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Rapid speciation and determination of vanadium compounds using ion-pair reversed-phase ultra-high-performance liquid chromatography inductively coupled plasma-sector field mass spectrometry

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ABSTRACT

Environmental vanadium contamination is a potential concern to public health, as evidenced by its place on the U.S. Environmental Protection Agency Drinking Water Contaminant Candidate List as a priority contaminant. Vanadium toxicity varies significantly between different oxidation states; therefore, it is crucial to be able to monitor the speciation of vanadium in environmental samples. In this study, a novel method is described that utilizes ion-pair reversed-phase ultra-high-performance liquid chromatography with inductively coupled plasma-sector field mass spectrometry (IP-RP-UHPLC-ICP-SFMS) to separate vanadyl and vanadate ions and resolve a major polyatomic spectral interference ($^{35}Cl^{16}O^+$) in less than a minute. Detection limits were obtained in the low ng L^{-1} (part per trillion) range with linear calibrations across several orders of magnitude (50 ng L^{-1}–100 μg L^{-1}). The mechanism of chromatographic retention was elucidated through investigation of the role of ethylenediaminetetraacetic acid, tetrabutylammonium ion and pH on elution. The optimized method was then applied to the speciation of vanadium in local lake water samples.

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1. Introduction

It is well established that the oxidation state of vanadium is related to its therapeutic or toxic properties in a biological system. Although vanadium exists in a variety of oxidation states from −1 to +5, the most stable and naturally prevalent species are the vanadyl (+4 formal oxidation state) and vanadate (+5 formal oxidation state) forms. Vanadate has been shown to be toxic to biological systems, while tetravalent vanadyl compounds exhibit the ability to reduce some symptoms of diabetes [1,2]. This therapeutic application has been proposed to stem from the inhibition of a phosphatase enzyme in the regulation pathway of insulin [3]. Vanadate, due to structural and electronic properties, is analogous to phosphate and can bind enzymes associated with phosphorylation [4] resulting in toxicity [5]. Vanadium is naturally present at trace levels in the environment (notably sea water) and is also introduced into the environment from a variety of anthropogenic sources [6]. The main source of vanadium contamination is fossil fuel combustion, with some crude oils containing vanadium levels as high as 1160 μg g^{-1} [7]. The United States Environmental Protection Agency (U.S. EPA) includes vanadium on the Drinking Water Contaminants Candidates List due to the potential health effects resulting from exposure and its environmental persistence [3,8]. Because the form of vanadium ultimately determines its biological properties, development of a rapid, accurate analytical method for speciation of this metal in environmental matrices is critical.

A variety of separation techniques have been applied to the speciation of vanadium. Solid phase extraction (SPE) [9–11], capillary electrophoresis (CE) [12,13], and several forms of liquid chromatography [14–17] have been used to analyze vanadium compounds in a variety of matrices including petroleum, fertilizers, steel, sediments, plant tissues and water. These separation techniques have been coupled to a variety of detectors such as UV–vis spectroscopy [18–20], atomic absorption spectroscopy [18,19,21,22], inductively coupled plasma optical emission spectroscopy (ICP-OES) [18,19,21], and inductively coupled plasma mass spectrometry (ICP-MS) [15,18,19,21], with reported detection limits ranging from the low-parts-per trillion to approximately 50 parts-per-billion [18]. SPE techniques have been shown to be less than optimal due to detector compatibility issues, forcing the use of less sensitive detectors such as UV, which requires a chromophore with high absorption to obtain acceptable detection

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limits [18]. CE methods have shown promise, however peak drift times have caused reproducibility issues [18]. LC techniques such as reverse phase (RP) [23], ion exchange chromatography (IEC) [14,15] and ion pair reverse phase (IP-RP) [16,17,24] methods have been extensively used in the speciation of vanadium, with the most common quantification techniques being electrospray ionization mass spectrometry (ESI-MS) [12,15], ICP-OES [25], and ICP-MS [14–16,24,26]. While the high levels of organic modifiers (30–60% v/v) that are used in traditional RP methods translate well to ESI-MS detection, they can result in instability of the plasma ionization source in ICP-MS. In addition, currently available IEC columns lack sub-2 μm particles, leading to longer retention times and lower sample throughput compared to reverse phase columns, making this method less than ideal.

IP-RP separations utilize a non-polar stationary phase to separate compounds by coupling them with less polar ion-pair reagents that provide retention. In the case of inorganic compounds, analytes are complexed with a strong chelating agent such as ethylenediaminetetraacetic acid (EDTA) to ensure stable complex formation. In the case of vanadium speciation utilizing EDTA, there is a charge on both complex species, 2− for the vanadyl complex and 3− for the vanadate complex at neutral pH. EDTA also can stabilize the redox state of vanadium and allow for decreased organic modifier, which also serves an important role in ion displacement. Such a separation approach is well-suited to ICP-MS quantification and has been used for a variety of matrices including water samples, sediments and mussel [18]. The most common form of mass analyzer for ICP-MS is a quadrupole system [14,24,26,27], which suffers from a chlorine oxide $^{35}Cl^{16}O^{+}$ polyatomic interference that complicates the analysis of the most abundant isotope of vanadium, ^{51}V. However, a sector field ICP-MS (ICP-SFMS) uses both a magnetic and electric sector to discriminate between analytes and can completely resolve ^{51}V, and $^{35}Cl^{16}O^{+}$, at a higher resolution setting, albeit with reduced sensitivity. Vachirapatama et al. performed IP-RP-HPLC analysis of vanadate and vanadyl ions in fertilizer and plant tissue samples and used a separate ICP-SFMS analysis to verify the quantified values [20,28]. In addition, the application of ultra-high-performance liquid chromatography (UHPLC) would allow for drastically increased throughput and sensitivity [29].

