oil refineries kept tanks with crude and refined petroleum, and asphalt, paint and solvents as byproducts for more than 80 years. Amarilla beach is a clean area. Negra beach is near an oil refinery, and Las Ventanas beach is next to a copper refinery. Samples were obtained at two occasions (May and July) in triplicate from three points of each beach (ends and centre). Samples were introduced in plastic bottles previously washed with 1% HNO_3 solution. Each analysis was carried out as triplicate. The averages for all the measurements are reported. To confirm the reliability of the method three samples were also analyzed by ICP-AES.

Procedure

10.0 mL of water, 1.0 mL of Britton-Robinson buffer, different volumes of oxine solution (1.0 or 2.0 mmol L^{-1}) and different volumes of 0.1 or 1.0 mg L^{-1} zinc solution were pipetted into the voltammetric cell. The solution was purged with argon (saturated with water vapor) for 5 min. Then, after 5 drops, a new mercury drop was extruded to initiate the preconcentration for a given t_{ads} and E_{ads} at a stirring speed of 1800 rpm. After a 10 s quiescent period, the potential was scanned between 0.00 and −1.40 V using square wave modulation with 0.005 V step amplitude, 0.050 V pulse amplitude, and a frequency of 50 Hz. The calibration curves were drawn and linear regression and detection limits were calculated.

Limit of detection (LOD)

The limit of detection was calculated using the approximation of Miller and Miller[46] for calibration curves. Minimum signal (y_{min}) was calculated from (y_{min}) = $a + 3s_{y/x}$, where a = intercept and $s_{y/x}$ = standard deviation of the calibration curve.

Results and Discussion

Effect of pH

The first step of this study was to find out the influence of pH on the peak current of the zinc complex in the 2.1 to 12.2 range (Figure 1). Zn(II) and oxine concentrations were 2.0 µg L^{-1} and 10 µmol L^{-1}, respectively (t_{ads} = 60 s, E_{ads} = 0.00 V). At pH values between 4.0 and 8.0 the Zn-Ox peak current had adequate values. At pH > 8.0 the peak current decreased, probably as a result of hydrolysis of Zn(II), and peak potential was shifted to more negative values. A pH of 7.3 was chosen for the whole study.

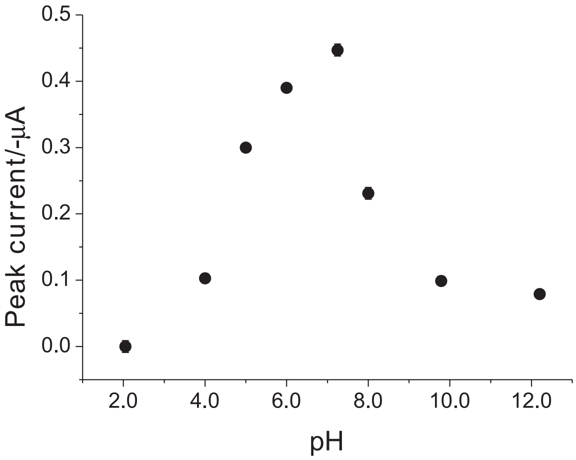

Figure 1. Influence of pH on the peak current of the Zn-Ox complex. Conditions: $C_{Zn(II)}$ = 2.0 µg L^{-1}; C_{ox} = 10 µmol L^{-1}; t_{ads} = 60 s; E_{ads} = 0.00 V. 5 mV step amplitude, 25 mV pulse amplitude and 25 Hz frequency.

Effect of oxine concentration

Oxine is strongly adsorbed on the mercury electrode between 0.10 and −0.25 V *vs*. SCE, favoring Hg oxidation through Hg_2Ox_2 formation.[26] In the pH range of our work (*ca*. 4.0 to 8.0) oxine in solution is an ionic compound (pK_1 = 5.2 and pK_2 = 9.6). It was seen that the current of the Zn-Ox complex increases linearly with oxine concentration up to 20 µmol L^{-1} (Figure 2, M:L ratio *ca*. 1:60), the peak current remained constant up to 40 µmol L^{-1}, and then decreased slightly with increasing concentration of oxine due to competition of free ligand with the Zn-Oxine complex for adsorption on HMDE. The optimum oxine concentration is dependent on accumulation time for a given Zn(II) concentration. For further study an oxine concentration of 20 µmol L^{-1} was chosen, and the

