Application of Synergistic Solvent Extraction by Formation of Ternary Complex for Determination of Trace Zn(II) in Water Samples

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The application of a synergistic solvent extraction by the formation of ternary complex with pyrocatechol violet (PV) and benzalkonium chloride (BC) was studied for determination of trace Zn(II) in water samples. The pH of sample solution and the amount of PV and BC added were optimized for the formation of the stable complex, a proper solvent was selected for the effective extraction, and the concentration of nitric acid was fixed for the back extraction of the complex from the solvent. After the ionic strength of 100 mL sample solution was adjusted to 0.1 M by adding NaCl and the pH was fixed at 9 with a carbonate buffer, 1.0 mL of 2% PV solution was added to form Zn(II)-PV complex then the Zn(II)-PV/BC ternary complex was made by adding 1.0 mL of 10% BC solution. The ternary complex was extracted into 10 mL of MIBK. And the ternary complex was back-extracted with 10 mL of 1.0 mol/L nitric acid to determine Zn(II) by a flame atomic absorption spectrophotometer (flame-AAS). The interference of concomitant ions on the extraction of Zn(II) was investigated. This procedure was applied to the analysis of three real samples such as Dalbang-dam water, laboratory tap water and Jungnajin seawater. The recoveries of Zn(II) in spiked samples were 86.58-104.1%.

Key Words : Synergistic solvent extraction, Ternary complex, Pyrocatechol violet (PV), Benzalkonium chloride (BC), Trace amount of zinc

Introduction

A zinc metal has been widely used in the many kinds of industries because of the low melting point and the ease to make alloys. And zinc had greatly contributed as a useful coating agent on an iron surface to be protected from corrosion.[1] In contrast, zinc itself or ion was known to affect the enzyme function of human being, the coagulation of blood, a dwarfish disease and the care ability of injuries and generative functions even a trace amount.[2] Therefore, the accurate determination of zinc was important to understand its elemental chemistry, the production and uses of zinc materials, and its pollutions.

Up to now, the solvent extraction has been widely used for the separation and determination of trace zinc. Although this technique is not a continuous method and needs some harmful organic solvents, this is a rapid and convenient method compared to other techniques.[3] If any proper chelating agents can be used for the solvent extraction, it is easy to apply for a trace analysis because of the good selectivity for target elements.[4]

The neutral complex is formed from metal ion with chelating agent in general solvent extraction. Alternatively, if the complex is charged, the synergistic solvent extraction[5-7] which use an ion of opposite charge (usually cationic surfactant) has widely used. The solvent extraction of Zn(II) has been widely investigated and applied in various kinds of fields such as material science and environmental chemistry. Smith and coworkers[8] have studied the deter-

mination of trace Zn(II) in seawater by the extraction of it into chloroform as a Zn(II)-dithizone complex for AAS determination. Djans and coworkers[9] studied the concentration of trace zinc(II) in the solution of cadmium matrix by a solid phase extraction with polyurethane form of thiocyanate salt. Elci and coworkers[10] reported the advanced method of the determination of trace zinc by the extraction of Zn(II)-diethyldithiocabamate precipitate in an aqueous samples followed the measurement of the emission intensity by ICP-AES. Ferreira and coworkers[11] determined a trace Zn(II) by the adsorption of zinc-chelate on synthetic Amberite 120 resin from an aqueous solution. In this case, the matrix of sample affected the extraction efficiency because the chelating agent was not so selective for every metal ion.

In this work, PV[12-15] was used as a chelating agent. Generally, the PV formed colored chelates with various metal ions. And the anionic chelate from zinc and PV was extracted into an organic solvent by forming a ternary complex with an appropriate cationic surfactant, BC. The ternary complex was formed at pH 9 and extracted into methyl isobutyl ketone (MIBK). The complex was redistributed into a diluted nitric acid to reduce a matrix effect and to expand the dynamic range. Finally, the concentrated Zn(II) in aqueous phase was determined by a flame atomic absorption spectrophotometer.

Experimental Section

Reagents and instruments. Chemicals used were of

Table 1. Operation conditions of atomic absorption spectrophotometer (Perkin-Elmer model 2380)

Parameters	Operation condition
Wavelength	213.85 nm
Slit width	0.7 nm
Lamp current	30 mA
Signal mode	Absorbance
Replicate	3

Figure 1. The structure of pyrocatechol violet (PV).

Figure 2. Effect of pH on the stability of Zn(II)-PV in the ternary complex system. The concentration of Zn(II) was 50 ng/mL in 100.00 mL solution including each 1.00 mL of 2 % PV and 10% BC solutions.

guaranteed reagent grade and distilled water used was further purified by the Millipore Milli-Q water system. All glasswares were washed with detergent, soaked in 15% nitric acid for over night, and then cleaned with the distilled water thoroughly. The concentration of Zn(II) in stock solution (NIST, U.S.A.) is 10,000 μg/mL, and it was diluted to the proper concentration for use. The concentration of PV (Sigma Co., U.S.A.) was 1% aqueous solution. It was prepared whenever it was needed for use. 10% ethanolic BC solution (Junsei Co. Japan) was used without any further purification. The reagent grade of MIBK and organic solvents (Junsei Co. Japan) were used without any further purification. The GR grade nitric acid (Avondale Laboratories Co., U.K.) was used. Sodium chloride (Junsei Co., Japan) was used to control the ionic strength of sample solution.

