Speciation of Vanadium(IV) and Vanadium(V) in Water Samples: Evaluation of Oxidation of V(IV) to V(V) during Sample Handling and Analysis

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For the determination of V(IV), an aliquot of the filtered sample was subjected to the selective separation of V(IV), removed into benzene by extraction with 1-butanol, immediately after an adjustment of the pH to 4.0 with nitric acid. After phase separation, V(IV) was extracted with 8-mercaptoquinoline into chloroform at pH 5.5, and subsequently back-extracted into a nitric acid solution. However, in real sample analysis, a small portion of V(IV) seemed to be oxidized and removed from an aqueous phase during the extraction step with 1-butanol. Moreover, the oxidation of V(IV) was related to co-existence of Fe(III). Therefore, the loss of V(IV) and remaining of V(V) should be evaluated to correct observed values of V(IV). Based on a few assumptions, they can be corrected to some extent by solving two simultaneous equations in two unknowns. The proposed correction method was applied to river water samples, and found that V(V) is the predominant species in samples of well-aerated and Fe(III)-rich river water.

(Received on August 9, 2001; Accepted on November 3, 2001)

Vanadium can exist in oxidation states from II to V in aqueous solutions. However, vanadium usually exists in the tetravalent and pentavalent states in the aquatic environment. Vanadium in trace amounts is an essential element for normal cell growth at μg/L levels, but can be toxic at higher concentrations, mg/L levels. Vanadium plays an important role in biochemistry and physiology, including normalizing glucose levels and stimulation of baxosome transport. It is an insulin mimetic agent, and it affects the cardiac muscle in mammals. The toxicity is dependent on its oxidation state, and V(V) is more toxic than V(IV). Thus, there has been an increasing interest in the chemical speciation of vanadium at μg/L levels during the last decade.

We have already reported on the determination of vanadium species in river water samples. Although several studies have been devoted to V speciation in natural water, little work in the stability of V(IV) in solutions sampled for the analysis, can be found in literature. V(IV) is generally accepted as being a stable species in acidic solution below pH 2, but is oxidized to the pentavalent form by atmospheric oxygen at higher pH. This complicates the determination of V(IV) in samples with pH>2, as stabilization of the V(IV) is necessary. Nakano et al. found that V(IV) was the predominant species in samples of natural water, whereas Hiraizama et al. found equivalent levels of V(IV) and V(V).

The proposed method is based on the solvent extraction of V(IV) with 1-butanol (BuOH) into benzene and V(V) with 8-mercaptoquinoline (thioxine) into chloroform. In this study, the loss of V(IV) by oxidation to V(V) during the removal step of V(IV) with BuOH, the oxidation efficiency, and the removal efficiency of V(V) with BuOH was evaluated to apply numerical corrections to the observed results. Moreover, we have investigated the losses of V(IV) during sample handling (preservation under natural pH or acidified).

Experimental

Apparatus

A Hitachi Model Z-5700 Polarized Zeeman graphite furnace atomic absorption spectrophotometer (GF-AAS) was used. A tube-type pyrolytic graphite coated cuvette was used. The absorbance signals were recorded at 318.4 nm, and the peak heights were taken as the analytical signals. The optimum conditions for vanadium measurements were as follows: Injection volume, 20 μL; Drying, 80-140 °C for 40 s; Ashing, 1000 °C for 30 s; Atomizing, 2800 °C for 5 s.

Reagents

A vanadium(IV) stock solution (1mg/ml) was prepared by dissolving appropriately weighed vanadyl sulfate n-hydrate (Kanto Chemical) into 1 v/v % H2SO4, and standardized by EDTA with Cu(II)-(2-pyridylazo)-2-naphthol as indicator. A vanadium(V) stock solution (1mg/ml, 0.1M HNO3) was obtained from Kanto Chemical. A nickel stock solution (1mg/ml, 0.1M HNO3) was obtained from Kanto Chemical and used as a matrix modifier. A 0.2 w/v % thioxine solution was prepared by dissolving the requisite amount of thioxine hydrochloride (Daijindo) into 6M HCl. All other chemicals were of analytical reagent grade. Distilled, deionized water was further purified using a Millipore Milli-Q system.

