Direct and simultaneous determination of molybdenum and vanadium in sea-water using a multielement electrothermal atomic absorption spectrometer

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Direct and simultaneous determinations of Mo and V in sea-water using a multi-element electrothermal atomic absorption spectrometer (Perkin-Elmer SIIAM 6000) are described. Three kinds of chemical modifier [Mg(NO$_2$)$_2$, Pd(NO$_2$)$_2$, and a mixture of both] were tested. A simple calibration curve method could be used to determine Mo in sea-water using Pd or a mixture of Pd and Mg as the chemical modifier. A standard additions method was used to determine V and to determine Mo and V simultaneously in sea-water. The detection limits were 0.35–0.60 µg L$^{-1}$ for Mo. The detection limit for V in this work (0.32–0.51 µg L$^{-1}$) is much lower than those reported in the literature (18–50 µg L$^{-1}$), such that direct determination of V in unpolluted sea-water (<2 µg L$^{-1}$) by ETAAS is possible. The RSDs for the simultaneous determination of Mo and V in nearshore or open ocean sea-water are <11% using a mixture of Pd and Mg as the chemical modifier. The accuracy of the method for Mo determination was confirmed by the analysis of two kinds of certified reference sea-water. There is no certified value of V for determination of Mo and V in nearshore or open ocean sea-water are

The applicability of ICP-based instruments has been limited by the difficulty in dealing with samples with high salt concentrations and the need for relatively large sample volumes. Consequently, separation or preconcentration of the analytes from the matrix prior to the measurement is necessary. Although ICP-MS has emerged as a method with a power of detection which is at least comparable to that of ETAAS, the MS detector is complex and expensive, which has limited the widespread use of ICP-MS in routine work. In recent years, many kinds of multi-element ETAAS instrument have been developed and become commercially available, hence the applicability of ETAAS in multi-element determinations is of great interest.

Several papers have appeared concerned with the direct determination of Mo and V in sea-water by ETAAS. The direct determination of Mo in sea-water by ETAAS has been reviewed by Huang et al. Several papers have appeared concerned with the direct determination of Mo and V in sea-water by ETAAS. The direct determination of Mo in sea-water by ETAAS has been reviewed by Huang et al.

Keywords: Multi-element analysis; electrothermal atomic absorption spectrometry; sea-water analysis; molybdenum; vanadium

Various techniques have been applied to the determination of trace heavy metals in sea-water. The direct determination of trace metals in sea-water is of interest because it implies simple and rapid analysis. However, the large salt content of sea-water and the minute concentrations of trace metals lead to considerable difficulties in the analysis. To resolve this problem, both careful selection of the temperature program and modification of the sample matrix to decrease interferences are extremely important. Chemical modifiers of many kinds, e.g., NH$_4$NO$_3$,$^{13,14}$ Mg(NO$_2$)$_2$,$^{3,4}$ NaOH,$^{9,10}$ EDTA,$^{5,6}$ H$_2$PO$_4$ and (NH$_4$)$_2$HPO$_4$,$^{9,10}$ H$_2$SO$_4$,$^{10}$ oxalic acid,$^{10}$ ascorbic acid,$^{10,18}$ tartaric acid,$^{10}$ citric acid,$^{10}$ a mixture of ammonium oxalate and tetraminepalladium chloride,$^{23}$ Pd(NO$_2$)$_2$,$^{3,4}$ NH$_4$VO$_3$,$^{43}$ and a mixture of Pd(NO$_2$)$_2$ and Mg(NO$_2$)$_2$,$^{3,4}$ have been used in the single-element ETAAS direct determination of trace metals in sea-water. Schlemmer and Wenzel$^{24}$ concluded that a mixture of Pd and Mg was a fairly universal and applicable chemical modifier in ETAAS, and therefore the mixture of Pd and Mg is generally recommended for multi-element analysis. An advantage of Pd-containing chemical modifiers is that high-purity reagents are available.

ETAAS is a well established technique, but it is generally used for single-element determinations and therefore it may be time consuming if several elements need to be determined in a sample. Many different multi-element instruments have been used for the simultaneous multi-element determination of trace metals in sea-water, such as inductively coupled plasma atomic emission spectrometry (ICP-AES)$^{25}$ and mass spectrometry (ICP-MS)$^{27,28}$ X-ray fluorescence spectrometry,$^{29}$ cathodic stripping voltammetry (CSV)$^{30}$ and multi-element electrothermal atomic absorption spectrometry (ETAAS)$^{31,32}$ in combination with THGA. Each instrument has its particular advantages and disadvantages.

