

## Simultaneous Multi-Element Extraction with High Efficiency by Dithizone and Other Ligands

Masahito SUGIYAMA\*, Hiroshi MUKAI\*\*, Noriyasu YASUDA\*\*, Sorin KIHARA\*\* and Masakazu MATSUI\*\*

Received November 9, 1987

Simultaneous multi-element extraction with high enrichment factor, ca. 250, was investigated for preconcentration method before determination of trace elements in natural waters by inductively coupled plasma emission spectrometry. Dithizone was used as a main extractant, and synergic effect with various neutral ligands and mixed ligand effect with other chelating agents were studied. Eleven elements (Cd, Ni, Fe, V, Cu, Pb, Zn, Ti, Al, Zr, and Co) were concentrated simultaneously ca. 250-fold by the extraction with dithizone, 1-phenyl-3-methyl-4-benzoylpyrazol-5-one and tri-*n*-octylphosphine oxide mixture in ethyl benzoate at pH 5.

KEY WORDS: Simultaneous multi-element extraction/ Dithizone/ Preconcentration/ Trace element/ Inductively coupled plasma emission spectrometry/

### INTRODUCTION

Simultaneous determination of trace elements in natural waters is very significant for geochemical and environmental chemical studies. However, this is possible, only when two methods of simultaneous determination and preconcentration are connected. Therefore, it is desirable to develop quantitative pretreatment technique applicable to as many elements as possible. From this point of view, in the previous paper<sup>1)</sup>, preconcentration method by dithiocarbamate extraction was discussed for the determination of trace elements in natural waters by inductively coupled plasma emission spectrometry (ICP-ES).

In this paper, simultaneous multi-element extraction by dithizone and other ligands was investigated. Dithizone is one of excellent chelating agents that form stable complexes with many elements<sup>2)</sup>. Dithiocarbamate contains S, S-coordination group, while dithizone contains S,N-coordination group and is a little harder base ligand than the former. Therefore, it is expected that this reagent can extract some elements difficult to be concentrated by dithiocarbamate. At very high volume ratio (aqueous/organic phase), 250, simultaneous multi-element extraction by only dithizone is considered to be very difficult. Accordingly, synergic effect with neutral ligand such as *o*-phenanthroline or tri-*n*-octylphosphine oxide (TOPO) was studied. In addition, mixed ligand effects with various chelating agents, for example, oxine or 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (HPMBP), were examined.

\* 杉山雅人 : Department of Chemistry, College of Liberal Arts and Sciences, Kyoto University, Kyoto 606.

\*\* 向井 浩, 安田憲康, 木原壯林, 松井正和 : Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

## EXPERIMENTAL

### *Apparatus and Reagents*

A Japan Jarrel-Ash model 96-953 inductively coupled plasma emission spectrometer was used. Some properties of the instrumentation are the same as previously reported<sup>1)</sup>.

All chemicals were reagent grade. Deionized/distilled water was used. Buffer solutions were prepared by mixing 1 M acetic acid and 1 M aqueous ammonia solution in the appropriate ratios.

Stock solutions ( $1000 \text{ mg l}^{-1}$ ) of the elements except for Se, Mo, Cr (VI), V, Zr and As were prepared by dissolving their salts in nitric or hydrochloric acid. Those of Se, Mo, Cr (VI), V and Zr were prepared by dissolving selenium dioxide in pure water, ammonium molybdate in pure water, potassium dichromate in hydrochloric acid, ammonium vanadate in sulfuric acid and zirconium oxychloride in hydrochloric acid, respectively. For the arsenic stock solution, arsenic(III) oxide was dissolved in sodium hydroxide solution, followed by adding hydrochloric acid.

### *Extraction Procedure*

A 2500 ml portion of an aqueous solution containing each element at  $10 \mu\text{g l}^{-1}$  was placed in 3000 ml separatory funnel. The pH was adjusted to the desired value, and 25 ml of 1 M buffer solution was added, if necessary. After addition of 10 ml of ethyl benzoate containing both dithizone and another ligand at  $5 \times 10^{-3} \text{ M}$ , the mixture was shaken for 1 h. The organic phase was separated after standing for 10 min and was directly used for ICP-ES measurement.

### *Preparation of Standard Organic Solutions*

Standard organic solutions were prepared by the extraction at the same volume (aqueous/organic phase). After extraction, aqueous concentrations were determined by ICP-ES, and organic ones were calculated from these values. By the use of these standard solutions, approximate organic concentrations in high volume ratio extraction were measured. Extraction efficiency was corrected by the volume loss of the organic phase by dissolution into the aqueous phase.