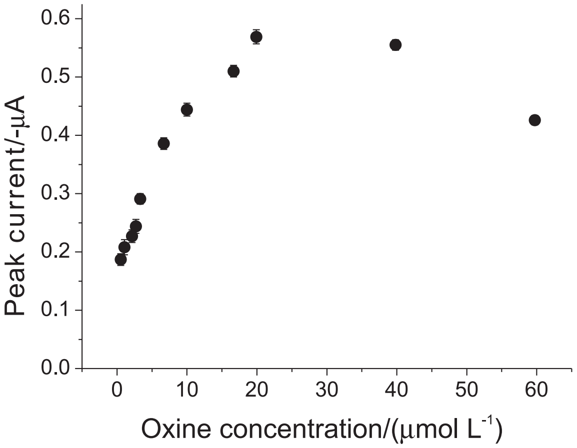

Figure 2. Influence of oxine concentration on the peak current of the Zn-Ox complex. Conditions: $C_{Zn(II)} = 10.0$ μg L^{-1}; pH = 7.3; $t_{ads} = 60$ s; $E_{ads} = 0.00$ V. 5 mV step amplitude, 25 mV pulse amplitude and 25 Hz frequency.

measurements were made with a zinc concentration of 10.0 μg L^{-1} ($t_{ads} = 60$ s; $E_{ads} = 0.00$ V; pH = 7.3).

Effect of adsorptive time and potential

Accumulation time is one of the important parameters in adsorptive stripping voltammetry that has a pronounced effect on both sensitivity and linear range. Accumulation times were examined in the range of 30-210 s while other standard measuring conditions remained constant (C_{Zn} 10.0 μg L^{-1}; C_{OX} 20 μmol L^{-1}; pH 7.3; E_{ads} 0.00 V). It was found that peak current increased linearly with accumulation time up to 120-150 s, but then decreased slightly with increasing time (Figure 3). An adsorption time of 60 s was used, as this was sufficient for the zinc analyses, but for determinations of lowest Zn(II) concentrations an extention of accumulation time is recommended.

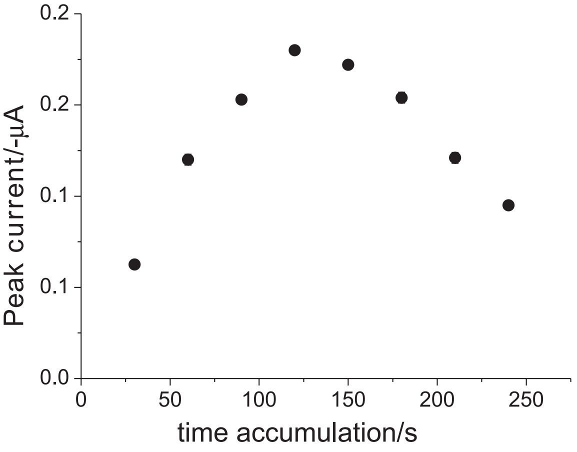

Figure 3. Influence of t_{ads} on the peak current of the Zn-Ox complex. $C_{Zn(II)} = 10.0$ μg L^{-1}; pH = 7.3; $E_{ads} = 0.00$ V. 5 mV step amplitude, 25 mV pulse amplitude, and 25 Hz frequency.

The influence of the accumulation potential was studied for Zn(II) concentration of 10.0 μg L^{-1} (C_{OX} 20 μmol L^{-1}; pH 7.3; t_{ads} 60 s), changing the potential from –0.00 to –1.10 V. It was found that the current of the Zn-Ox peak increases as the potential changes from –0.0 to –0.90 V and then slowly decreases. For further study an accumulation potential –0.90 V was chosen, but when analysis of real samples was made two peaks were observed for the Zn-Ox complex, and for that reason a potential of –0.70 V was chosen.

