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EVALUATION OF ANALYTICAL METHODS TO ADDRESS TUNGSTEN SPECIATION

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ABSTRACT

Tungsten in solution may exist as a wide variety of species depending on concentration, pH, and aging time. Despite a substantial number of studies on this topic, the speciation of tungsten in aqueous solutions is still not completely understood. To address issues of fate, transport and potential bioavailability, it is necessary to be able to assess the speciation of tungsten in environmental systems. This study investigates the use of Laser Desorption/Ionization mass spectrometry combined with a Time-of-Flight mass analyzer (LDI-TOF) as well as Raman spectroscopy as potential techniques in speciation studies. Raman spectroscopy has been successful in identifying the dominant species under a narrow range of conditions. The ultimate goal is to extend the range of conditions and concentrations while also identifying subordinate species.

KEYWORDS: Tungsten speciation, Environmental, LDI-TOF, Raman.

1. INTRODUCTION

Tungsten (chemical symbol W) has been used extensively in various applications including lighting applications, welding electrodes, tool steels, hard metal (tungsten carbide), super-alloys, x-ray tubes, glass-to-metal seals, solar energy devices, electrical contacts, electron emitters, golf club components, darts, and fishing weights. It has recently been touted as a replacement for lead in ammunitions for civil and military uses. The increasing use of tungsten has resulted in its widespread release into the environment. Previous research has shown that once released into the environment, tungsten heavy alloys (WHA) and composites release substantial amounts of W into the soil solution resulting in changes in the soil chemistry and microbiology (pH, dissolved oxygen, soil respiration, plant and earthworm toxicity) (Dermatas *et al*., 2004). In 2002, tungsten was recommended for toxicological and carcinogenesis studies by the National Center for Environmental Health of Centers for Disease Control and Prevention (ATSDR, 2003). Furthermore, in April 2008, the United States Environmental Protection Agency (USEPA) added tungsten to the list of emerging contaminants. However, very little information exists on tungsten toxicological effects, though preliminary studies indicate that these effects may be related to speciation. Tungsten exists as a wide variety of species in solution depending on concentration, pH, and aging time. Monotungstate, WO_4^{2-}, undergoes several polycondensation reactions forming polyoxotungstates. Tajima investigated the effect of polyoxotungstates on biological and biochemical systems. He reported that polyanionic species could be responsible for the observed biological effects including the inhibition of several anion-sensitive enzymes that could result in gene damage in microorganisms (Tajima, 2003). Recent studies by Strigul *et* *al.* (2008) indicate a significant difference in acute toxic responses by fish when exposed to polyoxotungstates compared to exposure to monomeric tungstate under similar conditions. The acute toxicity of metatungstate to *Poecilia reticulate* appears to be 4-6 fold larger than the tungstate toxicity (expressed in tungsten mg l^{-1}).

