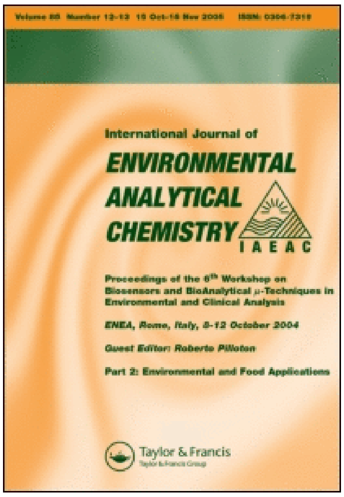

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Challenges and successes in using inductively coupled plasma mass spectrometry for measurements of tungsten in environmental water and soil samples

Jay L. Clausen[a]; Michael E. Ketterer[b]; Anthony J. Bednar[c]; Mark R. Koenig[d]
[a] US Army Corps of Engineers, Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH 03755, USA [b] Department of Chemistry and Biochemistry, Northern Arizona University, Flagstaff, AZ 86011-5698, USA [c] US Army Corps of Engineers, Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS 39180-6199, USA [d] US Army Corps of Engineers, Concord, MA 01742-2751, USA

To cite this Article Clausen, Jay L. , Ketterer, Michael E. , Bednar, Anthony J. and Koenig, Mark R.(2010) 'Challenges and successes in using inductively coupled plasma mass spectrometry for measurements of tungsten in environmental water and soil samples', International Journal of Environmental Analytical Chemistry, 90: 10, 773 — 783

To link to this Article: DOI: 10.1080/03067310903267323

URL: http://dx.doi.org/10.1080/03067310903267323

Intern. J. Environ. Anal. Chem.
Vol. 90, No. 10, 20 August 2010, 773–783

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Challenges and successes in using inductively coupled plasma mass spectrometry for measurements of tungsten in environmental water and soil samples

Jay L. Clausen[a]*, Michael E. Ketterer[b],
Anthony J. Bednar[c] and Mark R. Koenig[d]

[a]*US Army Corps of Engineers, Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, 72 Lyme Road, Hanover, NH 03755, USA;* [b]*Department of Chemistry and Biochemistry, Northern Arizona University, Box 5698, Flagstaff, AZ 86011-5698, USA;* [c]*US Army Corps of Engineers, Engineer Research and Development Center, Environmental Laboratory, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199, USA;* [d]*US Army Corps of Engineers, New England District, 696 Virginia Road, Concord, MA 01742-2751, USA*

(*Received 29 December 2008; final version received 11 August 2009*)

Military small arms ranges in the United States have been used for munitions training with tungsten rounds, which are comprised of powdered tungsten (W) pressed together with polymeric binders. As a result, W has been introduced into surface soils. The environmental and human health effects of W remain open questions. The US Army Corps of Engineers is responsible for environmental monitoring, site assessments, and cleanup of small arms ranges. This work requires routine measurements of tungsten in natural waters and soils. However, the existing sample preparation and analytical procedures were not specifically developed with W in mind for environmental analysis. Our work suggests modification of existing metal sample preparation and analytical procedures are necessary to accurately quantify W in environmental media. Our group has been actively conducting W measurements using inductively coupled plasma mass spectrometry (ICPMS), both with quadrupole and sector field ICPMS systems. We have used heavy rare earth elements and iridium as internal standards. For soils, the great majority of the W from small arms can be dissolved using acid leaching with HNO_3–H_3PO_4 mixtures; more rigorous preparations with fusion or HF digestions can also be used. In ICPMS analysis, the largest challenge involves dealing with the significant carry-over and memory of W in sample introduction systems. This ultimately limits measurement capabilities, particularly at sub-$\mu g\,L^{-1}$ levels. With careful attention to the sample and standards' matrix constituents, and proper washout time, successful analysis is possible and ICPMS is clearly the preferred technique. A commercially available fluoropolymer sample introduction system exhibits significantly improved memory characteristics.

