

Determination and Speciation of Vanadium(IV) and Vanadium(V) in Water Sample by Ion Chromatography in Combination with Electron Spin Resonance Analysis and/or Electrolysis-Induced Reduction of Vanadium(V)

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Summary

Attention has been paid to vanadium because of its antidiabetic action. There are a lot of natural water products whose sales point is to contain vanadium. However, in most cases, existing form of vanadium is not clear. There have been two methods developed for the differential determination of vanadium. One is graphite-furnace atomic absorption spectrometry based on the extraction of vanadium(V) and vanadium(IV) with different solvents. The other is the speciation method by using high performance liquid chromatography and inductively coupled plasma mass spectrometry. The present study demonstrated that an ion chromatography is very effective for the separation of vanadium(IV) and vanadium(V). If vanadium(V) is existed in aqueous samples, it can be reduced by electrolysis, resulting in the appearance of vanadium(IV). In addition, since electron spin resonance (ESR) spectrometry can be used to confirm the existence of vanadium(IV) based on the spectrum with eight signals, ESR spectrometry can detect the electrolysis-induced reduction of vanadium(V) to vanadium(IV). Therefore, we propose that the combination of these three methods is very useful for the determination and speciation of vanadium in water samples.

Key Words: vanadium, reduction, ion chromatography, electron spin resonance

Introduction

Vanadium is a group 5 transition metal, and under standard physiological conditions (pH 3-7, aerobic atmosphere, aqueous solution, ambient temperature), the oxidation states which are thermodynamically and kinetically possible are trivalent (III), tetravalent (IV), and quinquevalent (V)^{1, 2}. In some marine life forms such as ascidians, vanadium(III) is concentrated in specialized vanadocytes³.

Vanadium is suggested to be an essential trace

element for human body⁴, because it participates in glucose and lipid metabolic pathways. There have been many studies on the insulin-like and anti-diabetic effects of vanadium⁵⁻⁸, and some vanadium compounds have been reported to be effective in lowering blood glucose level⁹⁻¹³. Furthermore, pervanadium(V) has attracted pharmacologists' attention in terms of its insulin mimetic functions^{14, 15}. It was also reported that vanadium(V) exerts insulin-mimetic activities in a synergistic manner with peroxide¹⁶, and pervanadium(V) complexes such

as $K_2[VO(O_2)_2(C_5H_4NCOO)] \cdot 2H_2O$ are also effective insulin mimics¹⁷⁻¹⁹. In addition to peroxovanadium(V) complexes, vanadium(IV) salts such as $VOSO_4$ were clinically examined to ascertain their effectiveness on diabetes in humans^{20, 21}). However, bioavailability of these inorganic salts is generally very low. It was also reported that vanadyl(IV) compounds are less toxic in terms of LD50 values in rats than vanadium(V)^{22, 23}), and vanadium exists in the vanadyl(IV) state in the vanadium(V) salt-treated rats²⁴). Indeed, more recently, it was reported that oxovanadium(IV) complexes are effective as a potent antidiabetic agent²⁵).

In Japan, based on the beneficial aspects of vanadium as described above, a lot of natural water products whose sales point is to contain vanadium have been launched on the market. However, only a few studies have been conducted to analyze vanadium in natural water^{26, 27}), and in most cases the existent form or state of vanadium is not clear. In the present study, we propose a useful method for the determination and speciation of vanadium(IV) and vanadium(V) in water sample.

Materials and Methods

Reagents, test materials, and electrolyzer

Reagents were purchased from the following sources: Vanadium oxide (V_2O_5), and vanadyl sulfate ($VOSO_4$) from Wako Pure Chemicals (Osaka, Japan). All other reagents used were of analytical grade. Test water materials used were commercially available natural water whose sales point was to contain vanadium (henceforth described as natural water throughout the paper), and ultrapure water. As an electrolyzer, a diaphragm type electrolyzer in which the electrode material is platinum coated titanium plate and the interelectrode distance is 8 mm (Super Water Mini, Artec Co., Ltd., Tokyo, Japan) was upgraded to have an ability of varying freely electric current and applied voltage, and used in the present study (henceforth described as variable diaphragm electrolyzer throughout the paper).

