Determination of Trace Metals in Seawater by Graphite Furnace Atomic Absorption Spectrometry after Preconcentration Using Synergistic Extraction

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Trace Cd, Mn, Pb, Co, Ni, and Cu have been quantitatively separated and concentrated from seawater matrices with a low concentration (mmol dm^{-3} level) of 1,1,1-trifluoro-4-mercapto-4-(2-thienyl)-3-buten-2-one and trioctylphosphine oxide cyclohexane solution. The synergistic extract was directly injected into the furnace and a reproducible signal with little memory effect was obtained. The extracted adduct enhanced the AAS sensitivity during thermal decomposition processes, and simultaneously resulted in depression of the interferences. The detection limits of the analytes ranged from several ng dm^{-3} to 100 ng dm^{-3}. The proposed technique provides both the preconcentration and determination for trace analysis by a single extraction using a small volume of sample. Coastal seawater samples were analyzed by the method.

The determination of trace metals in seawater, particulary toxic or neutrient elements, has received increasing attension in analytical and environmental chemistry. Graphite furnace atomic absorption spectrometry (GF-AAS) is one of the most widely used methods for this purpose. Since the concentrations of many elements are extremely low, adequate preconcentration techniques are usually required prior to GF-AAS measurement.[1-5] However, most of them are troublesome due to the use of a large volume of sample and often cause contamination or loss of the analytes. A simple and reliable preconcentration method is required.

The synergistic extraction is a useful technique for separation and concentration of trace metals. Although the analytical importance has been well recognized, the applications combined with AAS are relatively few.[6,7] Recently, Itoh et al.[8] reported a convenient method for determining cadmium in river water, in which synergistic extract with dithizone-tributylphosphine oxide was directly injected into the furnace. Direct analysis of the organic extract is highly desirable to simplify sample pretreatment steps. Though similar attempts in GF-AAS have been undertaken by utilizing the conventional extraction, e.g., ammonium 1-pyrrolidinecarbodithioate[9] and thiocyanate-zephiramine systems,[10] they were not sufficiently sensitive for accurate analysis of seawater.

In this study, synergistic extraction with 1,1,1-trifluoro-4-mercapto-4-(2-thienyl)-3-buten-2-one (STTA)-trioctylphosphine oxide (TOPO) is evaluated for the preconcentration followed by GF-AAS measurement. The extraction conditions and recovery of trace metals from saline waters are examined in detail.

Experimental

Apparatus. A Nippon Jarrel-Ash Model AA-8500 atomic absorption spectrophotometer with a FLA-10 graphite furnace atomizer was used. A deuterium lamp was used for background correction and tube temparature was measured with a Keisoku Electric Co. Model OPA optical pyrometer.

Solvent extractions were carried out by a centrifuge tube (volume: 50 cm^3) with glass stopper. An Iwaki KM type shaker and a Kubota K80 centrifuge were also used.

Reagents. All reagents used were of analytical reagent or better grade. Deionized distilled water was used. The standard solutions (1000 mg dm^{-3}) for Cd, Mn, Pb, Co, Ni, and Cu were prepared by dissolving pure metals or their salts in 0.1 M (M=mol dm^{-3}) HNO$_3$. STTA was synthesized by the method of Berg et al.[11] and purified repeatedly by recrystallization from absolute ethanol. TOPO was purchased from Dojindo Co. Ltd. Stock reagent solutions (50 mM) for synergistic extraction were prepared by dissolving STTA and TOPO in cyclohexane. The working solution was prepared by mixing and diluting them with cyclohexane before use. HCl, HNO$_3$, and acetic acid were of extra pure grade purchased from Wako Chemical Co. Ltd., and NaOH was of suprapure grade from Merck. Buffer solutions were purified by washing with the extracting solution, and cyclohexane.

Seawater Samples. Surface seawater was collected at the coast of Noto Peninsula. The waters was filtered through a 0.45 μm Toyo Roshi membrane filter immediately after sampling, acidified to pH 1.5 with HNO$_3$ and stored in polyethylene bottles. Artificial seawater was prepared according to Japanese Industrial Standard K 2510. All glass wares and polyethylene bottles were rinsed well with pure water after soaking in (1+2) HNO$_3$ for over 3 days. Centrifuge tube was thoroughly washed with the extracting solution and cyclohexane just before use. Membrane filter was soaked in (1+1) HCl for over 5 days.