Keywords: tungsten; soil; water; ICPMS; small arms ranges

1. Introduction

Tungsten (W) is a transition metal that has a wide variety of industrial uses. The metal has also been used in military munitions applications, including high kinetic energy

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*Corresponding author. Email: jay.l.clausen@us.army.mil

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903267323
http://www.informaworld.com

penetrators and small-calibre ammunition, the latter comprised of powdered tungsten pressed together with polymeric binders. A United States (US) Army pollution prevention initiative, the Green Army Technology (GAT) programme, encouraged the substitution of lead ammunition with W rounds, which were presumably innocuous in the environment. Due in part to rising usage of W in GAT-related applications, W consumption is now 14,000–15,000 tonnes per year, with 2200–2700 tonnes being used in military applications in 2006 [1].

Recent studies suggest W has considerably more mobility in the geochemical environment than had been previously thought [2]. Historically, W metal was thought to be insoluble and have little or no mobility in the natural environment [3–5]. The Eh-pH diagram for W in water at 1 bar [6] indicates the soluble anionic species tungstate, WO_4^{2-} (aq), dominates under oxic conditions at neutral and alkaline pHs. Under acidic conditions, mononuclear WO_4^{2-} (aq) tends to polymerise to form polynuclear species [1,7]. Studies of the W powders used in the Army's tungsten/nylon rounds revealed the particles dispersed after use of the ammunition at small-arms ranges and would readily dissolve in water and become mobilised [2,8]. The W present in unfired rounds consists of sub μm to 100 μm particles [8] pressed together in a nylon matrix; unlike lead (Pb) projectiles, the tungsten/nylon rounds have a tendency to fragment and disperse upon impact [8–10]. Once deposited into the environment, the metal particles readily become oxidised at the surface, and the oxide coatings are rapidly dissolved by surface water or in the vadose zone under relatively mild environmental conditions [11].

The US Army Corps of Engineers (USACE) is responsible for environmental monitoring, site assessments and cleanup of small arms ranges where W munitions have been used in military applications. One range, Camp Edwards, located at the US Massachusetts Military Reservation (MMR), has been the subject of a recent detailed investigation [8].

Routine measurements of W in natural waters and soils require methods suitable for high volume, low-cost applications implemented in many government, academic and commercial laboratories. Among several candidate techniques, inductively coupled plasma mass spectrometry (ICPMS) is ideally suited. ICPMS is available at thousands of laboratories worldwide; it provides very low detection limits ($\ll \mu g\,L^{-1}$), high sample throughput (>100 samples/day), low cost per elemental determination ($10–20 US in commercial ICPMS labs) and generates relatively simple mass spectra that provide positive confirmation of the presence of an element. The US Environmental Protection Agency (EPA) has approved use of ICPMS in environmental analysis of waters and solid samples (soils, sludges, sediments and industrial wastes), and has developed standard methodologies (Methods 6020, 6020A, 200.8) for generating reliable analyses through contract commercial laboratories. These methods do not cover the use of ICPMS in W determinations, largely because this element has not been identified as a concern in major environmental legislation and regulatory policies. However, with W now drawing increasing attention as an emerging constituent of interest [8,12,13], suitable ICPMS techniques are required. Several previous groups have used ICPMS in research-mode applications to determine W in waters and soils [13,14]. These studies all point to the successful use of ICPMS in W determinations, with low detection limits and minimal problems with interfering polyatomic ions.

In the present study, we have evaluated the use of ICPMS for W determination in groundwater and soil from the Camp Edwards Small Arms Ranges, using two different laboratory facilities experienced in the use of ICPMS in non-routine, research-mode applications at USACE Engineering Research and Development Center (ERDC) and Northern Arizona University (NAU). The results indicate ICPMS is inherently well suited for W determinations in environmental samples and existing environmental analytical procedures can be adapted through slight modifications for W measurements. In this paper, we summarise the major issues and challenges in the application of ICPMS to W determination in environmental soil and water samples and demonstrate that, with due diligence, ICPMS can be successfully applied to this analytical problem.