Optimization of experimental variables

The response to be optimized was peak current intensity of the Zn-oxine complex (i_{peak}), which is notably influenced by pH, oxine concentration (C_{ox}), adsorption time (t_{ads}) and adsorption potential (E_{ads}) for a given Zn(II) concentration. The first optimization step was a 2^4 factorial design (pH, C_{ox}, E_{ads}, t_{ads}) with three replications in the central point (19 experiments performed in random order) using a solution with a Zn(II) concentration of 10.0 μg L^{-1}. Each of the experiments involved three adsorptive voltammograms. A high and a low level were selected for each of the factors to be optimized for the experimental designs. The values of the high (+) and low (-) levels were chosen taking into account the previous univariate study. These values for each factor were as follows: pH 5.0 to 9.0 (the maximum current was obtained at 7.3); C_{ox} 4 to 18 μmol L^{-1} (current increases linearly with C_{OX} up to 20 μmol); t_{ads} 10 to 80 s (current increases linearly with time up to 120-150 s), and E_{ads} 0.00 to –0.70 V (current increases linearly with potential up to –0.90 V). The values selected were chosen in the zone in which the current is increasing and nonsaturation of the mercury electrode was seen. The results obtained are shown in Table 1. Analysis of the variance indicated that pH and C_{ox} are the most important factors. The effect of pH shows a large negative slope (from 5.0 to 9.0. Figure 4), while C_{ox} shows a positive slope (from 4 to 18 μmol L^{-1}). On the other hand, the effect of t_{ads} and E_{ads} shows very slightly negative slopes (from 10 to 80 s and –0.70 to 0.00 V, respectively). To find the optimum pH and C_{ox} values an experimental 2^2 + star design was used. Values of 10 s for t_{ads} and –0.70 V for E_{ads} were selected for these experiments. The new experimental design conditions will move towards low levels of t_{ads} and higher C_{ox}. Figure 5 shows that the maximum intensity of the reduction peak of the Zn-Ox complex is reached under the following conditions: pH = 6.0; $C_{ox} = 25$ μmol L^{-1}; $t_{ads} = 10$ s; and $E_{ads} = –0.70$ V.

The results of univariate and multivariate design were slighly different. With the univariate method the optimum parameters obtained were pH 7.3; C_{ox} 20 μmol L^{-1}, and t_{ads}

Table 1. Results of the 2^4 central composite design for optimization of experimental variables in Zn(II) determination by adsorptive stripping voltammetry

pH	C_{oxine} (µmol L^{-1})	t_{ads} (s)	E_{ads} (V)	i_{peak} (µA)
5.0	18	80	–0.70	0.25
9.0	18	10	–0.70	0.00
9.0	4	80	0.00	0.00
9.0	18	80	–0.70	0.00
5.0	4	80	0.00	0.06
5.0	18	10	0.00	0.30
5.0	4	10	–0.70	0.08
5.0	4	10	0.00	0.08
9.0	4	80	–0.70	0.06
5.0	18	80	0.00	0.28
5.0	18	10	–0.70	0.31
5.0	4	80	–0.70	0.06
9.0	18	10	0.00	0.00
9.0	4	10	0.00	0.00
9.0	4	10	–0.70	0.00
9.0	18	80	0.00	0.00
7.0	11	45	–0.35	0.00
7.0	11	45	–0.35	0.00
7.0	11	45	–0.35	0.00

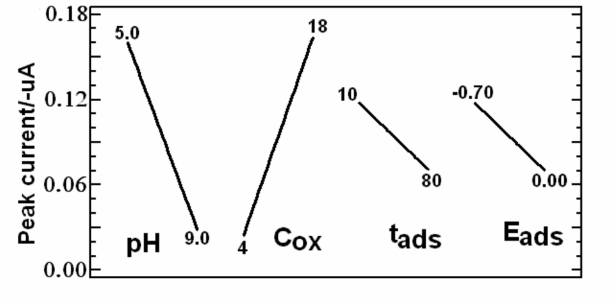

Figure 4. Influence of pH, C_{ox}, t_{ads} and E_{ads} in the response in the 2^4 factorial design. $C_{Zn(II)} = 10.0$ µg L^{-1}.

