

Accurate Quantification of Tungsten in the Environment

A Comparison of Analytical Methods

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Tungsten: an Emerging Contaminant of Concern

Tungsten (W) has been used by the military since 1999 as an alternative to lead (Pb) in military ammunition because it is theoretically more environmentally benign. However, the very characteristic that makes tungsten attractive as an alternative in military ammunition, its very low solubility, also makes it difficult to accurately quantify in environmental samples.

While tungsten has very low solubility, it is of course not entirely insoluble, and over time, especially in alkaline environments, it will slowly leach into soil and groundwater. Elevated tungsten concentrations in several drinking water aquifers has led to growing concerns about contamination and a growing interest in analytical techniques to accurately quantify it in environmental samples.

Once fully dissolved and properly chemically preserved, tungsten is fairly stable in solution, but many typical soil digestion techniques are insufficiently robust to fully extract tungsten from the matrix. In fact, in the analysis of actual environmental samples, it appears to be necessary to use a relatively extensive digestion of the sample with an acidic solution that includes hydrofluoric acid (HF) prior to analysis by ICP-MS.

Soil Preparation Methods

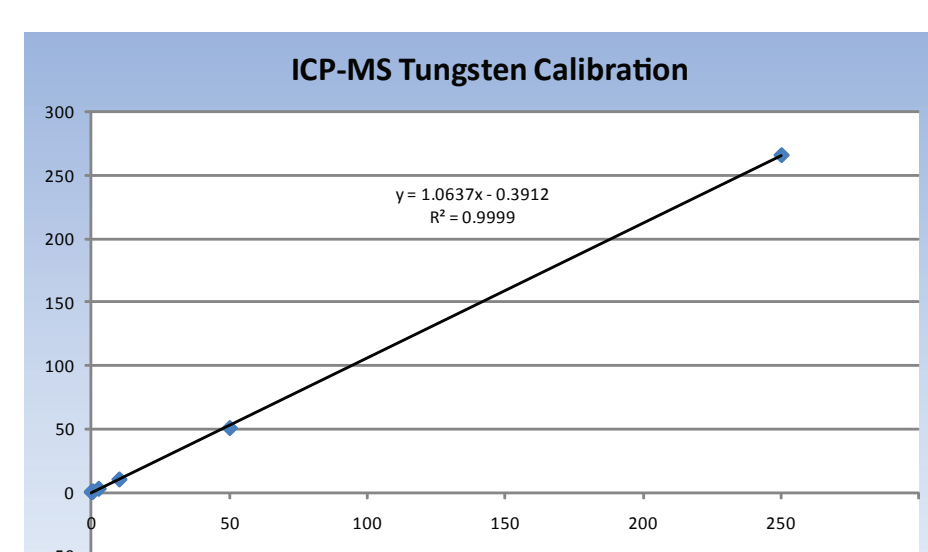
The sample preparation methods used are modifications of EPA Methods 3051 and 3052. We weighed the soil samples into Teflon® TFE digestion bombs, added spiking solution where appropriate, and then added the various acids.

Three different combinations of acids were tested: nitric acid (HNO₃) only; HNO₃ and hydrochloric acid (HCl); and HNO₃, HCl, plus hydrofluoric acid (HF). The TFE digestion bombs were then sealed and placed in an oven at 130 °C for at least eight hours.

ICP-MS Instrument Calibration

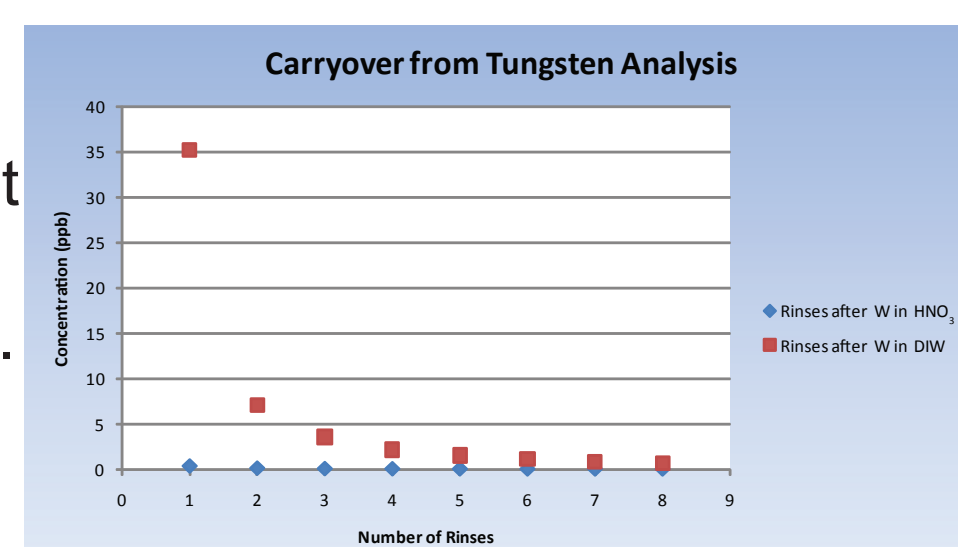
We calibrated the ICP-MS by applying weighed linear regression to 8 calibration points.

