
Generation and Detection of Gaseous $W_{12}O_{41}^{-\bullet}$ and Other Tungstate Anions by Laser Desorption Ionization Mass Spectrometry

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The presence of a peak centered near m/z 2862, observed for the first time for the caged dodecatungstate radical-anion, $[W_{12}O_{41}]^{-\bullet}$, enables distinguishing WO_2 from WO_3 by Laser Desorption Ionization mass spectrometry (LDI-MS). In addition to WO_2 , laser irradiation of dry deposits made from aqueous ammonium paratungstate, and calcium and lead orthotungstate also produce the $[W_{12}O_{41}]^{-\bullet}$. In contrast, spectra recorded from deposits made from aqueous Na_2WO_4 , sodium metatungstate, and WO_3 , or non-aqueous calcium and lead orthotungstate, and ammonium paratungstate, failed to show the m/z 2862 peak cluster. These observations support the hypothesis that polycondensation reactions to form $[W_{12}O_{41}]^{-\bullet}$ occur solely in the presence of water. Although dry spots are irradiated for ionization, the solvent used for sample preparation plays an important role on the chemical composition endowed to ions detected. For example, the m/z 2862 peak seen from deposits made from aqueous ammonium paratungstate, and calcium and lead orthotungstate, is absent in the spectra recorded either from pristine deposits or those derived from solutions made with organic solvents such as acetonitrile or ethanol. (J Am Soc Mass Spectrom 2009, 20, 1782–1789) © 2009 Published by Elsevier Inc. on behalf of American Society for Mass Spectrometry

Tungsten is a widely used metal. In fact, aqueous chemistry of tungsten oxo-salts such as tungstates and polytungstates has received considerable interest even as early as 1870s [1]. Moreover, heteropolyanions of tungsten, such as phosphotungstates, show catalytic and even antiviral properties. Tungsten oxide complexes are utilized in solar energy conversion and in breakdown of lignin in paper industry [2]. Recently, the Environmental Protection Agency has designated tungsten an emerging pollutant [3], giving new challenges to analytical chemists to develop novel procedures to detect and quantify species of tungsten present in ecological, food, and environmental samples.

In general, tungsten oxo-salts consist of a simple cation (sodium, potassium, or ammonium) and a simple tungstate or condensed polytungstate anion. Three groups of ammonium and alkali-metal tungstates have been recognized by Gibbs [1], namely the orthotungstates $[R_2WO_4]$ ($R = Na, K$), the metatungstates $[R_2W_4O_{13}]$ ($R = Na$), and the paratungstates $[R_{10}W_{12}O_{41}]$ ($R = NH_4^+, Na^+, K^+$).

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The aqueous chemistry of tungsten and its oxo-compounds is complex and elusive. Their characterization in aqueous solutions is complicated due to the occurrence of equilibrium aggregations and condensation reactions [4]. Undoubtedly, the aqueous chemistry of tungsten is challenging to all chemists interested in detecting inorganic ions. The methods employed for determination of tungstates include X-ray crystallography [4], ^{183}W and ^{17}O nuclear magnetic resonance (NMR) spectroscopy [5], potentiometry [6], Raman spectroscopy [7], calorimetry [8], chromatography [9, 10], and high performance liquid chromatography/inductively coupled argon plasma (HPLC-ICP) mass spectrometry [11]. One of the problems in tungsten chemistry is that not many polyoxoanions crystallize without submitting themselves to considerable lattice disorder [4]. Moreover, the abundance of NMR-active nuclei in such complexes is low. Not only techniques such as Raman spectroscopy, optical spectrophotometry, and polarography can only be used for relatively simple mixtures, but also their capabilities to discriminate among different anionic species are rather limited. Besides, Raman spectroscopy requires comparatively high analyte concentrations. The application of potentiometric techniques to polytungstates is rather problematic since the method demands the attainment of an

equilibrium state. Consequently, potentiometric techniques are unsuitable to investigate reaction kinetics or relatively unstable species.

Electrospray ionization mass spectrometry has been successfully used for aqueous polyoxometalate chemistry research [4, 12]. Le Quan Tuoi and Müller [13] and Lau et al. [14] studied phosphotungstates in organic solvents. Deery et al. [4] have extended the work to aqueous solutions. Walanda et al. [12] researched aqueous solutions of tungstates and provided comprehensive data on the observed species under electrospray conditions. However, under post-electrospray-ionization conditions, collision-induced dissociations frequently occur in-source. Apparently, it is difficult to ascertain which tungsten species were initially present in the analyte solution and which ions were formed by in-source gas-phase fragmentation. In the report by Walanda et al. [12], the electrospray ionization (ESI) peak intensities for tungstate anions, with the exception of $[HWO_4]^-$, were of very low abundance. As a consequence to this low signal-to-noise ratio, an unambiguous assignment of a chemical formula to an ion, based on isotope cluster determinations, appeared less reliable. In a more recent ESI-MS report by Ma et al. [15], possible structures for gas-phase phosphotungstate fragments, and charge assignments to tungsten species have been discussed on the basis of isotopic peak separations. They also carried out MS-MS analysis on phosphotungstate species, and some important neutral losses that take place were identified.

