RAPID SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM(VI) IN SEAWATER

Yoshio SHIJO,[®] Katsuji IDE, and Kaoru SAKAIDepartment of Environmental Chemistry, Faculty of Engineering,
University of Utsunomiya, Ishii-machi, Utsunomiya-shi, Tochigi 321

A rapid spectrophotometric method for the determination of molybdenum(VI) in seawater based on extraction and back extraction is described. Molybdenum(VI) is extracted as the thiocyanato complex from 400 cm³ of a seawater sample into 30 cm³ of 1 x 10⁻² mol dm⁻³ capriquat (trioctylmethylammonium chloride) benzene solution and then back-extracted into 3 cm³ of 4 mol dm⁻³ nitric acid-1 mol dm⁻³ trichloroacetic acid solution, followed by spectrophotometric determination of molybdenum(VI) as molybdenum(V) thiocyanato complex after reduction. The concentration of dissolved molybdenum(VI) in Ibaraki coast(seashore of The Pacific Ocean) seawater was found to be 11.3 µg dm⁻³ with a relative standard deviation of 2.1%. Other cations in seawater were found not to cause interference.

INTRODUCTION

For the analytical separation of molybdenum(VI) from seawater, several methods have been proposed based on techniques such as coprecipitation^{1) 6) 9)}, ion exchange²⁾, colloid flotation³⁾, adsorption on active carbon⁴⁾, collection on chelating resin⁵⁾, and solvent extraction^{6) - 9)}. Of these techniques, solvent extraction method appears to be the most convenient in view of simplicity and rapidity. Most of solvent extraction methods, however, lack the concentration efficiency, so that further concentration steps are needed. Kobrova⁶⁾ coprecipitated molybdenum in water with hydrated manganese dioxide and then extracted with toluene-3,4-dithiol into chloroform. Kim et al.¹⁾ studied the use of thorium hydroxide as a collector of traces of molybdenum from seawater before spectrophotometric determination as the thiocyanato complex. Ohta et al.⁹⁾ coprecipitated molybdenum in seawater with 8-hydroxyquinoline. The coprecipitate was then decomposed with nitric and perchloric acids and molybdenum was extracted as the 5-chloro-7-iodo-8-quinolinolate complex into chloroform, followed by spectrophotometry. However, these methods are troublesome and time-consuming.

In this paper, a rapid preconcentration method of molybdenum(VI) from seawater based on the extraction of molybdenum(VI) thiocyanato complex with capriquat in benzene and the back extraction with nitric acid-trichloroacetic acid solution is described. Molybdenum(VI) is successively determined by spectrophotometry as molybdenum(V) thiocyanato complex after reduction. Molybdenum(VI) can be concentrated about a thousandfold over original seawater with single extraction and the

back extraction.

EXPERIMENTAL

Reagents and apparatus

A 1000 $\mu\text{g cm}^{-3}$ molybdenum(VI) solution was prepared by dissolving a definite amount of sodium molybdate in deionized water. The solution was then diluted as required. A 1×10^{-2} mol dm^{-3} capriquat solution was prepared by dissolving capriquat (Dojindo Co., Japan) in benzene. A 4 mol dm^{-3} nitric acid - 1 mol dm^{-3} trichloroacetic acid solution was prepared freshly in each case by mixing 5 cm^3 of 8 mol dm^{-3} nitric acid and 5 cm^3 of 2 mol dm^{-3} trichloroacetic acid solution. All other chemicals used were of a guaranteed reagent quality. A Hitachi 100-10 spectrophotometer and a Hitachi Horiba F-7 pH meter were employed.

Procedure

A seawater sample acidified at 0.1 mol dm^{-3} hydrochloric acid was filtered through a 0.45 μm millipore filter. An aliquot (e.g. 400 cm^3) of the solution was taken in a separatory funnel. To this solution, 5 mol dm^{-3} potassium thiocyanate solution was added to be 5×10^{-2} mol dm^{-3} . The solution was shaken with 30 cm^3 of 1×10^{-2} mol dm^{-3} capriquat in benzene for 3 min. After 10 min, the phases were separated and 25 cm^3 of the organic phase was transferred to a dried separatory funnel. The organic phase was shaken with 3 cm^3 of 4 mol dm^{-3} nitric acid - 1 mol dm^{-3} trichloroacetic acid solution for 10 min. After 5 min, the phases were separated and 2 cm^3 of the aqueous phase was taken in a centrifuge tube. To this solution, 0.2 cm^3 of 10 w/v% hydroxylamine hydrochloride solution, 0.2 cm^3 of 20 w/v% potassium thiocyanate solution, and 0.2 cm^3 of 10 w/v% tin(II) chloride solution were added. The solution was centrifuged for 2 min at 3000 r.p.m.. The absorbance of the solution was measured at 460 nm against the reagent blank.