Analytical Procedure. An aliquot of seawater (up to 30 cm^3) was transferred into centrifuge tube and neutralized with 1 M NaOH. The pH was adjusted with 5 cm^3 of 0.1 M acetate or 0.05 M borax buffer solution; the total volume of the solution was controlled within the optimum volume for each metal. Then, 5.0 cm^3 of synergistic extracting solution was added and the mixture was shaked for 20 min. After centrifugal separation, 20 μL of the upper organic phase was directly injected into graphite furnace. The atomic absorption peak height for each metal was measured. The metal concentration was determined by the calibration method, except for Co by the standard addition method. Analytical conditions were determined for artificial or natural seawater by comparing the signal height with that for aqueous standard. Optimum analytical parameters obtained for furnace operation and synergistic extraction are shown in

Table 1.   Optimum Analytical Parameters for Furnace Operation and SynergistiC Extraction

Condition	Cd	Mn	Pb	Co	Ni	Cu
Wavelength(nm)	228.8	279.5	283.3	240.7	232.0	324.8
Drying current and time/A-s	14-20	14-20	14-20	14-20	14-20	14-20
(final temp/°C)	(80)	(80)	(80)	(80)	(80)	(80)
Ashing current and time/A-s	30-40	60-60	90-60	60-60	40-40	60-40
(final temp/°C)	(300)	(640)	(1000)	(640)	(420)	640
Atomizing current and time/A-s	270-5	320-5	270-5	350-5	330-5	350-5
(final temp/°C)	(2200)	(2550)	(2200)	(2700)	(2600)	(2700)
Ar flow rate: 2.0 dm³/min, Injection volume: 20 µL						
Exraction pH	8.0	9.3	5.5	5.5	8.0	5.5
STTA concentration/mM	5.0	2.0	1.0	1.0	5.0	1.0
TOPO concentration/mM	1.0	5.0	1.0	0.1	0.1	0.1
Volume ratio (V_{aq}/V_{org}): 4, Shaking time/min: 20						

Table 1.

Results and Discussion

Operating Conditions. Operating conditions for GF-AAS differ a little from those of the usual method, because synergistic extract is directly injected into the furnace. On graphite surface, the following chemical reactions will take place: evaporation of cyclohexane, fussion and decomposition of extracting reagents and adduct chelates, and vaporization of metals in drying, ashing, and atomization processes. The establishment of ashing temperature was especially important, because the extracting reagent acted as a flux. Figure 1 shows the effect of ashing current on the absorption signals of trace metals spiked into artificial seawater. The maximum absorbance was obtained at the current of 90 A (1000 °C) for Pb, up to 60 A (640 °C) for Mn and Co, and up to 100 A (1100 °C) for Cu. The signals for Cd and Ni markedly decreased even at low currents. Berg and Reed[11] have reported that the thermal stability of STTA chelate is relatively low. Although the
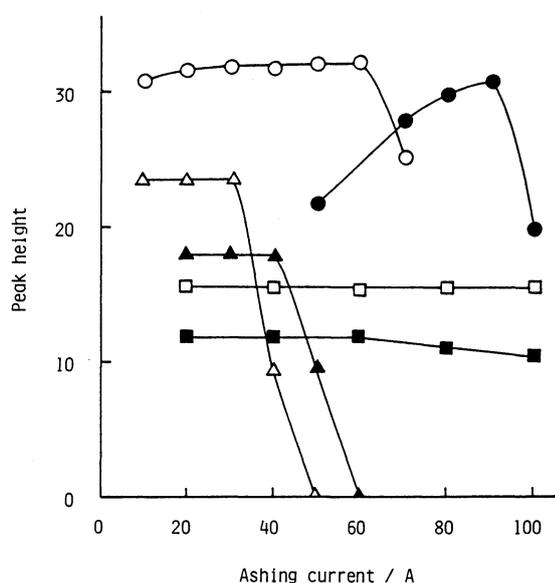

Fig. 1.   Effect of ashing current on absorption signal of each metal. O: Mn 40 ng, ●: Pb 125 ng, △: Cd 5 ng, ▲: Ni 300 ng, □: Cu 250 ng, ■: Co 100 ng.

thermal stability of TOPO adducts is not well-known, the abrupt decrease of Cd and Ni signals would be attributable to the sublimation of the adducts. On the other hand, the loss of Cu and Co by volatilization was little even at elevated temperatures, presumably due to forming a stable fussion product or metallic carbide during decomposition of chelating agents. The ashing temperature of each metal was set high enough to eliminate matrix interferences at the atomization step and ashing time was selected to make background signal became zero or minimum. The drying conditions were established by considering only the evaporation of cyclohexane.