2. Experimental

2.1 *Environmental setting and sampling*

This work focuses upon environmental water and soil samples collected from the Camp Edwards Small Arms Range, located at MMR [8]. Between 2000 and 2005, over one million individual tungsten/nylon rounds containing 2035 kg W metal were fired on 12 different ranges; all of this metal was presumably released into the surface and subsurface soils at the ranges. Surface soils from berms in the ranges contain up to 2080 mg kg W^{-1}. The concentration of W and other munition constituents (copper, zinc, lead) decrease markedly with depth, with a 10-fold decrease or greater at a depth of 25 cm; nevertheless, elevated W concentrations are still evident at depths of up to 150 cm. Concentrations of W in unaffected and background soils from the general vicinity are on the order of 1.5 mg kg^{-1}. The site has poorly developed soil profiles comprised of coarse sand and gravel; the contents of clay and organic matter are very low. These conditions, along with a shallow water table (30 m), exacerbate the transport of soluble W species through the vadose zone and into the underlying aquifer. Tension lysimeters installed in the berm area exhibit extremely high concentrations ($>$100 mg L^{-1}) of dissolved W, indicating the pronounced propensity for aqueous transport of W under the site conditions.

Surface soil samples (0–5 cm) were collected from a variety of locations on the firing range; a schematic of the respective areas of interest for one example (India Range) is depicted in Figure 1. Samples were collected with the multi-increment sampling approach Ramsey and Suggs [15]. A 100-increment sample of the top 5 cm was obtained at evenly spaced locations throughout each decision unit.

Plastic syringes (1.25-cm ID), metal scoops, or a metal corer (5-cm ID) were used to collect individual increments of surface soil; each primary sample typically had 3–5 kg dry mass. Subsurface soil samples were obtained from selected locations using a bucket auger. A multi-increment, subsurface soil sample was made by combining the soils from four cores from the same depth intervals; cores were sectioned in 25-cm depth intervals. Lysimeter water samples were collected from the vadose zone within the impact berm and trough at each range. Groundwater samples were also collected from existing monitoring wells.

Lysimeter and groundwater samples were collected both as ‘field-filtered’ (0.45 μm) and unfiltered samples, and in our initial work, we compared unpreserved/refrigerated samples versus HNO_3-preserved samples [8]; these comparisons indicated the W is essentially in dissolved form and it remains stable in solution irrespective of preservation, provided the samples are promptly analysed within approximately two weeks from collection.