RESULTS AND DISCUSSION

Kim and Kwon¹⁰⁾ studied the extraction of molybdenum thiocyanato complex with various types of long-chain alkylamines into chloroform. The best result was obtained with trioctylmethylammonium chloride (Aliquat 336). However, it is necessary to study the details of the optimum conditions for the extraction of molybdenum(VI) thiocyanato complex with capriquat from seawater into benzene.

Effect of experimental variables

Effect of acidity of the aqueous phase on the extraction of molybdenum(VI) was examined. Data for the extraction of 10 μg of molybdenum(VI) from artificial seawater containing 5×10^{-2} mol dm^{-3} thiocyanate in the various acidity with 1×10^{-2} mol dm^{-3} capriquat in benzene are given in Table 1. The maximum extraction of molybdenum(VI) was obtained within an acidity range of 1×10^{-2} mol dm^{-3} to 2 mol dm^{-3} hydrochloric acid solution.

Concentration effect of thiocyanate in artificial seawater was studied on the extraction of molybdenum(VI). The results are given in Table 2. The optimum con-

centration of thiocyanate in the aqueous phase is in the range of 1×10^{-2} to $1 \times 10^{-1} \text{ mol dm}^{-3}$. The extraction of molybdenum(VI) is suppressed by large excess thiocyanate over 1 mol dm^{-3} . It is evident that the excess thiocyanato ion is acting as a competitive ion to the molybdenum thiocyanato ion in the formation of ionic associate with capriquat. Absorbance of reagent blank increases abruptly over 1 mol dm^{-3} thiocyanate.

Table 1 Effect of acidity on the extraction of molybdenum(VI) from artificial seawater

Acidity	Absorbance (460 nm)
pH 7.0	0.013
pH 3.0	0.200
pH 2.6	0.277
$1 \times 10^{-2} \text{ mol dm}^{-3} \text{ HCl}$	0.293
$3 \times 10^{-2} \text{ mol dm}^{-3} \text{ HCl}$	0.282
$1 \times 10^{-1} \text{ mol dm}^{-3} \text{ HCl}$	0.288
1 $\text{mol dm}^{-3} \text{ HCl}$	0.291
2 $\text{mol dm}^{-3} \text{ HCl}$	0.289

Mo : $10 \mu\text{g}$, thiocyanate : $5 \times 10^{-2} \text{ mol dm}^{-3}$,
 capriquat : $1 \times 10^{-2} \text{ mol dm}^{-3}$, V_{aq} : 100 cm^3 ,
 V_{org} : 15 cm^3 , V_{back} : 3 cm^3

Table 2 Effect of thiocyanate concentration on the extraction of molybdenum(VI) from artificial seawater

Thiocyanate concentration (mol dm^{-3})	Absorbance (460 nm)
3×10^{-3}	0.140
5×10^{-3}	0.270
1×10^{-2}	0.288
5×10^{-2}	0.286
1×10^{-1}	0.289
1	0.276
2	0.260

Mo : $10 \mu\text{g}$. HCl : $1 \times 10^{-1} \text{ mol dm}^{-3}$, capriquat : $1 \times 10^{-2} \text{ mol dm}^{-3}$
 V_{aq} : 100 cm^3 . V_{org} : 15 cm^3 , V_{back} : 3 cm^3

The extraction of molybdenum(VI) with benzene containing capriquat in various

concentrations was examined. The data in Table 3 show that the maximum extraction is obtained within the concentration range of 1×10^{-3} to 5×10^{-2} mol dm⁻³ capriquat with slight decrease at 1×10^{-1} mol dm⁻³ which is caused by incomplete back extraction into aqueous phase.

