

SPECIATION AND GEOCHEMISTRY OF TUNGSTEN IN SOIL

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ABSTRACT

In order to limit the dispersive use of lead on small arms firing ranges, 5.56-mm bullets with tungsten-nylon composite material cores have been fired at a number of Army training ranges. Tungsten in bullet residues oxidizes when exposed to the atmosphere, yielding an amorphous tungsten oxide (WO_3) coating. This coating rapidly dissolves to yield the tungstate anion (WO_4^{2-}), which can migrate in saturated subsurface and surface water environments. The environmental geochemistry of dissolved tungsten species is complex, and consequently is not well characterized. Tungsten exists in most environmental matrices as the soluble and mobile tungstate anion, which can polymerize with itself and other anions, such as molybdate and phosphate, making determination of tungsten compounds important. Since the geochemical and toxicological properties of these polymer species may vary from monomeric tungstate, determination of tungstate is as critical as determination of total dissolved tungsten concentration. High performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS) has been used to determine tungsten speciation. Specifically, ion exchange chromatographic separations have been employed in investigations of tungsten leached from soil that was aged after amendment with metallic tungsten powder. Deionized water extraction of soil materials with HPLC-ICP-MS separation and detection indicated that up to approximately half of the extracted tungsten was in the form of polymers. Over 15 mg/L of soluble tungsten was measured in the extraction solution of soil aged for approximately 6 months. Further characterization experiments are in progress to elucidate the geochemical properties of the polymer species.

1. INTRODUCTION

Recently, interest in tungsten geochemistry and occurrence in groundwater has increased due to specific human toxicological events, specifically the cancer cluster located in Fallon, NV, and suspected cases in Sierra Vista, AZ and Elk Grove, CA, all related to local natural deposits of tungsten ore (Seiler, et al., 2005; Koutsospyros, et al., 2006). Additionally, industrial (e.g. tungsten carbide tools), civilian recreational (e.g. lead shotshell replacement), and military (e.g. kinetic penetrators and small arms ammunition) activities are under investigation as potential sources of tungsten to the environment (Strigul, et al., 2005; Koutsospyros, et al., 2006). Due to the potential impact to human health, the Centers for Disease Control is investigating the link of tungsten to human health in impacted areas (Seiler, et al., 2005). Tungstate is thermodynamically stable in most environmental matrices (Seiler, et al., 2005; Strigul, et al., 2005; Koutsospyros, et al., 2006), although tungsten chemistry is not limited to the soluble monomeric species, since polymerization with other common oxyanions (e.g. molybdate, phosphate, and silicate), can yield a variety of ill-defined poly-species with variable biogeochemical properties (Feigl, 1958; Seiler, et al., 2005).

Speciation of tungsten is important in toxicological and geochemical studies. Additionally, the ability to simultaneously determine concomitant analytes that may play a role in tungsten chemistry is crucial to forming a complete understanding of tungsten interactions in the environment, such as the polymerization with phosphate, which may affect sorption and mobility in soils as well as biological uptake of tungsten species. The ability to simultaneously detect various analytes can also greatly

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assist in understanding toxicological effects of tungsten. Tungsten is known to displace molybdenum in the active sites of several enzymes (Johnson, et al., 1974; Johnson and Rojagopalan, 1976). Additionally, tungstate may polymerize with phosphate *in vivo*, disrupting biological processes dependent on phosphates, such as energy production and cell signaling. Thus, the ability to simultaneously determine tungstate, molybdate, and phosphate at low levels in complex matrices will be critical in understanding tungsten biogeochemical processes.

In recent years, High Performance Liquid Chromatography (HPLC) coupled to element specific detectors, such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has proven valuable as a method of determining metal speciation at $\mu\text{g/L}$ and sub- $\mu\text{g/L}$ levels in environmental samples (Guerin, et al., 1997; Sarzanini and Mentasti, 1997; Das, et al., 2001; Huang, et al., 2002; Michalke, 2002; Bednar et al., 2004). Specifically, ion-exchange chromatography has been used successfully in speciation procedures because of the ionic nature of many metal species (Mattusch and Wennrich, 1998; Londesborough et al., 1999; Jain and Ali, 2000). The method reported in the current work is an HPLC-ICP-MS method developed to chromatographically separate and simultaneously determine tungstate, molybdate, and phosphate at sub- $\mu\text{g/L}$ to $\mu\text{g/L}$ levels.

