Determination of Trace Molybdenum in Water Samples by Electrothermal Atomic Absorption Spectrometry after Preconcentration with Miniaturized Coprecipitation

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Miniaturized coprecipitation with hydrous manganese(IV) oxide was studied for the preconcentration of sub μg dm^{-3} levels of molybdenum in water samples. Manganese(IV) oxide was produced by a reaction of permanganate ion with ethanol in the presence of 0.1 mol dm^{-3} hydrochloric acid. A nanogram amount of molybdenum in a 10 cm^3 sample was quantitatively coprecipitated. The amount of manganese required was 0.1—0.40 mg for a 10 cm^3 sample. The precipitate was collected on a 10 μm membrane filter, and then dissolved in 50 mm^3 of 5.6 mol dm^{-3} nitric acid and 75 mm^3 of 1% hydrogen peroxide. An 80-fold preconcentration factor was obtained by this procedure. The molybdenum concentration was determined by electrothermal atomic absorption spectrometry using a pyrolytic graphite coated cuvette. The detection limit (3σ) was found to be 8.9 ng dm^{-3}. The proposed method was successfully applied to river water and snow samples.

A simple and rapid preconcentration method for the determination of trace elements in natural water is required as a consequence of increased concern over environmental pollution. In 1992, new Tap Water Quality Standard and Standard Methods for Drinking Water were established in Japan, and molybdenum was specified to be monitored at a level below 70 μg dm^{-3}. If the molybdenum concentration, even in seawater, ranged from 10 to 100 μg dm^{-3}, molybdenum could be directly determined by electrothermal atomic absorption spectrometry (ETAAS).[1] However, since the molybdenum content of fresh water is often below μg dm^{-3} without any significant pollution, its determination requires preconcentration factors of 10—100 times.

We have already reported on two miniaturized preconcentration techniques, the micro solvent extraction method[2,3] and the mini-column chelating resin method.[4,5] This paper describes the miniaturized coprecipitation method.

The most common coprecipitants are hydrous oxides and hydroxides, such as manganese(IV) oxide and iron(III) hydroxide; the molybdenum content used to be determined by spectrophotometry.[6] Tanaka[7] has claimed that hydrous manganese(IV) oxide, produced by a reaction between manganese(II) and permanganate ion, is superior to iron(III) hydroxide for the coprecipitation of molybdenum.

Akagi and Haraguchi[8] have reported on the simultaneous multi-element determination of trace metals using 10 cm^3 of seawater by inductively coupled plasma atomic emission spectrometry with gallium hydroxide coprecipitation and a microsampling technique. However, the molybdenum content could not be determined because of poor recovery at pH 9.[9] Yamazaki et al.[10] have investigated the coprecipitation behavior of molybdenum with iron(III) hydroxide in various salt solutions, and found that molybdenum was almost completely coprecipitated at pH 4—5 as monohydrogen oxoanion, $HMoO_4^-$. The poor recovery of molybdenum at high pH may result from oxoanion, MoO_4^{2-}.[9,10] Coprecipitation with metal chelate complex formation has also been studied for determining molybdenum by ETAAS, operated in the conventional batch mode[11] or the flow injection online preconcentration mode.[12]

A coprecipitation method with hydrous manganese(IV) oxide is specified to the preconcentration of antimony, bismuth, and tin in the official method of spectrophotometric analysis.[13] In this work, the miniaturized coprecipitation method with hydrous manganese(IV) oxide was studied for the preconcentration of trace molybdenum in water samples.

Experimental

Apparatus. A Hitachi Model Z-7000 polarized Zeeman atomic absorption spectrometer was used. Argon was used as a sheath gas at a flow rate of 3.0 dm^3 min^{-1} and a carrier gas (internal gas) at 0.2 dm^3 min^{-1}. The carrier gas flow was interrupted during the atomization stage.

Reagents. All the chemicals used were of analytical reagent grade. Distilled, deionized water was further purified using a Millipore Milli-Q water purification system. A molybdenum working solution was prepared from a stock solution (1 mg cm^{-3}, dissolving ammonium molybdate in water) by dilution with water. As a buffer, a 1 mol dm^{-3} 3-(*N*-Morpholino)propanesulfonic acid (MOPS, Dojindo) solution was prepared by dissolving MOPS in water.

Procedure. The basic working procedure for the 20-fold preconcentration of molybdenum is as follows.

A 10 cm^3 water sample (3 ng Mo cm^{-3}, in 0.1 mol dm^{-3} hydrochloric acid) was taken in a polypropylene mini-column (ca. 15 cm^3, Muromac® Column L, Muromachi Kagaku) in which a 10 μm membrane filter (Omnipore, Millipore) was previously attached to a 35 μm perforated disc. Then, 20 mm^3 of ethanol and 20 mm^3 of 30 mg cm^{-3} potassium permanganate solution were successively added. After the solution was shaken for 10 min, the solution was drained through a 10 μm membrane filter by aspiration. The hydrous manganese(IV) oxide precipitate on the filter was rinsed with water, dehydrated by a hand-driven centrifuge, and dissolved in 200 mm^3 of 5.6 mol dm^{-3} nitric acid and 300 mm^3 of 1% hydrogen peroxide with ultrasonic irradiation for 15 min. After 30 min, the resulting solution was transferred into a collection vial by centrifugation, and the molybdenum concentration was determined by ETAAS. A 20 mm^3 aliquot of the solution was injected into a tube-type pyrolytic graphite coated cuvette. The absorbance signals were recorded at 313.3 nm, and the peak heights were taken as the analytical signals.

