Determination of Vanadium (IV) and (V) in Southern Nevada Groundwater by Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry

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Abstract: A rapid method is presented for measuring V(IV) and V(V) in groundwater, without preconcentration or complexing agents, using direct injection of the water samples (which were collected under an argon atmosphere) into an ion chromatograph-inductively coupled plasma mass spectrometer (ICPMS). The mobile phase is 1.5% v/v nitric acid, which minimizes the buildup of solids in the ultrasonic nebulizer, the torch, and on the entrance cones of the ICPMS - a problem with methods using organic complexing agents and inorganic salts. The result is much less instrument downtime for cleaning the affected parts. Limits of detection are 0.02 μg L^{-1} for V(IV) and 0.06 μg L^{-1} for V(V). The pentavalent form of vanadium represents 98% to 99% of the vanadium in these Southern Nevada groundwater samples and ranges from 3.7±0.1 μg L^{-1} to 82.1±0.5 μg L^{-1}. The remaining few percent is V(IV). Total vanadium was determined by ICPMS for a mass-balance comparison.

Keywords: Vanadium speciation, V(IV), V(V), IC-ICPMS, Groundwater, Argon collection.

1. INTRODUCTION

Anthropogenic vanadium enters the environment mainly from the burning of fossil fuels, such as residual oils and coal, and, from the production of steel and the manufacture of pigments and paints [1-5]. Vanadium has been shown to be an essential element in humans, playing an important role in the regulation of enzymes such as ATPase, phosphoryl-transfer enzymes, adenylate cyclase and protein kinases [4-6]. Vanadium can exist in oxidation states from (II) to (V) in aqueous solution [1,2,4]. Pentavalent vanadium is more toxic than other oxidation states [1,2,4,5]. Chronic exposure to inorganic forms of vanadium may result in hematopoietic changes, nephrotoxicity, and reproductive and developmental toxicity [1,6]. Vanadium pentoxide aerosols are "possibly carcinogenic to humans" [1,6,7]. Vanadium is an environmentally important trace element because of its redox sensitivity [2,8-10].

Total vanadium concentrations in groundwater are generally from 0.5 to 2.5 μgL^{-1} (ppb) [6,11]. However, the total vanadium in groundwater from volcanic areas in Italy ranges up to 140 μg L^{-1} [4], and, the concentrations in Argentinean groundwater extend from 50 to 2470 μg L^{-1} [3]. The most common oxidation states of vanadium in aqueous systems are V(IV) and V(V) [1,5,12,13]. The concentrations of vanadium are reported to decrease from oxidizing to reducing environments [1,4,5]. In oxidizing waters, the dominant vanadium species are the "phosphate-like anions" $H_2VO_4^-$ and HVO_4^{-2} [1,11]. In reducing environments, vanadyl ion VO^{+2} is the most stable oxycation [1,11]. The existence of each oxidation state species depends on the pH, redox potential and ionic strength of the aqueous system [1,4,5]. For these reasons, sample collection and storage techniques must be conducted in a manner that guarantees that the measured species are those representative of the groundwater that was sampled [5,13].

Many techniques have been used to separate the redox species of vanadium in natural waters, including capillary electrophoresis (CE) [14-18], reversed-phase liquid chromatography (RPLC) [19-22] (including ion-pairing (IP) RPLC), and, various forms of ion chromatography [1,3,4,14, 15,23-26]. After the species have been separated by any of these techniques, they are quantified by UV [14,17], chemiluminescence [27], ICP [28], or ICPMS [14].

In CE, the vanadium species are separated after complexation with various reagents such as ethylenediaminetetraacetic acid (EDTA) [14,18], diethylenetriaminepentaacetic acid (DTPA) [14,18], and a Mo(VI)-P(V) reagent [17]. In reversed-phase liquid chromatography [2,19-22], the chelating reagents include 4-(2-pyridylazo) resorcinol (PAR) [19-22,29], 2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)-phenol (5-Br-PAPS) [2], hydrogen peroxide-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) [21] and 2-(5-nitro-2-pyridylazo)-5-[N-n-propyl-N-(3-sulfopropyl)-amino]phenol (nitro-PAPS) [30]. Some of the ion-pairing reagents used in IP-RPLC are aminopolycarboxylic acids; e.g. EDTA) [1,2,4,12,14], 1,2-cyclohexanediaminotetraacetic acid (CDTA) [3], N-2-hydroxyethylethylenediaminetetraaceatic acid (HEDTA) [23] and 4-(2-pyridylazo) resorcinol (PAR) [15,24].