Ion chromatography and ESR analyses for vanadium

Standard aqueous solution was prepared to

contain V_2O_5 (20 ng/ml) and $VOSO_4$ (20 ng/ml). The standard solution, ultrapure water, and natural water were subjected to ion chromatography analysis. As needed, the natural water and V_2O_5 solution were electrolyzed with the variable diaphragm electrolyzer at applied voltage of 12 or 15 V for 15 min. To determine vanadium, a direct concentration method was used in the ion chromatographic analysis with the Dionex DX-500 high pressure liquid chromatography system (Dionex Corp., Sunnyvale, CA). Chromatographic separation was performed on IonPac CS5A (Dionex Corp.) as a guard column, IonPacTCC-2 (Dionex Corp.) as a concentration column, and IonPac CG5A (Dionex Corp.) as a separation column at the flow rate of 1.0 ml/min at 30-35°C. As for elution, a mixture containing 0.5 M oxalic acid, 75 mM sodium sulfate and 95 mM lithium hydroxide was used.

The natural water, V_2O_5 solution, and $VOSO_4$ solution were electrolyzed with the variable diaphragm electrolyzer at applied voltage of 12 or 15 V for 5 to 15 min. Then, each test sample in a sample tube ($\phi 4$ mm x 30 cm) was placed at 77 K in the ESR spectrometer (JES-FA-100, JEOL, Tokyo, Japan). ESR analysis was performed under the conditions as follows: field sweep, 322.861 ± 100 mT; field modulation frequency, 100 kHz; field modulation width, 2 mT; amplitude, 100; sweep time, 4 min; time constant, 0.1 s; microwave frequency, 9.054 GHz; microwave power, 8 mW.

Results and Discussion

Representative chromatogram of V_2O_5 and $VOSO_4$ analyzed by ion chromatograph is shown in Fig. 1, indicating that the peaks at 5-6 min and at 16-17 min corresponded to vanadium(IV) and vanadium(V), respectively. Figure 2 shows the chromatograms of the natural water and the ultrapure water. No clear peaks were observed in the chromatogram of the ultrapure water, whilst a large peak with a shoulder was observed at 14-17 min of retention time in the chromatogram of the natural water. Since it was thought that the large peak was derived from vanadium(V), the natural water was then electrolyzed at applied voltage of 12 V for 15 min.

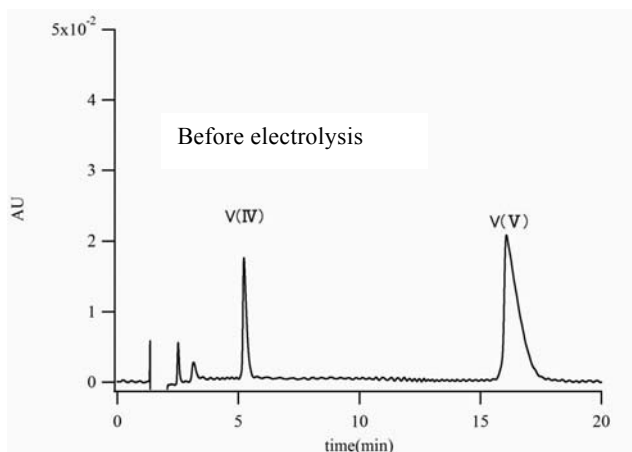


Fig. 1 Representative ion chromatogram of V_2O_5 and $VOSO_4$ aqueous solution.

The peaks at 5-6 min and at 16-17 min corresponded to vanadium(IV) and vanadium(V), respectively. The peak corresponds to vanadium(IV) is presumably derived from VO^{2+} , and that corresponds to vanadium(V) presumably from VO_2^+ .

