Trace element determination in seawater by ICP-MS using online, offline and bath procedures of preconcentration and matrix elimination

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In the present study, procedures for multielemental determination of V, Mn, Co, Ni, Cu, Zn, Cd and Pb in seawater using inductively coupled plasma mass spectrometry (ICP-MS) are described and evaluated. The methods involve chelation of the metals onto iminodiacetate resins: Toyopear® AF Chelate-650 M, using both off and online column procedures and SPR-IDA (suspended particulate reagent iminodiacetate) using batch procedure. The recoveries from seawater samples ranged from 75 to 110%. Calibrations (external and/or standard addition) performed using calibration solutions with concentrations ranging from 0 to 5 μg L−1 resulted in regression coefficients of 0.99–1. The limits of detection (LODs) ranged from 0.01 (for Co) to 0.08 μg L−1 (for Zn) for the offline column procedure, from 0.004 (for Cd) to 0.147 μg L−1 (for Ni) for the online column procedure and from 0.004 (for Cd) to 0.055 μg L−1 (for Cu) for the batch procedure, appropriate to the required analysis. Accuracy was assessed by the analysis of seawater certified reference materials (CASS-3 and CASS-4), and good agreement between found and certified values was found. These methods were used for the determination of trace metals in produced water, interstitial water and seawaters from the Brazilian shore.

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1. Introduction

Several techniques have been used to determine trace elements in environmental samples. These include flame and graphite furnace atomic absorption spectrometry [1], neutron activation analysis [2], inductively coupled plasma optical emission spectrometry (ICP-OES) [3] and inductively coupled plasma mass spectrometry (ICP-MS) [4]. However, trace analysis in sea water frequently requires a previous preconcentration and/or separation of the saline matrix for most instrumental analytical methods. Different procedures have been used successfully for this purpose, including coprecipitation and co-crystallization [5], solvent extraction [6], chelating ion exchange [7], electrolytic concentration [8] and electrothermal vaporization [9].

Direct analysis of sea-water by ICP-MS can cause serious physical damage to the cones (sampler and skimmer) through salt deposition and the consequent narrowing of orifices, resulting in sensitivity decreases and, in the long run, a decrease in the stability of the instrument. The saline matrix also contributes to sensitivity decreases due to ionization suppression and even if the sample is diluted several times, these interferences are still perceived. Interferences caused by the formation of polyatomic ions (particularly below m/z = 80), with elements such as Cl, O, Na, Mg and Ca [10] affect several determinations, i.e. 23Na40Ar in 63Cu or 23Na35Cl in 58Ni. The use of collision or reaction cells has been reported as a way of circumventing these interferences in the direct analysis of seawater [11–13], but at the expense of dilution factors or gas flows in the cell that can lead to prohibitive impoverishment of the limits of detection.

In the analysis of seawater by ICP-MS, most matrix separation and/or analyte preconcentration studies, with both offline and online sample introduction, have been conducted by using chelating agents based on iminodiacetate or 8-HQ (8-hydroxiquinoline) functional groups, immobilized onto several supports, such as polystyrene-divinylbenzene, controlled porosity glass and carboximethylcellulose, among others [14–17]. In most cases, the analytes retained in the column are eluted with acid mixtures, usually HNO3 and/or HCl. 8-HQ is one of the more used chelants for online systems, but, when used associated to ICP-MS presents some disadvantages. Given that the eluant used in this procedure is a HNO3 and HCl mixture, Cl polyatomic species can affect the determination of V and other elements of interest. On the other hand, and no less importantly, the fact that the 8-HQ resin is not available commercially should be taken into consideration.