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The major problem in RPLC and CE coupled with ICPMS is due to the organic complexing agents and other reagents used in the methods [13]. These organic compounds can clog the torch and cause instability in the plasma, which can lead to measurement problems and extinction of the plasma. They can also cause residue build-up on the entrance cones of the mass spectrometer, decreasing the performance of the ICPMS and requiring frequent cleaning [5]. Most of these limitations can be overcome by using ion exchange chromatography with ICPMS, because organic complexing reagents and organic solvents are generally not required. However, the use of various buffers and salts to control the ionic strength or pH in ion exchange also causes severe problems with the ICPMS due to salt deposition on the cones. These reagents should be avoided if possible.

Another problem when using the ICPMS as the vanadium detector is the formation of polyatomic ions in the plasma with the same mass as vanadium. The isobaric interference with the ^{51}V isotope (99.75% abundance) is the $[^{35}Cl^{16}O]^+$ ion [1,26,31,32]. However, this polyatomic ion can be eliminated by the introduction of a reaction cell or a collision cell between the plasma and the quadrupole analyzer [1,26,31,32].

Vanadium is one of 12 redox sensitive elements, also including arsenic, antimony, chromium, copper, iron, manganese, molybdenum, rhenium, selenium, tungsten, and uranium, that we are studying in order to develop an empirical relationship for predicting the redox states of many trace elements in groundwater near nuclear or other waste sites, based on the measurement of the speciation of a few. Such a relationship is needed since most attempts to predict trace element speciation in natural waters by measuring the E_H and pH have been unsuccessful [33-37]. In this report, we present a fast, selective, and sensitive method for establishing the speciation of vanadium using IC-ICPMS. The main advantages of the method include the direct injection of groundwater samples, without preconcentration or chelation, and the use of a dilute nitric acid mobile phase. This combination keeps the build-up of solids in the ultrasonic nebulizer, the torch, and the entrance cones of the ICPMS to a minimum, thereby contributing to low instrument down-time.

2. EXPERIMENTAL

2.1. Chemicals and Solutions

Ultrapure water with a specific resistance of 18.2 MΩ cm^{-1} was obtained from a Milli-Q Element A10 apparatus (Millipore, Bedford, MA, USA) and used to prepare the mobile phase and all calibration solutions. All V(IV) solutions were prepared from a 10 mg L^{-1} stock solution in 5% HNO_3 (Spex CertiPrep, Metuchen, NJ, USA) and all V(V) solutions prepared from $NaVO_3$ (96%, Alfa Aesar, Ward Hill, MA, USA). The total vanadium was determined in a routine where 54 elements were determined in all field samples by ICPMS, without the intervention of IC. Multielement standards (Spex CertiPrep, Metuchen, NJ, USA) were used as calibration standards. Yttrium (Y - 99.999%) 1000 mg L^{-1} solution, High-Purity Standards, Charleston, SC, USA) served as the internal standard. All solutions were stored in the dark in a refrigerator at 4±1° C and the calibration solutions were prepared daily. The mobile phase (1.5% v/v HNO_3) was prepared by the dilution of sub-boiling distilled in quartz 16 M HNO_3 (Seastar Chemicals INC., Sydney, BC, Canada) with Milli-Q water.

2.2. Instrumentation

The ICPMS used was an Elan 6100 with a Dynamic Reaction Cell (DRC) (PerkinElmer-Sciex, Norwalk, CT, USA). All liquid samples were introduced to the ICPMS with a Cetac U6000AT$^+$ ultrasonic nebulizer (Cetac Technologies, Omaha, NE, USA). The vanadium oxidation state species were separated by ion chromatography using a system which included a Dionex GP 50 Gradient pump (Dionex Corporation, Sunnyvale, CA, USA), a Dionex IonPac CG5A guard column (4×50 mm), a Dionex IonPac CS5A (4×250 mm) analytical column, and a six-way valve with a 200 µL loop. The effluent tubing from the analytical column was connected to the ultrasonic nebulizer whose output entered the ICPMS. The total vanadium analysis was carried out by introducing water samples directly to the ultrasonic nebulizer using an autosampler (AS93 Plus, PerkinElmer), without passing through the ion exchange column.