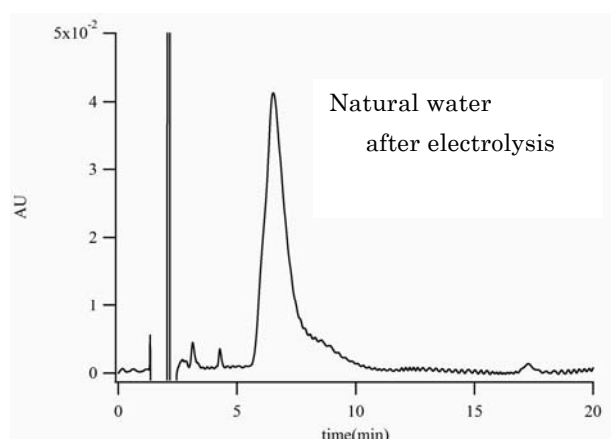
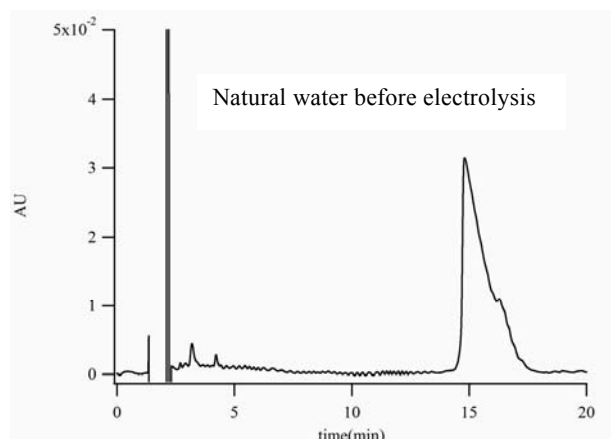
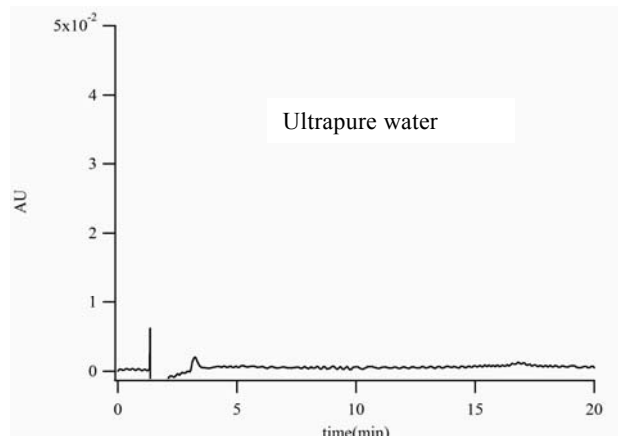


Figure 2 at the bottom shows the chromatogram of the sample taken from the cathode. Since retention time of the peak corresponded to that of $VOSO_4$, it was likely derived from vanadium(IV), a reduced form of vanadium(V). Electrolysis is a method applying the passage of an electric current through an ionic substance solution, which results in chemical reactions at the electrodes. Thus, we assumed that the method could be applied to reduce vanadium(V). To further confirm this, 0.05 mM (9.1 $\mu\text{g}/\text{ml}$) V_2O_5 aqueous solution was electrolyzed at applied voltage of 12 V for 15 min. Figure 3 shows the chromatogram of 0.05 mM V_2O_5 solution before and after electrolysis. A half-broad peak derived from V_2O_5 was observed before electrolysis. After electrolysis a peak at around 5 min of retention time appeared, suggesting that vanadium(V) was partially reduced to vanadium(IV). In this paper, we showed the data obtained by using the variable diaphragm electrolyzer at applied voltage of 12 V for 15 min. We firstly tried to electrolyze sample solutions by applying a commercially available diaphragm type electrolyzer (Super Water Mini). However, clear reduction of vanadium(V) was not observed. Thus, we changed electrolysis conditions and found that applied voltage of 12 V for 15 min could reduce vanadium(V) to vanadium(IV).

Fig. 2 Representative ion chromatograms of ultrapure water and natural water before and after electrolysis.

No clear peaks were observed in the chromatogram of the ultrapure water, whilst a large peak with a shoulder was observed at 14-17 min of retention time in the chromatogram of the natural water before electrolysis. After electrolysis at applied voltage of 12 V for 15 min, a clear peak at around 6 min appeared.

ESR spectroscopy is a technique for studying chemicals which possess one or more unpaired

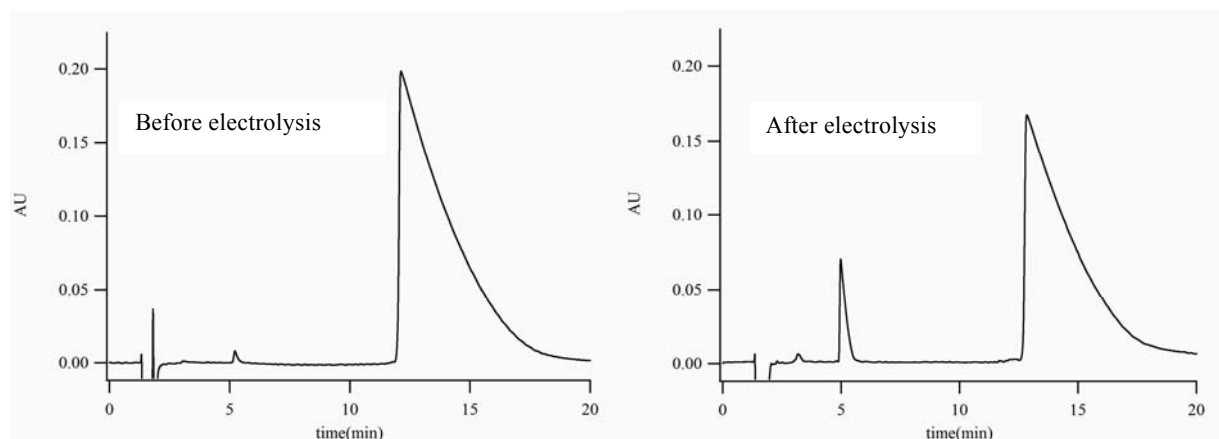


Fig. 3 Representative ion chromatograms of 0.05 mM V_2O_5 solution before and after electrolysis at applied voltage of 12 V for 15 min. After electrolysis, a peak at around 5 min appeared.