## RESULTS AND DISCUSSION

### *Selection of Organic Solvent*

The organic solvent to be used in high volume ratio extraction should have the following characteristics as previously mentioned<sup>1)</sup>. They are very low solubility in water, good applicability to ICP-ES measurement and high solubility of extractant in organic solvent. Dithizone is very soluble in chloroform, and this solvent is often used<sup>2)</sup>. However, as the volume loss of chloroform in the above procedure was 72%, the solvent is not adequate for this purpose. By contrast, solubility of dithizone in 2-ethylhexyl acetate, used in dithiocarbamate extraction, was low. As a result of investigation about a few solvents, ethyl benzoate was the most adequate. Loss of this solvent in the above procedure was 14%, and solubility of dithizone was approximately  $1.4 \times 10^{-2} \text{ M}$ .

Multi-Element Extr. by Dithizone and Other Ligands

Extraction with Only Dithizone

Figures 1 and 2 show the effect of pH on the extraction with only dithizone at the aqueous/organic phase volume ratio, 1 and 250, respectively. Seven ions (Cd, Ni, V, Cu, Fe(III), Mn and Cr (VI)) were studied, and mixed standard solutions were prepared from individual stock solutions. Distribution of these elements reached equilibrium within 1 h in every high volume ratio extraction system. Iron (III) was scarcely extracted at the same volume extraction owing to formation of hydroxide. When the two results were compared, extraction efficiencies at high volume ratio were generally low, but the tendency in extractability of elements was essentially identical. As shown in Figures 1 and 2, though Cd and Cu were quantitatively extracted in both experiments, extraction efficiencies of Ni, V, Mn and Cr in Figure 2 were decreased compared with the results in Figure 1. This was due to the difference in maximum distribution ratios of these elements.

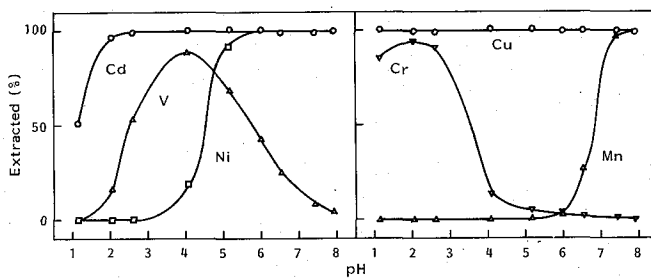


Fig. 1. Effect of pH on the extraction with dithizone. Each element concentration;  $2.5 \text{ mg l}^{-1}$  Dithizone;  $5 \times 10^{-3} \text{ M}$ . Aq. phase; 10 ml. Org. phase; 10 ml.

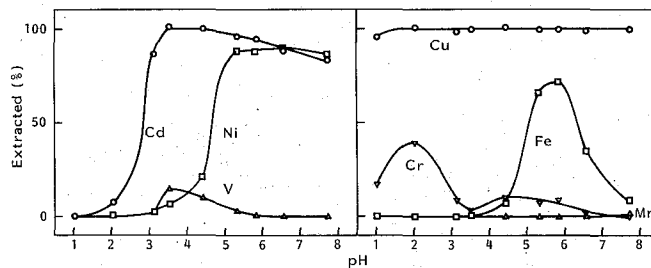


Fig. 2. Effect of pH on the extraction with dithizone. Each element concentration;  $10 \mu\text{g l}^{-1}$ . Dithizone;  $5 \times 10^{-3} \text{ M}$ . Aq. phase; 2500 ml. Org. phase; 10 ml.

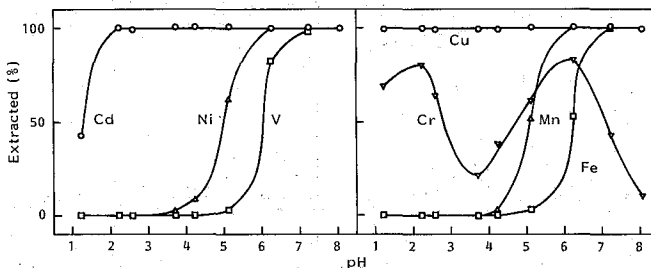


Fig. 3. Effect of pH on the extraction with dithizone and *o*-phenanthroline. Each element concentration;  $2.5 \text{ mg l}^{-1}$ . Dithizone;  $5 \times 10^{-3} \text{ M}$ . *o*-phenanthroline;  $5 \times 10^{-3} \text{ M}$ . Aq. phase; 10 ml. Org. phase; 10 ml.