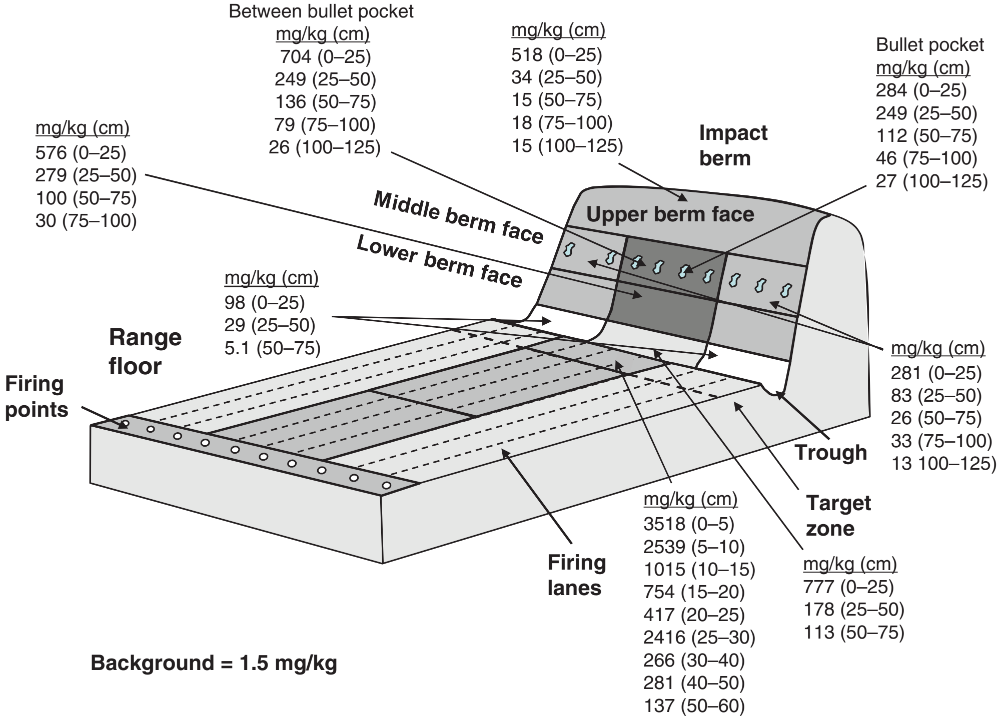

Figure 1. Construction of a typical berm depicting the targeted populations being sampled and showing concentrations of W in surface and subsurface soils at the Bravo Range.

2.2 *Subsampling and preparation of soil samples*

Soil samples were transported back to the laboratory and air-dried on aluminum-foil lined trays. Air-dried samples were passed through a 2-mm sieve, and subsequently ground using a Lab Tech ball mill (Model PM400) utilising a non-metallic agate bowl and balls. The ground portion of the samples (2–3 kg) was then homogenised and split into 1–1.5 kg portions. For analytical laboratory work, each ground sample was subsampled to produce a more workable aliquot of ~20 grams. The entire sample was spread into an elongated, flat pile on a strip of paper towel, and a subsample was removed by collecting 40–50 increments (~0.4–0.5 grams each) from random locations across the dimensions of the pile. The subsampled material was blended in a vial, and used for subsequent analysis.

A complete dissolution with HNO_3 and HF was performed as follows: approximately 0.2 grams of dried, pulverised soil were weighed to the nearest 0.1 mg into a 20 mL glass vial. Samples were placed in a muffle furnace at 450°C for two hours. The dry-ashed sample was quantitatively transferred to a 50 mL polypropylene centrifuge tube (pre-cleaned by heating at 75°C overnight after filling with 1 M aqueous HNO_3). Then 1.5 mL HF and 2.5 mL HNO_3 were added, and the tube was capped. The mixture was heated overnight (ca. 20 hours) at 75°C. After heating, the sample was diluted with water, and 0.50 g boric acid was added. The mixtures were diluted to 50 mL, and then were heated briefly in a microwave oven to dissolve all of the boric acid. Inspection of the sample solutions indicated a complete dissolution. As a simpler and safer alternative to the use of HF, other studies performed by the authors indicated the successful near-quantitative

Table 1. Comparison of ICPMS instrumentation and conditions at the two analytical laboratories.

A. ERDC

Instrumentation: Elan 6000; cross-flow nebuliser; double-pass Ryton spraychamber
Analytical isotopes: ^{182}W, ^{184}W (isobaric correction for ^{184}Os by monitoring ^{189}Os)
Internal standard: ^{159}Tb or ^{165}Ho, automated addition by online mixing
Calibration solution matrix: 0.16 M aqueous HNO_3
Standard concentrations: 0, 1, 10, 100 $\mu g\,L^{-1}$ W prepared by dilution of Spex Certi-Prep stocks
Replicates per sample: 3
Instrumental detection limit: 0.1–0.2 $\mu g\,L^{-1}$ W

B. NAU

Instrumentation: VG Axiom MC; ultrasonic nebuliser
Analytical isotope: ^{183}W
Internal standard: ^{191}Ir, manual addition with pipets
Calibration solution matrix: 0.32 M aqueous HNO_3
Standard concentrations: 0, 0.5, 1.0 $\mu g\,L^{-1}$ or 0, 1.0, 2.0 $\mu g\,L^{-1}$ W for general analysis; 0, 0.01, 0.04, 0.08 $\mu g\,L^{-1}$ W for ‘high-sensitivity’ analysis; solutions prepared by dilution of lab-prepared WO_3 and $(NH_4)_2WS_4$ aqueous stocks
Replicates per sample: 3 to 5
Instrumental detection limit: 0.1 $\mu g\,L^{-1}$ W; limited mainly by washout of ultrasonic nebulizer