General Procedure

The concentration of V species were determined by GF-AAS after solvent extraction with BuOH and thioxine in a manner similar to that described in the previous paper. As shown in Fig.1, using a 25 ml aliquot of the sample solution, V(IV) was first removed by BuOH extraction method. Then, V(IV) was concentrated 50-fold by thioxine extraction (and back-
V(IV)

Sample, 25 mL

pH 4 (Nitric Acid)

BuOH, 4 mL

Benzene, 15 mL

Shaking, 5 min

Centrifuging, 5 min

Aqueous phase

Organic phase

Boiling, 120 min

Cooling

Sample, 25 mL

5% Ascorbic acid, 0.5 mL
0.2% Thioisoxine, 0.2 mL
2M Ammonium acetate, 0.25 mL

pH 5.5 (Aqueous ammonia)

Chloroform, 5 mL

Shaking, 5 min

Centrifuging, 5 min

Organic phase, 4 mL

Aqueous phase

Nitric acid, 100 µg/L, 200 µg/L

Shaking, 5 min

Water, 220 µg/L, 440 µg/L

Shaking, 5 min

Centrifuging, 5 min

GF-AAS measurement

Fig. 1. Flow sheet of procedure for determination of V(IV) and total V [V(IV)+ V(V)].

Results and Discussion

Stability of V(IV)

Figure 2 shows the recovery of V(IV) in the presence of V(V) by the proposed method including BuOH extraction step and thioisoxine extraction step. When pure water or artificial river water was used in the absence of Fe(III), the recovery of V(IV) was 104 ± 4.4 %. However, using artificial river water containing 20 µg/L of Fe(III), the recovery of V(IV) was decreased to 76.4 ± 4.7 %. This fact can be explained by the oxidation of V(IV) with Fe(III). The resulting Fe(II) is oxidized with dissolved oxygen, and the resulting V(III) is removed into benzene with BuOH. It is insufficient to consider only Fe(III), however, it seems that the dissolved oxygen contributes a little to the oxidation of V(IV) than Fe(III) does during BuOH extraction step. On the other hand, the removal efficiency of V(V) with BuOH was not affected in the presence or absence of Fe(III), even if the concentration of V(V) was changed. In these conditions, the recovery of total V did not change very much.

Composition of artificial river water containing minor elements that can be extracted with thioisoxine is listed in Table 1.

Table 1 Composition of artificial river water

<table>
<thead>
<tr>
<th>Major components (mg/L)</th>
<th>Minor elements (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>5.38</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.11</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.16</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.78</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>9.97</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.03</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>26.1</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>3.89</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>11.4</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.02</td>
</tr>
</tbody>
</table>

V(V) was removed by extraction with 1-butanol method, then V(IV) was extracted and back-extracted with thioisoxine method. Measured absorbance was standardized by comparison with the absorbance obtained for V(IV) spiked into blank solution previously stripped of V(IV) by 1-butanol method.

Composition of major components was based on analytical values of Kinu river water, Usunomiya.

Evaluation of the loss of V(IV) during BuOH extraction step

If V(IV) was oxidized and removed from the initial solution, the observed value of V(IV) concentration was underestimated by the loss of V(IV), while it was overestimated by the remaining V(V). Based on a few assumptions, the observed values can be corrected to some extent by solving two simultaneous equations in two unknowns, i.e.:

\[
\begin{align*}
C_{\text{init}}^{\text{IV}} &= \frac{A(0)}{m} - \frac{tkR(1-\alpha)}{m} \\
C_{\text{int}}^{\text{IV}} &= \frac{A(0)}{Tkr} - C_{\text{init}}^{\text{IV}}
\end{align*}
\]

(See the Appendix section. For the definitions of the symbols used in these and subsequent equations, see the Nomenclature section.) The assumptions are that during BuOH extraction step a part of V(IV) was oxidized with Fe(III) or dissolved oxygen.
while \( V(V) \) was not reduced. The expected behavior of \( V(IV) \) and \( V(V) \) is represented as shown in Fig. 3.

![Diagram showing the expected behavior of \( V(IV) \) and \( V(V) \) during 1-butanol extraction step.]

To evaluate the values of \( \alpha, R \) and \( k \), the following additional experiments were carried out:

Exp.1: Using unspiked sample water, \( V(IV) \) is determined.
Measured absorbance = \( A(0) = A_1 \).

Exp.2: Using spiked (2 \( \mu \)g-\( V(V) \)/L) sample water, \( V(IV) \) is determined.
Measured absorbance = \( A_2 \).

Exp.3: Using unspiked sample water, total \( V \) is determined.
Measured absorbance = \( A'(0) = A_3 \).