Extraction with Dithizone and Neutral Ligand

In dithizone extraction, it has been reported that synergic effect with neutral ligand such as *o*-phenanthroline<sup>3-5)</sup> or  $\alpha, \alpha'$ -dipyridyl<sup>6)</sup> increases extraction efficiencies for some elements. Figure 3 shows the extraction curves in the presence of *o*-phenanthroline at the same volume

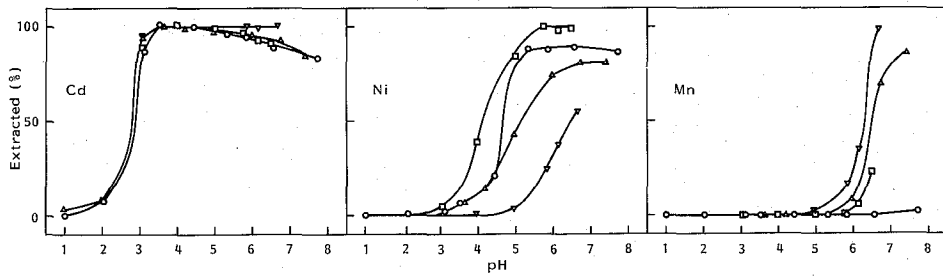


Fig. 4. Effect of *o*-phenanthroline concentration.  $\circ$ ; 0 M.  $\square$ ;  $1 \times 10^{-3}$  M.  $\triangle$ ;  $5 \times 10^{-3}$  M.  $\nabla$ ;  $2 \times 10^{-2}$  M. Each element concentration;  $10 \mu\text{g l}^{-1}$ . Dithizone;  $5 \times 10^{-3}$  M. Aq. phase; 2500 ml. Org. phase; 10 ml.

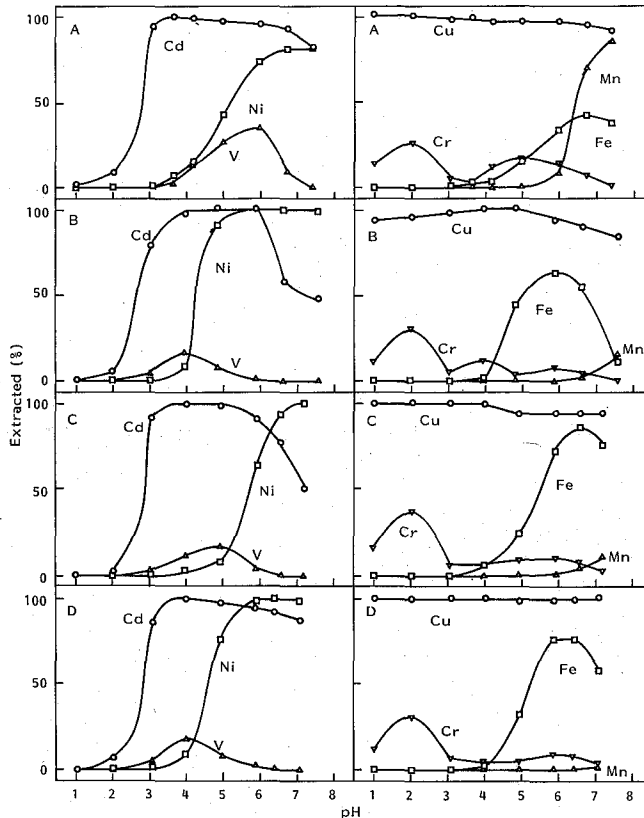


Fig. 5. Effect of pH on the extraction with dithizone and neutral ligand. (A) *o*-Phenanthroline, (B) Neocuproin, (C)  $\alpha, \alpha'$ -Dipyridyl, (D) *iso*-quinoline. Each element concentration;  $10 \mu\text{g l}^{-1}$ . Dithizone;  $5 \times 10^{-3}$  M. Neutral ligand;  $5 \times 10^{-3}$  M. Aq. phase; 2500 ml. Org. phase; 10 ml.

extraction. Quantitative extractions of V, Fe and Mn are made possible by synergic effect. The magnitude of this effect depends on the element itself and the neutral ligand concentration. Figure 4 shows the effect of *o*-phenanthroline concentration in high volume ratio extraction. Extraction curve for Cd scarcely depends on the concentration. Extraction efficiency of Mn was much increased by this effect and extraction in more acidic area became possible with increase of the concentration. However, for Ni, extraction efficiency decreased by addition of abundant *o*-phenanthroline. This is perhaps owing to the formation of water soluble Ni complex with *o*-phenanthroline. Therefore, selection of neutral ligand concentration is significant, and hence the concentration was set to  $5 \times 10^{-3}$  M in the present experiment.

