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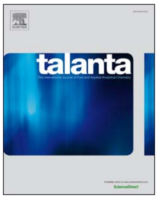

# Application of ESI-HRMS for molybdenum speciation in natural waters: An investigation of molybdate-halide reactions

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## ABSTRACT

High resolution electrospray ionization mass spectrometry (ESI-HRMS) was used to study the speciation of molybdate in interaction with halides (Cl, F, Br). Desolvation during electrospray ionization induced alteration of aqueous species but method optimization successfully suppressed artefact compounds. At low Mo concentrations, chloro(oxo)molybdate and fluoro(oxo)molybdate species were found and in natural samples, $MoO_3Cl$ was detected for the first time, to the best of our knowledge. Apparent equilibrium constants for Cl substitution on molybdate were calculated for a range of pH values from 4.5 to 8.5. A minor alteration in speciation during the gas phase (conversion of doubly charged $MoO_4^{2-}$ to $HMoO_4^-$) did not allow investigation of the molybdate acid-base properties; however this could be determined by speciation modeling. This study provides further evidence that ESI-HRMS is a fast and suitable tool to Deceasedassess the speciation of inorganic compounds such as Mo.

## 1. Introduction

Molybdenum and some other transition metals (e.g., V, W) differ from other members of transition elements in their ability to attract electrons, hydrolyze and form oxometalate complexes [1]. These elements have notable physico-chemical properties and a large diversity of applications (e.g., medicine, catalysis, biochemistry [2] and references therein). Also, being heteroatomic and negatively charged molecules, the environmental behavior and reactivity of molybdate species are complex. In surface waters, it is generally assumed that the doubly charged molybdate anion ($MoO_4^{2-}$) is the only dominant species [1,3,4] and also one of the best examples of a conservative-type trace metal in seawater [3]. Nevertheless, Mo behavior in estuarine systems has been reported to be either conservative [5–8], non-conservative [9,10] or both [11,12]. Hence, Mo reactivity in estuarine and coastal areas remains not totally understood despite the central role of Mo in N fixation in organisms and ultimately in global primary production [13,14].

Another important group of molybdenum species with significant applications encompasses chloromolybdenum compounds (e.g., $MoCl_3$, $MoCl_5$) [15]. In previous studies, thermic treatment of solid $MoCl_5$ with $O_2$ or dissolution of $MoO_3$ in 10 M HCl was shown to result in several molybdenum-oxo-chloro molecules ($MoO_nCl_{6-n}$, n = 1–3) containing 3 to 6 Cl [2,15–18]. However, the interaction between dissolved oxymolybdate and chloride has not yet been investigated; in natural water, this interaction may modify the reactivity of molybdate species, mostly during estuarine water mixing as has been observed for some metals, such as Cd [19].

Over the past decades, electrospray ionization - high resolution mass spectrometry (ESI-HRMS) has been widely used due its applicability in analyzing both organic and inorganic compounds with high resolution and selectivity [20]. Molybdenum speciation has been observed by its specific isotope pattern in mass spectra either in an aqueous/organic solvent mixture [21] or in purely aqueous media [22–24]. However, these experiments were carried out using high concentrations (1 mM, ~ 96,000 µg $L^{-1}$, or higher) of Mo, which can lead to potential polymerization [25]. Also, these concentrations are not necessarily reflective of natural conditions. Furthermore, even though ESI-HRMS is considered to be a soft ionization technique, the desolvation stage in which ions are transferred from solution to a gaseous phase, may modify the solution species, and potentially alter the applicability of ESI-HRMS for aqueous inorganic compounds [20,24].

In natural waters, Mo concentrations range from ca. 0.5 µg $L^{-1}$ in rivers [6,9] to ca. 10 µg $L^{-1}$ in oceans [4,26], with some exceptions for streams running through clay-rich or sulfide-mineralized formations or streams affected by local urban and industrialized contamination [27] (e.g., up to 230 µg $L^{-1}$ in UK surface and ground waters, 7,900 µg $L^{-1}$ in the Argentinian Cordoba oxic alkaline aquifers, and 4,740 µg $L^{-1}$ in the US Lithia reducing aquifer ([26] and references therein)). However,

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higher Mo concentrations could be found in waters in the vicinity of mining/mineralization facilities. Indeed, ground waters in the proximity of the Russian Uronai and Chilean Spence deposits contain up to 420–475 μg Mo $L^{-1}$ [28,29] while mine drainage from the Peruvian Antamina mine could be enriched up to 13,900 μg Mo $L^{-1}$ [30].