Exp.4: Using spiked (2 \( \mu \)g-\( V(V) \)/L) sample water, total \( V \) is determined.
Measured absorbance = \( A_4 \).

Exp.5: To 100 \( \mu \)L aliquot of back-extracted solution of Exp.3, 20 \( \mu \)L of 300 ng-\( V(IV) \)/mL is added, then absorbance is measured. Measured absorbance = \( A_5 \).

To calculate the following equations, the values of \( \alpha, R \) and \( k \) are obtained:

\[
\alpha = \frac{A_2 - A_1}{2(A_4 - A_3)} \quad (3)
\]

\[
R = \frac{A_5 - 5A_4}{6} \quad (4)
\]

\[
k = \frac{A_5 - 5A_4}{6} \quad (5)
\]

Moreover, the concentrations of \( V(IV) \) and total \( V \) in sample water were determined using the method of standard addition spiked with \( V(IV) \) according to the general procedure. The concentration factor of \( V(IV) \) was 50-fold (\( t = 50 \)), and that of total \( V \) was 25-fold (\( t = 25 \)). The observed value of total \( V \) concentration is the initial concentration of total \( V \), \( C_{I\text{init}} + C_{I\text{init}} \). The value of \( m \) is obtained by the slope of linear standard addition curve for \( V(IV) \), and the value of \( \beta \) is also calculated.

The initial concentrations of \( V(IV) \) and \( V(V) \) are obtained by solving Eq.(1) and Eq.(2), as follows:

\[
C_{I\text{init}} = \frac{A(0)\cdot t\cdot k\cdot R - A'(0)\cdot t\cdot k\cdot R(1 - \alpha)}{t\cdot k\cdot R\cdot m - (t\cdot k\cdot R\cdot (1 - \alpha))} \quad (6)
\]

\[
C_{I\text{init}} = \frac{A'(0)}{t\cdot k\cdot R} \quad (7)
\]

\[
\beta = \frac{k\cdot R}{t\cdot k\cdot R} \quad (8)
\]

**Analysis of river water**

To estimate the proposed correction method, spike tests were carried out on separate days using artificial river water in the presence or absence of \( Fe(III) \). The analytical results are shown in Table 2. The corrected values somewhat closer agreed with spiked values than the observed values by the ordinary standard addition method. Though these values varied slightly, it is due to a certain difference in elapsed time from sample solution was prepared until BuOH extraction step was carried out. Therefore, these experiments must be done carefully in the time. In particular, the results of Exp.1-5 may lead to large errors in calculations, then it is necessary to repeat the Exp.1-5 at least three times. In the presence of \( Fe(III) \), the values of \( \alpha \) and \( \beta \) Table 2 Analytical results of spike tests using artificial river water in the presence or absence of \( Fe(III) \) by the proposed correction method

<table>
<thead>
<tr>
<th>Added, ( \mu )g/L</th>
<th>Found, ( \mu )g/L</th>
<th>Total V</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V(IV) )</td>
<td>( V(IV) )</td>
<td>( V(V) )</td>
</tr>
<tr>
<td>0.4</td>
<td>1.6*</td>
<td>0.44(0.58)</td>
</tr>
<tr>
<td>0.4</td>
<td>1.6*</td>
<td>0.44(0.59)</td>
</tr>
<tr>
<td>0.4</td>
<td>1.6**</td>
<td>0.39(0.45)</td>
</tr>
<tr>
<td>0.3</td>
<td>1.7*</td>
<td>0.29(0.37)</td>
</tr>
<tr>
<td>0.3</td>
<td>1.7*</td>
<td>0.36(0.54)</td>
</tr>
<tr>
<td>0.3</td>
<td>1.7**</td>
<td>0.36(0.54)</td>
</tr>
</tbody>
</table>

* In the presence of 20 \( \mu \)g/L of \( Fe(III) \).
** In the absence of \( Fe(III) \).
† Values given in parentheses are the observed values by the ordinary standard addition method, and \( V(V) \) was calculated by total \( V \) and \( V(IV) \).