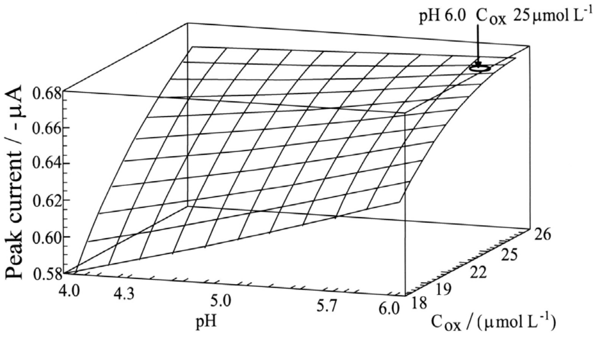

Figure 5. Response surface for 2^2 + star factorial design for pH and C_{ox}.

120-150 s. While the best conditions obtained with the second factorial design were pH = 6.0, $C_{ox} = 25$ µmol L^{-1} and $t_{ads} = 10$ s. Although the current maximum is reached at pH 6.0 in the 2^2 + star design, in the univariate method peak currents obtained at pH 6.0 and 7.3 were sligthy similar (390 and 447 nA respectively). However, the largest difference was obtained with the C_{ox} and t_{ads} parameters. The optimum oxine concentration is dependent on accumulation time for a given Zn(II) concentration. For low levels of t_{ads} higher C_{ox} increases the peak current of the Zn-Ox complex, while higher t_{ads} increases adsorption of free ligand and C_{ox} must be lower. On the other hand, the peak current of the Zn-Ox complex is higher at E_{ads} –0.90 V, but this increase came together with a loss of peak definition, therefore –0.70 V was chosen to carry out experiments because it offered good peak current values and good peak definition.

Effect of instrumental variables (frequency, step potential and amplitude)

A linear increase of the peak current of the complex was seen when the size of the mercury drop varied from 0.25 to 1.25 mm^2, and 0.75 mm^2 was adopted as optimum, with larger sizes not convenient because mercury drops fall more frequently. The peak current of the Zn-Ox complex increased when the frequency increased from 25 to 50 Hz. However, at frequencies of 50 Hz there was a deterioration of the peak shape and the backgroundand 25 Hz was adopted as optimum. Peak current increased linearly with step potential variations from 1 to 10 mV and pulse amplitude from 5 to 50 mV. The increase of the i_{peak} of the Zn-Ox complex as a function of pulse amplitude took place together with a displacement of the E_{peak} to a more positive potential, with good peak resolution. 5 mV and 50 mV were adopted as optimum for step potential and pulse amplitude, respectively. On the other hand, peak current increased as a function of stirring rate during the accumulation step from 0 to 800 rpm, remaining almost constant from 800 to 3000 rpm, and 800 rpm was adopted as optimum.

Linear range, detection limit, reproducibility

Under the best experimental conditions, pH = 6.0, $C_{ox} = 25$ µmol L^{-1}, $t_{ads} = 10$ s and $E_{ads} = -0.70$ V, peak current was proportional to Zn(II) concentration over the 0.1-48.0 µg L^{-1} range, with a detection limit of 0.05 µg L^{-1}. The detection limit of seawater samples by direct analysis was between 0.2 and 3.5 µg L^{-1} when the standard addition method was used. The reproducibility of 16 measurements of a Zn(II) concentration of 5.0 µg L^{-1} was 1.9%.

Interference studies and validation of the method

Because the peak potential of the Zn-Ox complex is about –1.18 V, it is well apart from several metallic ions, but the equilibrium constant for the Zn-Ox complex is lower than that of other metallic ions like Cu, Cd, Fe, and may compete for the oxine ligand. A 10 mL aliquot of synthetic sea water contaminated with a standard solution containing metal ions such as Ag, Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sr, Zn and others in equal concentrations (10.0 and then 20.0 µg L^{-1}), was added to the electrochemical cell that contained 1.0 mL of Britton Robinson buffer (pH 6.0). Due the great presence of metal ions unusual in natural water samples, a $C_{ox} > 25$ µmol L^{-1} was added before the analysis of zinc was carried out, using the standard addition method. Under these experimental conditions, Ni and Cr were not detected. The usefulness of the present method was also evaluated by examining the analysis of Zn(II) in certified reference sea water (10 mL. CRM-SW) containing Zn 5 µg kg^{-1} and fortified water (20 µL, GBW08607) containing Zn 5.00 mg kg^{-1}. Three replicate analyses were performed for each sample (pH = 6.0, C_{ox} = 25 µmol L^{-1}, t_{ads} = 10 s, E_{ads} = –0.70 V). The results obtained for Zn in the spiked synthetic water and in the sea water reference materials are given in Table 2. The values obtained for zinc in these water samples were in agreement with the added and certified values respectively. This indicates the accuracy of the proposed method.