dissolution of W in elevated-concentration berm soils using mixtures of HNO_3 and H_3PO_4. The HNO_3–H_3PO_4 acid mixture was developed in response to ERDC’s initial observations of systematically low W concentrations produced by HNO_3-only digests, such as implemented in EPA Method 3051. A microwave digestion procedure used at the ERDC consists of digestion of 0.5–2.0 grams pulverised sample with 8 mL HNO_3 and 2 mL H_3PO_4; following microwave heating as prescribed in EPA Method 3051, the mixture is filtered and diluted to 100 mL with deionised water. ERDC has also developed a similar HNO_3–H_3PO_4 acid digestion performed in a hot block digester. A non-microwave HNO_3–H_3PO_4 dissolution was used at NAU; the NAU method utilised 0.2 mL H_3PO_4 and 1.0 mL HNO_3 for a 0.2 g sample aliquot; the material was dry-ashed, digested at 75°C for 20 hours in a 50 mL polypropylene centrifuge tube, and diluted to 50 mL with deionised water.

2.3 *ICPMS analysis*

The ICPMS measurements described herein have been conducted at two different laboratories. Different parameters and conditions applicable to each lab are listed in Table 1. At the ERDC-EL, a Perkin Elmer ELAN 6000 quadrupole ICPMS system was used with the factory-supplied Ryton plastic spray chamber and fixed cross-flow nebuliser. At NAU, a VG Axiom MC sector-field ICPMS system was used; the Axiom was mainly used with a CETAC U- 5000AT ultrasonic nebuliser (CETAC, Omaha, NE); in more recent work (see below) the CETAC ultrasonic nebuliser has been replaced with a desolvating micro-nebuliser system (APEX HF, Elemental Scientific, Omaha, NE). The APEX configuration consisted of a self-aspirating (400 $\mu L\,min^{-1}$) concentric glass nebuliser, a heated (140°C) fluoropolymer spray chamber and Peltier-cooled (2°C) condenser.

3. Results and discussion

3.1 Detection limits for waters and soils

Detection limits for aqueous samples were determined for the ERDC laboratory's quadrupole ICPMS by analysing a 0.1 μg L^{-1} W standard eight times in sequence; the detection limit was taken as three times the standard deviation of the W concentration obtained from the eight measurements. This procedure resulted in a calculated detection limit of 0.04 μg L^{-1} W, with a resulting quantitation limit estimated at 0.04 μg L^{-1} W, which corresponds well with the instrument's performance for determination of other elements. Detection limits were not significantly different for measurements of 182W or 184W. These limits are obtained for clean, synthetic laboratory solutions, and as described below, are dramatically affected by instrumental wash times and prior sample analysis history. 'Unknown' samples that are not sufficiently diluted and have W concentrations >1000 μg L^{-1} can require 30 to 90 minutes of rinsing to return the instrument to baseline performance levels. This variable washout time is influenced by the W species present in the samples, and certain polymeric forms can take much longer to rinse out than monomeric tungstate.