Table 3 Analytical results of \( V(IV) \) and \( V(V) \) in Kino river water samples by the proposed correction method

<table>
<thead>
<tr>
<th>Sampling date</th>
<th>( V(IV) )</th>
<th>( V(V) )</th>
<th>Total V</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>0.28</td>
<td>0.08 (0.40)*</td>
<td>2.14 (1.82)*</td>
</tr>
<tr>
<td>1-2</td>
<td></td>
<td>(0.15)</td>
<td>2.20 (2.05)</td>
</tr>
<tr>
<td>No.2</td>
<td>0.13</td>
<td>0.02 (0.26)</td>
<td>2.48 (2.24)</td>
</tr>
<tr>
<td>No.3</td>
<td>0.14</td>
<td></td>
<td>1.34 (1.15)</td>
</tr>
<tr>
<td>No.4</td>
<td>0.09</td>
<td></td>
<td>1.61 (1.37)</td>
</tr>
<tr>
<td>No.5</td>
<td>0.07</td>
<td>(0.08)</td>
<td>1.65 (1.20)</td>
</tr>
<tr>
<td>No.6</td>
<td>0.07</td>
<td>0.10 (0.53)</td>
<td>1.94 (1.51)</td>
</tr>
<tr>
<td>Filtered</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Water samples were filtered through a 0.45µm membrane filter immediately after sampling, and subsequently analyzed except No.1-2.

* Values given in parentheses are the observed values by the ordinary standard addition method, and \( V(V) \) was calculated by total \( V \) and \( V(IV) \).
† Filtered sample was preserved under natural pH and analyzed on the next day.

were in the range 0.93 - 0.97, 0.09 - 0.62, respectively. In the absence of \( Fe(III) \), the values of \( \alpha \) and \( \beta \) were in the range 0.94 - 0.95, 0.23, respectively.

The proposed correction method and ordinary standard addition method were applied to the speciation of \( V(IV) \) and \( V(V) \) in real water samples. As shown in Table 3, it was found that \( V(IV) \) is the predominant species in samples of well-aerated and \( Fe(III) \)-rich river water. These samples were supersaturated with dissolved oxygen. The values of \( \alpha \) and \( \beta \) were in the range 0.79 - 0.90, 0.05 - 0.47, respectively.

**Preservation of water sample**

\( V(IV) \) is liable to oxidize with co-existence of \( Fe(III) \) or dissolved oxygen. As the potential of the system \( V(V)/V(IV) \) depends on the hydrogen ion concentration \([^\text{H}^+]\),

\[
\text{VO}_2^+ + 2\text{H}^+ + e^- \leftrightarrow \text{VO}^{2+} + \text{H}_2\text{O} \quad (9)
\]

the formal potential \( E'_{\text{V(III)}} \) of the system \( V(V)/V(IV) \) decreases with increasing pH:

\[
E'_{\text{V(III)}} = E'_{\text{V(III)}} - 0.12 \text{ p}H \quad (E'_{\text{V}} = 1.00 \text{ V vs. NHE}) \quad (10)
\]

It is clear that \( V(IV) \) is the stable species in the strongly acidic medium, whereas \( V(V) \) is stable in the alkaline. However, the
redox potential of this system can be modified by the co-existence of Fe(III) or dissolved oxygen:

\[
\begin{align*}
\text{Fe}^{3+} + \text{VO}^{2+} + \text{H}_2\text{O} &\rightleftharpoons \text{Fe}^{2+} + \text{VO}_2^+ + 2\text{H}^+ \\
\text{O}_2 + 4\text{VO}_2^+ + 2\text{H}_2\text{O} &\rightleftharpoons 4\text{V}^{2+} + 4\text{H}^+ \\
\end{align*}
\]

(11) (12)

Take this phenomenon into account, 0.1M of several acids (nitric acid, sulfuric acid, hydrochloric acid, and perchloric acid) were added to water sample, and the stability of V(IV) was investigated. One µg/L of V(IV) was added to the V(IV)-poor river water sample, and left it for a fixed time. The storage time investigated was in most cases up to 5 days. These samples were preserved in dissolved oxygen measuring bottles, the same as incubation bottles, at room temperature. Analyzing these samples and also the sample preserved under natural pH, the loss of V(IV) was rapidly progressing as the time goes. The measured absorbance was decreased to 17–32%. However, the values of total V concentration did not change very much.

In the similar experiments using artificial river water, the loss of V(IV) was larger in the presence of Fe(III) than in the absence of Fe(III). These results suggest that the oxidation of V(IV) is accelerated with co-existence of Fe(III) and/or dissolved oxygen even in acidic solution. However, additive effects of various factors, such as Cr(VI) and complexing agents, are expected.