Different exchangers based on iminodiacetate functional groups have been used in online systems, including the following commercial products: Chelex®–100 [18], MetPac® CC-1 [14,15,19], Chelite-C [18],...
Muromac A-1 [21], Prosep IDA [22] and Amberlite IRC-718 [23]. Although all of them are iminodiacetate based, their fabrication varies, resulting in differences in the analytical performance of the column. Chelex©-100 ion exchanger presented difficulties with salt retention [24], with the greatest problem being significant volume changes with pH variation [22,24]. This problem was eliminated in other resins, using a more rigid support. Chelite-C, a polystyrrene-divinylbenzene supported resin, was used by Taylor et al. [20] to determine Mn, Ni, Co, Cu, Zn, Cd, U and Pb in sea water. Calibration was conducted by analyte addition and the analysis time for each sample was 19 min. The disadvantage of this procedure was precisely the need to wash the column with 8 mL of buffer after sample loading. Ebdon et al. [19], for the determination of Cu, Mo, Ni, U and Zn, also needed to wash a column of Metpac CC-1 with a buffer, in order to remove the matrix. A similar need was also reported by Bloxham et al. [15], using a Metpac CC-1 column. The Prosep-1 chelating resin was successfully used for the determination of Co, Ni, Cu, Zn and Cd in seawater in online systems by ICP-MS [22,25]. In this case, external calibration was used with aqueous calibration curves and the analysis time for one sample was 5 min. The limits of detection calculated from the calibration curve ranged from 0.02 μg L⁻¹ for Co to 0.20 μg L⁻¹ for Zn.

Willie et al. [26] used the commercial resin Toyopearl AF-Chelate 650 M for multielement determination of trace metals in seawater, using a flow injection system (FI) coupled to a high resolution ICP-MS. V, Cu, Ni, Zn, Co, Pb and Cd in certified samples of seawater (NASS-4 and CASS-3) were determined. The analysis time was 3 min and the limits of detection ranged from 0.5 ng L⁻¹ for Co to 9.0 ng L⁻¹ for Zn. Later, Willie and Sturgeon [27] also used the same resin for the determination of rare earth elements (REE). A study of the same resin for the determination of Mn, Ni, Cu, Cd and Pb was reported by Warnken et al. [28]. In this study, a FI system directly connected to an ultrasonic nebulizer coupled to a high resolution ICP-MS was used. Internal standards of Sc, In and Bi were used for low, medium and high masses, respectively, and samples of certified seawater CASS-4 and NASS-4 were analyzed. The analysis time was 6 min and the limits of detection ranged between 0.06 ng L⁻¹ for Cd and 1.1 ng L⁻¹ for Mn. Beck et al. [29] also used the resin for the determination of Cd, Cu, Ni, Zn and Mn in estuarine water.

In the present paper, we investigated different modes of use of two commercial resins, Toyopearl AF-Chelate 650 M (column, off and online) and SPR-IDA (batch) for the determination of V, Mn, Co, Ni, Cu, Zn, Cd and Pb in seawater by ICP-MS.

2. Experimental

2.1. Instrumentation

The instrument used for the analysis with the Toyopearl AF-Chelate 650 M resin (Tosoh, Montgomerryville, PA, USA), both in the offline and online systems, was a model ELAN 5000A ICP-MS spectrometer (Perkin-Elmer-Sciex, USA), with a Meinhard concentric nebulizer and a cyclonic nebulization chamber (Glass Expansion, Au). The FI system used was a FIAS-200 model (Perkin-Elmer, Ueberlingen, Germany), in combination with an AS-90 sampler (Perkin-Elmer, Ueberlingen, Germany). Tygon tubing was used, black–black (0.76 mm internal diameter) for the buffer line and red–red (1.14 mm internal diameter) for the other lines, ultrapure water and eluent. For the transfer lines and connections, PTFE tubes of 0.8 and 1.0 mm internal diameter were used. To connect the pump tubes to the transfer lines and/or the solenoid valve plastic connectors were used (Perkin-Elmer, part numbers B0507918, B0501580, B0196704, B0199035).

The commercial iminodiacetate resin Toyopearl® AF-Chelate 650 M, which has particles of 65 μm in diameter, was packed onto a Teflon® (polytetrafluoroethylene, PTFE) column of 2.1 cm in length and 0.3 cm internal diameter, with the help of a peristaltic pump, model IPC-8 (Ismatec, Glattbrugg Switzerland), and a 50 μl pipette (Eppendorf, Eppendorf, Germany), to a final mass of 0.16 g. Each end of the column was closed with cellulose filters, which, besides having the ability to retain the resin, also serve as a filter for the seawater and prevent any particulate from interfering in the analysis.