Also recently, laser desorption-ionization time-of-flight mass spectrometry (LDI-TOF-MS), with and without the use of a matrix, has been found suitable for the determination of Mo:W ratio in mixtures of heteropolytungstates and molybdates [16]. However, LDI-MS has not been applied previously to determine different categories of tungstate anions, which are in fact the universal starting materials of tungsten chemistry. To ascertain whether LDI-MS is a valid procedure to determine speciation in aqueous solutions, it is necessary first to record their spectra from authentic standards, and then investigate how the spectral profiles change when samples are exposed to aqueous conditions. Ogundipe et al. [17] have reported some preliminary results on the feasibility of applying LDI-MS to problems of tungsten chemistry.

In this present paper, we demonstrate the applicability of LDI-MS technique to detect and study ortho- and polytungstates, deposited with or without the use of water or an organic solvent.

Experimental

Chemicals

Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), sodium metatungstate hydrate ($3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$), ammonium paratungstate (APT) [$5(NH_4)_2WO_4 \cdot 7WO_3 \cdot 5H_2O$], calcium tungstate ($CaWO_4$), lead tungstate ($PbWO_4$),

tungsten(VI) oxide (WO_3), tungsten(IV) oxide (WO_2), and ethanol (200 proof, spectrophotometric grade) were purchased from Aldrich Chemical Co. (St. Louis, MO, USA). The water and acetonitrile used were both HPLC grade and purchased from Fisher Scientific (Pittsburgh, PA, USA).

Sample Preparation

All solutions were prepared in water, acetonitrile, or ethanol at a concentration of 100 mg tungsten/L (500 pmol/ μ L), without any pH adjustments. Typically, 1 μ L of each solution was immediately deposited on a target plate and left to dry at room temperature. For the purpose of establishing the reproducibility of spectra, four deposits of each stock solution were applied to four different spots on the same target plate. Samples of pristine tungsten compounds (without the use of any solvent) were taken on the tip of a wooden toothpick and gingerly applied to the target plate.

Mass Spectrometry

Laser desorption/ionization (LDI) mass spectra were recorded on a ToFSpec-2E (Micromass, Manchester, UK) equipped with a pulsed nitrogen laser (337 nm, pulse width 520 ns, pulse voltage 1000 V). Source voltage was 20 kV and spectra were recorded in reflectron mode with voltage set at 26 kV. Sampling rate was set at 2 GHz. The instrument was operated in delayed extraction mode at an extraction voltage of 19,980 V, and focus voltage of 16,000 V. The energy of the laser beam was adjusted for the optimum ion yield. Generally, 100% coarse and 80% fine laser power setting were used, except in the case of $PbWO_4$ samples, for which the fine power was set at 40%. Spectra were acquired from m/z 0 to 4000 with a low mass cut-off setting at m/z 150. Mass axis calibration was performed using AgI deposited on lock-mass spots of the target plate. For the mass range around the cluster at m/z 2862, an additional calibration was performed using a mixture of standard peptides.

Results and Discussion

Spectra Recorded from Aqueous Analyte-Derived Spots

Mass spectra recorded under negative mode from all samples showed peaks corresponding to tungsten species. For the desorption of ions, the mediation of a laser-absorbing matrix was not necessary since peaks observed under direct laser ablation were sufficiently intense. In contrast to spectra recorded under negative-ion mode, the same sample deposits failed to produce any significant peaks under positive-ion conditions. The spots of $PbWO_4$ afforded some gaseous ions; however, none of the peaks recorded from $PbWO_4$ corresponded to tungsten-bearing ions.