Absorption Profiles. When the analyte spiked into alkali or alkaline earth metal chloride solution was directly supplied into the furnace, a background signal with multiple peaks appeared and a large depressive effect on the analyte peak was observed in the following sequence, Cs > Na > Mg > Ca. Whereas, when the synergistic extract was applied, a reproducible single peak with little memory effect was obtained, which was compatible with the aqueous analyte standard. Synergistic extraction was effective not only for preconcentration of trace metals from saline waters but also for reduction of the desired metal during thermal decomposition processes, because the synergist acted as a reductant.   Furthermore, the extracted adduct showed favorable effects on the AAS measurement, e.g., extension of thermal contact area in the furnace, depression of analyte volatilization at the ashing step, prevention of metal oxide formation, and acceleration of thermal decomposition of the extracted matrix.

Selection of Synergistic Extractants. When a common fluorinated β-diketone, such as thenoyltrifluoroacetone (TTA) or benzoyltrifluoroacetone, was used as a chelating reagent, matrix elements in seawater were coextracted and the detection of the analyte, especially Cd, Mn and Pb, became difficult. However, the interferences could be almost neglected when a low concentration of STTA was used. Figure 2 shows the effect of Ca or Mg matrices on Mn and Pb signals. The constant signals were obtained by the STTA-TOPO extraction at the seawater level of Ca and Mg, whereas the TTA-TOPO extraction gave the decreased signals
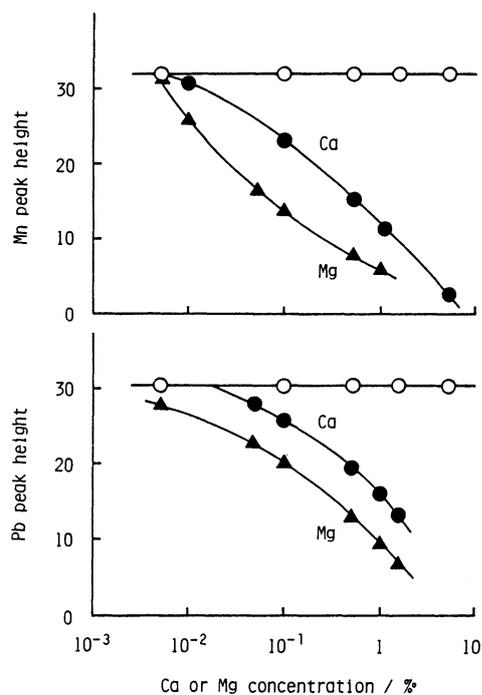
Fig. 2. Effect of Ca or Mg concentration on Mn and Pb absorption signals. Open symbols: 1 mM STTA–1 mM TOPO extraction. Closed symbols: 1 mM TTA–1 mM TOPO extraction.
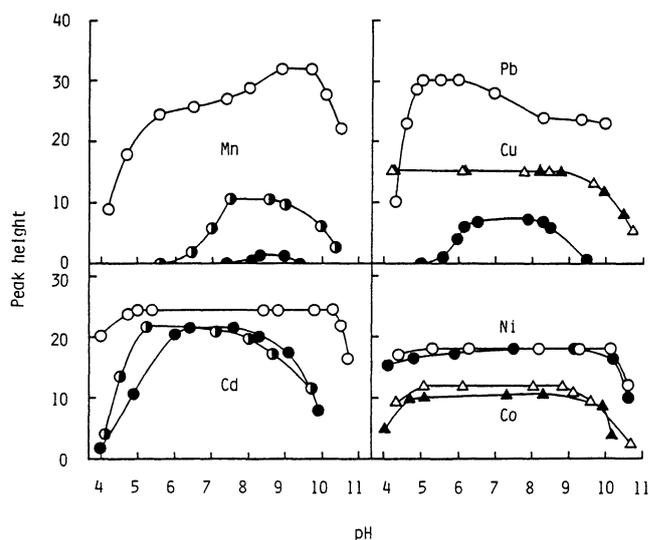

Fig. 3. Effect of extraction pH on absorption signals of each metal. Open and closed symbols denote the absorbances by STTA-TOPO and STTA extraction, respectively, except for STTA-TBP extraction (◐). The reagent and metal concentrations are identical to those shown in Table 1 and Fig. 1, respectively.