Despite a substantial number of studies on this topic, spanning several decades and featuring a wide variety of techniques, the speciation of tungsten in aqueous solutions is still not completely understood. This is largely due to the extremely slow kinetics of some of the condensation reactions and the poorly understood impact of concentration and time on speciation. It is agreed upon that at alkaline pH >10, monomeric WO_4^{2-} is the only species in solution. It has also been reported that at concentration values < 5 $x10^{-5}$M, no polyanions are formed (Ng and Gulari, 1984). However, differences in characterization techniques employed have often resulted in different conclusions adding to the confusion on the nature of the polyanionic species. For example, paratungstate A, the predominant species present in unaged samples between pH 5 and 7, was originally believed to have the formula $HW_6O_{21}^{5-}$ (Jander *et al.*, 1929). This position was upheld by many subsequent reports. Sasaki (1961) considered $W_7O_{24}^{6-}$ as a possible formula but ruled it out due to "better fit" to the experimental data of the $HW_6O_{21}^{5-}$ formula. Currently, $W_7O_{24}^{6-}$ is widely accepted as the correct formula for paratungstate A. Cruywagen and Van der Merwe (1987) have proposed, however, that the species $[W_6O_{20}(OH)_2]^{6-}$ exists, but is actually a minor unstable species that could attain only a maximum of 11% total tungsten in solution. Various techniques, including electrometric and conductometric titrations, spectrophotometric measurements, Glauber-salt cryoscopy isomatrix electromigration, proton magnetic resonance (PMR), and potentiometric and calorimetric titrations, have been used for the characterization of tungsten-water interaction products. Nuclear magnetic resonance (NMR), electrospray ionization mass spectrometry (ESI-MS) and Raman spectroscopy have also been used in recent studies. A Raman study by Shijun *et al*. (1998) presented a detailed analysis of the predominant species in solution at varying pH using very high concentrations of sodium tungstate. They successfully assigned Raman lines for the WO_4^{2-}, paratungstate A and paratungstate B species and suggested possible lines for the metatungstate species. In addition to the established predominant species, most new studies have also acknowledged the possibility of the existence of various low concentration species and metastable species, some of which might have been previously detected but discarded as non-probable. Although WO_4^{2-} is agreed upon as the only species present at pH >10, some studies have proposed the existence of a dimeric species $W_2O_7^{2-}$ in the pH range from 10 to 7 or even at lower pH. Chojnacka (1971) reports that this species could represent as much as 4.5% to 13.3% of the total amount of W in 0.01M and 0.02M samples, respectively and up to 20% in 0.05M samples. Ng and Gulari (1984) suggested the existence of a $[W_{24}O_{72}(OH)_{12}]^{12-}$ species in aged samples. Hastings and Howarth (1992) identified six metatungstate species and five metastable anions which are believed to slowly convert to metatungstate $(\alpha\text{-}[H_2W_{12}O_{40}]^{6-}$. They also proposed the existence of W_{11} species and provided a detailed scheme which Cruywagen (2000) adapted. Thermodynamic values of formation presented thus far (Cruywagen *et al.*, 2000; Smith *et al.*, 1987) are generally limited to certain species and are obtained under narrow ranges of conditions that limit severely their applicability. This accounts for the absence of tungsten equilibrium data in current equilibrium modeling software.

To address issues of fate, transport and potential bioavailability, it is necessary to be able to qualitatively and quantitatively assess the speciation of tungsten in environmental systems. In a recent study, Bednar *et al*. (2007) investigated the possibility of using an HPLC-ICP-MS technique for detection and characterization of tungsten species in aqueous samples. Their method was successful in quantitative detection of monomeric species. However, while the detection of polyoxotungstates as a group was achieved, the quantitative measurement of total polymeric species was only partially successful. The authors also showed that aqueous samples extracted from contaminated soils could contain polymeric species as much as fifty percent of the total tungsten concentration. The method was however unable to resolve and identify the different polymeric species present making it inapplicable for full qualitative/quantitative analysis.

Previous studies (Ogundipe, 2006) have shown the limitations of Fourier-transform infrared spectroscopy (FTIR) and ion chromatography-mass spectrometry (IC-MS), which relate to the weak signals of tungstate species in the IR region and the decomposition and formation of polytungstates in the MS cone. FTIR analyses of tungsten salt solutions suggest changes in molecular and bond structures of tungsten species in samples aged for 6 months. This current effort employs the use of Raman spectroscopy as well as Laser Desorption/Ionization mass spectrometry combined with a time-of-flight mass analyzer (LDI-TOF). Raman spectroscopy has been successful in identifying the dominant species under a narrow range of conditions. LDI-TOF makes use of the absorption of laser light by a solid sample layer. Preliminary studies using these two methods show promising results in the analyses of tungsten species.

2. MATERIALS AND METHODS

2.1 LDI-TOF

The general setup of LDI ion sources is comparatively simple (Figure 1). The pulse of laser light is focused onto a small spot (typically 0.05-0.2 mm in diameter). Variable beam attenuation in the laser optical path is employed to control the irradiance. LDI ion sources are generally operated at ambient temperature. The energy uptake upon laser irradiation causes evaporation and ionization of the sample. When combined with a time-of-flight (TOF) mass analyzer, the latter technique is capable of producing mass spectra of very large molecules, especially synthetic and biopolymers (proteins and nucleic acids), of up to about 100,000 u molecular mass. This has made LDI indispensable to biochemistry, but the technique has only recently started being applied to small molecules and inorganic materials. LDI-TOF mass spectrometry, given the right conditions, is a very sensitive analytical technique, requiring a sample load of about 1 microgram. The ionization method is very “soft”, that is, a molecular ion is generally present and little fragmentation (daughter-ion formation) occurs, even with very large molecules. In addition, very little sample preparation is necessary: all that is needed is a few microliters of solution deposited on a stainless steel plate and allowed to dry. In an effort to shed light on the tungsten speciation in aqueous solutions, LDI analysis was performed on a Micromass TofSpec-2E mass spectrometer using 100 mg l^{-1} (W) freshly made solutions of three tungsten salts - sodium tungstate ($Na_2WO_4.2H_2O$), sodium metatungstate ($3Na_2WO_4.9WO_3.xH_2O$) and ammonium paratungstate ($(NH_4)_{10}H_2(W_2O_7)_6.xH_2O$). The pH of the solutions was not adjusted. In each case, a 1 µL drop of analyte solution was allowed to dry on the LDI plate, yielding 1µg solid sample to be exposed to the laser.