This same analytical column (AC) was used in the offline and online systems. To reduce the blank, a cleaning column (CC), similar to the preconcentration column, but of 0.3 cm in diameter and 2.5 cm in length, also filled with same resin, was placed at the buffer line before the peristaltic pump. In the offline system, a peristaltic pump model IPC-8 and Tygon tubing were used to carry the sample to the analytical column (AC). The instrument used for the batch procedure using the SPR-IDA resin (CETAC, Nebraska, USA) was a model 7500 ICP-MS spectrometer (Agilent, Tokyo, Japan), coupled with a model AS-1 autosampler (Agilent). A centrifuge, model Excelsa II (Fanen, S. Paulo, Brazil), a mechanical stirrer, model SWB 20 (Haake Fisons, USA) and polypropylene centrifuge tubes (15 mL) were also used in this procedure. The SPR-IDA resin was used in the form of a 10% m/v suspension. For the determination of Ca, Mg and Na in the eluate a model 1000 ICP-OES spectrometer (Perkin Elmer, USA) was used.

2.2. Materials and solutions

The water used in this study (resistivity > 18.2 MW.cm) was purified by distillation and subsequent deionization with a Milli-Q system (Millipore, Bedford, MA, USA). The HNO₃ (Merck, Darmstadt, Germany) of analytical reagent grade was used in all tests was distilled (sub-boiling) in a quartz still (Hans Kuehner, Rosenheim, Germany). The ammonia–ammonium acetate buffer solution was prepared from PA reagents (Merck, Darmstadt, Germany). The analytical solutions were prepared by appropriate dilutions of 1000 mg L⁻¹ Titrisol® standard solutions (Merck), of V, Mn, Co, Ni, Cu, Zn, Cd and Pb. The certified reference materials, CASS-3 and CASS-4 from the National Research Council of Canada, for trace metals in seawater, were used to estimate the accuracy of the methods. This sample is acidified to pH 1.6 for the trace metals in the eluate. Seawater used for this study was collected from the north coast of the State of Rio de Janeiro, Brazil.

2.3. Procedures

2.3.1. Offline system

The offline cycle of the preconcentration and matrix elimination is composed of the following steps:

1. Column load: 4 mL of the sample is passed through the column at 2.8 mL min⁻¹.
2. Wash: Consists of washing the interstitial volume of the column with ultrapure water and the line itself, allowing the removal of residues of the saline matrix.
3. Elute: Conducted with 2 mL of 1 mol L⁻¹ HNO₃, resulting in a preconcentration factor of 2.
4. Reconditioning: The system is rinsed with ultrapure water, returning the column to a neutral pH before processing the next sample.

In the analysis of real samples, this procedure was proposed and implemented on board, directly after sampling, without the need for pH adjustment or addition of other reagents, avoiding, in this manner, unwanted manipulation of the samples, or their storage. For acidified samples, such as the reference samples CASS-3, the pH was previously adjusted to ≈ 8 with the ammonia–ammonium acetate buffer, which was previously passed through the CC in order to decontaminate this buffer solution. The ICP-MS spectrometer was used in the quantitative mode. External calibration was performed with aqueous calibration solutions (0.05 to 5 μg L⁻¹). The results were corrected by the recovery factors determined during the recovery tests of metals in the column as a function of pH.
2.3.2. Online system

A flow injection system was set up, and its schematic diagram and operation sequence are shown in Fig. 1. A complete cycle of the preconcentration and matrix separation is comprised of the following steps:

1. Prefill: The sample line is filled with the buffered samples up to the drain (W), where the pH of the resulting solution is measured for pH control.
2. Load: The buffered sample is passed through the analytical column (AC) at a flow rate of 2.2 mL min$^{-1}$.
3. Wash: The interstitial volume of the column and the line itself is washed with ultrapure water, to remove the sample matrix and the residue components of the saline matrix.
4. Elute: The elution is done with 1 mol L$^{-1}$ HNO$_3$, which carries the analyte to the ICP-MS.
5. Reconditioning: The column is washed with ultrapure water, to remove the remaining acid and ready it for the next sample.

A summary of the operational conditions of the ICP-MS in the online procedure is presented in Table 1. In the calibration studies for the preparation of calibration curves by analyte addition, micro-quantities of the standard solution were used, in order to avoid changes in the seawater pH $\approx$ 8.0. The calibration curves ranged from 0.05 to 5 $\mu$g L$^{-1}$.