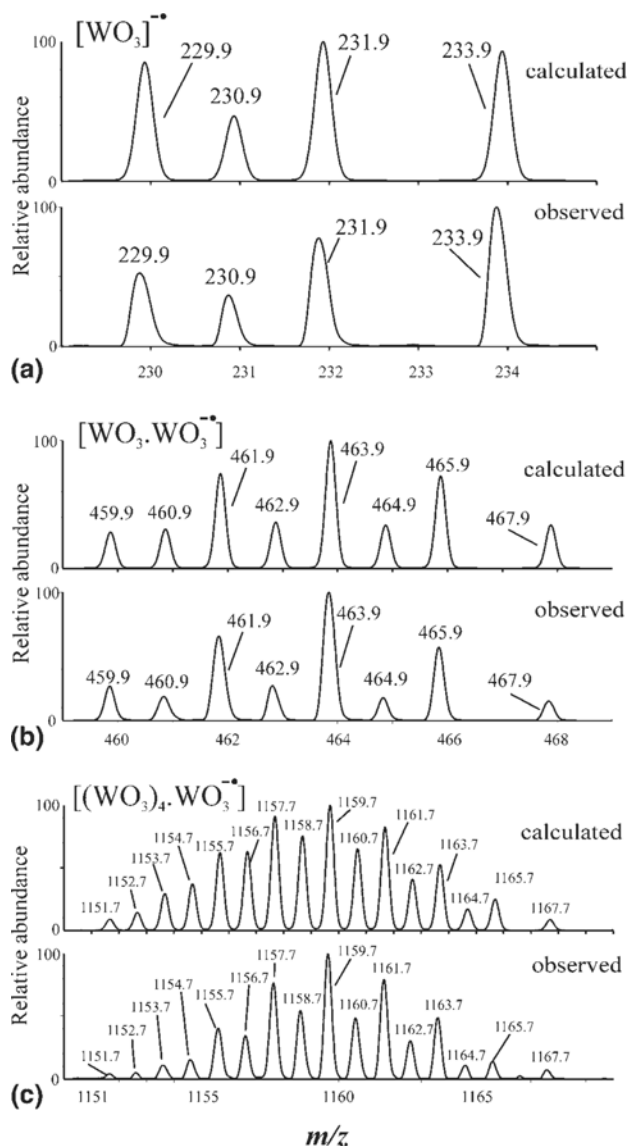


Figure 1. LDI mass spectrometric peak profiles of isotopic clusters of some tungsten species. (a) $[\text{WO}_3]^{-\bullet}$ recorded from PbWO_4 (lower spectrum) and that theoretically calculated for $[\text{WO}_3]^{-\bullet}$ (upper spectrum). (b) $[(\text{WO}_3)_2 \cdot (\text{WO}_3)^{-\bullet}]$ from CaWO_4 (lower) and theoretical isotopic distribution (upper). (c) $[(\text{WO}_3)_4 \cdot (\text{WO}_3)^{-\bullet}]$ from ammonium paratungstate $[\text{5}(\text{NH}_4)_2\text{WO}_4 \cdot 7\text{WO}_3 \cdot 5\text{H}_2\text{O}]$ (lower) and theoretical isotopic distribution (upper).

The recognition of tungsten-related peaks in a mass spectrum is straightforward since this element exists in nature as a five-isotope mixture [¹⁸⁰W (0.13%), ¹⁸²W (26.30%), ¹⁸³W (14.30%), ¹⁸⁴W (30.67%), and ¹⁸⁶W (28.60%)]. Under our LDI-TOF mass spectrometric conditions, all isotopic peaks were well-resolved, enabling the determination of the number of tungsten atoms present in an ion. The isotopic peak separations indicated that all the ions produced under our experimental conditions were singly-charged. Segments of spectra depicting typical tungsten isotopic clusters for $[(\text{WO}_3)^{-\bullet}]$, $[(\text{WO}_3)_2 \cdot (\text{WO}_3)^{-\bullet}]$, and $[(\text{WO}_3)_4 \cdot (\text{WO}_3)^{-\bullet}]$ are illustrated in Figure 1. The observed peak intensities were congruent

with those calculated for the proposed formulas (the upper set of spectra in Figure 1).

The heterogeneous nature of sample deposits is considered to give poor spot-to-spot reproducibility even for the same chemical substance under MALDI-TOF conditions. To verify the reproducibility of the peak intensities under the LDI conditions used in this study, samples of each analyte were deposited on four different spots on a target plate, and subjected to laser ablation. The spectra recorded from different sample spots were virtually identical, as illustrated in Figure 2, for ammonium paratungstate, indicating that peak intensities in a cluster can be used for unambiguous assigning of a chemical formula to an ion.

The spectra indicated the presence of peaks for anions of several distinct series of tungsten-bearing aggregates (Figure 2). The most intense series of peaks observed at m/z 232, 464, 696, 928, 1160, 1392, 1624, 1856... (note: the nominal mass corresponding to the most intense peak in each cluster is given here) in the spectrum of ammonium paratungstate represented the anionic series $[(\text{WO}_3)_n \cdot (\text{WO}_3)^{-\bullet}]$ ($n = 0$ to 7). The second most prominent series (m/z 249, 481, 713, 945, 1177, and 1409) represented the series $[(\text{WO}_3)_n \cdot (\text{HO})^-]$ ($n = 1$ –6). A third series of ions representing $[(\text{WO}_3)_n \cdot (\text{WO}_2)^{-\bullet}]$ ($n = 2$ to 7) was detected at m/z 448, 680, 912, 1144, 1376, and 1608.