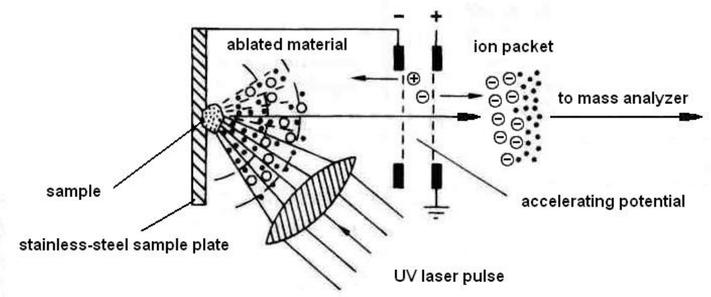


Figure 1. Schematic of a laser desorption ion source

2.2 Raman Spectroscopy

The Raman spectroscopic analyses of three pure salts of tungsten - sodium tungstate, sodium metatungstate, and ammonium paratungstate - were performed to obtain pure spectra of the three major tungsten species. The spectra were obtained using a Nicolet Almega XR Dispersive Raman spectrometer by Thermo Scientific. The samples were held for analysis in 10mm NMR tubes. Based on previous test runs, it was determined that the active region for the tungsten species is between 1050 cm^{-1} and 150 cm^{-1} consequently the analyses were limited to this region.

3. RESULTS AND DISCUSSION

3.1 LDI-TOF

Negative-ion LDI produced only singly charged ions, as evidenced by the 1 mass unit spacing between neighboring tungsten isotopic peaks. All clusters of peaks corresponded to tungsten species and displayed the characteristic tungsten isotopic patterns. The three tungstates subjected to LDI display distinctly different mass spectra. The spectra of sodium metatungstate and ammonium paratungstate are much richer, reflecting the tendency of tungsten to form polymeric ions.