electrons, so called free radicals, and inorganic complexes which possess a transition metal ion. Therefore, ESR analysis of the electrolyzed natural water was conducted. However, no clear spectra were observed, possibly because of the low sensitivity of ESR to detect the vanadium. Indeed, according to the ion chromatography analysis, the concentration of vanadium(IV) in the electrolyzed natural water was several dozen ppb (ng/ml). As a next step, $10\ \mu\text{g/ml}$ of V_2O_5 aqueous solutions electrolyzed at applied voltage 12 or 15 V for 5 to 10 min were subjected to the ESR analysis. Representative ESR spectra are shown in Fig. 4. When V_2O_5 aqueous solution was electrolyzed at 12 V, the signal intensity increased with electrolysis time. Also the higher the applied voltage was, the higher the signal intensity was. To confirm if the signal was derived from vanadium(IV), aqueous solution of $VOSO_4$ ($1\ \mu\text{g/ml}$) was subjected to the ESR analysis. A representative ESR spectrum derived from $VOSO_4$ is shown in Fig. 5. Since the nuclear spin of vanadium(IV) is $I=7/2$, the spectrum of vanadium

consists of eight signals because of the equation $2nI+1=8^{28}$. Thus, each ESR spectrum in Fig. 4 was most likely derived from vanadium(IV). In addition, we calculated the ESR parameters based on the anisotropy of spectra, which is a characteristic feature of vanadium(IV) complex^{24, 29}), as shown in Figs. 4 and 5. That is, $g_{\perp}=1.99$, $g_{\parallel}=2.08$, $g_0=2.02$, $A_{\perp}=92.0 \times 10^{-4}\ \text{cm}^{-1}$, $A_{\parallel}=190.3 \times 10^{-4}\ \text{cm}^{-1}$, $A_0=123.6 \times 10^{-4}\ \text{cm}^{-1}$ for $VOSO_4$ solution as shown in Fig. 5, and $g_{\perp}=1.99$, $g_{\parallel}=2.00$, $g_0=1.99$, $A_{\perp}=84.6 \times 10^{-4}\ \text{cm}^{-1}$, A_{\parallel}

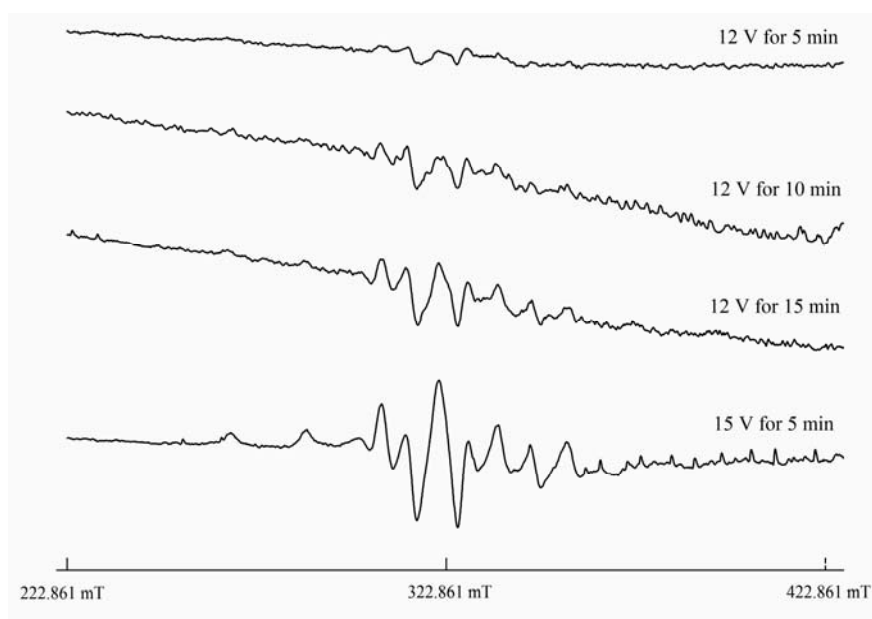


Fig. 4 Representative ESR spectra of V_2O_5 aqueous solution electrolyzed at applied voltage 12 or 15 V for 5 to 10 min.

