Accurate Determination of Trace Molybdenum in Drinking Water by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry

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A method for accurate and precise determination of trace molybdenum in drinking water by isotope dilution inductively coupled plasma mass spectrometry was developed, given the concentrations of Mo in drinking-water samples from Chaoyang and Changping districts of Beijing (China) as $1.017 \pm 0.008$ and $1.033 \pm 0.007 \mu g \text{ kg}^{-1}$ ($k = 2$), respectively. Special care was taken for the validation of the proposed ID-ICPMS method using CRM 7203-a, a certified reference material for elemental analysis of tap water.

Keywords Trace molybdenum, accurate determination, isotope dilution method, drinking water, uncertainty evaluation

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Introduction

As an essential trace element for human health, molybdenum draws attention in recent studies since it is an important enzyme cofactor in nearly all organisms. Particularly, Mo is a key element to the functioning of xanthine dehydrogenase, sulfite oxidase, and aldehyde oxidase, which play prominent roles in human metabolism. Insufficient intake of Mo may cause Keshan disease, anemia, and sulfite sensitivity, while an overdose of Mo is also harmful to human health, giving rise to ailments, including joint pain, gouty arthritis, arteriosclerosis, and deformity.

Drinking water is one of the major sources for the intake of Mo to the human body. The Mo concentrations in drinking water are usually very low and typically less than 2 $\mu g \text{ L}^{-1}$ based on investigations of the British Geological Survey and National Metrology Institute of Japan. In this case, the determination of trace Mo in drinking water demands the utilization of a high accurate and precise analysis method. Analytical methods including ion-selective electrode potentiometry (ISE), X-ray fluorescence spectrometry (XRF), inductively coupled plasma atomic emission spectrometry (ICPAES), and inductively coupled plasma mass spectrometry (ICPMS) have been applied to the determination of trace metals in various sample matrices. Amongst these, ICPMS has proven to be a powerful tool for water system characterization owing to its high sensitivity and advantages in isotopic analysis. The application of isotope measurement for the quantification of samples is well-known as an isotope dilution (ID) mass spectrometry, which is considered to be a potential primary method of the highest metrological quality for analysis. Since the ID approach is based on an isotope ratio rather than an absolute intensity measurement, it drastically eliminated the loss of analyte during sample preparation, matrix effects, and instrumental drifts, providing that the isotopic equilibration was achieved prior to ratio measurements. To date, ID-ICPMS has found limited achievements for the determination of trace metals at ppb levels in water systems. The application of ID-ICPMS for the quantification of Mo in drinking water still presents several challenges despite the robustness of the ID method. First, a suitable isotope pair for analysis is essential for reducing isobaric interferences. Second, accurate methods for the characterization of the isotope ratio and total Mo content of isotopically enriched Mo spike are required. Thirdly, the combined uncertainty of the methodology demands a full evaluation.

The objective of this research was to develop an ID-ICPMS method for the analysis of trace Mo in drinking water, which is highly accurate, precise, and without any preconcentration or matrix separation for samples. Herein, three efforts were made to overcome the present challenges: 1) a $^{97}\text{Mo}/^{95}\text{Mo}$ isotope pair was selected for ICPMS measurements to eliminate any isobaric interferences of Zr and Ru; 2) the isotopic composition of Mo in $^{97}\text{Mo}$ spike was determined by a multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) using the standard-sample bracketing method; while the accurate total content of Mo in $^{97}\text{Mo}$ spike was determined by a reverse ID approach; 3) the combined uncertainty of measurement results were evaluated according to the Guide to Expression of Uncertainty Measurement of ISO/BIPM with relative contributions of individual uncertainty components all being accounted for. The proposed ID-ICPMS method was further applied for the determination of the Mo concentration in a certified reference material for elemental analysis of tap water, NMIJ CRM 7203-a, to validate the analytical approach.

Experimental

An optimum $^{97}\text{Mo}/^{95}\text{Mo}$ ratio of 11 was obtained by Eq. (1) to achieve a minimum error multiplication factor, and hence lowered the measurement uncertainty. 

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\[ R_{\text{opt}} = \frac{x_a \cdot x_b}{x_a \cdot x_b} \]  

(1)

where \(x_a\) and \(x_b\) denote the isotope abundances of \(^{97}\text{Mo}\) in the sample and spike solution, respectively; \(x_s\) and \(x_p\) denote the isotope abundances of \(^{95}\text{Mo}\) in the sample and spike solution, respectively.