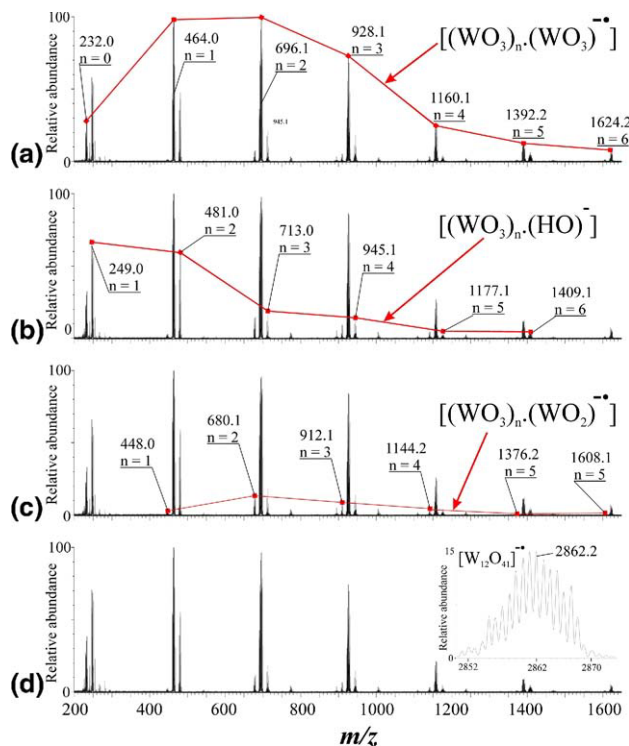


Figure 2. LDI mass spectra (a)–(d) recorded under identical mass spectrometric conditions from four different sample deposits of ammonium paratungstate (APT) $[\text{5}(\text{NH}_4)_2\text{WO}_4 \cdot 7\text{WO}_3 \cdot 5\text{H}_2\text{O}]$. An example of the cluster corresponding to $[\text{W}_{12}\text{O}_{41}]^{-\bullet}$ is shown as an inset in (d).

Interestingly, the relative abundances of peaks belonging to the three most abundant series of peaks displayed different intensity trends with increasing mass-to-charge ratios. The distribution of peaks for the series $[(WO_3)_n \cdot (WO_3)^{-\bullet}]$ and $[(WO_3)_n \cdot (WO_2)^{-\bullet}]$ were more or less bell-shaped, with the most intense peaks appearing at m/z 464 (Figure 2a) and 680 (Figure 2c) for the two series, respectively. The peak intensities for the series $[(WO_3)_n \cdot (HO)^-]$, on the other hand, decreased gradually with increasing mass-to-charge ratio. For example, the most intense peak for this series appeared at m/z 249, which was the first peak in the series (Figure 2b).

The sodium tungstate, Na_2WO_4 , and sodium metatungstate (SMT), displayed a characteristic set of peaks for a sodiated series at m/z 271, 503, 735, and 967, of composition $[(WO_3)_n \cdot (NaO)^-]$ with $n = 1-3$ for Na_2WO_4

(Figure 3a), and $n = 1-4$ for SMT (Figure 3b). These two compounds also displayed a few peaks for the $[(WO_3)_n \cdot (WO_3)^{-\bullet}]$ and $[(WO_3)_n \cdot (HO)^-]$ series, which were observed in the spectra of ammonium paratungstate, albeit extending only to $n = 2$ species for Na_2WO_4 , and to $n = 4$ for SMT (Figure 3a, b).

Similarly, spectra recorded from aqueous deposits of calcium and lead orthotungstates, and WO_2 showed peaks for the $[(WO_3)_n \cdot (WO_3)^{-\bullet}]$ and $[(WO_3)_n \cdot (OH)^-]$ series ions. The spectrum of $PbWO_4$ displays an additional and a characteristic set of low-intensity peaks centered at m/z 456, 688, and 920, respectively, for a “plumbated” series of ions of general formula $[(WO_3)_n \cdot (PbO)^{-\bullet}]$ ($n = 1-3$).

The spectrum of WO_3 displayed peaks only for the $[(WO_3)_n \cdot (WO_3)^{-\bullet}]$ and $[(WO_3)_n \cdot (OH)^-]$ series, with $n = 1-7$. It is particularly noteworthy that all series of peaks