2.3. Sampling

Groundwater samples were collected from: 1) wells drilled by the Nye County Early Warning Drilling Program (NCEWDP) in the Amargosa Valley, NV, USA and, 2) springs in the Ash Meadows National Wildlife Refuge, NV, USA. The well samples were collected after pumping out a minimum of three well volumes and stabilization of pH, conductivity, and dissolved oxygen. Spring water was pumped through Teflon tubing from as near as possible to the source of discharge. All water samples were filtered through an inline 0.45 µm filter (AquaPrep, Pall, East Hills, NY, USA) and collected under an inert atmosphere (argon).

The samples were collected in 250 mL polyethylene wash bottles (Nalgene, Rochester, NY, USA), modified as shown in Fig. (**1**). Before collection trips, the sample bottles were rinsed five times with 18.2 MΩ cm^{-1} deionized water and allowed to air dry in a laminar flow hood. They were then stored in zip-lock bags until needed. Before being taken into the field, they were fitted with the introduction tube and clamp, filled with argon, and rebagged. The water samples were collected by connecting the output from the 0.45 µm filter to the wash bottle spout (see Fig. **1**), while partially loosening the top in order to allow argon to be expelled as the water flowed into the bottom of the bottle. Sample introduction was stopped before all of the argon was displaced, then the cap was tightened leaving the sample covered with argon, the plastic clamp closed, and the 0.45 µm filtered water-source removed. The sample bottles were returned to the zip-lock plastic bags which were flushed with argon. The bagged samples were placed in coolers with frozen ice packs and transferred to the laboratory where they were stored in argon-filled zip-lock bags in a refrigerator at 4±1 °C until analysis, usually one to three days. Duplicate samples were also collected from the same wells and springs. The E_H and pH of all waters were measured in the field immediately using an oxidation reduction potentiometer (Hach, Loveland, CO, USA) and a pH meter (model HQ 40d; Hach, Loveland, CO, USA). Samples were collected at all locations for other studies, including measurement of the

major ions including chloride, which might have some bearing on the formation of isobaric ions during the analysis of vanadium.

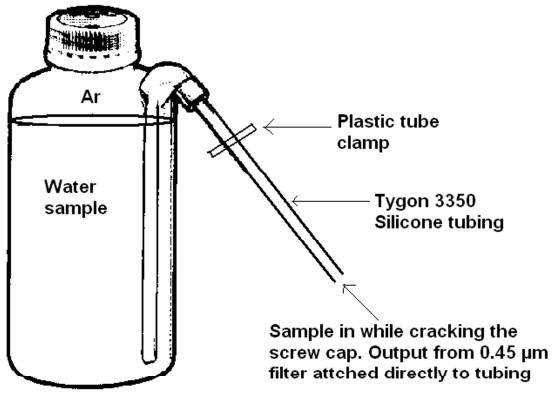

Fig. (1). Sample collection bottle.

2.4. Vanadium Speciation Analysis

First, the sample bottle, stored in an argon-filled plastic bag, was removed from the 4° C refrigerator and placed in a glove box (Erlab, North Andover, MA, USA), which was continually purged with argon. The bottle was removed from the plastic bag and the plastic clamp opened. The bottle was then squeezed to expel a few milliliters of sample into a 20 mL styrofoam disposable beaker (VWR Scientific Products, West Chester, PA, USA). When pressure on the bottle was released, argon flowed in to replace the expelled sample. The plastic clamp was closed and the sample bottle placed into its argon-filled zip-lock bag, and returned to the refrigerator. Next, a 3 mL disposable syringe (Becton Dickson & Co., Franklin Lakes, NJ, USA) was filled from the expelled sample in the argon glove box. The syringe was removed from the glove box and immediately attached to the IC injection valve. The 200 µL sample loop was flushed with sample and closed. When the valve was turned to introduce the sample into the mobile phase, a signal was sent to the ICPMS and the run was started. Table **1** summarizes the chromatographic conditions and ICPMS parameters. The signal at m/z ratio of 51 was monitored for quantification (^{51}V is 99.75% abundant). An external calibration method was used with five points for both V(IV) and V(V). The R^2 values were required to be $\geq$ 0.998. The vanadium concentrations in each oxidation state were calculated based on peak heights. Initial calibration verification solutions, continuing calibration check solutions, reagent blank solutions, spiked sample solutions, and duplicate sample injections were included routinely in the sample train as quality control measures. The stability of the oxidation state species in the 1.5% v/v HNO_3 mobile phase over time was investigated and the results are presented in the results and discussion.