2.3.3. Batch

The batch procedure proposed in this paper builds on small diameter polymer beads (10 $\mu$m) derivatized with the chelating agent iminodiacetate providing a greater contact surface and better metal percolation efficiency. 15 mL of the seawater sample was transferred to a centrifuge tube and 100 $\mu$L of the SPR-IDA suspension (10% m v$^{-1}$) was pipetted directly in the sample. The tube was capped and the contents were mixed. The tube was placed in a shaker for approximately 45 min and the mixture centrifuged at 3500 rpm for 5 min. The supernatant was carefully discarded, avoiding any loss of the resin that adheres to the bottom of the tube. After this, 3 mL of HNO$_3$ 1 mol L$^{-1}$ was added to the residue in the tube, for extraction of the metallic ions from the resin. The tube was then shaken for 1 min. The mixture was once again centrifuged and the supernatant transferred to the ICP-MS autosampler vial for metal determination. For resin reconditioning, 15 mL of a 0.01 mol L$^{-1}$ HNO$_3$ solution was used, followed by centrifugation and supernatant discarding. The operating conditions of the ICP-MS

![Diagram of the FI system.](image)

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ICP-MS Online</th>
<th>ICP-MS Batch</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power</td>
<td>1200 W</td>
<td>1500 W</td>
</tr>
<tr>
<td>Nebulizer Ar flow</td>
<td>0.95 L min$^{-1}$</td>
<td>1.0 L min$^{-1}$</td>
</tr>
<tr>
<td>Plasma Ar flow</td>
<td>15.0 L min$^{-1}$</td>
<td>15.0 L min$^{-1}$</td>
</tr>
<tr>
<td>Auxiliary Ar flow</td>
<td>1.0 L min$^{-1}$</td>
<td>1.0 L min$^{-1}$</td>
</tr>
<tr>
<td>Nebulizer chamber</td>
<td>Concentric</td>
<td>Concentric</td>
</tr>
<tr>
<td>Calibration</td>
<td>Cyclonic</td>
<td>Scott double-pass</td>
</tr>
<tr>
<td>Aspiration rate</td>
<td>1.0 mL min$^{-1}$</td>
<td>1.0 mL min$^{-1}$</td>
</tr>
<tr>
<td>Acquisition mode</td>
<td>Peak hopping</td>
<td>Scanning</td>
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<tr>
<td>Dwell time</td>
<td>20 ms</td>
<td>20–30 ms</td>
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<tr>
<td>Calibration</td>
<td>Analyte addition/external</td>
<td>Analyte addition</td>
</tr>
<tr>
<td>Replicates</td>
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<td>3</td>
</tr>
<tr>
<td>Readings per replicates</td>
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<td>300</td>
</tr>
<tr>
<td>Isotopes</td>
<td>$^{51}$V, $^{55}$Mn, $^{59}$Ni, $^{60}$Co, $^{62}$Ni, $^{63}$Cu, $^{64}$Zn, $^{65}$Cu, $^{66}$Zn, $^{114}$Cd and $^{208}$Pb</td>
<td>$^{51}$V, $^{55}$Mn, $^{60}$Ni, $^{62}$Cu, $^{64}$Zn, $^{65}$Cd and $^{208}$Pb</td>
</tr>
</tbody>
</table>
spectrometer are shown in Table 1. Calibration was performed by analyte addition in the range of 0.25 to 1 μg L⁻¹.