Table 3 Effect of capriquat concentration on the extraction of molybdenum(VI) from artificial seawater

Capriquat concentration (mol dm ⁻³)	Absorbance (460 nm)
2×10^{-4}	0.215
5×10^{-4}	0.267
1×10^{-3}	0.287
2.5×10^{-3}	0.285
1×10^{-2}	0.285
5×10^{-2}	0.285
1×10^{-1}	0.260

Mo : $10 \mu\text{g}$, HCl : 1×10^{-1} mol dm⁻³ , thiocyanate : 5×10^{-2} mol dm⁻³
 V_{aq} : 100 cm^3 , V_{org} : 15 cm^3 , V_{back} : 3 cm^3

Effect of nitric acid concentration on the back extraction of molybdenum(VI) from benzene into aqueous phase was examined. The results are given in Table 4. The optimum concentration of nitric acid in the back extracting solution is in the range of 3 to 4.5 mol dm⁻³.

Table 4 Effect of nitric acid concentration on the back extraction of molybdenum(VI) from the benzene layer

Nitric acid concentration (mol dm ⁻³)	Absorbance (460 nm)
1	0.250
1.5	0.275
2	0.275
3	0.286
4	0.287
4.5	0.287
5	0.0

Mo : $10 \mu\text{g}$, HCl : 1×10^{-1} mol dm⁻³ ,
 thiocyanate : 5×10^{-2} mol dm⁻³ , capriquat : 1×10^{-2} mol dm⁻³ ,
 V_{aq} : 100 cm^3 , V_{org} : 15 cm^3 , V_{back} : 3 cm^3

The molybdenum thiocyanato complex decomposes rapidly over 5 mol dm⁻³ nitric acid. The clarity of the back-extracted solution improves with the addition of trichloroacetic acid solution into nitric acid. The rate of the back extraction of molybdenum decreases at temperatures below 20°C.

Extraction and back extraction of molybdenum(VI) were studied by varying the volume ratio of the aqueous to the organic phase. For the back extraction, 3 cm³ of 4 mol dm⁻³ nitric acid - 1 mol dm⁻³ trichloroacetic acid solution was used. The results are given in Table 5. The maximum extraction of molybdenum(VI) was obtained in the volume ratio of the aqueous to the organic phase less than 40 to 1 for the first extraction and more than 1 to 30 for the back extraction. Consequently, about a thousandfold preconcentration of molybdenum(VI) from seawater can be achieved by single extraction and back extraction. Recovery of 10 µg of molybdenum(VI) from 400 cm³ of artificial seawater by the foregoing procedure was 94.7%.

Table 5 Effect of the volume ratio on the extraction and the back extraction of molybdenum(VI)

V _{aq} / V _{org}	Absorbance (460 nm)	
	Extraction	Back extraction
5	0.282	—
20	0.286	—
40	0.288	—
60	0.272	—
1 / 4	—	0.290
1 / 15	—	0.288
1 / 30	—	0.286
1 / 50	—	0.268

Mo : 10 µg , HCl : 1 × 10⁻¹ mol dm⁻³,
capriquat : 1 × 10⁻² mol dm⁻³

Interference

A study of interference was made for the metals in seawater in amounts ranging up to 1 mg with 10 µg of molybdenum(VI). Among the metals tested, the considerable interferences were from cobalt, iron(III), uranium(VI), vanadium(V), and tungsten(VI). However, these elements can be neglected in applications to seawater analysis because of their rarities. Interference data are summarized in Table 6.

Calibration curve

A calibration curve for the determination of molybdenum(VI) in 400 cm³ of artificial seawater was made by the foregoing procedure. A linear calibration curve was obtained in the range of 3 to 60 µg dm⁻³ molybdenum(VI).