Effect of neutral ligands containing various coordination groups are shown in Figures 5 and 6. Triphenylphosphine sulfide and 2-(2-thienyl)pyridine, both of which contain S-coordination group, were not effective. Extraction of Mn was improved in the presence of *o*-phenanthroline or TOPO. TOPO was also effective for Fe and Cr. However, for Cd and Cu, capable of quantitative extraction with only dithizone, the extraction efficiencies were decreased in high pH region. From these results, TOPO was the most adequate as a reagent for synergic effect.

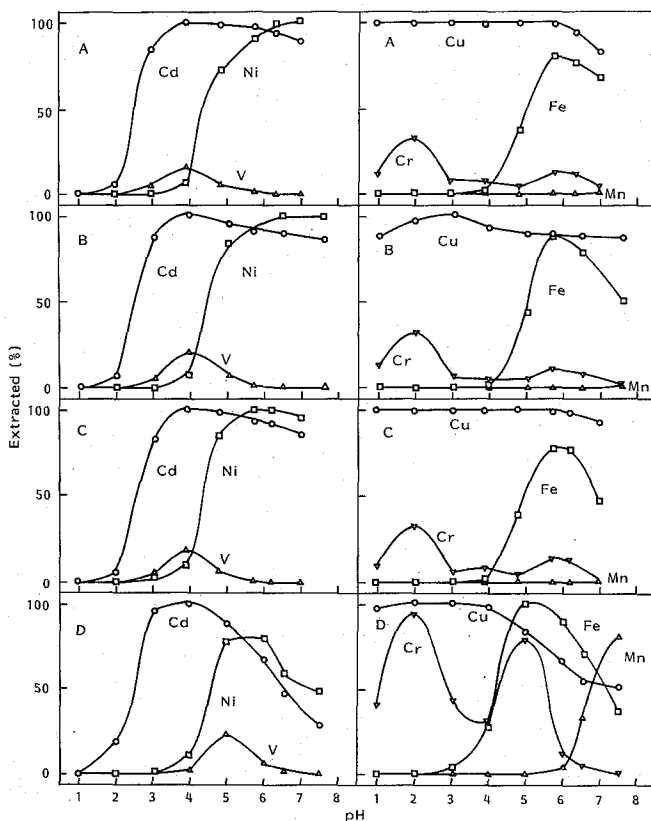


Fig. 6. Effect of pH on the extraction with dithizone and neutral ligand. (A) Triphenylphosphine sulfide, (B) 2-(2-Thienyl)-pyridine, (C) 2-Benzoylpyridine, (D) TOPO. Each element concentration;  $10 \mu\text{g l}^{-1}$ . Dithizone;  $5 \times 10^{-3}$  M. Neutral ligand;  $5 \times 10^{-3}$  M. Aq. phase; 2500 ml. Org. phase; 10 ml.

*Extraction with Dithizone and Another Chelating Agent*

It has been reported that a combination of two chelating agents is effective for quantitative extraction of a number of trace elements with dithiocarbamate<sup>1,7-9</sup>. In this study, effects of four chelating agents, di- $\beta$ -naphthylthiocarbazon that is a dithizone derivative, oxine containing O, N-coordination group, and so on, were investigated. These results are shown in Figure 7. Extraction of Fe was improved by di- $\beta$ -naphthylthiocarbazon, oxine and HPMBP. In addition, HPMBP enabled quantitative extraction of V. This is based on the fact that HPMBP is the hardest chelating agent containing O, O-coordination group in four agents. However, extraction of Mn was not sufficient by any reagent. Figure 8 shows the extraction curves for other elements with dithizone and HPMBP. It is shown that quantitative extractions for Co, Zn, Pb, Sn and Ti are possible. If extraction is carried out at pH 5, nine elements (Cd, Ni, Fe, Cu, Zn, Pb, Sn and Ti) are simultaneously concentrated at high enrichment factor, 250. Compared to the dithiocarbamate extraction, the extraction efficiency of Ti, Al, Zr and Be increased in this extraction system. These come from the fact dithizone and HPMBP are harder bases than dithiocarbamate as chelating agents, and this system is suitable for