3. RESULTS AND DISCUSSION

3.1. Vanadium Speciation Method Development

A study was conducted to determine the effectiveness of the dynamic reaction cell (DRC) with NH_3 as the reaction gas, to destroy $[^{35}Cl^{16}O]^+$. This molecular ion is isobaric with ^{51}V and could lead to false positive measurements. Samples of groundwater and standards with vanadium concentrations in the range of 0.05 μgL^{-1} to 100 μgL^{-1} were analyzed using IC-ICPMS with and without the DRC. The results showed that the background was higher (~25 000 cps) with the DRC "off" than with the DRC "on" (~5 000 cps, gas flowing in the cell). When NaCl solutions covering and exceeding the concentrations found in the environmental water samples (0-100 mgL^{-1} chloride) were injected into the IC-ICPMS with the DRC "off", no false ^{51}V peaks were observed, and the background was high. Similarly, with the DRC "on", no false peaks were observed and the background was lower. Therefore, the DRC mode was used for all analytical runs, because it reduced the background signal and did not significantly reduce the analytical signal. Figs. (**2**, **3**) show the IC-ICPMS chromatograms obtained for 1 µg L^{-1} calibration solutions of V(IV) and V(V) under the optimized conditions in Table **1**. The detection limit (3σ; n=7 runs) is 0.02 µg L^{-1} for V(IV) and 0.06 µg L^{-1} for V(V).

Table 1. Operating Analytical Conditions

Chromatographic Conditions	
Analytical column	IonPac CS5A (4×250 mm)
Guard column	IonPac CG5A (4×50 mm)
Injection volume	200 µL
Pressure	2000 PSI
Mobile phase	1.5% v/v HNO_3
Flow rate	1.50 mL min^{-1}
Elution	Isocratic
Time of analysis	5 min
ICPMS Parameters	
ICPMS	Elan 6100 DRC
Sample introduction system	Cetac ultrasonic nebulizer model U6000AT$^+$
RF power	1.3 kW
Mode	DRC
Plasma gas flow	15.00 L min^{-1}
Auxiliary gas flow	1.10 L min^{-1}
Nebulizer gas flow	1.06 L min^{-1}
DRC - cell gas A (NH_3)	0.5 mL min^{-1}
Internal standard	^{89}Y (for total vanadium)
Isotope monitored (m/z ratio)	51

The mobile phase, flowing continuously through the chromatographic-nebulizer-ICPMS system was 1.5% v/v HNO_3. One might be concerned about using dilute nitric acid because of its oxidizing properties, and thus the possibility of altering the vanadium speciation during the analysis. However, the clean chromatograms of 1 µg L^{-1} for the two oxidation states in Figs. (**2**, **3**) suggest that contact with the mobile phase does not alter the redox state of vanadium during the 5-minute analysis time. To substantiate this

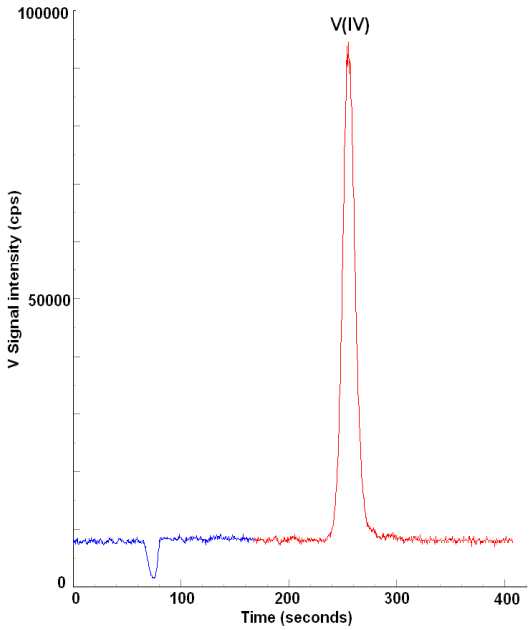

Fig. (2). Chromatogram of a 1 µg L^{-1} standard of V(IV) prepared in ultrapure deionized water. Experimental conditions are listed in Table **1**.

