Comment on:

"Generation and Detection of Gaseous $W_{12}O_{41}^{-•}$ and Other Tungstate Anions by Laser Desorption Ionization Mass Spectrometry" by Julius Pavlov, Washington Braida, Adebayo Ogundipe, Gregory O'Connor, and Athula B. Attygalle, *J. Am. Soc. Mass Spectrom.* 2009, 20, 1782–1789.

Tungsten and its alloys are widely used in industry. During the past 15 y, there has been a significant environmental push in Europe and the United States to stop using lead in various applications involving bullets, wheel balancing weights, fishing weights, and other lead products. Tungsten was the major substitute component for lead cores of bullets in the U.S. Green Bullet Program. The degree of tungsten's leachability in water strongly depends on the environmental conditions, especially on the water's pH, but also on the nature of the soil [1]. The initial interaction between tungsten and oxygen-containing water can be described as follows [1]:

$$W + H_2O + 1.5\,O_2 \rightarrow WO_4^{2-} + 2H^+.$$
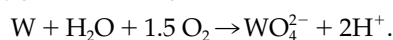
The monotungstate ion, WO_4^{2-}, reacts with H^+, resulting in the formation of the metatungstate ion $[H_2W_{12}O_{40}]^{6-}$:

$$12\,WO_4^{2-} + 18\,H^+ \rightarrow [H_2W_{12}O_{40}]^{6-} + 8\,H_2O.$$
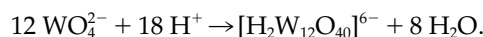
There is no doubt that for the sake of protecting our environment, a careful testing of tungsten's potential toxicity is an obligation. Therefore, the tungsten-containing species, formed under various environmental conditions, must be identified with all certainty. To identify the suitable analytical technique can be a challenge, even more to draw the correct conclusions from the obtained analytical data. After studying the publication very carefully, we would like to make the following comments, which include also the correction of factual inaccuracies.

The authors claimed that the detection of the caged dodecatungstate radical-anion $[W_{12}O_{41}^{-•}]$ enables the distinction of WO_2 from WO_3. In our opinion, their identification could be done by X-ray diffraction. Furthermore, the question arises: Why is their distinction relevant from an ecological standpoint? It is very unlikely that the intermediate tungsten dioxide, WO_2, would be a chemical present in any non-manufacturing location.

The authors claimed on the basis of laser desorption ionization mass spectrometry (LDI-MS) 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." In our opinion, based on the authors' experimental material, the radical ion is

indeed formed as a result of a gas-phase interaction in the ion source, with one exception. The exception is ammonium paratungstate, which already contains the dodecatungstate anion, $[H_2W_{12}O_{42}]^{10-}$ (Figure 1).

The formation of W_{12}-species in water without any pH adjustment from virtually insoluble compounds, such as $CaWO_4$ and $PbWO_4$, is contrary to the voluminous literature over decades in peer-reviewed journals on this subject.

The authors claimed that "all solutions were prepared in water, acetonitrile, or ethanol at a concentration of 100 mg tungsten/L without any pH adjustments." The four chemicals WO_3, WO_2, $CaWO_4$, and $PbWO_4$ are characterized by a very minute solubility in water at 25 °C, namely by 22 mg W/L for WO_3 [2], 10 mg W/L for WO_2 [3], 4 mg W/L for $CaWO_4$ [4], and 1.7 mg W/L for $PbWO_4$ [5]. Even though quantitative data for their solubilities in acetonitrile and ethanol are not available, one can be confident that the solubilities of these inorganic compounds in organic solvents will be distinctly lower than in water.

We suggest that when water is used during the sample preparation, $CaWO_4$ and $PbWO_4$ form a low concentration (cf. the solubility data) of hydrated Ca^{2+}, Pb^{2+}, and monomeric WO_4^{2-}. The dried spots (prepared before LDI analysis) contain sufficiently reactive oligomeric "clusters" of the starting monotungstates, which are being converted into the radical ion $W_{12}O_{41}^{-•}$ in the ion source. The polymeric WO_3 (distorted structure of cubic ReO_3), though better soluble in water, can not generate the discussed oligomeric species.

In our opinion, the absence of the $[W_{12}O_{41}^{-•}]$ cluster from all spectra of tungsten compounds other than that of WO_2, originating from the organic solvents and also from their pristine state, is explainable by the fact that the interaction of $CaWO_4$ and $PbWO_4$ with water is the precondition for forming the cluster in the ion source.

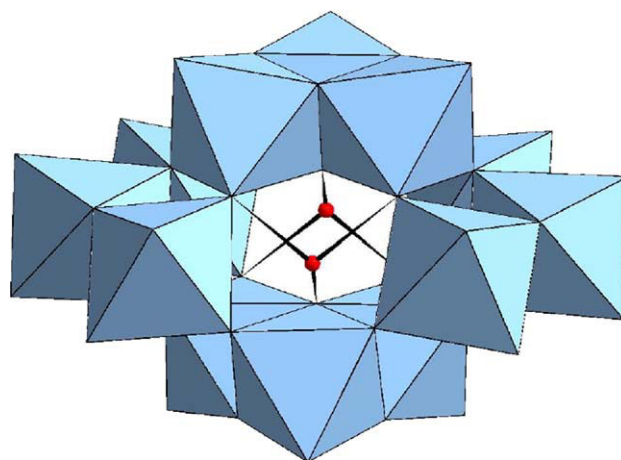Tungsten dioxide, WO_2, is a special case. In our opinion, the only way to explain the formation of the

Figure 1. Polyhedral representation of the paratungstate 'Z' anion $[H_2W_{12}O_{42}]^{10-}$.