Cr(VI) is a fairly strong oxidizing agent in sulfuric acid, and a weaker oxidizing agent in hydrochloric acid, but no difficulty is encountered in the oxidation of V(IV). Water pollution with EDTA, a typical complexing agent, is becoming a problem in the developed countries.° The redox potential of a system involving metal ions can be modified by the complexation of metal ions with a suitable ligand. Therefore, these factors are the subjects for a future study.

Consequently, with regard to the speciation of vanadium, the addition of acids is not good for the preservation of water samples, similarly to the speciation of chromium.° The content of V(IV) tends to change according to the quality of sample water. We feel there is still room for further study.

Appendix

From the Lambert-Beer law, the following equation can be set up between the concentration of vanadium and measured absorbance, A (See Fig. 3):

\[
A = k(C^\text{IV}_\text{init} (1 - \beta) + C^\text{V}_\text{init} \beta (1 - \alpha) + C^\text{V}_\text{init} (1 - \alpha) \beta) t R
\]

(13)

When the determination of V(IV) was carried out using the method of standard addition spiked with V(IV), x µg/L, according to the general procedure, the following functional equation can be derived:

\[
A(x) = t' k R ([C^\text{IV}_\text{init} + x (1 - \beta) \gamma (1 - \alpha) + C^\text{V}_\text{init} (1 - \alpha) \gamma (1 - \alpha) \beta])
\]

(14)

In Eq.(14), replacing the slope of linear standard addition curve, tkR(1-α β), by m, yields the following functional equation:

\[
A(x) = A(x') + m x
\]

(15)

If A(x) is taken as zero, then the observed value of V(IV), \(\gamma x\), can be obtained from Eq.(15):

\[
\gamma x = m C^\text{V}_\text{init} + tk R (1 - \alpha) C^\text{V}_\text{init}
\]

(16)

As is evident from Eq.(16), in order to find out the value of \(C^\text{V}_\text{init}\), it is necessary to correct the term \(C^\text{V}_\text{init}\). When \(x = 0\), then the following equation can be obtained from Eq.(15):

\[
A(0) = \frac{A(0)}{m} + tk R (1 - \alpha) C^\text{V}_\text{init}
\]

(17)

\[
C^\text{V}_\text{init} = \frac{A(0) - \frac{1 - \alpha}{1 - \alpha \beta} C^\text{V}_\text{init}}{m}
\]

(18)

On the other hand, when the determination of total V was carried out using the method of standard addition spiked with V(IV), x' µg/L, according to the general procedure, the following functional equation can be derived:

\[
A'(x') = t R k [C^\text{IV}_\text{init} + C^\text{V}_\text{init} + x']
\]

(19)

\[
\text{Total } V = C^\text{IV}_\text{init} + C^\text{V}_\text{init} + A'/t R
\]

(20)

By solving two simultaneous equations in two unknowns, Eq.(1) and Eq.(2), the concentrations of V(IV), \(C^\text{IV}_\text{init}\), and V(V), \(C^\text{V}_\text{init}\), can be obtained.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C^\text{IV}_\text{init}</td>
<td>the initial concentration of V(IV).</td>
</tr>
<tr>
<td>C^\text{V}_\text{init}</td>
<td>the initial concentration of V(V).</td>
</tr>
<tr>
<td>α</td>
<td>the removal efficiency of V(V) with BuOH extraction step.</td>
</tr>
<tr>
<td>β</td>
<td>the oxidation efficiency of V(IV) to V(V) during BuOH extraction step.</td>
</tr>
<tr>
<td>R</td>
<td>the recovery of V(IV) and/or V(V) with thiooxine extraction method.</td>
</tr>
<tr>
<td>k</td>
<td>the absorption coefficient including length of light path.</td>
</tr>
<tr>
<td>t</td>
<td>the concentration factor of V(IV) with BuOH and thiooxine extraction method.</td>
</tr>
<tr>
<td>t'</td>
<td>the concentration factor of total V with thiooxine extraction method.</td>
</tr>
<tr>
<td>m</td>
<td>the slope of linear standard addition curve for V(IV), tkR (1-α β).</td>
</tr>
<tr>
<td>A(x)</td>
<td>the absorbance for V(IV) as a function of standard addition concentration, x.</td>
</tr>
<tr>
<td>A'(x')</td>
<td>the absorbance for total V as a function of standard addition concentration, x'.</td>
</tr>
</tbody>
</table>

References