In the case of an 80-fold preconcentration, the precipitates were dissolved in 50 mm^3 of 5.6 mol dm^{-3} nitric acid and 75 mm^3 of 1% hydrogen peroxide.

Results and Discussion

Optimum Furnace Conditions of ETAAS. The effect of the ashing temperature was investigated by varying it from 700 to 2200 °C. The maximum, constant absorbance was obtained at approximately 700—1600 °C. At the atomization stage, the maximum absorbance was obtained at around 3000 °C.

The optimum furnace conditions for molybdenum measurements were as follows: Drying, 100—200 °C for 50 s; Ashing, 1200 °C for 30 s; Atomizing (rapid-heating atomization with an optical temperature control device), 3000 °C for 10 s.

Optimum Conditions for Coprecipitation. Hydrous manganese(IV) oxide is usually produced by a reaction between manganese(II) and permanganate ion, where the reaction is accelerated by heating the solution.[7,13,14] However, its can be readily precipitated by a reaction at room temperature between the permanganate ion and ethanol.[6] The effect of the experimental variables on the recovery of molybdenum was examined.

Chan and Riley have reported on the optimum pH conditions of 1.3 to 5.5 in seawater.[6] In this study, the coprecipitation of molybdenum was complete in the pH range of 1.0—6.0, and even in an acidic solution of 0.1—0.4 mol dm^{-3} hydrochloric acid. Therefore, the acidity of 0.1 mol dm^{-3} hydrochloric acid was chosen because natural water samples are commonly stored at this acidity. In the case of iron(III) hydroxide,[15] the recovery of molybdenum depended markedly on the pH, and the optimum pH range was 5.25—6.25.

Generally, the recovery of a trace element is achieved with a milligram quantity of a coprecipitant element. Figure 1 shows the effect of the amount of added manganese. The recovery of molybdenum abruptly increased along with an increase in manganese, and became almost constant. The recovery of molybdenum gradually decreased as the added amount of manganese increased by more than 0.4 mg. However, with an excess of manganese, the absorbance of molybdenum drastically decreased. The interference from manganese in an ETAAS measurement was investigated. With 0.4 and 0.5 mg of manganese, the absorbances of molybdenum were 9.4 and 26.7% lower than the value with 0—0.3 mg of manganese. Therefore, the amount of manganese added was optimized to be 0.2 mg (0.6 mg as potassium permanganate) for a 10 cm^3 sample.

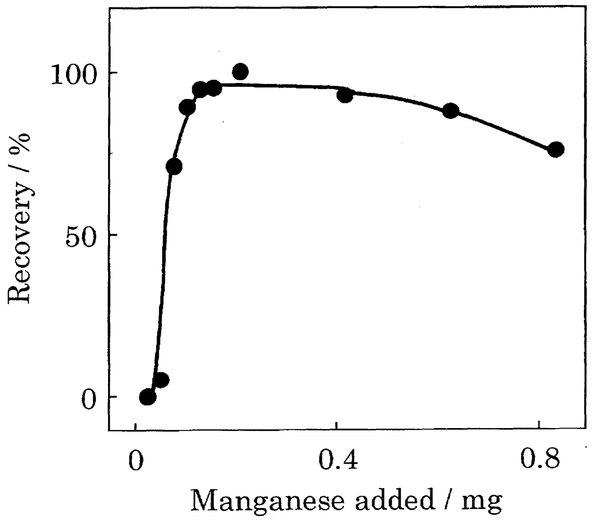

Fig. 1. Effect of the amount of manganese on the recovery of 30 ng of molybdenum from 10 cm^3 of water.

The reaction of permanganate ion and ethanol was performed by shaking the mixture for 10 min, but the manganese(IV) oxide precipitated was ca. 53% of the yield of the added manganese. As shown in Fig. 2, a standing time of more than 60 min was required for complete precipitation. Chan and Riley have aged precipitates overnight.[6] However, the recovery of molybdenum was not affected by the standing time, as can be seen in Fig. 2. Therefore, the aging step was no longer necessary.