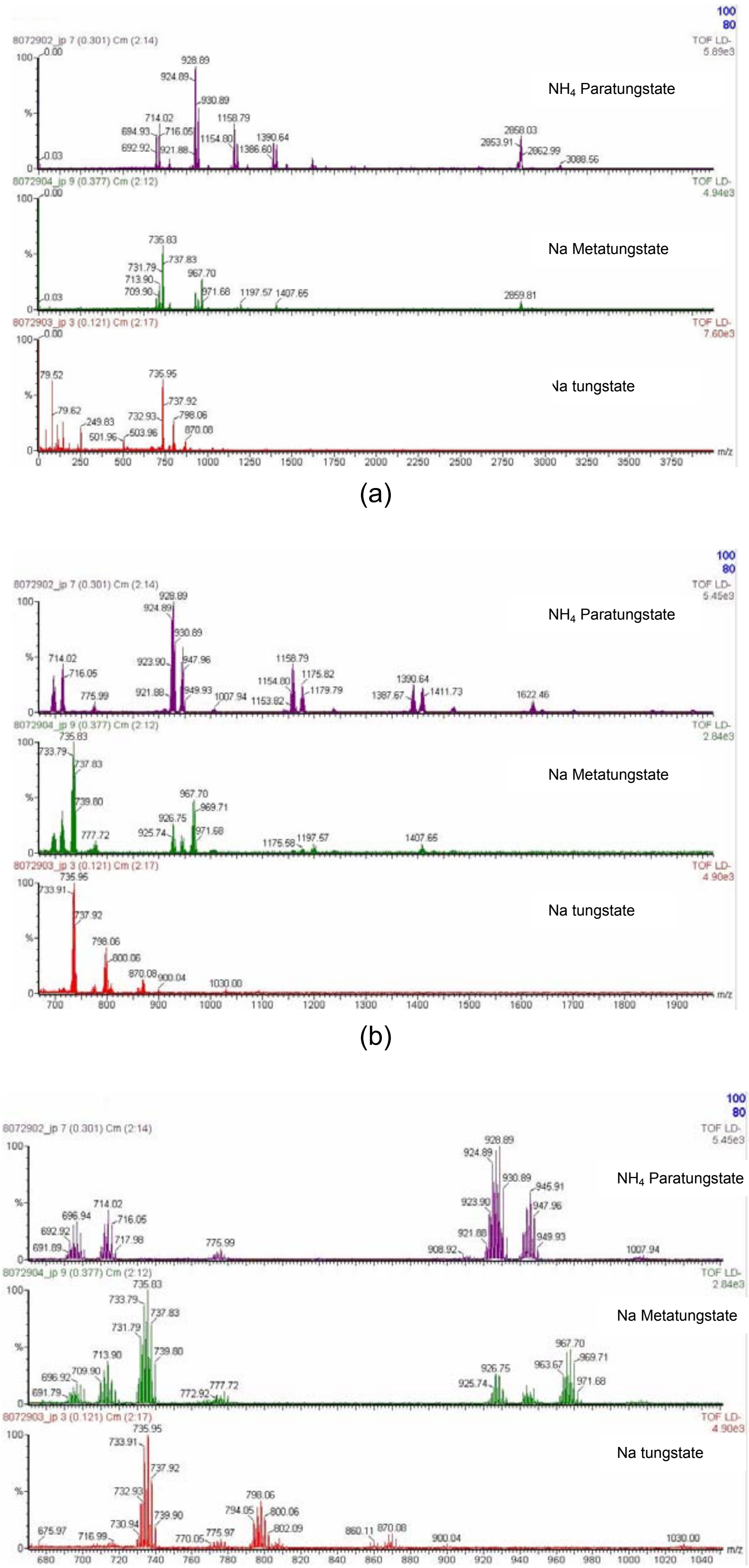
The spectra are presented in various zoom scales highlighting the peaks that are characteristic to each sample. This is the key to potentially using the method for qualitative and semi-quantitative analyses of environmental samples. The spectra obtained from the three different samples are compared in Figure 2. The stacked view indicates that sodium tungstate (representing the monomeric form of tungsten) features some unique peaks below m/z 600 which are not present in the polymeric samples. A strong peak cluster centered at m/z 249 corresponds to HWO_4^- (Figure 3). The sodium tungstate spectrum also features a cluster centered at m/z 798 and absent from the polymeric samples.

In addition, sodium tungstate displays no significant peaks above m/z 900. Hence the presence of peaks above m/z 900 is indicative of polymeric tungsten species. Comparing the two polymeric samples, ammonium paratungstate and sodium metatungstate, some similarities are observed. Generally, there are shifts in comparable peak clusters featured by both samples. These shifts could be due to the differences in the structure and arrangement of each species. Sodium metatungstate has a cluster m/z 735 which is also present in sodium tungstate but absent in the paratungstate sample. In addition, ammonium paratungstate has a cluster centered at m/z 3088 (Figure 5) which was not observed in sodium metatungstate (Figure 4). However, considering that comparable peaks generally had higher intensities in the paratungstate spectra, it could be that the 3088 peak was too weak in the sodium metatungstate spectra. These higher intensities correspond to a higher abundance which suggests that paratungstate is ultimately a more stable form. More detailed analysis needs to be performed to qualitatively assign all peaks. However, it is clear that this technique shows promise in the distinguishing and identification of tungsten species in environmental samples.