In 2006 and 2007, the NAU laboratory analysed W in water samples as 11 different analytical batches. For nine batches, where high-concentration samples were known or anticipated, calibration standards of 0, 0.5 and 1.0 μg L^{-1} W were prepared in 0.32 M aqueous HNO_3 media. Under these conditions, detection limits (the concentration equivalent to three times the standard deviation of the calibration blank response) ranging from 0.02 to 0.2 μg L^{-1} W were achieved. Two batches were analysed under 'high-sensitivity' conditions, for use with samples expected to contain low or 'background' levels of W. For high sensitivity conditions, the ICPMS instrument was specifically tuned with the calibration blank to obtain maximal signal of the iridium (Ir) internal standard, and the standard concentrations were 0, 0.01, 0.04 and 0.08 μg L^{-1} W in 0.32 M aqueous HNO_3, thus limiting the exposure of the sample introduction system to lengthy exposure of high W concentrations. Detection limits for the high sensitivity batches were 0.003 and 0.004 μg L^{-1} W. It is noted the detection limits are generally constrained by the W signal from the calibration blank arising from residual W in the sample introduction system; thus, detection limits vary depending upon the recent history of W concentrations in introduced standards and samples. Moreover, the ultrasonic nebuliser system has a complex sample flow path with large glass surface areas, and as such is not well suited for rapid washout; rinse times of one hour or more were sometimes needed following undiluted samples $\gg$1 μg L^{-1} W in order to restore the W signal to levels approaching the initial response of the calibration blank. The NAU lab also conducted W measurements in soil digests prepared using the HNO_3/HF and HNO_3/H_3PO_4 procedures described previously. Both types of digests require a 50-fold dilution prior to ICPMS analysis in order to limit the dissolved solids content of the analysed solutions. Using total procedural blanks diluted in the same manner, detection limits of 0.5 and 0.3 μg g^{-1} were achieved for W in soil samples using the HNO_3/HF and HNO_3/H_3PO_4 procedures, respectively. The soil detection limits are also constrained (as noted above for water analysis) by the unfavourable washout characteristics found with higher concentration standards and/or samples.

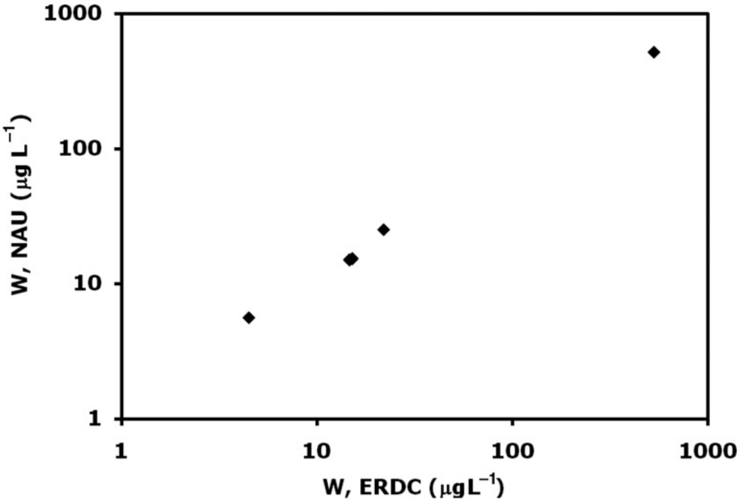

Figure 2. Interlaboratory comparison of results for W determination in water by quadrupole ICPMS (ERDC) and sector field ICPMS (NAU).

3.2 *Interlaboratory comparison of results for W in water samples*

Natural water samples, consisting of both groundwater and soil pore-water samples, were split and analysed independently at the ERDC and NAU labs. These samples span many orders of magnitude W concentration, from <1 μg L^{-1} for some baseline natural waters to >100,000 μg L^{-1} for soil pore-water samples collected from the vadose zone underlying the range berm soils. A comparison of W standards was performed by the ERDC and NAU laboratories (Figure 2), indicating excellent agreement between the two laboratories. It is apparent that both quadrupole and sector field ICPMS are useful for W analysis over a wide range of concentrations.

3.3 *Interlaboratory comparison for W in soils: HNO_3/HF and HNO_3/H_3PO_4 procedures*

The HNO_3/HF and HNO_3/H_3PO_4 dissolution procedures were compared for 14 soil samples; the results of this comparison are shown in Table 2. These results are described by linear relationship as follows: $[HNO_3/H_3PO_4] = (0.783 \pm 0.019) * [HNO_3/HF]$, $r^2 = 0.985$. The intercept term is not significant at the $p = 0.10$ level. These results suggest the great majority of W is dissolved by the HNO_3/H_3PO_4 dissolution procedure, but a minor portion is refractory and can only be recovered with complete dissolution. We note that the NAU procedure used relatively mild (75°C) heating conditions; other work done at ERDC indicates comparability between microwave HNO_3/H_3PO_4 dissolution and X-ray fluorescence spectrometric W measurements. This could arise from the much higher temperatures achieved by pressurised vessel heating in the microwave digestion. It is prudent to conduct additional work in this area, since W in soil is a concern at Camp Edwards as well as at other military small arms range sites in the United States.