The instrument response was linear from 0.01 µg/L to 250 µg/L.



Carryover or Memory Effects of Tungsten

The poor solubility of tungsten is illustrated when we serially diluted a tungsten standard solution with reagent water. We compare this to tungsten recoveries in an acid-preserved spike mixture of the same concentration. Note the effect of preservation on instrument carryover.



Limits of Detection and Quantification

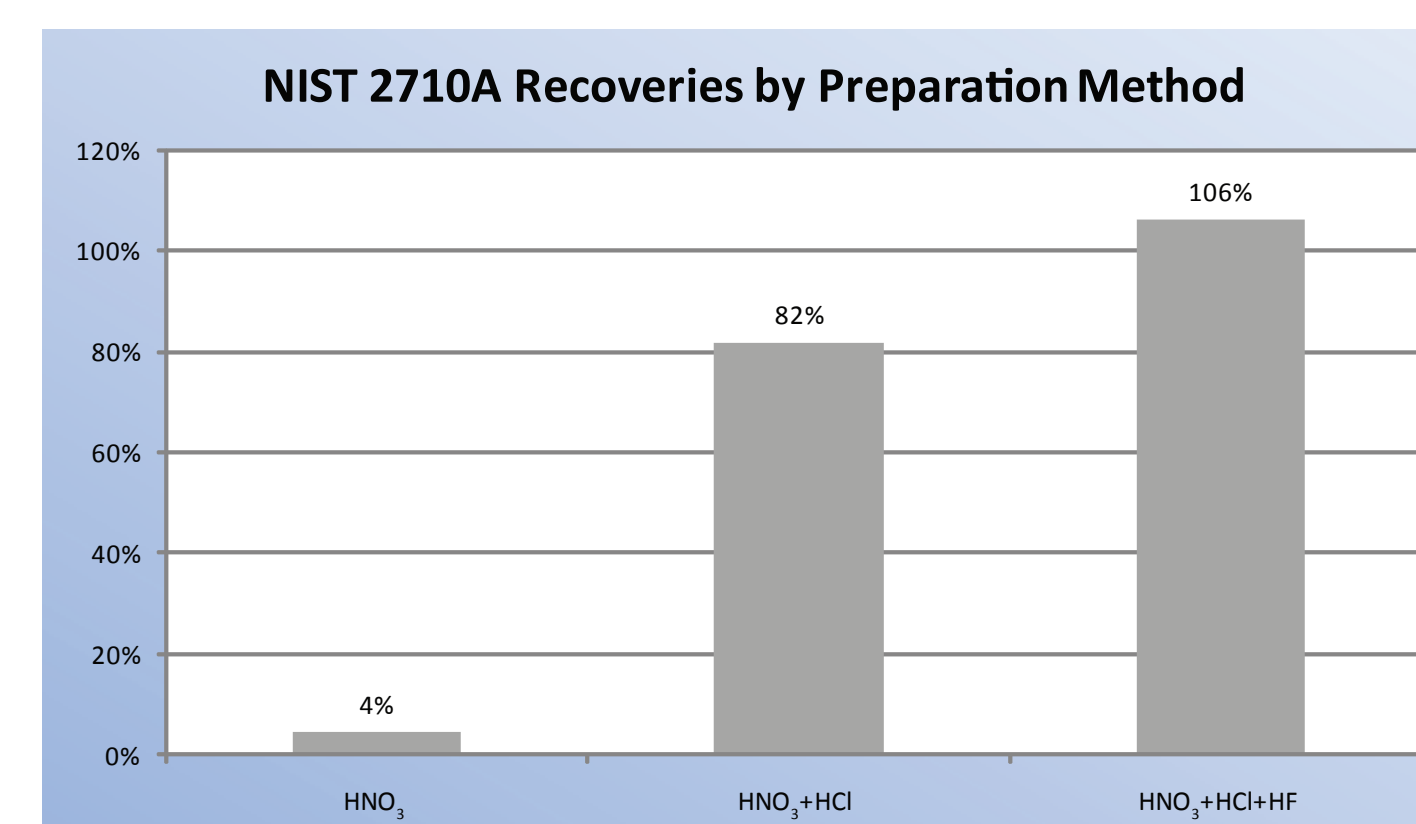
Low detection limits are essential to quantify low-level concentrations in environmental samples, monitor for minor concentration changes, and accurately establish trends.