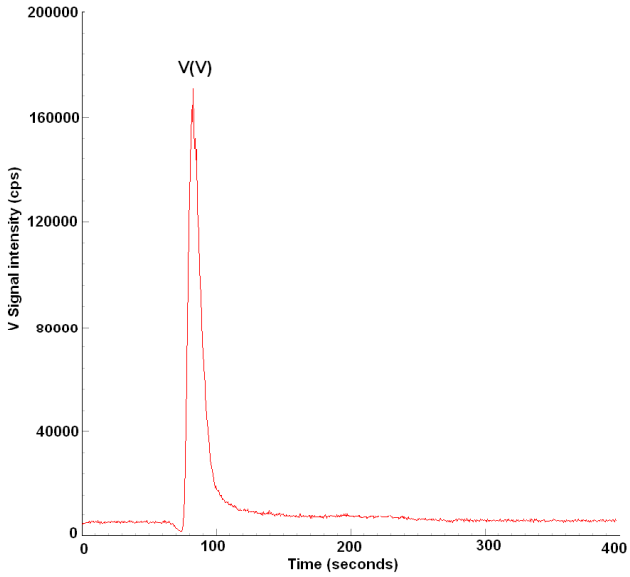

Fig. (3). Chromatogram of a 1 µg L^{-1} standard of V(V) prepared in ultrapure deionized water. Experimental conditions are listed in Table **1**.

observation, the effect of a 1.5% v/v HNO_3 on vanadium speciation over a longer time was evaluated. This was performed by preparing 10 µg L^{-1} solutions of V(IV) and V(V) in pure water and in 1.5% v/v HNO_3. The solutions were analyzed immediately after preparation, and, at 5 hr, 72 hr and 7 days intervals. The results showed that in pure water, V(IV) converts slowly to V(V) and is stable in 1.5%. HNO_3. Conversely, V(V) is slowly reduced to V(IV) in 1.5% HNO_3 and is stable in deionized water. Thus, the use of 1.5% HNO_3 as the mobile phase does not produce a change in the the redox species ratio during the five minute analysis time.

3.2. Vanadium Speciation in Southern Nevada Groundwater

The groundwater sampling sites are located near Las Vegas and are given in Figs. (**4**, **5**). The Nye County Early Warning Drilling Program (NCEWDP) is a part of the research umbrella supported by the DOE scientific investigation of Yucca Mountain as a suitable site for the long-term storage of high-level nuclear waste from commercial electrical power reactors and military sources. It has been extensively studied since 1978 and its fate is still unclear (as of 2009). The NCEWDP research targets the complex hydrology of the area located just east of Yucca Mountain. The NCEWDP site is also adjacent to the Nevada Test Site (NTS), where many nuclear devices were tested underground near or in the water table. The redox condition of the groundwater is just one of the minor phases of the overall study of Yucca Mountain and the NTS. The general consensus is that reducing groundwater impedes the movement of most trace elements, including their radioactive isotopes, and oxidizing conditions favor such movement. Water from springs in the Ash Meadows National Wildlife Refuge, located about 60 miles to the northwest of Las Vegas and about 25 miles south of Yucca Mountain, is thought to consist of water originating on the eastern side of the NTS (the Pahranagat Valley) along with recharge from the nearby Spring Mountains, just east of Ash Meadows [38]. It is not known if any component of this water originates from the NTS.

Figs. (**6**, **7**) show typical chromatograms of vanadium in groundwater samples from the NCEWDP wells and natural springs of Ash Meadows. Fig. (**6**) shows the lowest V(IV)/V(V) ratio observed and Fig. (**7**) shows the highest ratio observed. Although the concentration of vanadium is over twenty times higher in the NCEWDP well than in the Ash Meadows spring, V(V) is clearly the predominant oxidation state in these chromatograms and, in fact, the predominant species in all of the samples collected from the nine locations in the study.

The vanadium results are found in Table **2** for groundwater from wells in the NCEWDP and springs from Ash Meadows. Also listed are the measured pH, measured E_H, sum of the experimental V(IV) and V(V) concentrations, total vanadium by ICPMS (without the IC), the percentage of mass balance, and the percentage of V(V) in these samples.

The reproducibility of the vanadium redox species measurements can be evaluated by comparing the results obtained for the duplicate samples, which were collected in tandem at J-12 and 33P. The reproducibility of J-12 and 33P samples were 19% and 5% for V(IV) and, 5% and 7% for V(V). Spiking experiments (standard additions) were carried out to demonstrate the accuracy of the vanadium concentrations. The average recoveries were 98% and 102% for V(IV) and V(V) respectively, demonstrating that there are no measurable matrix interferences.