Table 2. Intralaboratory comparison of two different dissolution methods for the determination of W in soils by sector field ICPMS using HNO_3/HF and HNO_3/H_3PO_4 procedures.

Sample	W, HNO_3/HF ($\mu g\, g^{-1}$)	W, HNO_3/H_3PO_4 ($\mu g\, g^{-1}$)
1	3.7	3.1
2	321	294
3	10.6	9.0
4	588	474
5	208	187
6	207	207
7	310	282
8	471	423
9	381	250
10	35.7	29.9
11	154	161
12	576	400
13	30.6	24.1
14	1470	1130

It is also noted there is a lack of soil standard reference materials certified for W in either naturally occurring or anthropogenically derived forms. As part of this work, W was determined in two materials using the HNO_3/HF dissolution procedure; 2.5 and 80 $\mu g\, g^{-1}$ W were found in NIST soil SRM's 2709 and 2710. The corresponding uncertified 'recommended' values are 2 and 93 $\mu g\, g^{-1}$ W, respectively. Though this comparison is relatively good, the emerging importance of W as a soil (and water) constituent of concern mandates development of better certified reference data and interlaboratory check samples.

3.4 *Performance of the APEX HF fluoropolymer sample introduction system with SF-ICPMS*

Both the EDRC and NAU labs have noted significant difficulties in routine W analysis by ICPMS due to memory effects in the sample introduction system. Different rinse procedures have been attempted, with no apparent advantage being found over time-consuming rinsing with 0.32 M aqueous HNO_3. However, the NAU lab has recently installed an APEX HF sample introduction system. The system is described in detail elsewhere [16].

The Apex HF uses a high-purity fluoropolymer flow path to provide resistance to hydrofluoric acid. Though the environmental sample data reported herein were acquired with the ultrasonic nebuliser system, we have briefly investigated the suitability of the APEX HF for routine W analysis. An experiment was conducted with a series of W standards (0, 0.01, 0.05, 0.2, 1.0, 5.0 $\mu g\, L^{-1}$) in 0.32 M aqueous HNO_3 media; all contained 1.0 $\mu g\, L^{-1}$ as an internal standard. The APEX system was first flushed with 0.32 M aqueous HNO_3 heated to 75°C; then the W standards were run in order of increasing concentration; thereafter, the 5.0 $\mu g\, L^{-1}$ standard was introduced continuously for 15 minutes. Subsequently, the 0 $\mu g\, L^{-1}$ calibration blank was reintroduced and the