Six independent blend solutions of spike and drinking-water samples were prepared gravimetrically to provide an isotope ratio of \(^{97}\text{Mo}/^{95}\text{Mo}\) close to 11. To ensure isotopic equilibration, spiked samples were well-mixed and stored over night before ICPMS measurements.

For reverse ID, the same amount of spike solution used for the drinking-water samples were accurately weighed and mixed with a known mass of Mo primary assay standard solution to result in a ratio of \(^{97}\text{Mo}/^{95}\text{Mo}\) near to 11. Six replicate blend solutions were prepared. Equations (2) and (3) were utilized for calculating the Mo concentrations of \(^{97}\text{Mo}\) spike solution and the drinking-water samples, respectively:

\[ C_s = \frac{C \cdot m_p \cdot x_p - R_w \cdot m_s \cdot x_s}{R_p \cdot m_s \cdot x_s - m_p \cdot x_p} \cdot M_s \]  

(2)

\[ C_s = \frac{C \cdot m_s \cdot x_s - R_w \cdot m_p \cdot x_p}{R_p \cdot m_p \cdot x_p - m_s \cdot x_s} \cdot M_s \]  

(3)

in which \(C_s\), \(C_a\), and \(C_p\) are the Mo concentrations (\(\mu\)g kg\(^{-1}\)) in drinking-water sample, \(^{97}\text{Mo}\) spike, and primary assay standard; \(m_s\) and \(m_p\) are the masses (g) of drinking water sample and \(^{97}\text{Mo}\) spike used for preparing the blend solution of the sample and spike; \(m_s\) and \(m_p\) are the masses (g) of the \(^{97}\text{Mo}\) spike and the primary assay standard used for preparing the blend solution of the spike and primary assay standard solution for reverse ID; \(R_w\) and \(R_p\) are the mass bias corrected \(^{97}\text{Mo}/^{95}\text{Mo}\) ratios for blend solutions of the sample and spike, and blend solutions of the spike and primary assay standard; \(x_s\) is the abundance of \(^{97}\text{Mo}\) isotope in primary assay standard; \(x_p\) is the abundance of \(^{97}\text{Mo}\) isotope in primary assay standard; \(M_s\), \(M_s\), and \(M_p\) are the molar mass (g mol\(^{-1}\)) of Mo in drinking water, \(^{97}\text{Mo}\) spike, and primary assay standard.

Inductively coupled plasma mass spectrometry (NexION 300D, Perkin Elmer Inc., USA) was used for trace Mo determinations in samples. The instrument was operated in standard mode with a low-mass resolution. Daily optimization was performed using a standard tuning solution in order to obtain maximum sensitivity and reduce spectral interferences. The parameters, including the number of sweeps/reading, dwell time and replicates were optimized to obtain precise isotope ratio measurement (see Experimental in Supporting Information). Typical operation parameters of ICPMS are listed in Table S2 (Supporting Information). After the measurement for each sample, 0.3 M HNO\(_3\) was used for rinsing the nebulizer and spray chamber until the signal intensity had dropped to the background level to eliminate any memory effect. Then, a blank solution was measured before each sample, and its intensity was always subtracted.

**Results and Discussion**

The ID and reverse ID equations (Eqs. (2) and (3)) require accurate measurements of Mo isotopic compositions for the enriched \(^{97}\text{Mo}\) spike. Since the Mo isotope ratios for enriched \(^{97}\text{Mo}\) were in a large dynamic range, a determination of the Mo isotope-abundance values for \(^{97}\text{Mo}\) spike was carried out by MC-ICPMS to achieve higher precision for the isotope ratio measurement (see Experimental in Supporting Information). The determined isotopic compositions for the \(^{97}\text{Mo}\) spike were: \(x^{(\text{Mo})} = 0.002084 \pm 3\), \(x^{(\text{Mo})} = 0.001897 \pm 3\), \(x^{(\text{Mo})} = 0.0046505 \pm 11\), \(x^{(\text{Mo})} = 0.012359 \pm 4\), \(x^{(\text{Mo})} = 0.942136 \pm 16\), and \(x^{(\text{Mo})} = 0.033813 \pm 12\), respectively.