3.2 Raman Spectroscopy

From Figure 6a, three major peaks are identified at 929 cm^{-1}, 837 cm^{-1} and 333 cm^{-1} for sodium tungstate salt. These are in agreement with the peaks observed by Shijun *et al.* (934 cm^{-1}, 834 cm^{-1} and 325 cm^{-1}). In addition, some minor peaks are observed at 892 cm^{-1}, 809 cm^{-1}, 282 cm^{-1} and 168 cm^{-1}. The peak identified at 441 cm^{-1} does not appear to be significant compared to the others. Figure 6b shows peaks associated with the paratungstate species. Raman shifts associated with the NH_4^+ occur outside the current scanning range. More peaks are observed with the paratungstate salt than with any of the other salts. Major peaks occur at 948 cm^{-1}, 872 cm^{-1}, 804 cm^{-1}, 350 cm^{-1}, 317 cm^{-1}, 206 cm^{-1}, and 164 cm^{-1} with minor peaks at 649 cm^{-1}, 568 cm^{-1}, 491 cm^{-1}, and 428 cm^{-1}. The peak at 948 cm^{-1} may be related to a similar peak in the spectrum of sodium tungstate at 929 cm^{-1}. It is possible that these peaks originate from similar vibrations and the difference in the shifts may be due to the larger molecular structure of the paratungstate and the effects of other vibrations from the molecule. It is also observed that the base of this peak is broader than the one in the sodium tungstate spectrum. The Raman spectrum of pure sodium metatungstate salt (Figure 6c) shows major peaks at 979 cm^{-1}, 965 cm^{-1}, 233 cm^{-1}, 195 cm^{-1}, and 163 cm^{-1}. The bases of these peaks are generally broader than the other salts. The region between 1000 cm^{-1} and 900 cm^{-1} reveals two peaks which may be related to the previously discussed peaks in the same regions of the sodium tungstate and ammonium paratungstate spectra. However, these peaks are less acute which may also be indicative of the influence of other molecular bonds and vibrations.

From the comparison of Figures 6 a, b, and c, the active regions for each salt can be easily identified. The Raman spectra of these three species are quite distinct and could hold the key to possible qualitative analysis.

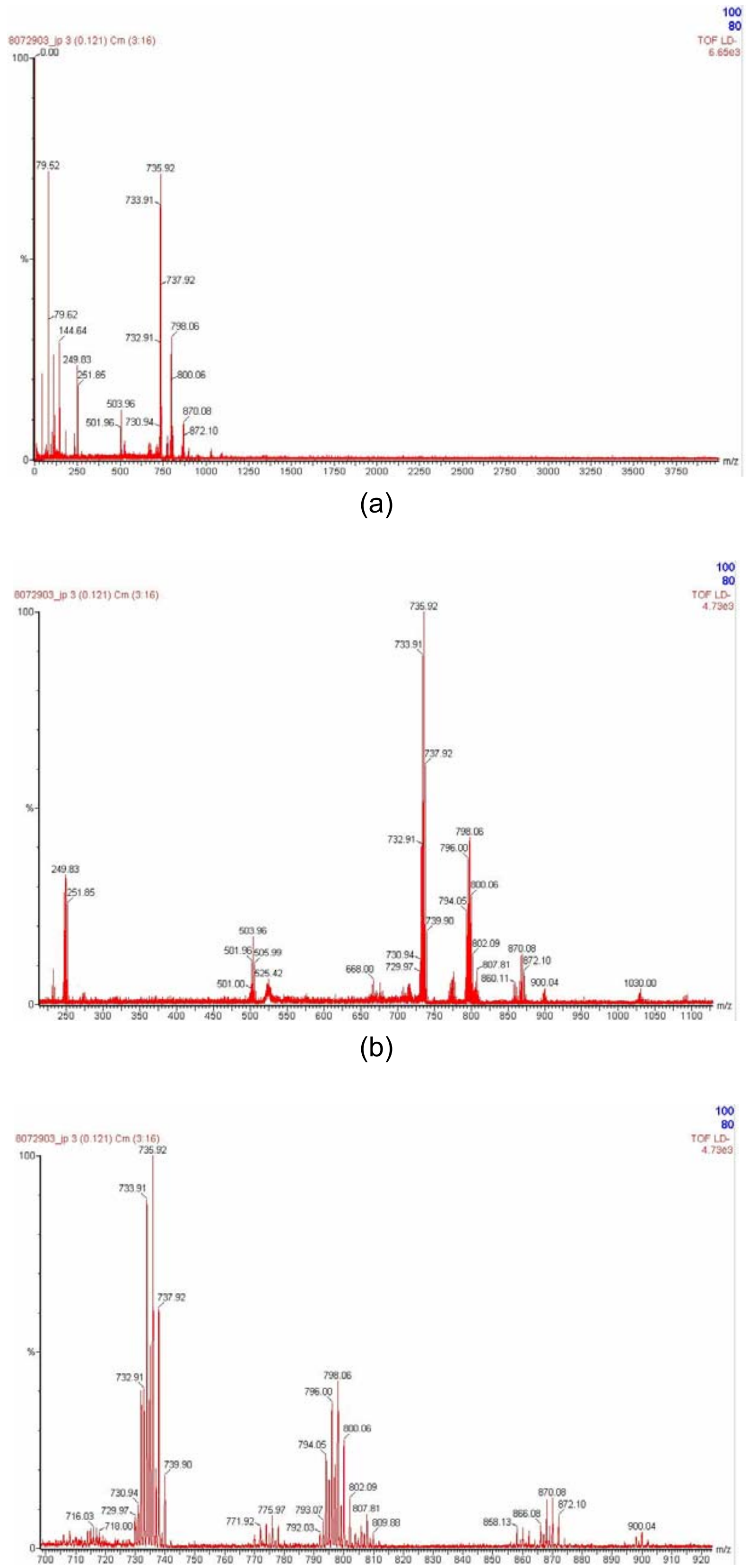


(a)