With the demand for energy driving fossil fuel exploration, a rapid method to analyze vanadium species in environmental samples would be valuable to regulatory agencies charged with monitoring water quality [8]. Environmental disasters such as the Deep Water Horizon oil spill, and alternate methods of fuel exploration such as hydraulic fracturing, exacerbate this need. In this paper, a method utilizing ion-pair reversed-phase ultra-high-performance liquid chromatography inductively coupled plasma-sector field mass spectrometry (IP-RP-UHPLC-ICP-SFMS) is used to achieve sample redox stability and low detection limits for vanadium species with high-throughput capabilities for environmental samples. The mechanism of retention is examined in detail, along with species stability and the analysis of real world samples.

2. Experimental

2.1. Reagents

Analytical grade UHPLC reagents were used in all standards and solutions. Approximately 18 MΩ cm deionized water (DI H_2O), was obtained from a Pure Water Solutions system (Hillsborough, NC, USA) and was used for all solutions. Mobile phase eluent was prepared daily to obtain a concentration of 18 mM EDTA, 0.5 mM Tetrabutyl ammonium (TBA^+) and 20 mM phosphoric acid (H_3PO_4). Stock solutions used to prepare the mobile phase included 0.5 M EDTA and 1 M TBA(OH) (Fluka, Buchs, Switzerland) and concentrated H_3PO_4 (Sigma–Aldrich, St. Louis, MO, USA). The pH of the eluent was adjusted to 7.00 with concentrated ammonium hydroxide (NH_4OH) (Sigma–Aldrich, St. Louis, MO, USA). Finally, the mixture was diluted with semiconductor grade methanol (CH_3OH) (Sigma–Aldrich, Munich, Germany) to obtain a final concentration of 4% (v/v). Vanadium stock solutions (200 mg L^{-1}) were prepared daily in DI H_2O from vanadyl sulfate ($VOSO_4{\cdot}3H_2O$, 99.99%) (GFS Chemicals, Columbus, OH, USA) and sodium orthovanadate (Na_3O_4V, 99.98%) (Sigma–Aldrich, St. Louis, MO, USA). Calibration standard solutions ranging from 50 ng L^{-1} to 100 μg L^{-1} were prepared fresh daily by dilution of standard stock solutions with mobile phase eluent. Sodium chloride (NaCl) (≥99.999%) (Fluka) was used to prepare a 20 mM NaCl solution for interference resolution experiments.

2.2. Sample preparation

The mechanism of retention was studied by assessing the impact of sequential removal of EDTA and TBA^+ from the eluent for DI H_2O samples containing nominal 5 μg L^{-1} concentrations of vanadyl and vanadate ions. The same nominal vanadium species concentrations in DI H_2O were used to assess the impact of variation of eluent pH by addition of NH_4OH from 5.00 to 9.00. A 20 mM NaCl solution in eluent was also spiked with 5 μg L^{-1} of both vanadium species to demonstrate interference resolution. Vanadyl single spike stability experiments were performed by diluting individual stock solutions to 100 mg L^{-1}, 50 mg L^{-1}, 1 mg L^{-1}, and 100 μg L^{-1} vanadyl in DI H_2O and 50 mg L^{-1} vanadyl in tap H_2O. These samples were evaluated at 7 time points (t = 0, 10, 20, 30, 60, 120, and 240 min) by diluting samples in eluent to a final concentration of 5 μg L^{-1} and evaluated in medium resolution ICP-SFMS. Vanadate single spike samples were prepared similarly to vanadyl samples, and evaluated the same time points.

Lake water was obtained and stored in refrigerated conditions was collected from Falls Lake (36.0167° N, 78.6958° W), located northeast of Durham, NC. The sample was filtered through an Acrodisc LC 13 mm syringe filter with 0.2 μm polyvinylidene fluoride membrane (Pall, Port Washington, NY, USA), to remove particulate matter, and then diluted by a factor of 5 with eluent mobile phase. The sample matrix was evaluated within 24 h of collection by spiking 5 μg L^{-1} of both vanadium species and compared to non-spiked samples.

2.3. Instrumentation

A Waters ACQUITY UPLC (Milford, MA, USA) equipped with an ACQUITY UPLC BEH C_{18} 1.7 μm (2.1 mm × 50 mm) separation column (Waters) was used for separation of species and mated to the Element 2 ICP-SFMS (Thermo, Bremen, Germany). Samples (20 μL) were injected using a Waters ACQUITY UPLC autosampler. An isocratic eluent program with a flow rate of 0.6 ml min^{-1} was used at an approximate pressure of 10,000 psi. The chromatography system was controlled using E-pro Empower 3V 7.10.00.00 software (Waters). The outlet of the chromatograph was connected to an ESI PC3 Peltier cooled cyclonic spray chamber at −5 °C (Electron Scientific, Appleton, WI, USA) which directly interfaced with the ICP-SFMS. The ICP-SFMS was operated at 1475W with a Pt guard electrode (Thermo) using Element ICP-MS software V. 3.1.2.242 and tuned by monitoring the ^{51}V signal to obtain the highest signal-to-noise ratio. Analysis was completed in low ($M/\Delta M$ = 300–400) and medium ($M/\Delta M$ = 5900–6800) resolution modes and exported via the Xcalibur Export Plugin V 1.0 (Thermo, Franklin, MA, USA). All data analysis was performed using Xcalibur V 2.0.6.

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