3. Results and discussion

3.1. Preconcentration column performance

The recovery of the elements of interest as a function of pH (solutions in ultrapure water and seawater enriched with 3 μg L⁻¹ of the investigated elements) was studied, in order to establish the optimal conditions for metal adsorption onto the column. Fig. 2 shows the recovery of the investigated elements in spiked seawater. This experiment was performed offline, following the methodology described above. The sorption of V onto the column, both in ultrapure water and in seawater, decreases from pH ~6 on, with a more pronounced decrease in seawater. Thus, the pH range for optimal V recovery is from 4 to 6, which complicates the direct analysis of seawater for this metal, since the pH of seawater is about 8. For Ni, similar recovery trends were observed in both ultrapure water and seawater, demonstrating that the saline matrix exerts no influence on the adsorption of this element throughout the studied pH range. The recovery percentages measured by the detection of three studied Ni isotopes show that the elimination of the saline matrix avoids possible polyatomic interference, such as 23NaCl⁺ on 59Ni (67.84% abundance), 44CaO on 60Ni (26.23% abundance) and 23NaNaCl⁺ on 62Ni (3.66% de abundance). For Cu, similar recovery in ultrapure water (from pH ~5.5) and in seawater was observed, and, in the latter, results from the 65Cu and 64Cu isotopes were also very similar, indicating that the possible polyatomic ion interference of 23NaAr⁺ on 64Cu (the main Cu isotope, with 69.09% of abundance) was virtually eliminated. The 65Cu (30.91% abundance), could also suffer spectral interferences from polyatomic S ions, present in seawater, but such interferences would not be as severe as those of Na (high content in seawater) on 63Cu. The recovery of 114Cd (28.86% abundance) in ultrapure water was constant (~82%) in the pH range of 4.0 to 9.6, but for seawater, the same constancy was only observed from pH 5.4 onwards. Mn recovery in ultrapure water was ~100% in the pH range of 4.0 to 9.6. In seawater, the maximum recovery of Mn (~90%) was in the pH range of 7.0 to 9.5. In the case of 55Mn (100% abundance), spectral interferences due to the polyatomic ion 37ClH⁺ could also be expected.

Lead showed a recovery in seawater near to 100%, in a wide pH range (3.3 to 9.5). The recovery of 59Co (100% abundance) in ultrapure water was ~100% in almost the whole studied pH range, with the optimal range of recovery in seawater in the pH interval of 4.7 to 8.5.

Table 2 shows the metal recoveries in ultrapure water and seawater for pHs 5.5 and 8.2. The quantitative recovery is evident for most elements in both cases, illustrating that, with the exception of Mn (pH 5.5) and V (pH = 8.2), the matrix saline does not influence the analytical performance of the column.

The elimination of the major matrix components of seawater is a determinant factor for the reduction of interferences from polyatomic ions and the minimization of signal suppression caused by ion–ion interactions or by the space-charge effect. Concentrations of Ca²⁺, Mg²⁺, Na⁺ and Cl⁻ in 2 mL of eluate at pH = 5.4, measured by ICP-OES, were lower than 4 mg L⁻¹, which means a reduction of approximately 400 mg L⁻¹ for Ca, 1400 mg L⁻¹ for Mg, 12,000 mg L⁻¹ for Na and 12,500 mg L⁻¹ for Cl, which represents almost the whole totality of

![Fig. 2. Recovery (%) vs. pH for V, Cd, Mn, Co, Ni, Cu and Pb in spiked seawater using column preconcentration procedure. Other factors as in procedures, offline system.](image-url)
these components in seawater. For pH 8.0, the retention of Mg\(^{2+}\), Na\(^{+}\) and Cl\(^{-}\) was also below 4 mg L\(^{-1}\), however Ca\(^{2+}\) concentration was around 15 mg L\(^{-1}\). With this evidence, for Co determination the pH 5.5 was chosen, in order to minimize any possible isobaric interference of \(^{42}\)Ca\(^{16}\)OH and \(^{43}\)Ca\(^{16}\)O on the monoisotopic element \(^{59}\)Co.

A seawater sample enriched with 5 \(\mu\)g L\(^{-1}\) of the studied elements was analyzed, in order to observe the influence of increasing the sample volume (higher preconcentration of the metals of interest and increase in salinity) on the metal recovery in the eluate. Fig. 3 presents the metal recovery in the eluate for the different sample volumes (4, 8, 12 and 16 mL) that were passed through the analytical column. Mn was the only element that proved to be volume-dependent, experiencing a drop in metal recovery with the increase of sample volume of seawater. For pH 5.4, where Mn adsorption to the resin is very poor, the recovery decreases from 12% (4 mL) to 0% (12 and 16 mL), while for pH 8.0 Mn recovery also decreases dramatically from 85% (4 mL) to 55% after pre-concentration of a 16 mL volume. The other studied metals showed similar recoveries for the four volumes studied and a RSD of less than 7% for most of the metals in question. For pH 8.0 V recovery is practically null.