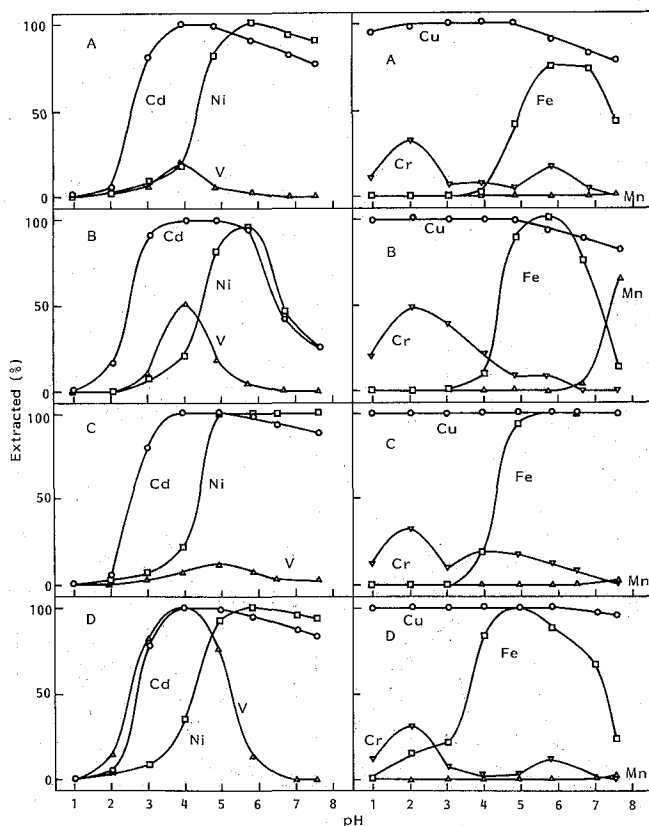


Fig. 7. Effect of pH on the extraction with dithizone and another chelating agent. (A) Dimethylglyoxime, (B) Di- $\beta$ -Naphthylthiocarbazon, (C) oxine, (D) HPMBP. Each element concentration;  $10 \mu\text{g l}^{-1}$ . Dithizone;  $5 \times 10^{-3}$  M. Another chelating agent;  $5 \times 10^{-3}$  M. Aq. phase; 2500 ml. Org. phase; 10 ml.

Multi-Element Extr. by Dithizone and Other Ligands

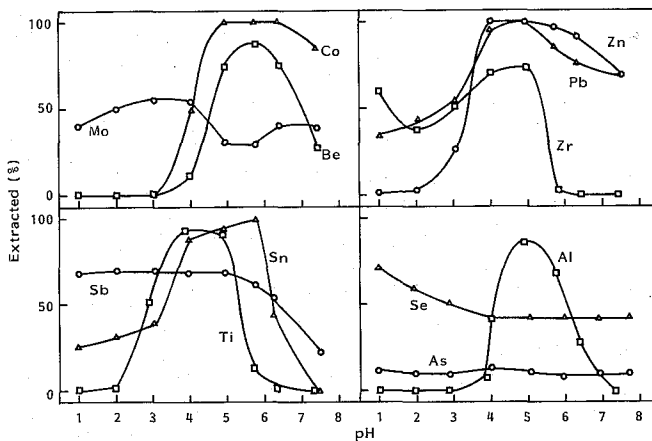


Fig. 8. Effect of pH on the extraction with the combination of dithizone and HPMBP. Each element concentration;  $10 \mu\text{g l}^{-1}$ . Dithizone;  $5 \times 10^{-3}$  M. HPMBP;  $5 \times 10^{-3}$  M. Aq. phase; 2500 ml. Org. phase; 10 ml.