(b)

(c)

Figure 2. Comparison of the LDI-TOF spectra of sodium tungstate, sodium metatungstate, ammonium paratungstate at different zoom scales



(a)

(b)

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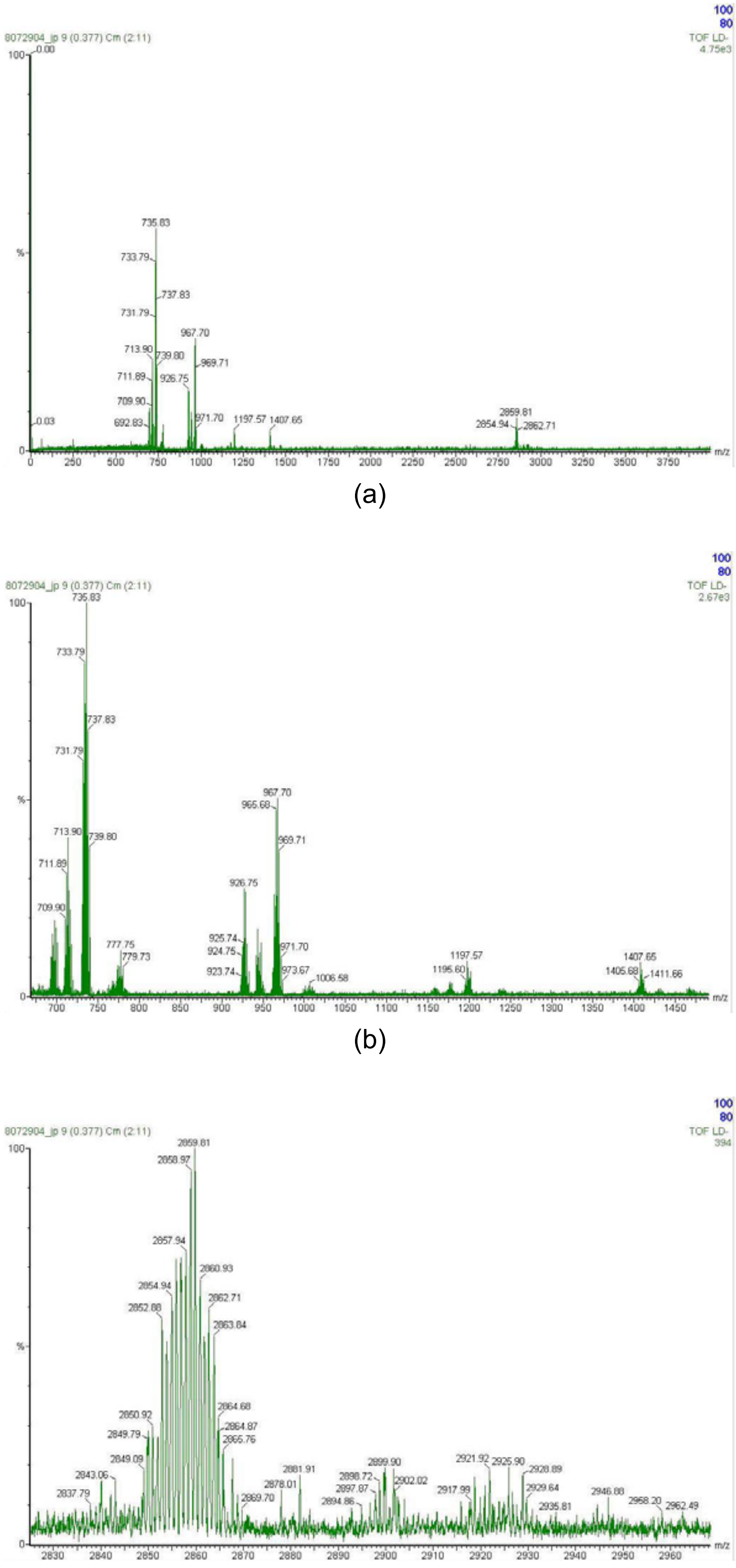
Figure 3. LDI-TOF spectra of sodium tungstate at different zoom scales