The most important commercially available multi-element instruments for trace elemental determination are ICP-based. The applicability of ICP-based instruments has been limited by the difficulty in dealing with samples with high salt concentrations and the need for relatively large sample volumes. Consequently, separation or preconcentration of the analytes from the matrix prior to the measurement is necessary. Although ICP-MS has emerged as a method with a power of detection which is at least comparable to that of ETAAS, the MS detector is complex and expensive, which has limited the widespread use of ICP-MS in routine work. In recent years, many kinds of multi-element ETAAS instrument have been developed and become commercially available, hence the applicability of ETAAS in multi-element determinations is of great interest.

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simultaneously. Three kinds of chemical modifier (Mg, Pd and a mixture of Pd and Mg) were tested. For the direct determination of Mo in sea-water, a simple calibration curve method can be used when using Pd or a mixture of Pd and Mg as the chemical modifier. We also found that the direct determination of V in unpolluted sea-water or the simultaneous determination of Mo and V in unpolluted sea-water is possible, but the method of standard additions should be used. The detection limits were 0.35–0.60 μg l⁻¹ for Mo, which are comparable to those reported previously.⁴⁻⁶ The detection limit for V (0.32–0.51 μg l⁻¹) in this work is much lower than those reported in the literature.⁴⁻⁶

EXPERIMENTAL

Reagents and samples

High-purity water (18 MD cm) was prepared using Milli-Q, a de-ionized water purification system (Millipore, Bedford, MA, USA). Nitric acid (Suprapur grade, Merck, Darmstadt, Germany) was purified by sub-boiling distillation. Commercial molybdenum and vanadium standards (1000 mg l⁻¹) (Merck) were used. Pd(NO₃)₂ solution was prepared by dissolving 100 mg of palladium metal powder (Merck) in 1 ml of concentrated nitric acid and diluting to 100 ml with de-ionized water. If dissociation was incomplete, 10 μl of Suprapur grade concentrated hydrochloric acid were added to the cold nitric acid solution, which was then heated gently until the solution cleared. The solution was then heated to gentle boiling in order to volatilise the excess of chloride.⁴² Mg(NO₃)₂ solution (15% v/v HNO₃, 10,000 mg l⁻¹, AA reagent grade) was obtained from Kanto Chemical, Tokyo, Japan. The Mg(NO₃)₂ solution (10,000 mg l⁻¹) was diluted to the desired concentration with 15% v/v HNO₃. Sea-water reference materials, CASS-3 (near-shore sea-water) and NASS-4 (open ocean sea-water), were obtained from the Marine Analytical Chemistry Standards Program of the National Research Council of Canada (Ottawa, Ontario, Canada).

Sea-water blank preparation

Sea-water blanks were prepared by adjusting the pH of the sea-water samples (CASS-3 and NASS-4) to 5.0 and then passing them through a column (Chelex-100, sodium form, 100–200 mesh) (Bio-Rad Laboratories, Richmond, CA, USA) at a flow rate of 0.2–0.3 ml min⁻¹. The procedure for purifying the (Chelex-100) resin was similar to that used by Sturgeon et al.³⁸ The resin (4 g) was placed in a PTFE beaker with nitric acid (2 ml, 30 ml) overnight, then transferred to a column. The resin was washed with HNO₃ (2 ml, 30 ml) and de-ionized water (50 ml). Aqueous ammonia (2 ml, 20 ml) was added to convert the resin from the hydrogen to the ammonium form. Finally, the resin was washed with de-ionized water (40 ml).

Contamination control

All reagents were prepared in a class-100 laminar-flow clean hood. All sample containers, autosampler cups, etc., were acid washed with 50% v/v nitric acid for 24 h and then rinsed five times with de-ionized water before use.

Instruments and analysis

A multi-element ETAAS system (SIMAA 6000, Perkin-Elmer, Norwalk, CT, USA) with transverse-heated graphite atomizer (THGA), longitudinal Zeeman-effect background correction and autosampler (AS-72) was used. A pyrolytic graphite-coated THGA graphite tube with integrated platforms was used. The flow rate of the inert gas (argon) was 230 ml min⁻¹. This flow was stopped during atomization. The procedure was controlled by AA Winlab software version 2.3 (Perkin-Elmer). The lamps used were hollow-cathode lamps (HCL) from Perkin-Elmer and the wavelengths used and reading times were 313.3 nm, 7 s and 318.4 nm, 5 s for Mo and V, respectively. The peak area of the atomic absorption signal was used for the determination. Unless specified otherwise, each experimental value is the arithmetic average of three determinations.

RESULTS AND DISCUSSION

Optimum conditions using Mg(NO₃)₂, Pd(NO₃)₂ or mixture of Pd and Mg as chemical modifier

The reference sea-water NASS-4 (20 μl) with added Mo (20 μg l⁻¹) and V (2 μg l⁻¹) was used to establish the optimum temperature program.

