The determination of tungsten, molybdenum, and phosphorus oxyanions by high performance liquid chromatography inductively coupled plasma mass spectrometery

A.J. Bednar [a],*, J.E. Mirecki [a], L.S. Inouye [a], L.E. Winfield [a], S.L. Larson [a], D.B. Ringelberg [b]

[a] *U.S. Army Engineer Research and Development Center, Environmental Laboratory,*
3909 Halls Ferry Road, Vicksburg, MS 39180, United States
[b] *U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory,*
72 Lyme Road, Hanover, NH 03755, United States

Abstract

The toxic properties of tungsten compounds have recently been brought to the forefront with clusters of human cancer cases, such as in Fallon, NV. Such instances have made the determination of tungsten in natural water supplies vitally important. Tungsten exists in most environmental matrices as the soluble and mobile tungstate anion, although it can polymerize with itself and other anions, such as molybdate and phosphate. Because the geochemical and toxicological properties of these polymer species will vary from the monomeric tungstate parent, determination of tungstate speciation is as critical as determination of total dissolved tungsten concentration. Use of chromatographic separations, followed by element-specific detection is a proven technology for elemental speciation. In the present work, anion exchange chromatography has been coupled to inductively coupled plasma mass spectrometry to determine tungstate, molybdate, and phosphate species at the sub-$\mu g\,l^{-1}$ and $\mu g\,l^{-1}$ levels. The method provides quantitative determination of these species in about 10 min with the capability to simultaneously determine other oxyanion species. The method has been applied to groundwater and extracts of soils amended with tungsten powder. The water soluble tungsten in 1-h deionized water extracts after six months of soil aging was $>15\,mg\,l^{-1}$, however, only $\sim50\%$ of the tungsten was present as monomeric tungstate.
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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 [1,2]. 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 in the environment [2,3]. The potential impact to human health has made

the Centers for Disease Control investigate the link of tungsten to human health in impacted areas [1]. Tungsten metal is not found in nature, but oxyanion species of tungsten are found in a variety of minerals, which can dissolve to yield the thermodynamically stable tungstate in most environmental matrices [1–3]. The chemistry of tungstate is not limited to the soluble monomeric species, as polymerization with other common oxyanions, such as molybdate, phosphate, and silicate, can yield a plethora of ill-defined poly-species with variable biogeochemical properties [1,4].

Speciation of tungsten is important for 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. For example, it is suspected that one mode of tungstate toxicity is its replacement

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of molybdate active sites in enzymes, necessitating the need to simultaneously determine tungstate and molybdate at low levels in complex matrices [5,6]. Furthermore, polymerization with phosphate may affect tungstate sorption in soils and biological uptake and phosphorylation mechanisms.

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 for determining elemental speciation at $\mu g\,l^{-1}$ and sub-$\mu g\,l^{-1}$ levels in environmental samples [7–12]. Specifically, ion-exchange chromatography has been used successfully in speciation procedures because of the ionic nature of many elemental species [13–15]. Methods involving other mass spectrometric techniques have also been employed, but have not been used as extensively as ICP-MS [16]. Chelation ion chromatography with ICP-MS detection has been reported as a method for the determination of vanadium, molybdenum, and tungsten, however, because the three species eluted in the chromatography void volume, the method relied solely upon the element specific capabilities of the ICP-MS detector, limiting the ultimate speciation ability of the method [10]. The method reported in the current work is an ion chromatographic HPLC–ICP-MS method developed to chromatographically separate and simultaneously determine tungstate, molybdate, and phosphate at sub-$\mu g\,l^{-1}$ to $\mu g\,l^{-1}$ concentrations.

The method has been tested on laboratory spike samples, field-collected groundwater, and deionized water extracts of aged tungsten metal-spiked soils. These matrices were used to test the reliability, robustness, and versatility of the method. The results indicate that in soil with pH < 6, significant amounts (up to 50+ %) of the water-leachable tungsten is present as polymeric species, whereas neutral to alkaline water samples primarily contain monomeric tungstate.

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 MΩ cm. Sodium hydroxide, sodium phosphotungstate, tungstosilicic acid, and phosphotungstic acid were purchased from Sigma–Aldrich (St. Louis, MO). Sodium tungstate dihydrate was purchased from Alfa Aesar (Ward Hill, MA). Sodium Polytungstate was purchased from Fluka (Sigma–Aldrich, St. Louis, MO). 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 samples were processed through a 0.45 μm pore-size syringe filter to obtain classically defined 'dissolved' constituents. Four groundwaters were collected from a military installation into polypropylene 1 l bottles, stored at 4 °C and used as test solutions. Tungsten-containing soil was created by

adding metallic tungsten (<1 μm particles) to a Grenada Loring soil, mixing, and allowing it to age approximately six months to oxidize the metallic tungsten. The silty loam soil of the Grenada-Loring series (Alfilsols order) was collected from the Brown Loam Experimental Station, Learned, MS. The soil was collected with a front-end loader after the top 12 cm were removed to eliminate unwanted vegetation. Following transport to the US Army Engineer Research and Development Center at Vicksburg, MS, the soil was sieved (<1 cm) prior to use. The soil was characterized, including: texture (3% sand, 72% silt, and 26% clay), total organic carbon analysis (0.7% organic carbon), percent organic matter (1% loss on ignition), pH (6.7), and cation exchange capacity (0.108 meq. g^{-1}). The water extracts used for tungsten speciation analysis were produced by shaking 1 g of air-dried ground soil with 10 ml of deionized water for 24 h. Samples were prepared and analyzed in triplicate. The solutions were filtered to 0.45 μm and diluted with deionized water for analysis.

2.3. Instrumentation

Total tungsten, molybdenum, and phosphorus concentrations were determined directly using nebulization ICP-AES (atomic emission spectroscopy) or ICP-MS as appropriate for the concentration ranges observed (following modifications of EPA Methods 6010B and 6020) [17], using a Perkin Elmer (Wellesley, MA) Optima 3000 DV or Elan 6000, respectively. Molecular weight cut off (MWCO) centrifuge filter devices (Millipore Amicon Ultra, Billerica, MA), with nominal filter pore sizes of 5 and 50 kilodaltons (kDa), were used to separate polymeric tungsten complexes based on relative molecular size. The filtrate was then analyzed by ICP-MS or ICP-AES as above.

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, sample introduction system, and ICP-MS are listed in Table 1. The retention time and the chromatographic peak width

Table 1
Instrumentation and operating conditions for the HPLC–ICP-MS system

HPLC	
Agilent 1100	
ChemStation software	
Mobile phase vacuum degassed	
Dionex AMMS-III chemical regenerant suppressor	
Sample introduction	
Nebulization	
PE Sciex cross flow nebulizer argon flow rate	$0.85\,l\,min^{-1}$
ICP-MS detector	
PE Sciex Elan 6000 ICP-MS	
Plasma power	1200 W
Typical tungsten dwell time	300 ms
Typical molybdenum dwell time	300 ms
Typical phosphorus dwell time	500 ms
Readings per replicate	540
Acquisition delay	5 s
Masses monitored (m/z)	31, 95, and 182