Table 6 Effect of diverse ions on the determination of molybdenum(VI)

Ions	Amount added (mg)	Molybdenum(VI) found (μg)	Relative error (%)
	0	10.0	0
Ag^+	1	10.2	+ 2.0
Al^{3+}	1	9.83	- 1.7
As^{3+}	1	10.2	+ 2.0
Bi^{3+}	1	10.13	+ 1.3
Cd^{2+}	1	10.38	+ 3.8
Co^{2+}	1	12.58	+ 25.8
Co^{2+}	0.1	10.42	+ 4.2
Cr^{3+}	1	10.04	+ 0.4
Cu^{2+}	1	9.63	- 3.7
Fe^{3+}	1	11.17	+ 11.7
Fe^{3+}	0.1	10.08	+ 0.8
Mn^{2+}	1	10.21	+ 2.1
Ni^{2+}	1	10.33	+ 3.3
Pb^{2+}	1	10.08	+ 0.8
Sn^{4+}	1	9.87	- 1.3
Ti^{4+}	1	10.38	+ 3.8
U^{6+}	1	11.75	+ 17.5
U^{6+}	0.1	10.38	+ 3.8
V^{5+}	1	10.75	+ 7.5
V^{5+}	0.1	10.42	+ 4.2
W^{6+}	1	5.46	- 45.4
W^{6+}	0.1	9.08	- 9.2
Zn^{2+}	1	10.08	+ 0.8

Mo : $10 \mu\text{g}$, HCl : $1 \times 10^{-1} \text{ mol dm}^{-3}$, thiocyanate : $5 \times 10^{-2} \text{ mol dm}^{-3}$,
capriquat : $1 \times 10^{-2} \text{ mol dm}^{-3}$.

V_{aq} : 400 cm^3 , V_{org} : 30 cm^3 , V_{back} : 3 cm^3

Analysis of seawater

A near-shore surface sample (Isozaki coast, Ibaraki, Japan) was analysed for molybdenum(VI) content by the foregoing procedure, using 400 cm^3 seawater. The result is given in Table 7. The average molybdenum(VI) concentration and relative standard deviation of Isozaki coast (Seashore of Pacific Ocean) seawater were $11.3 \mu\text{g dm}^{-3}$ and 2.1%, respectively. The time required for the analysis was about 1.5 h.

Table 7 Determination of molybdenum(VI) in seawater

Sample	Molybdenum(VI) found ($\mu\text{g dm}^{-3}$)	R.S.D.† (%)
Isozaki coast (Seashore of Pacific Ocean)	11.3	2.1

† Relative standard deviation (eight determinations)

CONCLUSION

Spectrophotometric determination of molybdenum(VI) in a ppb range has been demonstrated using a seawater sample. The spectrophotometric methods^{1) 6) 9)} recently reported are troublesome and time-consuming. The proposed method offers significant advantages as a simple, rapid, sensitive procedure with few interferences. About a thousandfold preconcentration of molybdenum(VI) can be rapidly achieved by single extraction and back extraction. It has been shown that the molybdenum(VI) content of seawater can be determined in the range 3 - 60 $\mu\text{g dm}^{-3}$ with about a hundredfold preconcentration. The detection limit of molybdenum(VI) will further go down by use of large volume samples.

REFERENCES

- 1) Y. S. Kim, H. Zeitlin: Anal. Chim. Acta, 51, 516 (1970).
- 2) K. Kawaguchi, R. Kuroda: Anal. Chim. Acta, 46, 23 (1969).
- 3) Y. S. Kim, H. Zeitlin: Separ. Sci., 6, 505 (1971).
- 4) H. A. Van der Sloot, G. D. Wals, H. A. Das: Anal. Chim. Acta, 90, 193 (1977).
- 5) H. M. Nakagawa, F. N. Ward: U. S. Geol. Surv. Bull., 1408, 65 (1975).
- 6) M. Kobrova: Chem. Listy, 66, 768 (1972).
- 7) C. H. Kim, P. W. Alexander, L. E. Smythe: Talanta, 23, 229 (1976).
- 8) M. Otto, H. Mueller: Talanta, 24, 15 (1977).
- 9) N. Ohta, M. Fujita, K. Tomura: Bunseki Kagaku, 28, 277 (1979).
- 10) C. H. Kim, K. S. Kwon: Haksul yonguchi-Chungnam Taehakkyo, Chayon Kwahak Yonguso, 1976, 63; Chem. Abstr., 91, 77278h (1979).

Keyword phrases

Spectrophotometry of molybdenum(VI) in seawater; rapid preconcentration method of molybdenum(VI) from seawater; solvent extraction of molybdenum(VI) thiocyanato complex with capriquat; back extraction of molybdenum(VI).

(Received June 1, 1983)