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cluster $[W_{12}O_{41}]^{-\bullet}$ from WO_2 in all four experimental conditions is to accept that they are also formed in the mass spectrometer ion source. In this case, the incorporated oxidation of W(IV) to W(VI) obviously facilitates the formation of the observed cluster.

It is surprising to us that sodium metatungstate (SMT), $Na_6[H_2W_{12}O_{40}]\bullet nH_2O$, which also contains a W_{12}-species (Figure 2), does not produce a detectable LDI-MS signal. The use of ammonium metatungstate $[NH_4]_6[H_2W_{12}O_{40}]\bullet nH_2O$ would answer the question whether or not "the presence of sodium cations appears to suppress the formation of high-mass aggregates."

The formulae $3Na_2WO_4\bullet 9WO_3\bullet H_2O$ and $5(NH_4)_2$ $WO_4\bullet 7WO_3\bullet 5H_2O$ given in the paper are outdated and also misleading. A preferable formula (meaning reflecting the anion's structure as a member of the KEGGIN-family) of sodium metatungstate is $Na_6[H_2W_{12}O_{40}]\bullet nH_2O$. An acceptable formula of ammonium paratungstate is $(NH_4)_{10}[H_2W_{12}O_{42}]\bullet 4H_2O$. The centrosymmetric paratungstate 'Z' anion $[H_2W_{12}O_{42}]^{10-}$ of $APT\bullet 4H_2O$ consists of four corner-sharing W_3O_{13} groups and two non-acidic protons. Every W_3O_{13} group consists of three edge-sharing WO_6 octahedra. The two protons in the center of the anion are essential for the existence of this polyoxotungstate anion (Figure 1). The distance between the two non-acidic protons was determined by broad-line ^{1}H-NMR spectroscopy as 2.22 Å [6]. Later on, this result was confirmed by neutron diffraction experiments [7]. Therefore, the formula $(NH_4)_{10}[H_2W_{12}O_{42}]\bullet 4H_2O$ is a better representation of the structure than the out-dated, but still used, formula $(NH_4)_{10}W_{12}O_{41}\bullet 5H_2O$.

The authors stated that "the ion $[W_{12}O_{41}^{-\bullet}]$ belongs to a group of dodecatungstates, of which the best-known examples are $[H_2W_{12}O_{42}]^{10-}$ and $[H_2W_{12}O_{40}]^{6-}$" and that "these ions have a caged structure with a prominent tetrahedral hole inside the 12 tungstate units." It is well know that only the metatungstate anion $[H_2W_{12}O_{40}]^{6-}$ has a structure with a "tetrahedral cavity" in its center. The metatungstate anion realizes a structure type, known as KEGGIN anion structure. The structure is based on a central XO_4 tetrahedron surrounded by 12 WO_6 octahedra arranged in four groups of three edge-shared octahedra, W_3O_{13}. These groups are linked by shared corners to each other and to the central XO_4 tetrahedron [8] (Figure 2).

The paratungstate anion $[H_2W_{12}O_{42}]^{10-}$, on the other hand, is characterized by a hexagonal close packing ABAB of 42 oxygen anions O^{2-}. The tetrahedral and octahedral vacancies, generated by such a packing, are too small for incorporating heteroelements.

To our knowledge, there are KEGGIN-anions with 13 (not 35, as the authors stated) elements, occupying the central tetrahedral coordination. These elements are "H_2", B, Al, Ga, C, Si, Ge, P(V), As(V), Cr(III), Fe(III), Co(II/III), Zn, where the metatungstate anion represents a special case. A KEGGIN anion with Pb(IV) at its center is currently unknown. Its correct formula would be $[PbW_{12}O_{40}]^{4-}$, not $[Pb(W_{12}O_{42})]^{-\bullet}$, as the authors claimed.

The statement that ". . . small amounts of $[W_{12}O_{41}]^{-\bullet}$ and tungsten aqua-hydroxo complexes formed during the production might be present in WO_2 samples" is incomprehensible. On page 150 of the literature source [9], quoted by the authors of the article under their reference 19 one finds: "In a pure state WO_2 can be obtained, for example, at 900 °C in hydrogen atmosphere and a water vapor partial pressure of 0.5 bar." WO_2 made under these conditions cannot contain the mentioned species.

Finally, $R_2W_4O_{13}$ (R = Na) is not the formula for *meta*-tungstates, as the authors claimed, but it is rather the formula of sodium *tetra*tungstate [10]. Although the Na:WO_3 ratio is the same as for the metatungstate anion, its structure is quite different from the KEGGIN structure (Figure 2).

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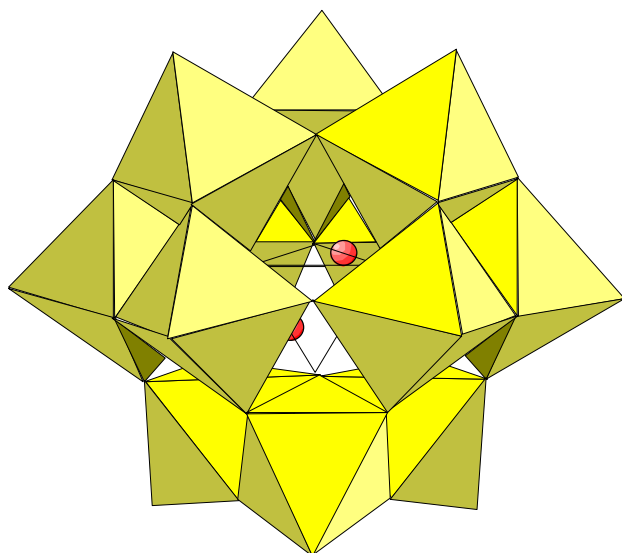Pennsylvania, USA

Figure 2. Polyhedral representation of the metatungstate anion $[H_2W_{12}O_{40}]^{6-}$.

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