with the increase of matrix concentration, especially for Mg. Similar decreased signals were also recognized for Cd, Co and Ni, except for Cu. As a synergist, alkylphosphine oxides and pyridine bases were examined. The analyte peaks were generally enhanced in the following order: pyridine, piperidine < α-picoline, α-pipecoline, 2,6-lutidine < γ-picoline, γ-pipecoline, 2,4-lutidine ≪ tributyl phosphate (TBP) < TOPO. Although the order differed a little from the ordinary base effect for synergistic extraction,[12] TOPO showed a constant signal over wider pH region with the largest enhancement effect. As for the diluent, the signals were increased in the following sequence: chloroform < carbon tetrachloride < benzene < hexane < cyclohexane. Cyclohexane was easier to volatilize than chlorinated solvent, that showed the depressive effect in pH range over 9.

Effect of Extraction pH. Figure 3 shows the effect of pH on the signals of each metal by extraction with STTA-TOPO (or TBP) or STTA only. The maximum and constant absorbances were obtained over wider pH ranges of 8.9—9.7 for Mn, 5.0—10.3 for Cd, 5.0—6.0 for Pb, 4.2—8.5 for Cu, 5.3—10.1 for Ni, and 5.0—8.8 for Co, respectively. Comparing with the signal of STTA only, the peak height increased about 23-fold for Mn and 4.2-fold for Pb, and these enhancement effects were recognized in the following order: Mn ≫ Pb > Cd > Co > Ni ≈ Cu. The order agrees nearly with that of synergistic extractability, but Cu and Ni did not show any significant effect, presumably due to low stability of the adducts. In order to

make the phenomena clearer, the extraction equilibria of the TOPO adducts were analyzed by the curve fitting method with 0.05 M STTA at μ=0.1 (NaClO$_4$). The extracted species of Cd, Pb and Zn were found to be MR$_2$·L type adduct with one molecule of TOPO, and those of Mn and Co are of MR$_2$·L$_2$ type, while Ni formed an ambiguous adduct. Copper was completely extracted with STTA only even at pH 0.5 or below. The primary stability constants of the adducts increased in the order of Cd > Mn > Pb > Co > Zn. These facts suggest that the more STTA chelate is stabilized by adduct formation, the more the sensitivity for GF-AAS is increased.

STTA and TOPO Concentrations. The maximum and constant signals were obtained in the following STTA concentration ranges; 0.1—1 mM for Cu, 0.1—5 mM for Cd, 0.5—1 mM for Pb and Co, 1—5 mM for Mn, and 5—50 mM for Ni. Above the concentrations, the decreases of the signal height, except for Ni, were observed, especially for Mn and Pb. The effect of TOPO concentrations is shown in Fig. 4, where constant absorbances are obtained in the following ranges: 5—10 mM for Mn, 1—10 mM for Pb, 0.5—5 mM for Cd, up to 1 mM for Ni and 0.1 mM for Cu, and 0.1—10 mM for Co, respectively. Above 10 mM, the decreases of absorbance arising from the antagonism were observed for Cd, Ni, and Cu.

Shaking Time and Aqueous Phase Volume. The constant signals were obtained by shaking for over 5 min for Mn, Co, Ni and Cu, 10 min for Pb, and 15 min for Cd, respectively, up to 60 min in each case. The effect of aqueous phase volume was also examined by shaking for 20 min with 3.0 cm^3 of organic phase. The peak height of each metal was little affected by the
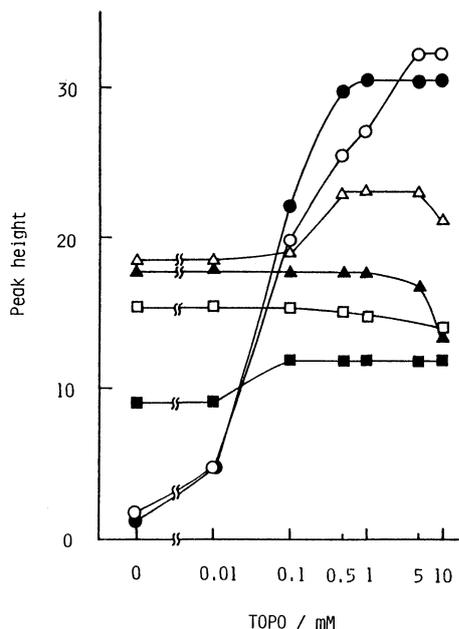
Fig. 4. Effect of TOPO concentration. Symbols and experimental conditions are identical to those shown in Fig. 1 and Table 1, respectively.

volume ratio (V_{aq}/V_{org}) up to 10, but at the ratio of 15, peak height of Cd, Mn, and Ni decreased by about 7, 8, and 15%, respectively.