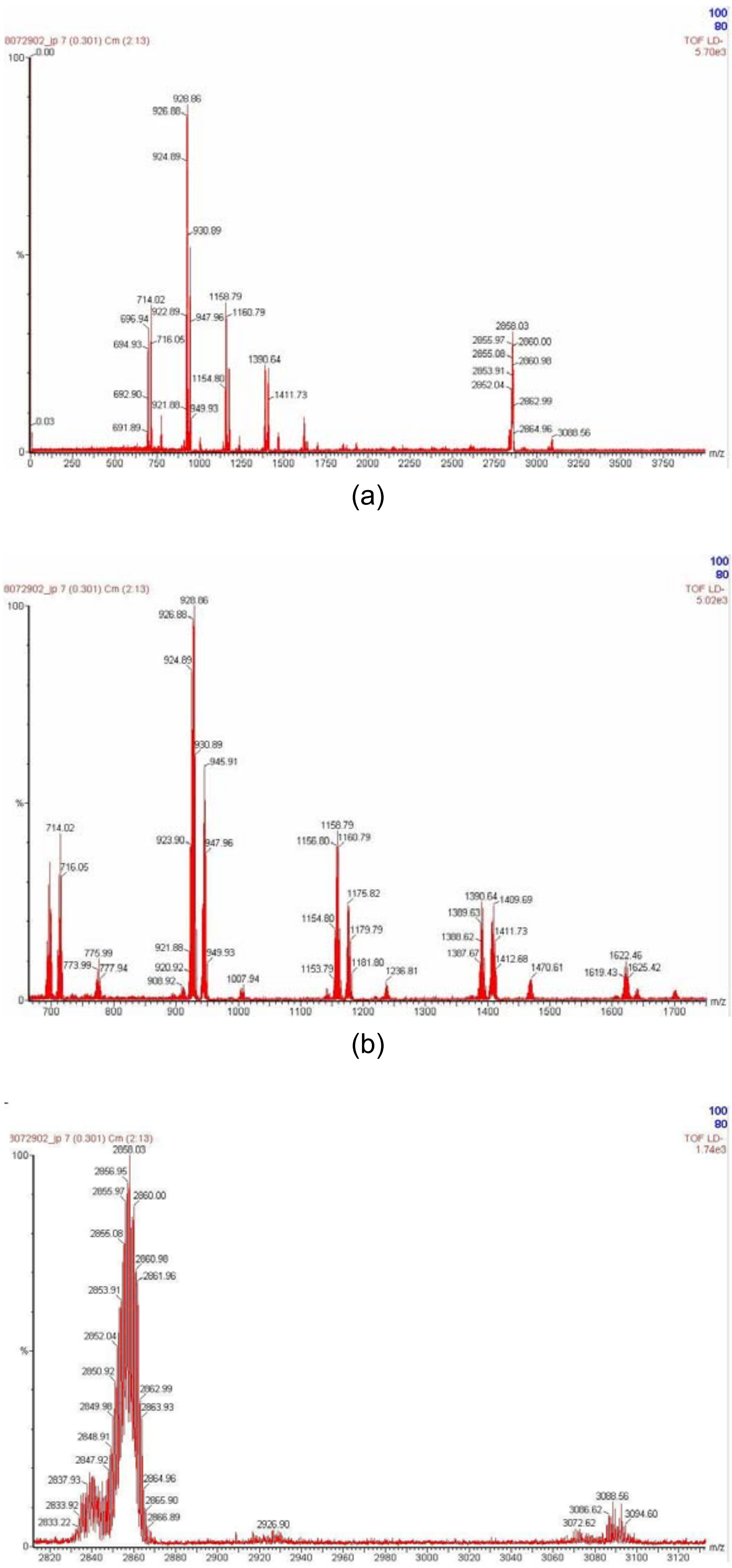


(a)

(b)

(c)