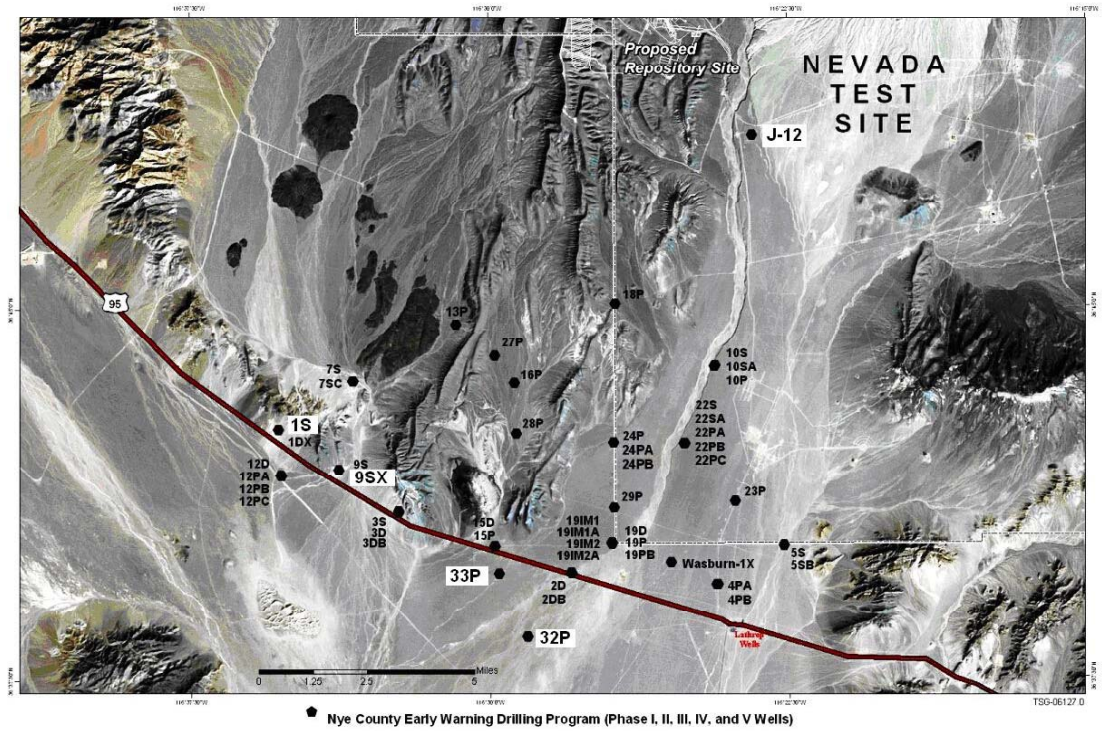

Fig. (4). Map of the NCEWDP well locations on and adjacent to Yucca Mountain and the Nevada Test Site [http://www.nyecounty.com/ewdpmain.htm].