This study focuses on the optimization of ESI-MS parameters to assess a potential interaction between oxomolybdate and chloride at low concentrations (10 μM, ~ 960 μg Mo $L^{-1}$) of Mo and across a large pH range (4.5–8.4). In addition, application of a data processing program (Winnow [31]) on large mass spectra lists was used to simplify and reveal all potential species of the target elements. The purpose of this investigation was to provide a novel approach to better understand Mo behavior in surface waters.

## 2. Materials and methods

### 2.1. Chemicals and sample preparation

Stock solutions of molybdate, selenite, selenate and NaCl were prepared in glass vials by dissolving reagents (99% min; $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Acros organic), $NaSeO_4$ (Alfa Aesar), $NaSeO_3$ (Alfa Aesar), NaCl (Bioshop)) in 18 MΩ.cm water. Phosphate buffer stock solutions ($Na_2HPO_4$, $NaH_2PO_4$ (Baker)) were prepared at 0.2 M and readjusted for pH with $HNO_3$ (double distilled trace-metal grade, BHD Aristar plus/DuoPUR Milestone) and $NH_4OH$ (Fisher). Molybdate solutions at a final concentration of 10 μM (~ 960 μg Mo $L^{-1}$) were mixed with phosphate buffer (final concentration of 0.4 mM) and different concentrations of Cl (0–180 mM). Prior to ESI-HRMS analysis, aqueous samples were mixed with methanol (HPLC-grade, BDH) at a ratio of 50/50 (v/v).

Natural water samples were collected from Bow Lake (BLW: Ontario, Canada; 45°00'49.8"N 77°56'21.0"W) and the Otonabee River (ORW: 44°21'23.1"N 78°17'23.9"W, Ontario, Canada). Water from Bow Lake was collected, filtered through 0.7-μm filters and stored at 4 °C in the dark. Water collected from the Otonabee River was sand filtered and ozonated before it was filtered through the 0.7-μm filters and stored at 4 °C in the dark. Additionally, a soft water river sample (PERADE-09, certified reference material) was purchased from Environment Canada. Also, a seawater sample was collected from Clear Water Bay (CWB, Hong Kong) and was subjected to the same treatment and preservation as river and lake waters above.

### 2.2. Instrumentation

Mass spectra were collected using an Orbitrap Q Exactive (Thermo Fisher Scientific) in infusion mode at the Water Quality Center (WQC, Trent University, Canada). Negative ions were examined at a resolution of 140,000, using either a full MS scan of the $m/z$ range of 50–750 or a narrower range depending on the analyte - typically 140–260 $m/z$ for diluted molybdate species. The S-lens level was set at 50. Other ESI-HRMS parameters were subjected to optimization: syringe flow rate from 5 to 20 μL $min^{-1}$, spray voltage from 2 to 7 kV, capillary temperature from 180 to 350 °C, sheath gas pressure from 10 to 22 (arbitrary units: arb), auxiliary gas from 0 to 6 arb. Prior to ESI-HRMS data acquisition, a routine mass calibration was carried out with Pierce™ LTQ ESI Positive/Negative Ion Calibration Solution (88322/88324, Thermo Fisher Scientific) using the recommended manufacturer parameters (sheath gas = 12 arb, auxiliary gas = 0 arb, spray voltage = 4 kV, capillary temperature = 320 °C). Mass spectra were acquired in duplicate with the 2 microscans, lasting 1–1.5 min each, corresponding to 60–80 scans to reach 100% of the Automatic Gain Control (AGC) target. The maximum injection time was set to 10 ms.

Ion fragmentation was performed at different in-source CID (collision-induced dissociation) voltages from 0 to 60 eV.