The signal intensity increased dependently on electrolysis time and applied voltage.

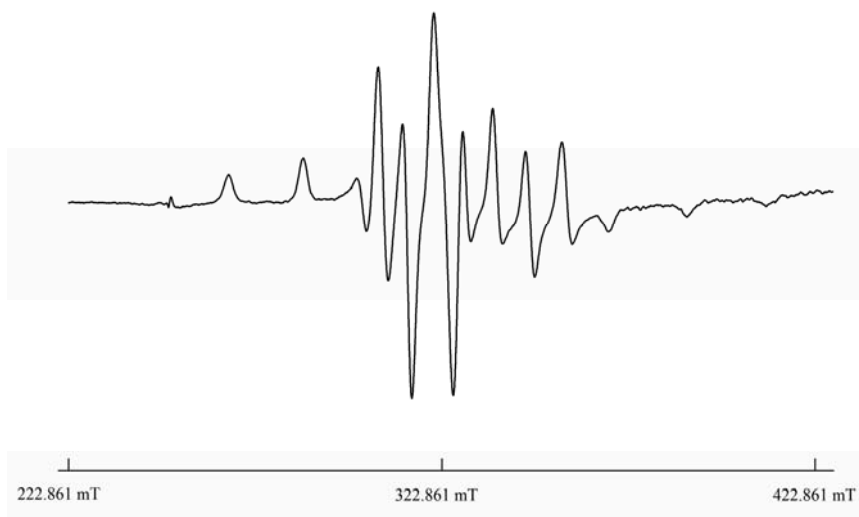


Fig. 5 Representative ESR spectrum of VOSO₄.
Eight signals were observed as the spectrum of vanadium(IV).

$g = 1.849$, $A_0 = 118.0 \times 10^{-4} \text{ cm}^{-1}$ for electrolyzed V₂O₅ solution as shown in Fig. 4. Since the values of these parameters obtained from the spectra in Figs. 4 and 5 are very close to each other, each spectrum in Fig. 4 was surely derived from vanadium(IV).

For analysis of vanadium in water samples by graphite-furnace atomic absorption spectrometry, it was reported that separation and preconcentration method based on the solvent extraction of vanadium(V) with 1-butanol and vanadium(IV) with 8-mercaptquinoline is effective for differential determination of vanadium(V) and vanadium(IV)³⁰. More recently, it was reported that a simple and sensitive method for the speciation of vanadium(III), (IV), and (V) was developed by using high performance liquid chromatography and inductively coupled plasma mass spectrometry (HPLC-ICPMS)³¹. The present study demonstrated that the ion chromatography coupled with ESR analysis could be a tool effective for detection and speciation of vanadium in solutions. Even if the concentration of vanadium is too low to detect by ESR spectroscopy, electrolysis under the certain conditions could reduce the vanadium(V) to vanadium(IV), supporting the evidence for the existence of vanadium.

List of Abbreviations

tetravalent vanadium;
vanadium(IV)
quinquevalent vanadium;
vanadium(V)
electron spin resonance; ESR

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電子スピン共鳴解析、五価バナジウムの電気分解還元とイオンクロマトグラフィーの組合せによる水試料の四価バナジウムと五価バナジウムの分別定量

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要旨

バナジウムの抗糖尿病作用が注目されており、バナジウム含有をセールスポイントとする天然水が多数販売されているが、多くの場合バナジウムの存在形態は不明である。これまでバナジウムの分別定量のために二つの方法が開発されている。四価および五価バナジウムを異なる溶媒で抽出し、黒鉛炉原子吸光で分析する方法と液体クロマトグラフィー・誘導結合プラズマ質量分析法である。本研究ではイオンクロマトグラフィーが四価および五価バナジウムの分離に有効であることを示した。次に五価バナジウムが水試料中に存在する場合には、水試料を電気分解することで四価バナジウムに還元できることを示した。最後に、電子スピン共鳴分光法は、四価バナジウムに由来する 8 本のシグナルを検出することができることから、水の電気分解による五価バナジウムへの還元の際の四価バナジウムへの還元を検出に有効であることを示した。以上より、我々は、これら三つの方法の組合せは、天然水などの水試料中のバナジウムの分別定量に非常に有効であることを提示した。

キーワード：バナジウム、還元、イオンクロマトグラフィー、電子スピン共鳴