The determined Mo concentrations in drinking-water samples (DW-1 and DW-2) were measured with six replicates. The horizontal lines represent the mean values (solid line) and the expanded uncertainty (\(k = 2\) (dot line)) of the Mo contents in DW-1 and DW-2 samples, respectively. Each data point is the average of two measurement results.

For achieving an accurate quantification result by the ID-ICPMS method, an insignificant spectral interference for the isotope ratio measurement is essential. The isotope ratio of \(^{97}\text{Mo}/^{95}\text{Mo}\) was selected as the measured isotope pair to eliminate the potential isobaric interferences from Zr and Ru. The signal intensities for \(^{95}\text{Mo}\) and \(^{97}\text{Mo}\) were optimized to be as high as possible for reducing any potential molecular interferences, such as \(^{40}\text{Ar}^{18}\text{O}\) on \(^{97}\text{Mo}\). As a result, the typical background to signal ratios were <0.35% for \(^{96}\text{Mo}\) and <0.08% for \(^{98}\text{Mo}\) when measuring the blend solutions using ICPMS.

In our analytical procedure, a Mo primary assay standard solution was repeatedly introduced as a bracketing standard to monitor the instrumental sensitivity and correct the mass bias drift. The measurement sequence is outlined in Table S4 (Supporting Information). The Mo concentrations in drinking-water samples obtained from two districts of Beijing were determined by the proposed ID-ICPMS method. Results for the analysis are plotted in Fig. 1, in which the relative standard deviations of six replicates were 6.2% for DW-1 and 4.8% for DW-2, respectively. The detection limit of Mo in this method was calculated as 0.002 – 0.003 \(\mu\)g kg\(^{-1}\) by the 3\(\sigma\) criterion (3\(\sigma\)DS).

Relative contributions of individual uncertainty components were all evaluated according to the Guide to Expression of Uncertainty in Measurement of ISO/BIPM (Eq. (4)).

\[
u_C(y) = \sum_{i=1}^{\nu_1} \left( \frac{\partial f}{\partial x_i} \right)^2 \sigma_y(x_i) + 2 \sum_{i=1}^{\nu_1} \sum_{j=i}^{\nu_2} \left( \frac{\partial f}{\partial x_i} \right) \left( \frac{\partial f}{\partial x_j} \right) \sigma_y(x_i) \sigma_y(x_j) \]  

(4)

A detailed budget of potential uncertainties and the relationships between these parameters and the uncertainty budget are summarized in Table S5 (Supporting Information). The overall combined standard uncertainties were evaluated as 0.0038 for DW-1 and 0.0034 for DW-2, respectively.
in which the individual partial derivatives (sensitivity coefficients) $x_i, x_j$ were derived from all variables in Eqs. (2) and (3).

As a result, the assessment of the uncertainty budget for determining the Mo content using the double ID-ICPMS method is dominated by the standard deviations of the six replicate measurement results for drinking-water samples $u_c (\sim 56.9\%)$ and $^{97}$Mo spike $u_c (\sim 10.5\%)$. The uncertainty for the certified value of the primary assay standard $u_p$ is responsible for $\sim 20.6\%$ of the overall combined uncertainty. The typical uncertainty budget for the measurement results is displayed in Fig. 2.

The ID-ICPMS method was further applied for the determination of the Mo content in CRM 7203-a, given the Mo concentration as $1.021 \pm 0.010 \mu g kg^{-1}$ ($k = 2$), which is identical to the certified value of CRM 7203-a ($1.02 \pm 0.09 \mu g kg^{-1}$, $k = 2$). The good agreement between the results validated the analytical procedure we applied for determining the trace Mo concentration in drinking water.

**Conclusions**

In this study, an ID-ICPMS analytical protocol was developed and allowed for the determination of trace Mo in drinking water. The good agreement of the achieved results with the certified values of NMIJ CRM 7302-a had validated the newly developed analytical procedure. As a result, the total Mo content in drinking-water samples were determined as $1.017 \pm 0.008$ and $1.033 \pm 0.007 \mu g kg^{-1}$ ($k = 2$) for Chaoyang and Changping districts of Beijing, China. This ID-ICPMS approach provided high accuracy, absolute quantification and reduced uncertainty for the determination of trace Mo in drinking water.

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**Supporting Information**

The additional experimental descriptions and discussions are available in Supporting Information. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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