The recovery of the metals for different concentrations of the HNO\(_3\) acid eluent (0.1, 0.5, 1, 2 and 3 mol L\(^{-1}\)) was studied. For this experiment, a sample of seawater enriched with 5 mg L\(^{-1}\) of the studied elements was also used. Small variations were observed, with a slight tendency of recovery increase by increasing the eluent concentration for most elements of interest, with this increase being more pronounced for vanadium. The HNO\(_3\) concentration of 1 mol L\(^{-1}\) was chosen as a good compromise between recovery and not being a too elevated concentration representing a risk to the instrument.

A column saturation test was conducted by adding a sample of seawater with different concentrations of the elements of interest from 0.05 \(\mu\)g L\(^{-1}\) to 100 \(\mu\)g L\(^{-1}\). With the exception of vanadium, which from the concentration of 25 \(\mu\)g L\(^{-1}\) onwards completely loses its sorption capacity to the column, for the other metals a constant recovery was observed in the concentration range investigated.

### 3.2. Offline preconcentration

Calibration curves were constructed with aqueous calibration solutions that went through the preconcentration procedure. The figures of merit associated to these curves, with the studied isotopes, are presented in Table 3.

The LOD results demonstrated that this technique is suitable for the determination of metals in seawater. For most of the studied

```markdown
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<thead>
<tr>
<th>Isotope</th>
<th>pH 5.5</th>
<th>pH 8.2</th>
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</thead>
<tbody>
<tr>
<td>UPW (%)</td>
<td>Seawater (%)</td>
<td>Resp. (%)</td>
</tr>
<tr>
<td>(^{51})V</td>
<td>104±5</td>
<td>103±6</td>
</tr>
<tr>
<td>(^{55})Mn</td>
<td>100±2</td>
<td>32±1</td>
</tr>
<tr>
<td>(^{59})Co</td>
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<tr>
<td>(^{114})Cd</td>
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</tr>
<tr>
<td>(^{208})Pb</td>
<td>94±3</td>
<td>100±9</td>
</tr>
</tbody>
</table>
```

**Table 2**

Spike recovery from ultrapure and sea water at pH 5.5 and pH 8.2. Resp. = response seawater to ultrapure water, UPW = ultrapure water.

![Fig. 3](image-url)
metals, the concentrations are above the obtained values, with the exception of cadmium and lead, which are in the same concentration order.

To validate the developed methodology, certified seawater samples CASS-3 buffered with ammonia-ammmonium acetate (pH~8.2) were used. As shown in Table 4, the results showed good agreement between the measured and certified values, considering the concentration ranges and the uncertainties of the results.

### 3.3. Online preconcentration

The figures of merit for the analyte addition curves in seawater using the online preconcentration procedure are shown in Table 3. Good linearity, with correlation coefficients always higher than 0.98, was observed. Although the method chosen for analysis was calibration by analyte addition, external calibration curve with aqueous calibration solutions could also have been used, since there was no significant difference regarding the results obtained by this manner. Analysis of the blank, with and without the cleanup column, showed a clear decrease (50 to 90%) of the signals associated with it when the column was used.

The limits of detection obtained in the present study were somewhat larger than those reported in the literature in studies conducted with the same resin, with the exception of vanadium. This was due to the larger blanks associated to the use of non ultrapure reagents for the buffer, showing that the use of the cleaning column compensated, but only partially, the use of analytical reagent grade reagents. However, in comparison with the studies using different resins for the determination of metals in seawater, using an online system with ICP-MS, the limits of detection obtained are lower than those reported in literature [22,25,30].

The methodology accuracy was assessed by the analysis of the certified reference material CASS-3 seawater. Due to the acidity of CASS-3 (pH=1.6) and, therefore, the difficulty of adjusting, in line, a pH of 8.2, the validation was performed using the ammonia-ammmonium acetate buffer (pH 5.5), resulting in a pH=5.0 measured at the drain. The results for the studied elements are presented in Table 4.