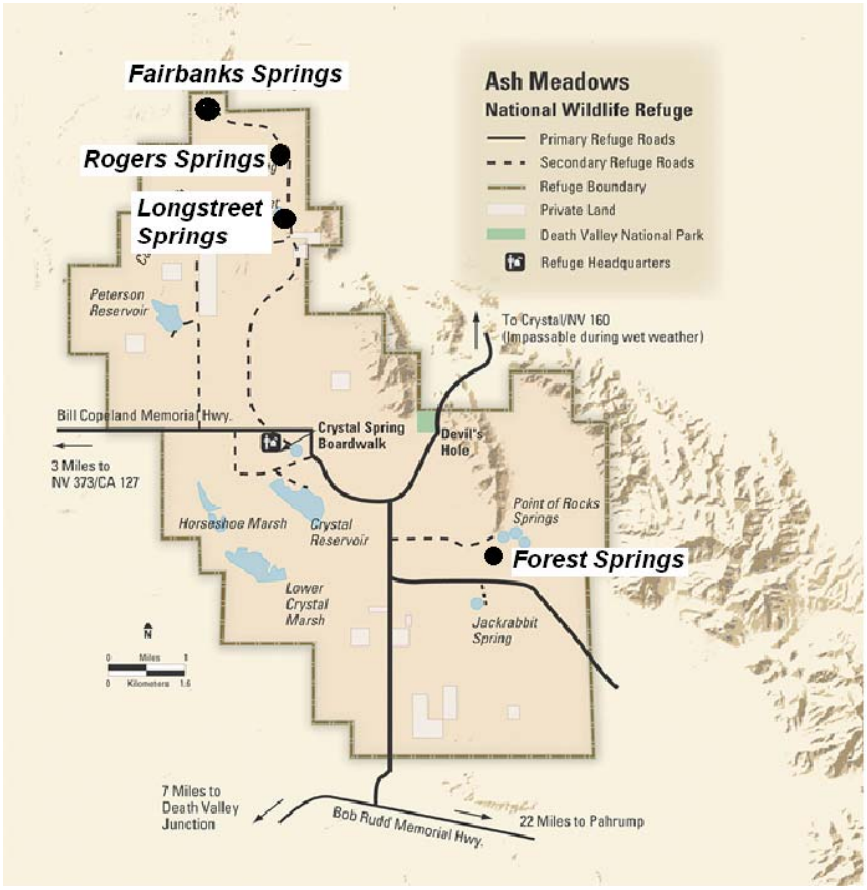

Fig. (5). Map of the Ash Meadows National Wildlife Refuge showing locations of springs. Samples were collected from Fairbanks, Rogers, Longstreet and Forest springs [http://www.fws.gov/desertcomplex/ashmeadows/map.htm].

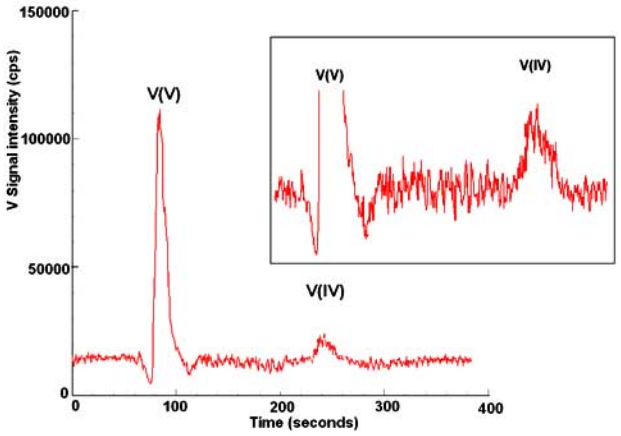

Fig. (6). Chromatogram of vanadium species in groundwater from the NCEWDP (well ID: 32P Deep). Experimental conditions as in Table **1**. V(IV) = 0.47 ±0.06 µg L^{-1} and V(V) = 82.1±0.5 µg L^{-1}.

Pentavalent vanadium represents 98% to 99% of total vanadium in the well water samples, and 99% in spring water samples. The sum of total vanadium concentration ranged between 7.0 ±0.1 µg L^{-1} and 82.6±0.5 µg L^{-1} for well water and 3.8±0.1 µg L^{-1} and 5.8±0.1 µg L^{-1} for spring water. The total vanadium concentration (without IC) ranged between 7.7±0.2 µg L^{-1} and 78±2 µg L^{-1} for well water and 3.5 ±0.1 µg L^{-1} and 4.9±0.1 µg L^{-1} for spring water. The mass balance calculations comparing the sum of total vanadium (IC-ICPMS) with the total vanadium (ICPMS) ranged between 86±1% to 105±2% for well water and 90±10% to 124±2% for spring water.

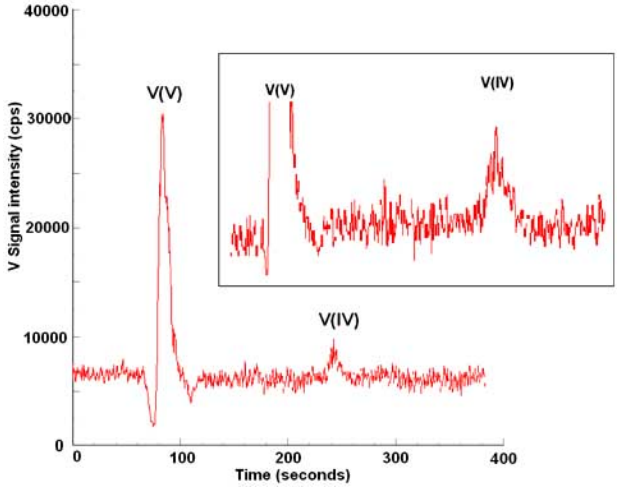

Fig. (7). Chromatogram of vanadium species in groundwater from Ash Meadows (Fairbanks Spring). Experimental conditions as in Table 1. V(IV) = 0.06 ±0.02 µg L^{-1} and V(V) = 4.3±0.1 µg L^{-1}.

Also listed in the last column of the table is the E_H calculated from the Nernst relationship shown in equation 1, where, E^0 is the standard electrode potential [8-10,34,39,40].