The method has been tested on laboratory spike samples and deionized water extracts of aged tungsten metal-spiked soils. These matrices were used to test the reliability, robustness, and versatility of the method.

2. EXPERIMENTAL

2.1 Reagents

All chemicals used were of reagent grade or higher purity and used without further purification; the deionized water used had a resistivity of $18.3 \text{ M}\Omega \cdot \text{cm}$. Sodium hydroxide and sodium tungstate dihydrate was purchased from Sigma Aldrich (St. Louis, MO) and Alfa Aesar (Ward Hill, MA), respectively. Single element and mixed analyte standards for tungsten, molybdenum, and phosphorus were purchased from SPEX CertiPrep (Metuchen, NJ) and PlasmaCal (Champlain, NY).

2.2 Sample collection and preservation

All liquid samples were processed through a $0.45\text{-}\mu\text{m}$ pore-size syringe filter to obtain classically defined 'dissolved' constituents. A tungsten-containing soil was

created by adding metallic tungsten ($10 \mu\text{m}$ particles) to a Grenada Loring soil, mixing, and allowing it to age approximately six months, for the metallic tungsten to oxidize. The silty loam soil of the Grenada-Loring series (Alfilsols order) was collected from the Brown Loam Experimental Station, Loring, MS. The soil was collected with a front-end loader after the top 12 cm were removed to eliminate unwanted vegetation.

2.3 Instrumentation

Total tungsten, molybdenum, and phosphorus concentrations were analyzed directly using nebulization Inductively Coupled Plasma Atomic Emission Spectroscopy or Mass Spectrometry (ICP-AES or ICP-MS) as appropriate for the concentration ranges observed (Following modifications of EPA Methods 6010B and 6020, US EPA, 1996), using a Perkin Elmer (Wellesley, MA) Optima 3000DV or Elan 6000, respectively. Speciation samples were analyzed using an Agilent (Palo Alto, CA) 1100 HPLC interfaced to the Perkin Elmer Elan 6000 ICP-MS with a cross-flow pneumatic nebulizer. Details of the HPLC, chromatographic conditions, sample introduction system, and ICP-MS are listed in Table 1. Retention time and chromatographic peak width determined the ICP-MS dwell time and number of readings per replicate and were selected so that data were collected for the entire length of the chromatogram.

The HPLC analytical column, mobile-phase composition, flow rate, and typical injection volume are listed in Table 1. Chromatographic resolution was attained isocratically with a 20-mM sodium hydroxide mobile phase at a flow rate of 1.5 mL/min . A Dionex (Sunnyvale, CA) AMMS-III conductivity suppressor was used to remove sodium from the column effluent prior to introduction into the ICP-MS to prevent salt buildup on the interface cones. The suppressor used 18 mM sulfuric acid pumped at a flow rate of approximately 1.4 mL/min . The 100 mM sodium hydroxide mobile phase concentrate was prepared by dissolving 4.00 g of sodium hydroxide pellets into 1 L of deionized water. The molarity of the hydroxide mobile phase was adjusted on-line with deionized water by using the proportioning valves of the HPLC.

2.4 Calibration

Graphical AnalysisTM software (Vernier Software & Technology, Beaverton, OR) was used to integrate the chromatographic peaks (Bednar, et al., 2004). Linear regression analysis established the response function with calculated intercept from the reagent blank and the

series of three standard solutions (1, 10, 100 µg/L) with typical correlation coefficients >0.999 for tungstate and molybdate and >0.995 for phosphate.

Table 1: Instrumental Operating Conditions for the HPLC-ICP-MS System.