Concentrations of dissolved Mo were measured using an 8800 Triple Quadrupole ICP-MS (Agilent Technologies) at the WQC (see [32] for further details). Briefly, Mo was analyzed in MS/MS mode with $O_2$ as the reaction gas and indium as the internal standard. Analytical recovery was determined using certified materials; the measured Mo concentration in certified ground water (ES-L1, EnviroMat) was 11.0 ± 0.9 μg $L^{-1}$ (n = 16), in agreement with the certified value of 11 ± 1 μg $L^{-1}$. The certified seawater (CASS-6, National Research Council Canada) was diluted by tenfold prior to ICP-MS analysis; the Mo concentration was 9.9 ± 0.7 μg $L^{-1}$ (n = 9), compared to the certified value of 9.15 ± 0.52 μg $L^{-1}$.

The pH values reported in this study were measured in a water/methanol mixture after pH calibration in aqueous standard solutions (referred to as , ${}^{S}_{W}pH$ according to Suu et al. [33]). Solution pH and Cl concentrations were measured on an Accumet AB250 meter using a pH combination electrode (Fisher Scientific) and a Cole-Parmer combination chloride ion selective electrode, respectively.

### 2.3. Data processing

Mass spectra were processed using Thermo Xcalibur Qual Browser software after an automatic processing defining mass tolerance of 10 ppm and mass precision at four decimals. For each compound, the elemental composition was assigned and checked by the isotope simulation module of the software. In addition, the spectrum list was exported to be processed by Winnow, a program that scans the mass spectrum list for the presence of target elements or ions based on isotope pattern (isotopologue mass difference and intensity ratio [31]). Examples of Mo isotope patterns in oxomolybdate and chloro(oxo) molybdate that Winnow aims to extract from an ESI-HRMS spectrum list are given in Fig. 1.

## 3. Results and discussion

### 3.1. Preliminary measurements of Mo and Se speciation

We conducted some preliminary measurements of Mo speciation (15 solutions containing 10 μM Mo (~ 960 μg Mo $L^{-1}$), 0–17 mM Cl at pH 5 in glass vials) using the ESI parameters recommended by the manufacturer for routine mass calibration, i.e., sheath gas = 12 arb, auxiliary gas = 0 arb, spray voltage = 4 kV, capillary temperature = 320 °C [34]. The Winnow program identified 12 compounds of monomolybdate (Table 1) in the mass spectrum of a solution containing 10 μM molybdate (~ 960 μg Mo $L^{-1}$), 0.13 mM Cl at pH 5 (Fig. 2A; note that for this test only, an intermediate solution of molybdate (1 mM, ca. ~ 96,000 μg Mo $L^{-1}$) was stored in a 10 mL plastic (Falcon) centrifuge tube rather than in the glass vials used for other solutions carried out in this study). The detected molybdate monomers are unlike the large polyoxomolybdate species found in previous studies carried out at a 100-fold higher Mo concentration [24,35]. The 12 molybdate monomers identified by Winnow include (i) oxomolybdate ($HMoO_4$, $MoO_5$, $HMoO_5$, $NaMoO_4$, $MoO_4NO_2$), (ii) chloro(oxo)molybdate ($MoO_3Cl$, $MoO_4Cl$, $MoO_5Cl$), (iii) organic molybdate ($CH_3O_4Mo$, $C_3H_5O_6Mo$), (iv) organic chloro(oxo)molybdate ($C_3H_4O_5MoCl$) and (v) one unassigned compound (Mo-X) (Table 1). No Mo compound was found below 140 $m/z$, showing that $MoO_4^{2-}$ (theoretical $m/z$ = 80.943), generally considered to be the main species in natural surface water [1,3,4], was not detected.

Two solutions of selenate and selenite (0.12 mM) in 10 mM $NaNO_3$ were also analyzed revealing $HSO_4$, $HSeO_4$, $SeO_2$, $HSeO_2$, $SeO_3$, $HSeO_3$, $CH_3SeO_3$ (Fig. 2b and c). Similar to $MoO_4^{2-}$, the dominant doubly charged sulfate and selenate species in natural waters ($SO_4^{2-}$ and $SeO_4^{2-}$, [36]) were not detected. In fact, modifications of these aqueous anions during ESI desolvation has been observed previously for S [37], Mo [22–24,35] and W [22,23]. These multi-charged small aqueous species tend to become protonated during ESI to enhance their stability by accepting a proton from water [23]. In addition, it appears that oxygen was added to the most dominant $HMoO_4^-$ compound (peroxo-