The results showed good agreement between the measured and certified values of CASS-3, except for Mn, as expected, because of its poor recovery at pH=5. In a further analysis of CASS-3, at pH 8.2, a Mn concentration value of 2.51 μg L⁻¹ was obtained, in excellent agreement with the certified value. The concentration obtained for vanadium, even though this is not a certified value, did not correspond to the values reported by Willie et al. [26] (1.18±0.05 μg L⁻¹), Chapple et al. [31] (1.50±0.15 μg L⁻¹) and Pozebon et al. [32] (1.47±0.22 μg L⁻¹). In the case of lead, the concentration to be determined (0.012 μg L⁻¹) was below the limit of detection of the technique (LOD = 0.032 μg L⁻¹).

In the case of the V, in order to confirm the accuracy of the procedure, the recovery of this metal in seawater and ultrapure water was further studied at concentrations of 0.1, 0.5, 1, 2 and 3 μg L⁻¹. Recovery ratios (seawater/ultrapure water) of 99% at pH 5.5 were observed, illustrating that the saline matrix does not influence the column performance at this pH.

### Table 4

Analytical results for CASS-3 and CASS-4 using the ICP-MS offline, online and batch preconcentration procedures.

<table>
<thead>
<tr>
<th>Element</th>
<th>CASS-3</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>CASS-4</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>ICP-MS Offline</td>
<td>ICP-MS Online</td>
<td>Certified (μg L⁻¹)</td>
<td></td>
<td>ICP-MS Batch</td>
<td>Agilent 7500</td>
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<tr>
<td>V</td>
<td>n.m.</td>
<td>0.70 ± 0.07</td>
<td>n.c.</td>
<td></td>
<td>n.m.</td>
<td>1.18 ± 0.16</td>
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<tr>
<td>Mn</td>
<td>2.26 ± 0.09</td>
<td>2.51 ± 0.25</td>
<td>2.51 ± 0.36</td>
<td></td>
<td>2.78 ± 0.19</td>
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</tr>
<tr>
<td>Co</td>
<td>0.055 ± 0.014</td>
<td>0.045 ± 0.001</td>
<td>0.041 ± 0.009</td>
<td></td>
<td>0.026 ± 0.003</td>
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<tr>
<td>Ni</td>
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<td>0.433 ± 0.061</td>
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<td>0.314 ± 0.030</td>
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<tr>
<td>Cu</td>
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<td>0.517 ± 0.062</td>
<td></td>
<td>0.592 ± 0.055</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>n.m.</td>
<td>1.28 ± 0.19</td>
<td>1.24 ± 0.23</td>
<td></td>
<td>0.381 ± 0.057</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.040 ± 0.007</td>
<td>0.031 ± 0.009</td>
<td>0.030 ± 0.005</td>
<td></td>
<td>0.026 ± 0.003</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.030</td>
<td>&lt;0.030</td>
<td>&lt;0.012</td>
<td></td>
<td>0.009 ± 0.0036</td>
<td></td>
</tr>
</tbody>
</table>

m.n.: not measured; n.c.: not certified.

### Table 3

Figures of merit of the ICP-MS offline, online and batch procedures.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Sensitivity (cps L μg⁻¹)</th>
<th>R²a</th>
<th>LODb (μg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ICP-MS Offline</td>
<td>ICP-MS Online</td>
<td>ICP-MS Batch</td>
</tr>
<tr>
<td>51V</td>
<td>2479</td>
<td>4881</td>
<td>0.9995</td>
</tr>
<tr>
<td>55Mn</td>
<td>3181</td>
<td>4527</td>
<td>283,602</td>
</tr>
<tr>
<td>54Co</td>
<td>2804</td>
<td>3934</td>
<td>0.9994</td>
</tr>
<tr>
<td>58Ni</td>
<td>1614</td>
<td>2143</td>
<td>0.9990</td>
</tr>
<tr>
<td>60Ni</td>
<td>653</td>
<td>884</td>
<td>45,110</td>
</tr>
<tr>
<td>62Ni</td>
<td>93</td>
<td>138</td>
<td>0.9656</td>
</tr>
<tr>
<td>63Cu</td>
<td>1570</td>
<td>1047</td>
<td>0.9996</td>
</tr>
<tr>
<td>65Cu</td>
<td>777</td>
<td>511</td>
<td>0.9982</td>
</tr>
<tr>
<td>66Zn</td>
<td>779</td>
<td>733</td>
<td>0.9926</td>
</tr>
<tr>
<td>68Zn</td>
<td>488</td>
<td>363</td>
<td>29,906</td>
</tr>
<tr>
<td>69Zn</td>
<td>850</td>
<td>1069</td>
<td>37,887</td>
</tr>
<tr>
<td>76Sr</td>
<td>488</td>
<td>363</td>
<td>29,906</td>
</tr>
<tr>
<td>86Sr</td>
<td>850</td>
<td>1069</td>
<td>37,887</td>
</tr>
</tbody>
</table>