To a quantitative collection of the precipitate, filtration with a 10 μm membrane filter was successfully applied. The dehydration step was essential for accurate results, because a small amount of water retained with the precipitate affects the dissolution step and the precision. Since the precision

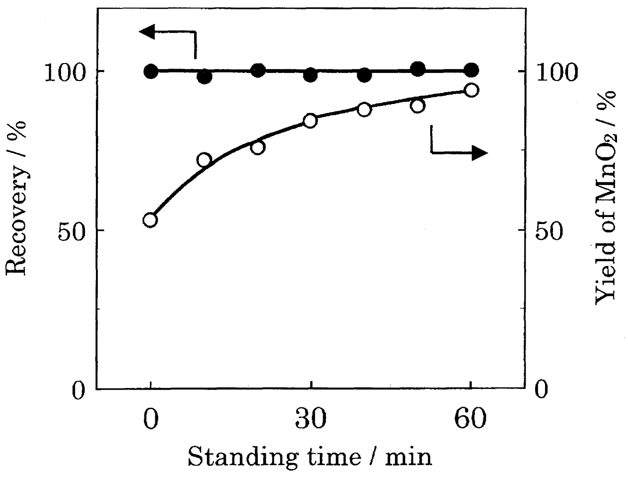

Fig. 2. Effects of the standing time on the recovery of 30 ng of molybdenum (●) from 10 cm^3 of water and the yield of manganese(IV) oxide (○) from 0.20 mg of manganese.

(relative standard deviation) for eight replicate determinations of 3 ng cm^{-3} level was 1.4%, dehydration with a hand-driven centrifuge appeared to be effective.

For the dissolution of manganese(IV) oxide, nitric acid was better than hydrochloric acid. The addition of hydrogen peroxide and ultrasonic irradiation were necessary for complete dissolution in a limited-volume solvent.

Detection Limit and Interference. A linear calibration curve for 80-fold preconcentration was obtained over the range of 0 to 1.25 μg dm^{-3}. The molybdenum concentration corresponding to 1% absorption (absorbance = 0.0044) was 16 ng dm^{-3}. The detection limit, defined as three times the standard deviation of the blank signals (n = 10), was 8.9 ng dm^{-3}.

The interference of various metal ions in the determination of molybdenum was investigated with a mixture of metal ions, at concentrations approximately equal to, or exceeding, those normally found in river water.[16)] However, the mixture of metal ions tested was found not to cause severe interference with the determination of molybdenum. Furthermore, it can be seen in Table 1 that the proposed method is applicable to the analysis of saline water.

Analysis of Fresh Water. The concentrations of molybdenum in river water and snow samples were determined according to the proposed method using the standard addition method and the matrix matching method of calibration. The matrix-matched calibration standards were prepared by adding the requisite volumes of a 30 mg cm^{-3} potassium permanganate solution, 5.6 mol dm^{-3} nitric acid and 1% hydrogen peroxide. The collected river water samples were filtered through a 0.45 μm membrane filter (MF-Millipore) and acidified to 0.1 mol dm^{-3} hydrochloric acid. The collected snow sample was acidified to 0.1 mol dm^{-3} hydrochloric acid and filtration was performed after one week. For all samples, the determination was performed within one week after filtration. The analytical results are given in Table 2.

The concentrations of molybdenum in fresh water have been reported to be 0.32 μg dm^{-3},[17)] 0.15—0.49 μg dm^{-3}.[18)] The analytical values obtained by the proposed method are approximately in the same range as those reported. Moreover, the analytical values obtained by the two calibration methods were in good agreement, and no interferences from humic substances[19)] were observed.

Table 1. Influence of Foreign Ions on the Determination of Molybdenum in Seawater

Ions	Concentration/μg dm^{-3}				
Al^{III}	0	0	5	25	50
Ti^{IV}	0	0	1	5	10
V^{V}	0	0	1.5	7.5	15
Fe^{III}	0	0	3	15	30
Ni^{II}	0	0	2	10	20
Cu^{II}	0	0	3	15	30
Zn^{II}	0	0	5	25	50
As^{V}	0	0	2.3	11.5	23
Sb^{III}	0	0	0.2	1	2
W^{VI}	0	0	0.12	0.6	1.2
U^{VI}	0	0	3.3	16.5	33
Artificial seawater	None	Add	Add	Add	Add
Relative absorbance	100	99.6	104.4	101.0	90.2

Composition of the artificial seawater(in g dm^{-3}) is Na^+: 11.03, Mg^{2+}: 1.33, Ca^{2+}: 0.42, K^+: 0.39, Sr^{2+}: 0.013, Cl^-: 19.84, $SO_4{}^{2-}$: 2.77, Br^-: 0.067, $BO_3{}^{3-}$: 0.028, and F^-: 0.0014.

Table 2. Analytical Results of Molybdenum in Fresh Water

Sample	Mo found/μg dm^{-3}	
	Method A	Method B
Kinu river[b)]	0.30 ± 0.03[a)]	0.30 ± 0.02
Kuro river[c)]	0.27 ± 0.01	0.29 ± 0.02
Snow[b)]	0.091 ± 0.010	0.092 ± 0.011

Method A: Standard addition method. Method B: Matrix matching method. a) Mean ± standard deviation, n = 4. b) Utsunomiya, Tochigi Pref. c) Kanuma, Tochigi Pref.

The proposed method combined with the matrix matching method of calibration is simple and rapid, and allows the determination of trace molybdenum using only 10 cm^3 of water samples, such as river water, wet precipitation and saline water. Moreover, the proposed method has applicability in the field analytical chemistry[20)] and is also applicable to the determination of antimony, bismuth, and tin.

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