A tungsten method detection limit (MDL) of 0.005 µg/L was established for water samples, with an associated limit of detection (LOD) of 0.010 µg/L and a limit of quantitation (LOQ) of 0.017 µg/L.

For soil samples, an MDL of 0.025 mg/kg was determined based on the water MDL.

Analysis of a Standard Reference Material

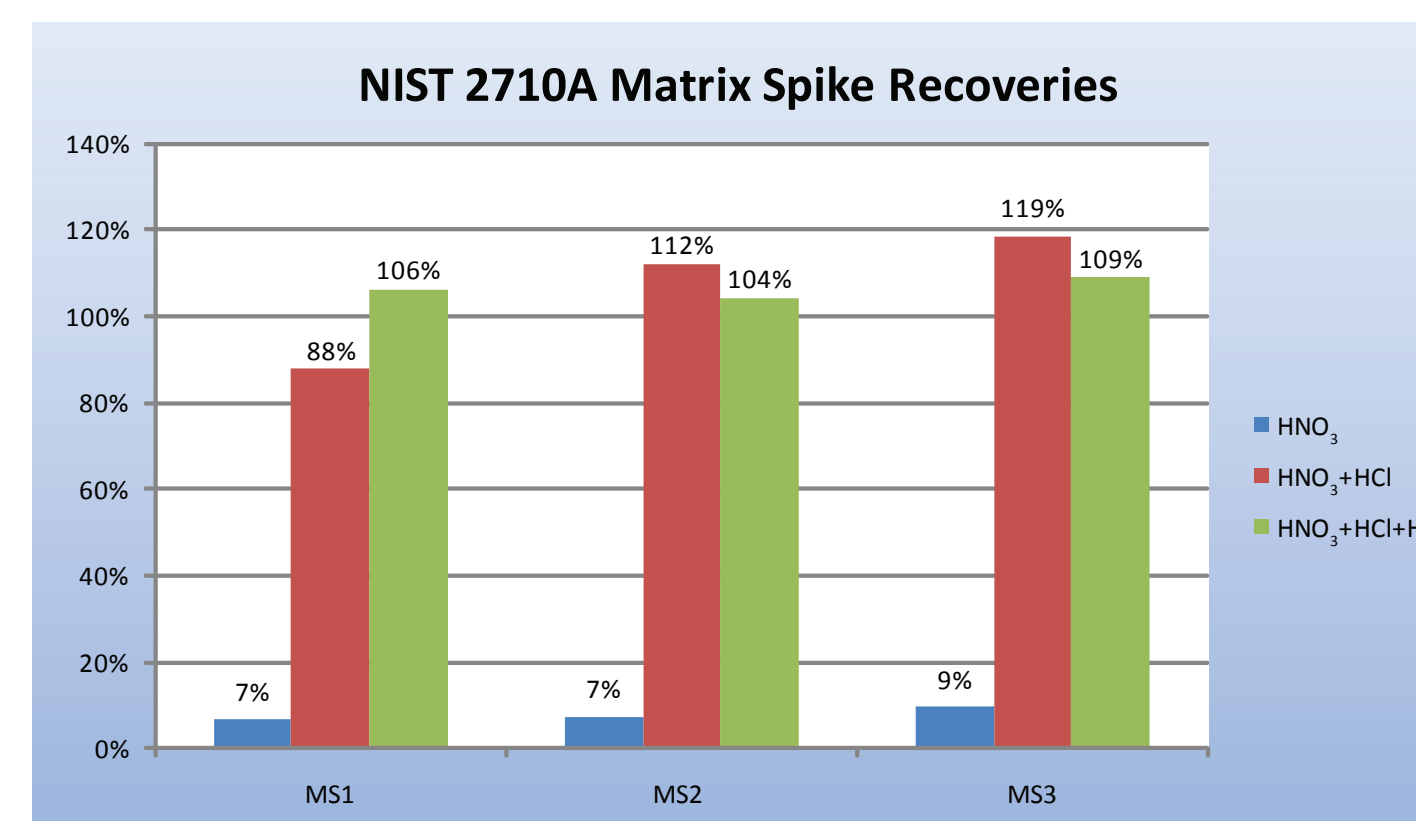
A comparison of the analytical results for Standard Reference Material (SRM) NIST 2710A, a Montana soil with elevated trace metals concentrations, after each of the preparation methods described above.



NIST 2710A has an informational (as opposed to certified) tungsten concentration of 190 mg/kg. Certified values for tungsten in soil reference materials are exceedingly rare. These results clearly demonstrate that the digestion that includes HF is superior to the other methods.