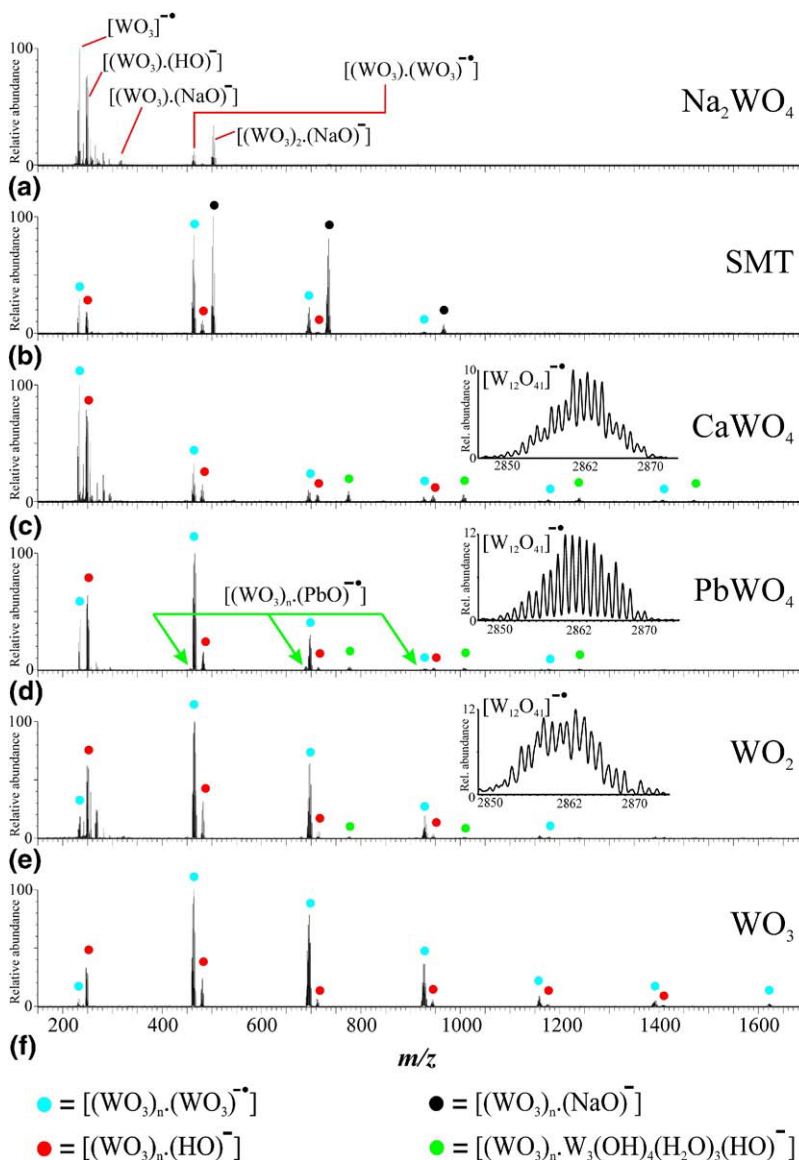


Figure 3. LDI mass spectra recorded from deposits made from aqueous solution of Na_2WO_4 (a), SMT (b), $CaWO_4$ (c), $PbWO_4$ (d), WO_2 (e), and WO_3 (f).

are not present to the same extent of spread in all seven analytes investigated in this study (Figure 3). In fact, the observations made here could be used to determine the identity of tungsten compounds in uncharacterized samples. In all metal tungstates, (Na_2WO_4 , CaWO_4 , PbWO_4 , and SMT), the highest value observed for n was 6 for CaWO_4 . For Na_2WO_4 , it was less than 3. The presence of peaks for the sodiated series $[(\text{WO}_3)_n(\text{NaO})^-]$ is a diagnostic marker for sodium salts such as Na_2WO_4 and SMT. The presence of sodium cations appears to suppress the formation of high-mass aggregates. In the spectra of Na_2WO_4 and CaWO_4 the base peaks represent ions that bear only one tungsten atom. Moreover, the peak intensities rapidly decrease with increasing mass-to-charge ratio. With SMT and PbWO_4 , a somewhat bell-shaped distribution of relative abundances of peaks is observed. Similar distributions were observed in the spectra of WO_2 , WO_3 and APT (Figure 2). However, the spectra of these three compounds show many more peaks for the high mass aggregates.

An interesting low-abundance series appeared at m/z 777, 1009, 1241, and 1473 in the spectra of CaWO_4 , PbWO_4 , and WO_2 (Figure 3c, d, e). This series of ions appear to fit to the general formula $[(\text{WO}_3)_n\text{W}_3(\text{OH})_4(\text{H}_2\text{O})_3(\text{OH})^-]$ with $n = 0$ –3. Similar aqua–hydroxo complexes of tungsten have been reported by Lassner and Schubert [19]. However, further collision-induced dissociation experiments are necessary to establish their exact composition.