Table 2. Analytical results of Zn determination in synthetic sea water, certified reference materials, and sea water samples

Sample	Zn found (µg L^{-1})	Zn certified (µg L^{-1})
Synthetic sea water	9.6 ± 0.6	10.0 spiked*
Synthetic sea water	19.7 ± 0.4	20.0 spiked*
CRM-SW	5.2 ± 0.5 µg kg^{-1}	5.0 ± 0.25 µg kg^{-1}
GBW 08607	4.98 ± 0.04 mg kg^{-1}	5.00 mg kg^{-1}
Sea water (1)	22.3 ± 1.3	20.1 ± 0.6**
Sea water (2)	21.8 ± 0.8	20.9 ± 0.5**
Sea water (3)	19.3.0 ± 1.0	18.4 ± 0.7**

*These solutions contained metals such as Ag, Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sr, Zn and others in equal concentrations. **Values obtained with ICP-AES.

Seawater sample analysis

The proposed method was successfully applied to the determination of zinc in seawater samples using the standard addition method. Samples were analyzed without prior treatment. Depending of the level of Zn(II) in the samples different aliquots were added to the voltammetric cell and completed up to 10.0 mL with deionized water. These samples were obtained from 4 beaches which are close to several industries, in a sector with a large population and tourism. Low reproducibility was obtained with some samples that had high concentrations of organic matter and these were previously digested under UV radiation in the presence of H_2O_2 solution at 90 °C for 3 h. The level of zinc in Las Ventanas beach was the highest, with 177.3 ± 76.1 µg L^{-1}, followed by Las Salinas beach with 52.2 ± 16.4 µg L^{-1}, Amarilla beach with 35.8 ± 8.2 µg L^{-1}, and Negra beach with 29.9 ± 9.5 µg L^{-1}. High levels were found in the Las Ventanas beach next to a copper refinery. Figure 6 shows a map with the place where the samples were collected. To test the accuracy of the method, Zn(II) in three seawater samples was also determined by ICP-AES. The results are given in Table 2.

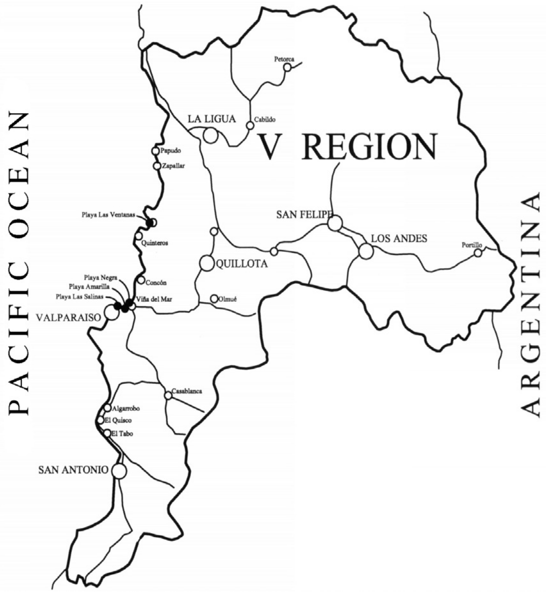

Figure 6. Map of the 5th Region of Chile, showing the samples sites for sea water samples.

Conclusions

The method of multivariate experimental design has a practical potential for use with the adsorptive stripping voltammetry technique in the selection of the best parameters. The values obtained with univariate and multivariate design are similar. The multivariate method indicates that lower t_{ads} with higher C_{ox} is better than higher t_{ads} with lower C_{ox}. Also, for the determination of zinc in HMDE, adsorptive voltammetry showed excellent experimental simplicity, speed, reproducibility, a very wide range of application, selectivity, and sensitivity for the determination of low levels in the presence of others metal ions. The ability of the method was confirmed by the analysis of sea water samples.

Acknowledgments

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