<u>HPLC</u>	
Agilent 1100	
Chemstation Software	
Mobile Phase	Vacuum Degassed
Ionization Suppressor	Dionex AMMS-III
Analytical Column	Dionex AS-11
Guard Column	Dionex AG-11
<u>Chromatographic Parameters</u>	
Elution and Mobile Phase	Isocratic, 20mM Sodium Hydroxide
Flow Rate	1.5 mL/min
Suppressor Regenerant and Flow Rate	18 mM Sulfuric Acid at 1.4 mL/min
Injection Volume	25 µL
Tungstate Detection Limit	0.4 µg/L
Molybdate Detection Limit	0.5 µg/L
Phosphate Detection Limit	5 µg/L
Total Chromatographic Time	10 min
<u>Sample Introduction</u>	
Cross Flow Nebulizer Argon Flow Rate	0.85 mL/min
<u>ICP-MS Detector</u>	
Perkin Elmer Sciex Elan 6000	
Plasma Power	1200 W
Tungsten Dwell Time	300 ms
Molybdenum Dwell Time	300 ms
Phosphorus Dwell Time	500 ms
Readings per Replicate	540
Acquisition Delay	5 s
Typical Masses Monitored	m/z 31, 95, & 182

The linear dynamic range extends to at least 1,000 µg/L for each species when using a 25-µL sample-injection and pulse-counting detection mode on the ICP-MS. Method detection limits for tungstate, molybdate, and phosphate were determined to be 0.4, 0.5, and 5 µg/L, respectively using the U.S. Environmental Protection Agency's protocol (U.S. Environmental Protection Agency, 2000).

3. RESULTS AND DISCUSSION

3.1 HPLC-ICP-MS Method

A typical chromatogram for reagent water containing 10 µg/L of each species is shown in figure 1. The bias and variability of the method was established using laboratory solutions made from separate commercially available standards having known concentrations. Concentrations of check standards at 10 µg/L for tungstate and molybdate and 100 µg/L

phosphate had a relative percent difference less than 10 % from the nominal values. The three isotopes selected for the current work are free of direct isobaric interferences from other elements. The most abundant isotopes of molybdenum and tungsten, 98 and 184, respectively, have minor interferences from ruthenium and osmium, respectively. Shown in figure 2 is an HPLC-ICP-MS chromatogram where signals from ⁹⁸Mo, ¹⁸⁴W, ¹⁰¹Ru, and ¹⁸⁹Os, and were collected from a 100 µg/L ruthenium and osmium standard. The chromatography spreads out the potential interferents due to their low solubility in the alkaline mobile phase, thereby reducing the likelihood of a significant interference. The small tungstate and molybdate peaks observed are trace contaminants in the ruthenium and osmium standard. However, to avoid the possibility of false positives, the clean isotopes were used (⁹⁵Mo and ¹⁸²W).

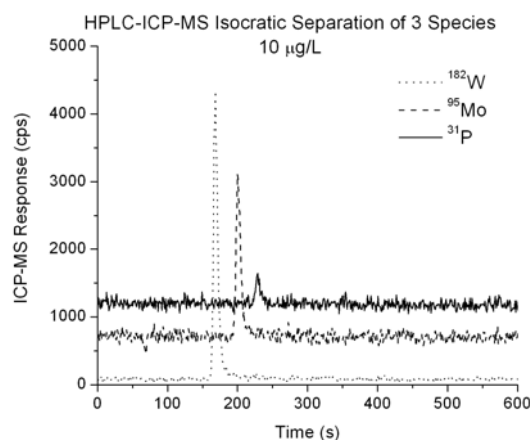


Figure 1. A typical HPLC-ICP-MS chromatogram obtained using the described method. The peaks represent a 25-µL injection of a standard containing 10 µg/L of tungstate, molybdate, and phosphate.