An additional feature observed in some spectra of tungsten compounds shown here is the presence of a multitude of peaks centered at m/z 2862 (Figure 3c, d, e, and Figure 4). A comparison of peak intensities theoretically calculated for the formula $[\text{W}_{12}\text{O}_{41}]^{\bullet-}$ with the

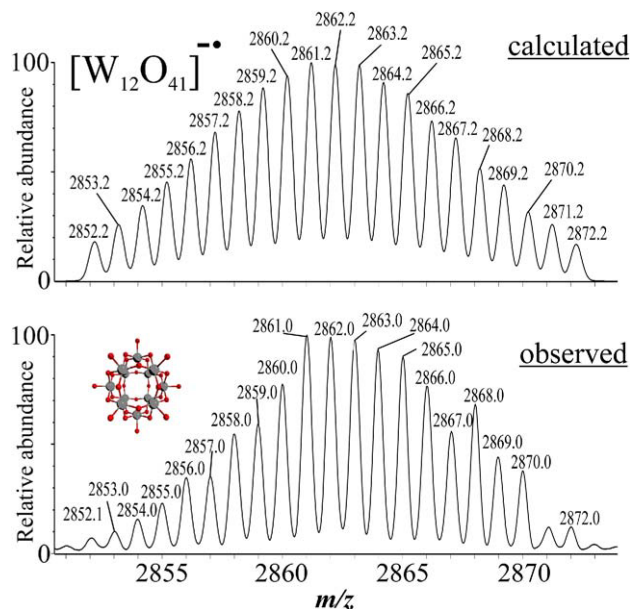


Figure 4. An expansion of the m/z 2850 to 2875 section of the spectrum of PbWO_4 (bottom), and that theoretically calculated for $[\text{W}_{12}\text{O}_{41}]^{\bullet-}$ at a resolving power of 6000 (top). Bottom, inset: structure of the dodecatungstate cage.

relative abundances observed, confirmed that the peak cluster represented a dodecatungstate. Clearly, the m/z 2862 peak is a diagnostic marker useful for the identification of unknown tungsten compounds.

A peak for the $[\text{W}_{12}\text{O}_{41}]^{\bullet-}$ radical ion is observed in the spectra recorded from CaWO_4 , PbWO_4 , APT and WO_2 . The ion belongs to a group of dodecatungstates, of which the best-known examples are $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ and $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$. These two ions have a caged structure [18] with a prominent tetrahedral hole inside the 12 tungstate units (Figure 4). It is known that this tetrahedral coordination site is spacious enough to accommodate one of at least 35 different cations to yield heteropolytungstates, which are also known as Keggin structures. In fact, a low-abundance peak in the spectrum of PbWO_4 , centered at m/z 3085, can be attributed to $[\text{Pb}(\text{W}_{12}\text{O}_{42})]^{-\bullet}$, a Keggin-type species (Figure S1 in Supplementary Material, which can be found in the electronic version of this article).

There are several important features about the dodecatungstate $[\text{W}_{12}\text{O}_{41}]^{\bullet-}$ radical-ion. The detection of a Keggin precursor has not been unequivocally established previously by mass spectrometric techniques, although a few attempts have been made [7–9]. Lubal et al. [16] employed LDI-MS and MALDI-MS with a fullerene matrix, but failed to establish the presence of W_{12} species unequivocally. By electrospray ionization mass spectrometry of aqueous tungstate solutions, Walanda et al. [12] showed some peaks as multiply charged W_{12} species; however, those peaks were of such low abundance and such poor resolution that their composition remained ambiguous. Recently, using ESI-MS, Ma et al. [15] unambiguously assigned gas-phase Keggin-type structures to phosphotungstate species with 12 or 18 tungsten atoms. However, these researchers did not work with tungsten compounds without heteroatoms.

The second important point is about the relative abundance of the $[\text{W}_{12}\text{O}_{41}]^{\bullet-}$ peak. Although low intensity peaks for W_6 or W_7 aggregates were observed under LDI-MS conditions, those bearing nine to 11 tungsten atoms were not detected in any of our experiments. Thus, we conclude that the caged structure of the radical-ion is bestowed with some stability that allows its detection in the gas-phase.

The third important point about the $[\text{W}_{12}\text{O}_{41}]^{\bullet-}$ species is the question whether it is formed in the original aqueous solutions or is it a species produced by combining lighter ions formed during the LDI process itself. To answer this question, we performed LDI-MS analysis of the same tungsten compounds using deposits made from solutions of organic solvents, and those without the intervention of any solvent.