Equation 1

$$VO_2^+ + e^- + 2H^+ \Leftrightarrow VO^{2+} + H_2O \quad E^0 = 1016 \pm 2mV$$

$$E_{H(VO_2^+/VO^{2+})} = E^0 + 59Log\frac{[VO_2^+]}{[VO^{2+}]} - 2 \times 59 \times pH$$

For the first well, 1S Zone 1: E_H = 1016 mV + 99 mV - 894 mV = 221 ± 10 mV compared to the measured value of

Table 2. Vanadium Speciation in Southern Nevada Well Water and Spring Water

Sample	pH ±0.05	E_H ±5 (mV)	V(IV) (µg L^{-1})	V(V) (µg L^{-1})	VTot sum[a] (µg L^{-1})	VTot[b] (µg L^{-1})	Mass Balance(%)	V(V) %	E_H Calculated (mV)
Wells									
1S Zone 1	7.58	133	0.14±0.03	12.2±0.2	12.3±0.2	13.3±0.1	93±2	99±2	221±10
1S Zone 2	7.35	140	0.16±0.04	8.3±0.1	8.5±0.1	8.2±0.4	103±5	98±2	235±7
9SX Zone 2	7.76	121	0.09±0.04	9.1±0.1	9.2±0.1	10.2±0.3	90±2	99±2	210±30
9SX Zone 3	8.17	132	0.07±0.02	7.7±0.1	7.8±0.1	8.1±0.4	96±5	99±2	158±14
9SX Zone 4	7.64	128	0.12±0.03	9.0±0.1	9.1±0.1	10.1±0.2	91±2	99±2	210±9
J-12	8.23	154	0.20±0.04	19.7±0.3	19.9±0.3	22.0±0.1	91±1	99±2	148±12
J-12 Dup	8.18	154	0.24±0.04	18.7±0.2	18.9±0.2	21.9±0.1	86±1	99±2	148±7
33P Deep	8.37	172	0.14±0.04	6.9±0.1	7.0±0.1	7.9±0.3	89±4	98±2	114±8
33P Deep Dup	8.30	164	0.13±0.03	7.4±0.1	7.5±0.1	7.7±0.2	98±3	98±2	126±7
33P Int	8.34	167	0.18±0.04	9.2±0.1	9.4±0.2	10.3±0.2	91±3	98±2	119±7
32P Deep	8.49	163	0.47±0.06	82.1±0.5	82.6±0.5	78±2	105±2	99±1	132±12
32P Int	8.33	167	0.22±0.05	20.4±0.4	20.6±0.4	21.2±0.3	97±2	99±3	135±13
Springs									
Forest	8.22	165	0.05±0.01	5.7±0.1	5.8±0.1	4.6±0.1	124±2	99±1	154±20
Longstreet	8.70	138	0.06±0.03	4.3±0.1	4.4±0.1	4.9±0.1	90±10	99±3	87±20
Rogers	8.14	172	0.05±0.03	3.7±0.1	3.8±0.1	3.5±0.1	107±4	99±4	154±30
Fairbanks	8.47	165	0.06±0.02	4.3±0.1	4.4±0.1	3.6±0.1	120±5	99±4	114±20

All ± values one sigma. [a] Sum of V(IV) and V(V) using IC-ICPMS. [b] Total vanadium using ICPMS.

133. The species ratio yields 99, an order of magnitude lower than the other two wells and in order to get a value of 133 from the relationship in Equation 1, the species ratio would have to be 11, or about 10% of the vanadium would have to be found in the reduced state. Clearly, this is not the case for this water sample. On the other hand, the calculated and measured E_H values are within experimental error for about half of the sites, in most cases due to the very low concentrations of V(IV) and the associated high error. Even though the lower limits of detection for vanadium (IV) and (V) are quite good, 0.02 µg L^{-1} for V(IV) and 0.06 µg L^{-1} for V(V), the limit for V(IV) would have to be improved, if this element could be used to rigorously evaluate the relationship between the measured and calculated E_H.

4. CONCLUSIONS

A method was developed for measuring vanadium (IV) and (V) in groundwater by IC-ICPMS, using cation exchange and 1.5% v/v HNO_3 as the mobile phase. It is fast (about five minutes), selective, and sensitive, with detection limits of 0.02 µg L^{-1} for V(IV) and 0.06 µg L^{-1} for V(V). No chelating agents are involved. This combination keeps the build-up of solids in the ultrasonic nebulizer, the torch, and the entrance cones of the ICPMS to a minimum, thereby contributing to low instrument down-time. The pentavalent oxidation state of vanadium is, by far, the dominant species in all of the groundwater samples analyzed in Southern Nevada.

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