3.2 Water Extraction of Tungsten

The method was applied to the determination of tungstate in deionized water extracts of soil amended with tungsten metal. The water extracts were produced by shaking 1 g of air-dried ground soil with 10 mL of deionized water for 1 hour. Samples were prepared and analyzed in triplicate. The solution was filtered to 0.45 µm and diluted for analysis. Table 2 also lists the concentrations of the analytes of interest in the soil extracts determined by direct nebulization ICP-MS and by HPLC-ICP-MS. The HPLC-ICP-MS chromatogram in figure 3 shows a tailing of the tungstate peak in the tungsten-soil extract. This tail is indicative of poly-species, rather than concomitant metal ions pairing with

tungstate, as determined by monitoring the isotopes: ^{24}Mg , ^{27}Al , ^{44}Ca , ^{55}Mn , and ^{57}Fe with the ICP-MS. The data graphed in figure 4 for a separate extract sample shows that integration of the peak tail can lead to excellent mass balance of the speciation analysis with the direct quantification by ICP-AES.

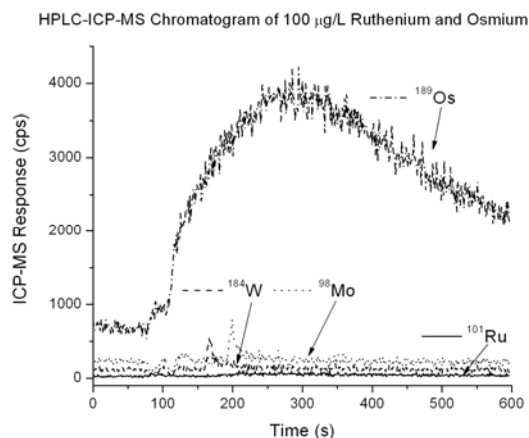


Figure 2. An HPLC-ICP-MS chromatogram obtained by monitoring m/z 98, 101, 184, and 189, showing the potential for interference from ruthenium and osmium.

Table 2: Comparison of Analyte Concentrations Using ICP-MS and HPLC-ICP-MS Techniques.

Sample	ICP-MS $\mu\text{g/L}$		
	Tungsten	Molybdenum	Phosphorus
Clean Soil*	<1	<1	35 $\pm$ 10
Tungsten Soil	133.8 $\pm$ 8.7		
	HPLC-ICP-MS $\mu\text{g/L}$		
	Tungstate	Molybdate	Phosphate
Spiked Clean Soil	10.2 $\pm$ 0.3	10.7 $\pm$ 0.3	9.4 $\pm$ 1.6
Tungsten Soil	52.48 $\pm$ 7.8†		

*ICP-MS values indicate ‘natural’ analyte concentrations in clean soil deionized water extractions.

†Significant tailing of tungstate peak observed.

A tungsten-free soil extract was also prepared by using the parent soil that had not been amended with tungsten metal. These extracts were then spiked with tungstate, molybdate, and phosphate at 10 $\mu\text{g/L}$, each, yielding percent recoveries of 102, 107, and 94 %, respectively (Table 2). The soil extracts do contain trace levels of phosphorus, approximately 35 $\mu\text{g/L}$ (Table 2), therefore the recovery reported in table 2 for the HPLC-ICP-MS analysis was corrected for this naturally present phosphorus.

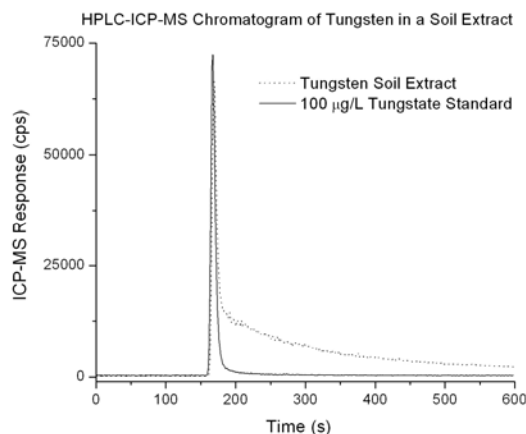


Figure 3. An HPLC-ICP-MS chromatogram of a tungstate standard overlain by tungsten-spiked soil deionized water extract, showing significant tailing, indicating poly-species were present.