Spectra Recorded from Authentic Compounds With or Without the Intervention of an Organic Solvent

Sets of LDI mass spectra were recorded from deposits of the seven tungsten compounds discussed above as acetonitrile or ethanol solutions (Figures 5 and 6, re-

spectively). These spectra show some striking differences from those derived from aqueous solutions. In all cases, the peak intensities showed a bell-shaped distribution profile. Since many peaks are common to spectra obtained from different compounds, it is not straightforward to identify a compound directly from its LDI spectrum. Interestingly, peaks for the $[W_{12}O_{41}]^{-\bullet}$ radical-ion are absent in the spectra from organic-solvent derived spots. However, an unexpected peak was observed for $[W_{12}O_{41}]^{-\bullet}$ in the spectrum of WO_2 recorded even from non-aqueous solutions (Figures 5e and 6e). Likewise, the series $[(WO_3)_n \cdot W_3(OH)_4(H_2O)_3(OH)^-]$ was also observed only in that particular spectrum. WO_2 is generally synthesized by a hydrothermal procedure [19]; thus, it is likely small amounts of $[W_{12}O_{41}]^{-\bullet}$ and tungsten aqua-hydroxo complexes formed during the production might be present in WO_2 samples. This is not surprising because of the extra stability of $[W_{12}O_{41}]^{-\bullet}$, and would indicate a similar stability for the aqua-hydroxo complexes. Furthermore, because of

its very low water solubility, it is unlikely that WO_2 interacts directly with water to undergo chemical changes required for the formation of $[W_{12}O_{41}]^{-\bullet}$ during the sample preparation for deposition on the target plate. In addition, peaks for plumbated ions are absent in the organic-solvent-derived spectra of $PbWO_4$, suggesting that water is a necessary factor for their formation as well. Finally, the aqua-hydroxo series is absent in the spectra derived from $CaWO_4$ and $PbWO_4$ deposited using organic solvents. This indicates that, for these complexes too, water is an essential factor for their formation.

The absence of the $[W_{12}O_{41}]^{-\bullet}$ cluster from all spectra of tungsten compounds other than that of WO_2 , originating from organic solvents shows that the dodecatungstate radical-ion is formed in solution, and it is not a product of chemical processes occurring in the mass spectrometric ion source. To confirm this hypothesis, we obtained the LDI mass spectra of the same tungsten compounds in their pristine state, without

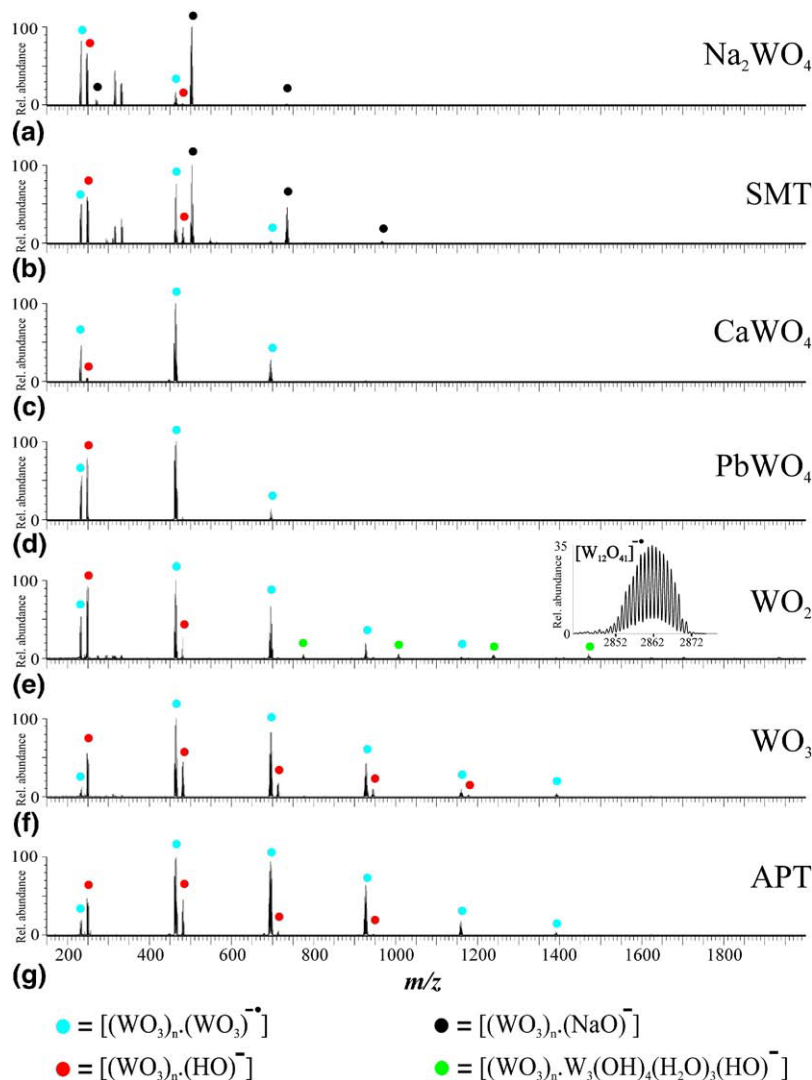


Figure 5. Spectra recorded from acetonitrile solutions of Na_2WO_4 (a), SMT (b), $CaWO_4$ (c), $PbWO_4$ (d), WO_2 (e), WO_3 (f), APT (g).