Use of Mg(NO₃)₂ as the chemical modifier

The atomic absorption signals obtained using Mg (10 μg) as the chemical modifier are shown in Fig. 1. The atomic absorption signals remained approximately constant as the ashing temperature varied from 1000–1300 and from 1000–1400°C for Mo and V, respectively. The atomic absorption signals were maximum at an atomization temperature of 2400°C for both Mo and V. An ashing temperature of 1300°C and an atomization temperature of 2400°C were chosen as the optimum. The effect of Mg dosage was studied. For Mo, the maximum atomic absorption signal and best precision were achieved with addition of 10 μg of Mg. For V, the atomic absorption signal remained approximately constant with addition of Mg (10–30 μg); 10 μg of Mg was used in subsequent studies. The atomic absorption and background absorption profiles of a sea-water sample (NASS-4) using Mg as the chemical modifier are shown in Fig. 2(a).

Use of Pd(NO₃)₂ as the chemical modifier

The atomic absorption signals obtained using Pd (5 μg) as the chemical modifier are shown in Fig. 3. For V, the atomic absorption signals remained approximately constant as the ashing temperature varied from 1200 to 1500°C; for Mo, the atomic absorption signal with the greatest precision was achieved at an ashing temperature of 1400°C. The background absorption signals decreased with increasing ashing temperature. An ashing temperature of 1400°C was used. The atomic absorption signals were maximum at an atomization temperature of 2400°C for Mo and V. The effect of the dosage of the chemical modifier (Pd) was studied. The atomic absorption signals remained approximately constant on addition of Pd
Fig. 2. (A) Atomic absorption and (B) background absorption signals of Mo and V in sea-water samples. Analytical conditions are given in Table 1. NASS-4 (20 μl, unspiked), modification with (a) Mg, (b) Pd and (c) Pd + Mg.

Fig. 3. Effects of ashing and atomization temperatures on atomic and background absorption signals. Sample and symbols as in Fig. 1; modification with Pd (5 μg). Atomization temperature, 2400 °C for ashing curve; ashing temperature, 1400 °C for atomization curve. Use of a mixture of Pd(NO$_3$)$_2$, and Mg(NO$_3$)$_2$ as the chemical modifier.

(1–5 μg for Mo and 1–10 μg for V) and the background absorption signal increased with increasing dosage of Pd. For multi-element analysis, 3 μg of Pd were used as this addition yielded results with the greatest precision and lowest background. The atomic and background absorption profiles of the sea-water sample (NASS-2) with Pd as the chemical modifier are shown in Fig. 2(b).

Fig. 4. Effects of ashing and atomization temperatures on atomic and background absorption signals. Sample and symbols as in Fig. 1; modification with a mixture of Pd (5 μg) and Mg (3 μg). Atomization temperature, 2400 °C for ashing curve; ashing temperature, 1400 °C for atomization curve.

3 μg amount of Pd was used in subsequent work because it offered results with the greatest precision and lowest background. When the dosage of Pd was kept at 3 μg, the optimum dosages of Mg were 3–5 and 3–15 μg for Mo and V, respectively. A mixture of Pd (3 μg) and Mg (3 μg) was used as this yielded results with the greatest precision and lowest background. The atomic and background absorption profiles of a sea-water sample (NASS-4) with a mixture of Pd and Mg as the chemical modifier are shown in Fig. 2(c). Background correction is most accurate when the background absorbance is small relative to the atomic absorption. Fig. 2 shows that the background absorption signal is approximately the same magnitude as the atomic absorption signal for Mo and is considerably larger for V. This may affect the accuracy and precision of the determination of V, although the background absorbance at a level <0.2 is not too large to be corrected by the Zeeman background corrector.

Sea-water analysis
The optimum temperature programs are summarized in Table 1. The slopes of the standard addition curves for the sea-water samples are compared with those based on simple aqueous solution, with various chemical modifiers (shown in Table 2). The differences in slope between the two curves are ~10% for the determination of Mo using Pd or a mixture of Pd and Mg as the chemical modifier. The differences in slope between the two curves are >20% for V determination, which indicates that significant matrix effects exist. Mo and V in the certified reference sea-water samples (CASS-3 and NASS-4) were determined and the results are given in Table 3. For Mo, when Pd or a mixture of Pd and Mg was used as the chemical modifier, the concentrations obtained were within the ranges of the certified values when either the method of standard additions or a calibration curve was used. When Mg was used as chemical modifier, the method of standard additions should be used. For the direct determination of V or the direct and simultaneous determination of Mo and V, the method of standard additions was used to compensate for matrix effects. There are no certified values of V provided for CASS-4 or NASS-4, which makes it impossible to evaluate the accuracy as chemical modifier, the method of standard additions should be used. For the direct determination of Mo and V, a simple calibration curve can be used when Pd or a mixture of Pd and Mg was used as the chemical modifier.