Figure 4. LDI-TOF spectra of sodium metatungstate. at different zoom scales

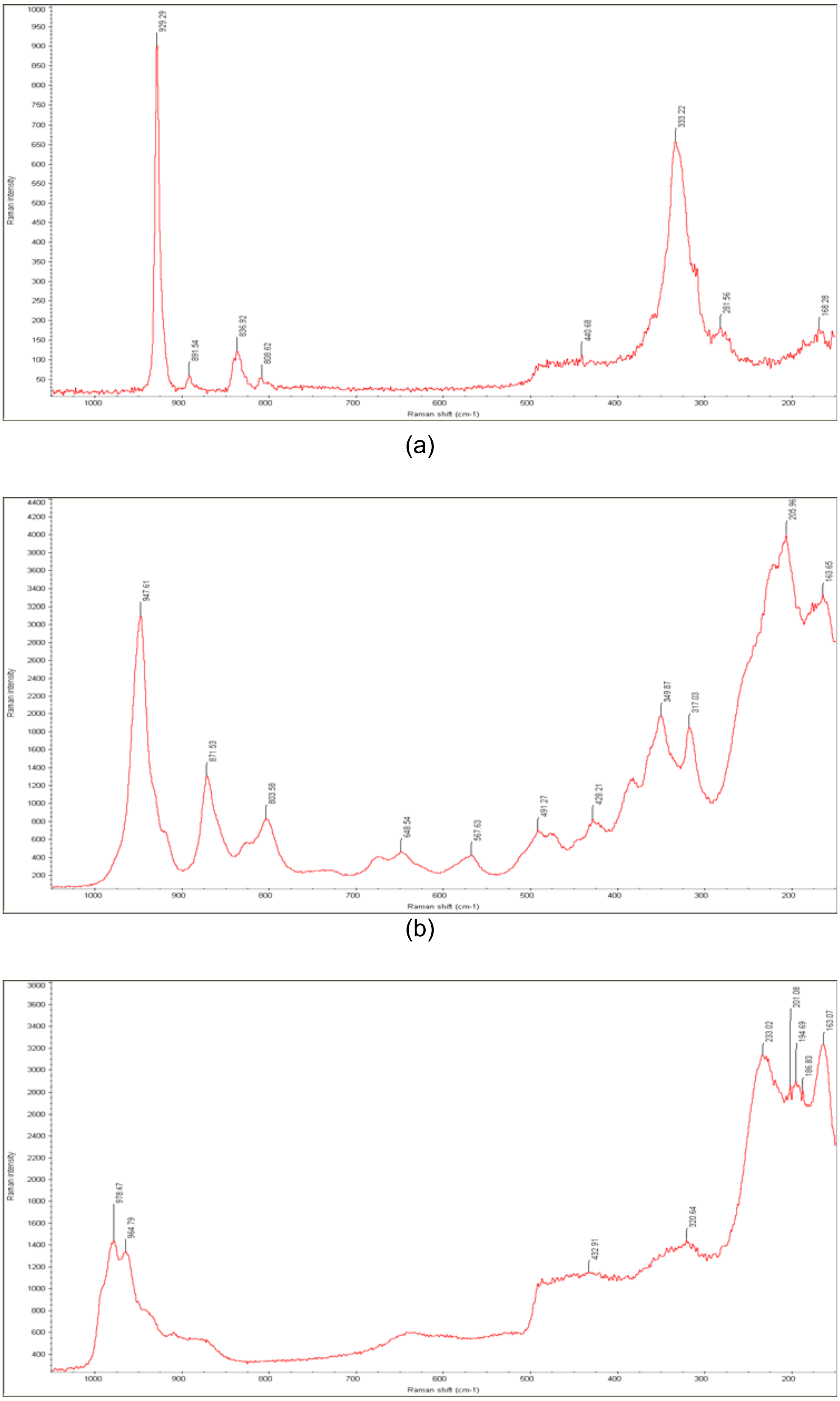


(a)

(b)

(c)

Figure 5. LDI-TOF spectra of ammonium paratungstate at different zoom scales



(a)

(b)

(c)

Figure 6. Raman Spectrum of: a) pure sodium tungstate, b) ammonium paratungstate, and c) sodium metatungstate

4. CONCLUSIONS

Currently, there are not analytical techniques available to assess speciation of tungsten in environmental samples beyond the distribution between monomeric and polymeric species. The results presented here show that both LDI-TOF and Raman spectroscopy appear to be viable methods for qualitative and semi-quantitative analysis of tungsten speciation. However, more detailed analyses need to be performed to assign all MS peaks and to improve the resolution of Raman spectra.

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