Matrix Spikes of the Standard Reference Material

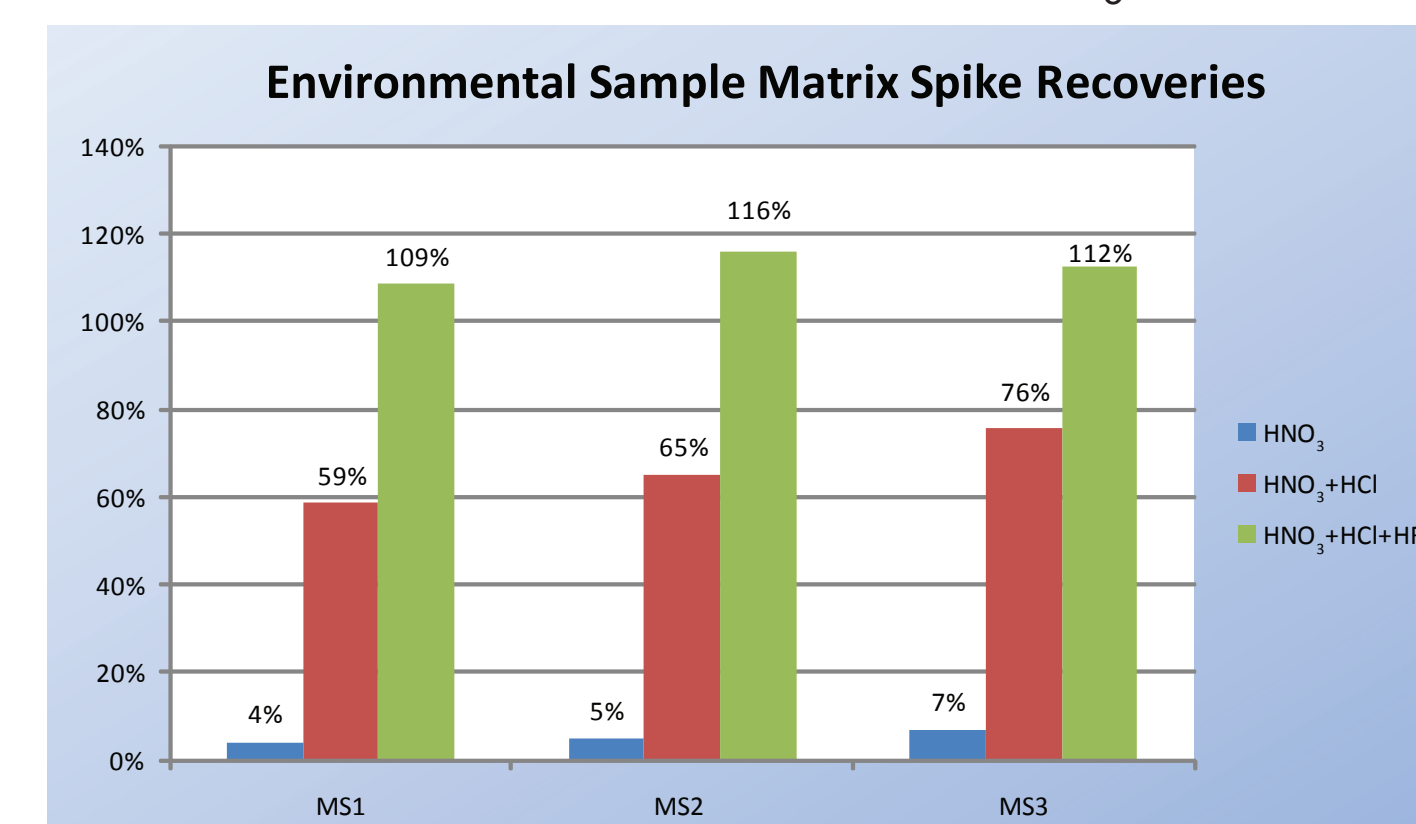
We used a Method of Standard Additions (MSA) curve to evaluate the efficiency of the three digestion methods. We used an aqueous tungsten standard to spike a matrix of SRM NIST 2710A.



The samples were spiked with 50 mg/kg, 100 mg/kg, and 200 mg/kg. The tungsten spike appears to have adsorbed to the soil and was not efficiently solubilized by the HNO₃ only digestion or the HNO₃ + HCl digestion.

Matrix Spikes of an Environmental Sample

Additionally, we analyzed a soil sample from northern California by all three methods. We measured concentrations of 0.10 mg/kg from the HNO₃ only digestion, 0.16 mg/kg from the HNO₃ + HCl digestion, and 1.12 mg/kg from the HNO₃ + HCl + HF digestion.



The HNO₃ only and the HNO₃ + HCl digestion methods produced significantly lower results for the soil sample than the digestion including HF.