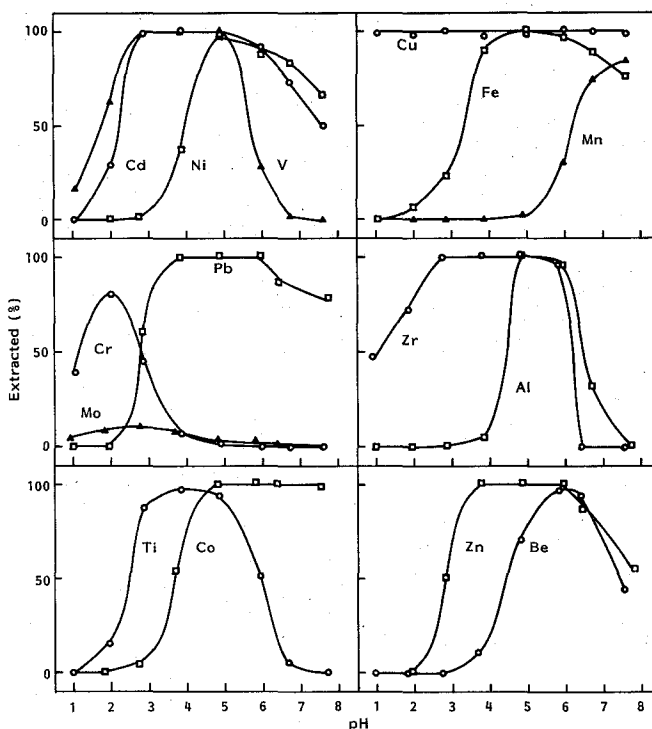


Fig. 9. Effect of pH on the extraction with dithizone, HPMBP and TOPO mixture. Each element concentration;  $10 \mu\text{g l}^{-1}$ . Dithizone;  $5 \times 10^{-3}$  M. HPMBP;  $5 \times 10^{-3}$  M. TOPO;  $5 \times 10^{-3}$  M. Aq. phase; 2500 ml. Org. phase; 10 ml.

concentration of harder acid elements. Therefore, in order to extract these elements more quantitatively, TOPO was added to this dithizone-HPMBP extraction system. TOPO is the most adequate reagent for synergic effect from the above results, and the neutral ligand also

produces good synergic effects in the extraction with 1-phenyl-3-methyl-4-acylpyrazol-5-one<sup>10-12</sup>. As shown in Figure 9, extraction efficiencies of V, Be, Zr, Ti and Al were further increased, and simultaneous extraction of eleven elements (Cd, Ni, V, Cu, Fe, Pb, Zn, Ti, Al, Zr and Co) was possible at pH 5. Though it is inferred from the previous report<sup>10</sup> that Mg and Ca, major elements in natural waters, are extracted at the same time, these elements were scarcely extracted in the pH region studied in the present extraction system.

Quantitative extraction pH regions are generally narrow in this extraction system compared to the previous report<sup>11</sup>, but this system is applicable to harder acid elements and is useful as a preconcentration method for trace elements in natural waters.

This work was supported partly by a Grant from the Nippon Life Insurance Foundation and partly by a Grant in Aid for Scientific Research (61035035) from the Ministry of Education, Science and Culture of Japan.

#### REFERENCES

- (1) M. Sugiyama, O. Fujino, S. Kihara and M. Matsui, *Anal. Chim. Acta*, **181**, 159 (1986).
- (2) E. B. Sandell and H. Onishi, "Photometric Determination of Traces of Metals", Wiley-Interscience, New York, 1978.
- (3) K. S. Math, K. S. Bhatki and H. Freiser, *Talanta*, **16**, 412 (1969).
- (4) H. Akaiwa, H. Kawamoto and E. Yoshimatsu, *Chem. Lett.*, 421 (1978).
- (5) H. Akaiwa, H. Kawamoto and S. Kogure, *Bunseki Kagaku*, **28**, 498 (1979).
- (6) H. Akaiwa, H. Kawamoto, K. Ogura and M. Konishi, *Bunseki Kagaku*, **27**, 329 (1978).
- (7) C. W. McLeod, A. Otsuki, K. Okamoto, H. Haraguchi and K. Fuwa, *Analyst (London)*, **106**, 419 (1981).
- (8) B. Magnusson and S. Westerlund, *Anal. Chim. Acta*, **131**, 63 (1981).
- (9) H. Tao, A. Miyazaki, K. Bansho and Y. Umezaki, *Anal. Chim. Acta*, **156**, 159 (1984).
- (10) S. Umetani, K. Sasayama and M. Matsui, *Anal. Chim. Acta*, **134**, 327 (1982).
- (11) S. Umetani, M. Matsui, T. Kuzunishi and Y. Nishikawa, *This Bulletin*, **60**, 254 (1982).
- (12) K. Sasayama, S. Umetani and M. Matsui, *Anal. Chim. Acta*, **149**, 253 (1983).