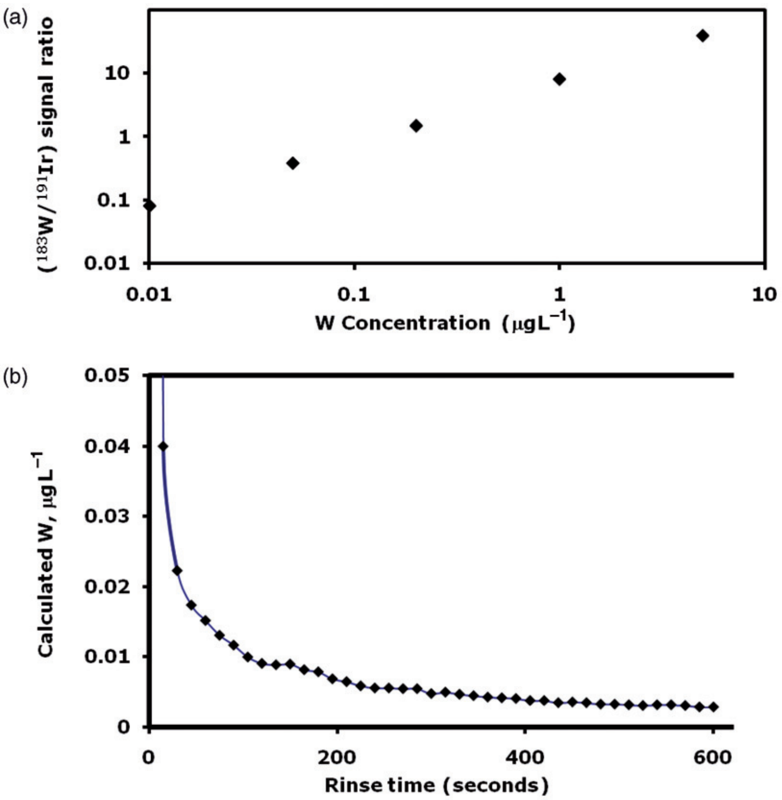

Figure 3. Calibration curve (A) and washout behaviour (B) for the determination of W with sector field ICPMS using the APEX HF fluoropolymer sample introduction system. The data collection was initiated at $t = 0$ defined as the point in time when the sample arrived at the nebuliser tip. The first 15 second integration (not shown) resulted in concentration of 0.62 μg L^{-1} W found in the calibration blank.

washout behaviour monitored over a 10 minute timeframe. The resulting calibration curve and washout profile are depicted in Figure 3. It is evident that the calculated concentration in the calibration blank decreases to 0.02 μg L^{-1} within 30 seconds and is less than 0.01 μg L^{-1} after two minutes before reaching a quasi-plateau of 0.003–0.004 μg L^{-1}. This is in contrast to the ultrasonic nebuliser, which in a similar experiment required more than one hour washout to decrease the calibration blank-equivalent concentration to 0.01 μg L^{-1}. While even the APEX system still does not reach the calibration blank's original W signal level within the 10 minute timeframe depicted in Figure 3, the behaviour indicates there would be little problem with utilising an automated rinse time of 2–3 minutes for most analytical circumstances.

3.5 *Tungsten concentrations at Bravo Range, Camp Edwards*

The methods described above were applied in the analysis of soil and water samples from Camp Edwards [8]. The W concentrations in surface and subsurface soils for a representative berm (Bravo Range) are depicted in Figure 1. Thirty-seven surface soil samples (0–5 cm) were collected from 14 separate sampled populations. The concentrations follow an expected pattern, with the highest mean W levels (1030 $\mu g\,g^{-1}$) observed near the bullet pockets. The second highest W concentration based on the mean were observed in the trough area (549 $\mu g\,g^{-1}$), followed by the lower berm (498 $\mu g\,g^{-1}$), upper berm (369 $\mu g\,g^{-1}$), target (95 $\mu g\,g^{-1}$), range floor (26 $\mu g\,g^{-1}$), and firing point (5.0 $\mu g\,g^{-1}$). Concentrations at the firing point approach the geochemical background of $\sim$1.5 $\mu g\,g^{-1}$. Subsurface profiles indicate sharp decreases in W concentrations with depth; nevertheless, obviously elevated W levels are present down to at least 125 cm depth. Lysimeter samples revealed W concentrations ranging from non-detect to 400,000 $\mu g\ L^{-1}$ with W found in groundwater up to a level of 560 $\mu g\ L^{-1}$ [8].

4. Conclusions

As illustrated in our work, ICPMS is a well-suited, lab-based technique for the determination of W in environmental soils and waters, both at naturally occurring and elevated levels. ICPMS provides detection limits for W in waters well below any possibly anticipated maximum contaminant levels, and detection limits are sufficient for the determination of geochemical baseline W concentrations in soils. Both quadrupole and sector field ICPMS are wellsuited, with no strong advantage noted for the latter, more sensitive but more complex technique. Dissolution methods for routine determination of W in soils deserve additional attention, and there is a clear need for high-quality W-certified reference soils at baseline and elevated levels; ideal elevated soil SRM's would contain W in physico-chemical forms emulating anticipated environmental species. The largest pragmatic problem in applying familiar ICPMS methodologies to W analysis is this element's persistence in many sample introduction systems; the use of a specialised desolvating fluoropolymer system significantly improves the washout situation.

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