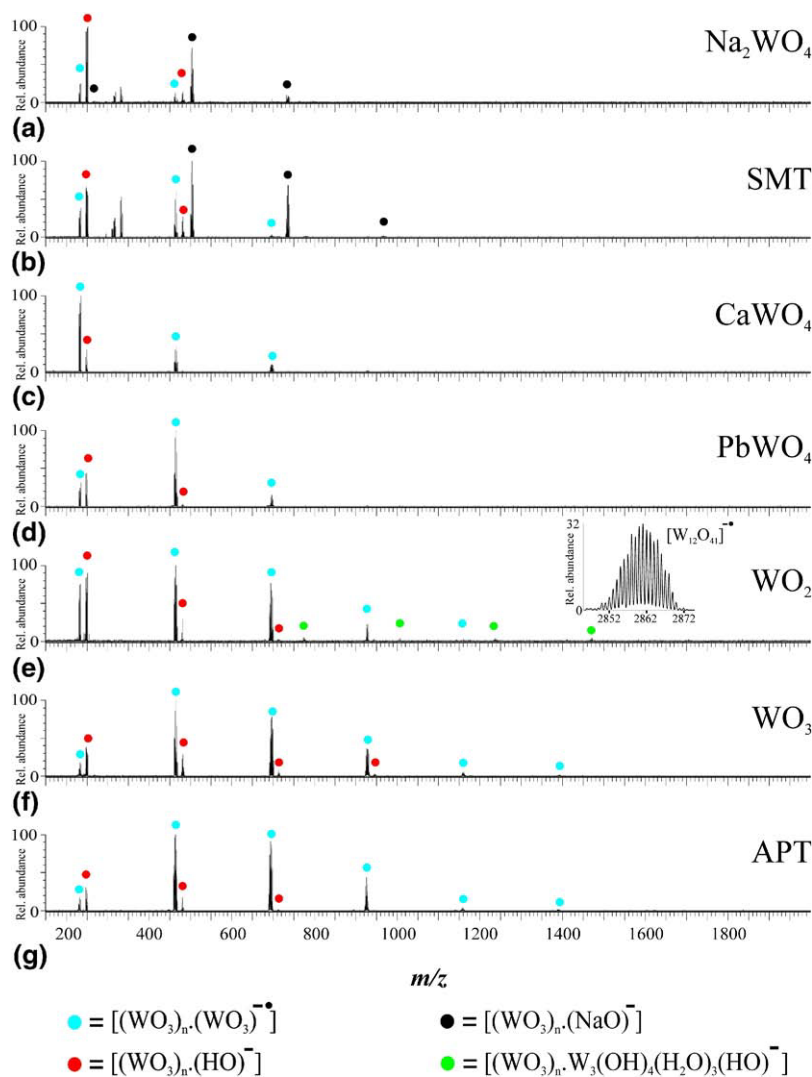


Figure 6. Spectra recorded from ethanol solutions of Na_2WO_4 (a), SMT (b), CaWO_4 (c), PbWO_4 (d), WO_2 (e), WO_3 (f), APT (g).

using a solvent at all. These spectra were essentially identical to those obtained from organic solvents, hence not shown here (Supplementary Figure 2). The series of peaks corresponding to plumbated species were absent from the spectrum of PbWO_4 , as was the case with its spectra taken from deposits from organic solvents. Yet again, the peak cluster corresponding to $[\text{W}_{12}\text{O}_{41}]^{-\bullet}$ was observed solely in the spectrum of WO_2 , confirming the initial presence of the ion in the oxide, as mentioned above.

We conclude that the dodecatungstate is rapidly formed even in neutral aqueous solutions, contrary to previous reports which state that the formation of W_{12} -species is slow (days to weeks) and takes place only under acidic conditions (pH 4–6) [19]. Furthermore, the $[\text{W}_{12}\text{O}_{41}]^{-\bullet}$ species readily forms even from sparingly soluble tungsten compounds, such as CaWO_4 and PbWO_4 , when they are left in contact with water. However, a peak for $[\text{W}_{12}\text{O}_{41}]^{-\bullet}$ was not observed in the spectra of sodium tungstate or SMT samples pre-

pared in organic or aqueous solvents. We have shown that many tungsten compounds can be detected and differentiated by LDI-MS. The ability to obtain mass spectra directly from tungsten species enables the observation of tungsten corrosion products. LDI-MS will allow for nearly real-time monitoring at least of some aqueous tungstate equilibria, especially when long-term ones, such as aging, are involved. Considering the recent decision of the Environmental Protection Agency to designate tungsten an emerging pollutant, LDI-MS could well become a preferred research tool in tungsten chemistry.

Appendix A Supplementary Material

Supplementary material associated with this article may be found in the online version at [doi:10.1016/j.jasms.2009.05.015](https://doi.org/10.1016/j.jasms.2009.05.015).

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