Table 1. Optimum temperature program for simultaneous determination of Mo and V

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature/°C</th>
<th>Ramp/s</th>
<th>Hold/s</th>
<th>Gas flow rate/ ml min⁻¹</th>
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</thead>
<tbody>
<tr>
<td>Drying</td>
<td>110</td>
<td>1</td>
<td>30</td>
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<tr>
<td>Ashing</td>
<td>Various*</td>
<td>15</td>
<td>30</td>
<td>250</td>
</tr>
<tr>
<td>Cooling</td>
<td>20</td>
<td>1</td>
<td>10</td>
<td>250</td>
</tr>
<tr>
<td>Atomization</td>
<td>2400</td>
<td>0</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>Clean-out</td>
<td>2450</td>
<td>1</td>
<td>5</td>
<td>250</td>
</tr>
<tr>
<td>2450</td>
<td>1</td>
<td>5</td>
<td>250</td>
<td></td>
</tr>
</tbody>
</table>

*Temperature: Mg, 1300°C; Pd, 1400°C; and mixture of Pd and Mg, 1450°C.

Table 2. Results of simultaneous determination of Mo and V in reference sea-water

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyte</th>
<th>Modifier</th>
<th>SA*</th>
<th>CC</th>
<th>Mo found/µg ¹⁻¹</th>
<th>V found/µg ¹⁻¹</th>
<th>Mo certified/µg ¹⁻¹</th>
<th>V certified/µg ¹⁻¹</th>
<th>V reference value/µg ¹⁻¹</th>
</tr>
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<tbody>
<tr>
<td>CASS-3</td>
<td>Mo</td>
<td>Mg</td>
<td>0.098</td>
<td>0.048</td>
<td>0.9996</td>
<td>0.9998</td>
<td>0.048</td>
<td>0.9996</td>
<td>0.9998</td>
</tr>
<tr>
<td>V</td>
<td>0.0014</td>
<td>0.0012</td>
<td>0.9797</td>
<td>0.9988</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.0044</td>
<td>0.0041</td>
<td>0.9900</td>
<td>0.9994</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>V</td>
<td>0.0014</td>
<td>0.0011</td>
<td>0.9999</td>
<td>0.9986</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.0038</td>
<td>0.0035</td>
<td>0.9900</td>
<td>0.9983</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NASS-4</td>
<td>Mo</td>
<td>Mg</td>
<td>0.0477</td>
<td>0.0040</td>
<td>0.9977</td>
<td>0.9988</td>
<td>0.040</td>
<td>0.9977</td>
<td>0.9988</td>
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<tr>
<td>V</td>
<td>0.0018</td>
<td>0.0012</td>
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<td>0.9988</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.0037</td>
<td>0.0041</td>
<td>0.9963</td>
<td>0.9994</td>
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</tr>
<tr>
<td>NASS-4</td>
<td>Mo</td>
<td>Mg</td>
<td>0.0023</td>
<td>0.0011</td>
<td>0.9999</td>
<td>0.9986</td>
<td>0.0011</td>
<td>0.9999</td>
<td>0.9986</td>
</tr>
<tr>
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<td>0.0038</td>
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<td>V</td>
<td>0.0018</td>
<td>0.0011</td>
<td>0.9998</td>
<td>0.9986</td>
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</table>

Table 4. Detection limits (DL) and relative standard deviations (RSDs) obtained for the simultaneous determination of Mo and V in reference sea-water

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modifier</th>
<th>DL,µg ¹⁻¹</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CASS-3</td>
<td>Mg</td>
<td>0.042</td>
<td>4.4</td>
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<tr>
<td>V</td>
<td>0.042</td>
<td>8.5</td>
<td></td>
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<tr>
<td>CASS-3</td>
<td>Pd</td>
<td>0.035</td>
<td>4.6</td>
</tr>
<tr>
<td>V</td>
<td>0.035</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>CASS-3</td>
<td>Pd + Mg</td>
<td>0.049</td>
<td>3.7</td>
</tr>
<tr>
<td>V</td>
<td>0.035</td>
<td>9.9</td>
<td></td>
</tr>
<tr>
<td>NASS-4</td>
<td>Mg</td>
<td>0.031</td>
<td>7.8</td>
</tr>
<tr>
<td>V</td>
<td>0.031</td>
<td>14.0</td>
<td></td>
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<tr>
<td>NASS-4</td>
<td>Pd</td>
<td>0.060</td>
<td>0.6</td>
</tr>
<tr>
<td>V</td>
<td>0.055</td>
<td>0.5</td>
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<tr>
<td>NASS-4</td>
<td>Pd + Mg</td>
<td>0.049</td>
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</tr>
<tr>
<td>V</td>
<td>0.060</td>
<td>0.36</td>
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*Detection limits calculated as three times the standard deviation of seven replicate measurements of a sea-water blank.
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REFERENCES