a: Calculated as the correlation coefficient.

b: Calculated as the concentration equivalent to 3σ—the standard deviation of the blank (n = 10).
The Fl system proposed in this paper demonstrated a capacity for the analysis of 25 readings per hour (~2.4 min per reading), which puts it at an advantage in comparison to other similar systems, saving time and argon consumption by the ICP-MS.

3.4. Batch procedure

The studied samples presented a pH of approximately 8.1, similar to the pH used in the offline procedure with the Toyopearl® AF-Chelate 650 M column. The metal recoveries for this procedure are shown in Table 5. Good recoveries were observed in all cases, comparable or better than those obtained with the offline column procedure.

The calibration data and limits of detection are shown in Table 3. The LODs obtained demonstrated that, as the previously reported methods, the batch procedure is suitable for the determination of metals in seawater, highlighting the LOD for Pb, which was three times lower than in the column procedures.

The certified seawater sample CASS-4 was used to validate the present methodology. The pH was adjusted to 8.1 with ammonium hydroxide. In Table 4, the results showed good agreement between the measured and certified values for Co, Ni, Cu, and Cd. However for Mn, Zn and Pb unsatisfactory results were obtained. In this case, despite property conducted blanks and careful correction to compensate the reagent contamination, disagreement with certified values still occurs. For lead, the concentration to be determined (0.0098 μg L⁻¹) was, in any case, below the limit of detection.

3.5. Application of procedures

The procedures described in this paper were used for the determination of trace metals in seawater during the performance of several environmental studies of the Brazilian shore. In Table 4 are shown the range of concentrations of metals in seawater samples collected around the two oil platforms (Pampo and Pargo) at the Bacia de Campos oil field (located 60 km from the coast of the state of Rio de Janeiro). In the referred study, for each site, six samples were collected at three different depths (superficial (5 m), middle (45 m) and bottom waters (95 m)), giving a total of 18 samples for each platform studied. In order to evaluate the suitability of the methods for use with real samples, the LODs of the proposed procedures are also shown in Table 6. As shown in Table 6 for V, Co, Ni, Cu, Zn and Cd the limits of determination reached in this work for all three procedures were suitable for this study at the Brazilian shore. On the other hand the concentration of Mn was below the limit of detection of 0.014 μg L⁻¹ for seven samples of Pampo platform. And for lead, in only three samples of each platform was detected concentration above the limit of detection of 0.030 μg L⁻¹, showing that for the low concentrations of Pb in seawater the proposed methods should be improved.

4. Conclusions

The proposed offline column procedure was adequate for the determination of the natural levels of Co, Ni, Cu and Cd in seawater and is especially suitable for field sampling on board, since buffering is not necessary and the samples are ready to be analyzed by ICP-MS. V could also be determined at pH = 5.5. The Fl system also showed adequate performance, and the presence of the cleaning column was essential in obtaining lower blanks and good LODs. A sample throughput of 25 h⁻¹ was possible, and the column showed a life time long enough for the analysis of more than 250 seawater samples, without any performance change. The batch procedure could also be used for seawater analysis, with adequate LODs. Large batches were easily managed. Good agreement between found and certified values was observed in the analysis of seawater certified reference materials for the studied metals. Recoveries always close to 100% at the low μg L⁻¹ level were observed in all cases. External calibration with aqueous calibration solutions could be employed in all cases, once they were submitted to the same analytical procedure. These procedures were used with success for the determination of trace metals in seawater, interstitial water and produced water (the largest wastewater stream in the offshore oil, gas exploration and production process) during the performance of several environmental studies of the Brazilian shore.

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References