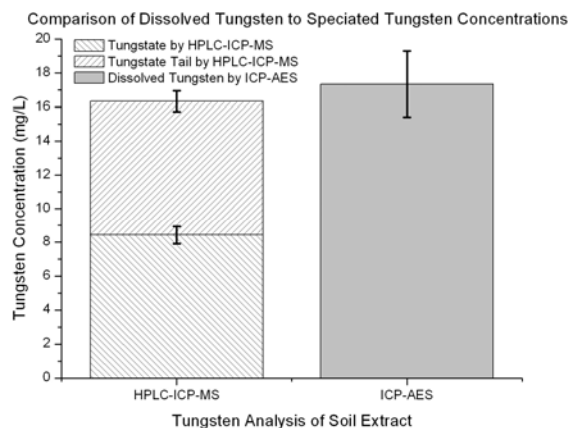


Figure 4. Comparison between dissolved tungsten concentrations determined by ICP-AES and integration of tungstate peak and tail on HPLC-ICP-MS. Error bars given are the standard deviation of three replicate soil extractions.

3.3 Geochemical Parameters

The soluble tungstate extracted from the Grenada Loring tungsten amended soil has a 2 day equilibration time before a constant concentration is observed, as shown in figure 5. The delay is critical when experimental determinations of geochemical parameters are performed. Following the method of Langmuir (1997), an effective K_d was measured for tungstate in the Grenada Loring soil of approximately 590 mL/g after a 5 hour equilibration period, the value did not change after a one week equilibration period (600 mL/g). However, when a commercially available polytungstate compound

was used, the K_d value determined changed from 730 to 370 mL/g over the same one week time period, indicating a redistribution of the polymer species.

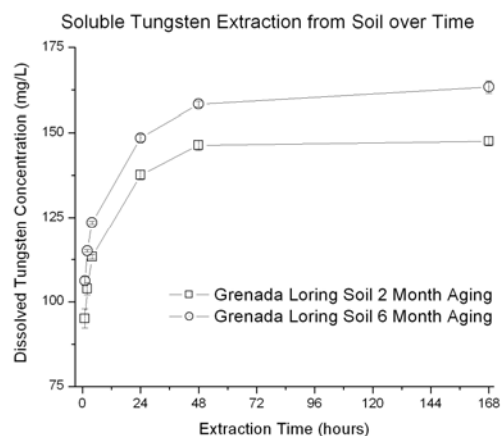


Figure 5. Time dependence of deionized water extraction of soluble tungsten compounds from the Grenada Loring soil aged for different lengths of time after amendment with tungsten metal. The error bars shown are the standard deviation of triplicate experiments.

4. CONCLUSIONS

A method is described for the speciation of tungstate, molybdate, and phosphate in aqueous matrices. Poly- and heteropoly-tungstates, as a group, can also be semi-quantitatively determined with this method, because of their polydisperse nature and non-specific interaction with the anion exchange column, by integration of the tungstate peak tail. Detection limits for the species determined ranged from 0.4 to 5 $\mu\text{g/L}$, however, the sensitivity can be increased by selection of a more abundant isotope, or increasing the integration dwell time per isotope measured. Deionized water extractions of tungsten from the Grenada Loring soil is time dependant and reaches a steady state concentration in about 2 days. The dissolved tungsten extracted has a polydisperse nature, with only about half of the soluble tungsten present as monomeric tungstate. The resultant partition coefficients determined for the soil indicate the time and species dependant nature of this geochemical parameter, with polytungstate K_d values changing by a factor of 2 over a one week equilibration period.

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otherwise noted, were obtained from research conducted under the Environmental Quality Technology Program of the United States Army Corps of Engineers by the USAERDC. Permission was granted by the Chief of Engineers to publish this information; Distribution is unlimited. The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents. The authors also thank Jeffrey Davis and Deborah Felt of the USACE for their editorial comments.

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