Recovery of Spikes and Calibration Curves. Known amounts of metals were spiked into seawater aliquots (20 cm^3) to evaluate the net recovery of the extracted metals by comparing with the aqueous standards. The spikes were added before pH adjustment and the solutions were equilibrated for at least 6 h prior to extraction. The spikes were extracted into 5.0 cm^3 of organic phase with above 99% recovery at the concentration up to 5 ng for Cd, 40 ng for Mn, and 125 ng for Pb and Co, and below these concentrations, favorable linear relationships were obtained by a single extraction. The straight lines were also obtained for Cu up to 250 ng and Ni up to 400 ng, although the mean recovery fell to 94.5 and 87.3%, respectively. Since the spikes of Cu and Ni can be quantitatively extracted by synergistic extraction with 1 mM STTA-TOPO,[13] low recovery from seawater matrices would be attributed to the non-extractable metal species.[14] In practice, found values

Table 2. Blanks and Detection Limits

	Blank/ng cm^{-3}[a]	Detection limit/ng cm^{-3}
Cd	0.010±0.004	0.008
Mn	0.10±0.05	0.10
Pb	0.84±0.16	0.32
Co	<0.20	<0.20
Ni	0.3±0.1	0.2
Cu	0.5±0.1	0.2

a) Mean and standard deviation for five determinations.

of Cu and Ni were corrected by the calibration graphs.

Blanks and Detection Limits. The blank in the extraction procedure consists of metals in the reagents used as well as those introduced during sampling and extraction steps. A reagent blank was prepared by re-extracting the previously extracted seawater. A preextracted seawater sample (500 cm^3) was washed with two 10 cm^3 portions of cyclohexane, and the aliquots were submitted to the analysis. Replicate blanks for each metal studied are shown in Table 2. As for Co, the metal concentration corresponding to the peak unit of 0.1 is regarded as a blank, due to it's weak signal. The detection limits are based on twice the standard deviation of the blank, which are lower than those obtained by the dithiocarbamate extraction-GF-AAS.[9]

Analysis of Seawater. The analytical results of coastal seawater samples are summarized in Table 3. Each metal was determined within the relative standard deviation of 10%, but the concentration of Co was near or below the detection limit and the values found had poor analytical precision. The results of six elements were lower than those found in Seto Inland Sea and Tokyo Bay,[15] especially for Mn and Pb. The results of Monzen were compared with those obtained by the chelex-100 resin preconcentration-GF-AAS.[16] The concentrations obtained by two analytical methods were agreed closely with each other, indicating that the proposed method is accurate enough to apply to the determination of trace metals in seawater.

Conclusion

Synergistic extraction by using a low concentration synergist is useful for preconcentration of trace metals

Table 3. Analytical Results of Trace Metals in Seawater

	Concentration/ng cm^{-3}[a]					
	Cd	Mn	Pb	Co	Ni	Cu
Wajima	0.038±0.001	0.92±0.08	1.84±0.08	0.35±0.05	1.2±0.1	1.1±0.1
Sosogi	0.033±0.003	0.80±0.03	0.71±0.03	0.17±0.03	1.1±0.1	1.4±0.1
Noroshi	0.031±0.002	0.96±0.02	0.66±0.03	0.29±0.04	1.2±0.1	1.4±0.1
Koiji	0.031±0.002	0.92±0.08	0.78±0.01	N.D.[b]	0.7±0.1	1.1±0.1
Anamizu	0.088±0.003	7.70±0.12	0.73±0.05	0.21±0.03	1.0±0.1	1.0±0.1
Monzen	0.029±0.005	0.66±0.03	0.71±0.04	N.D.	1.1±0.1	1.0±0.1
	0.025±0.005[c]	0.60±0.05	0.75±0.08	N.D.	1.2±0.1	0.8±0.1

a) Mean and standard deviation for three determinations. b) Not detected. c) Chelex-100 resin preconcentration method.[16]

in saline water. The method is convenient and rapid, as the extraction is carried out in a centrifuge tube and an aliquot of cyclohexane extract in the upper layer can be directly served for GF-AAS. This enables the use of smaller amounts of samples and reagents compared with those in the conventional methods. As an another merit of synergistic extraction, the group separation of trace metals is achievable, that is now under investigation for simultaneous multielement analyses.

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