Perkin-Elmer model 2380 AAS was used with a hollow cathode lamp. The operating conditions for determining Zn(II) are shown in Table 1. Eyela pH meter, PHM-2000 of Tokyo Rikakikai Co., Japan, and Ingold glass electrode were used after correction with a buffered solution.

Experimental procedures. After 100.0 mL of sample solution was taken in 250 mL separatory funnel, 0.58 g of NaCl was added to fix the ionic strength at 0.1 mol/L. The pH of solution was adjusted to 9.0 with buffer solution. And each 1.0 mL of 2% PV and 10% BC solution were added to this solution, together. The solution was shaken for a while to form the ternary complex. The complex was extracted into 10 mL of MIBK by a vigorous shaking for 30 minutes and the solution was stood for 40 minutes. After the phase separation, only the organic phase was moved to other separatory funnel of 10 mL of 1 mol/L nitric acid. And also it was vigorously shaken in a mechanical shaker for 10 minutes to strip the Zn(II). The absorbance of zinc was measured in the aqueous phase by a flame-AAS.

Results and Discussion

The effect of pH on extraction of Zn(II)-PV/BC complex. The stable formation of Zn(II)-PV chelate ion was very important to extract zinc ion in a solution as a ternary complex of Zn(II)-PV/BC. The formation of Zn(II)-PV chelate was known to be greatly influenced by the solution pH because the PV had three hydroxyl groups to be ionized as shown Figure 1. The stability of Zn(II)-PV was investigated by changing the pH under other optimized conditions for the efficient extraction of the ternary complex. The pH
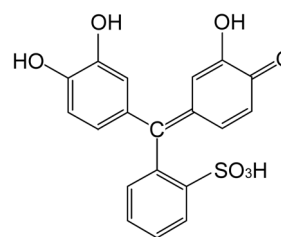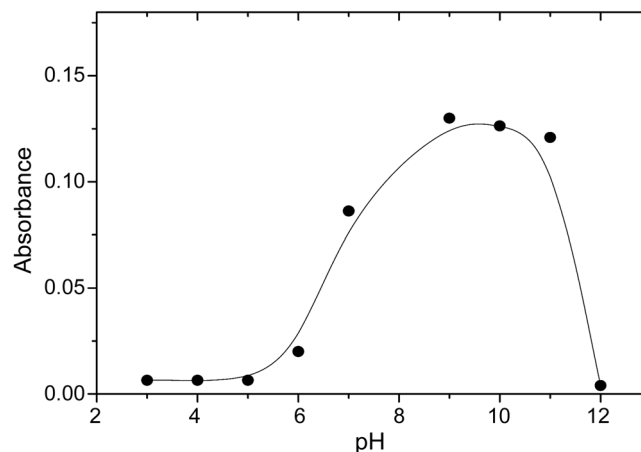
was changed from 3 to 12 with dilute nitric acid and NaOH solution (Fig. 2). And the extraction efficiency was compared at each pH by measuring the zinc absorbance of the back-extracted solutions.

As shown in Figure 2, the maximum absorbance of zinc was obtained at pH 9. The absorbance was decreased in the acidic solution of less than pH 9 because the hydroxyl protons of PV were difficult to be dissociated. On the other side, the decrease of the absorbance was due to the formation of zinc hydroxide precipitate in the alkaline solution above pH 10. Therefore the solution pH was adjusted at 9 in this experiment with a carbonate buffer solution.

The quantity of PV to be needed for the efficient extraction The minimum quantity of chelating agent, PV, was determined for the efficient extraction of zinc in this system because the PV was an important factor for the extraction of zinc. The quantity of PV needed was investigated for the effective extraction of zinc by varying the volume of 1% PV solution from 0.01 to 1.0 mL added to 100.00 mL of 50 ng/mL zinc solution. The experiment was done at pH 9 and under given conditions. The absorbance of the zinc extracted was plotted against the volume of 1% PV solution added (Fig. 3).

Figure 3 showed the absorbance plateau from 0.1 mL addition of the PV solution. This represented that the volume was the minimum quantity of PV to extract zinc into MIBK as a ternary complex at pH 9. But the absorbance increased slowly with the increase of the volume added. That meant
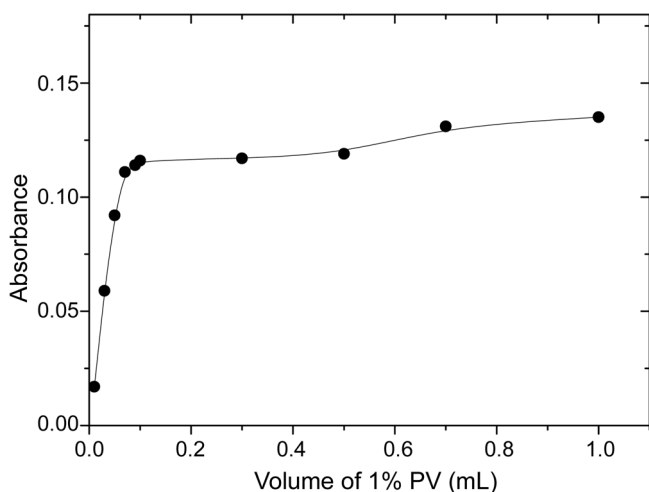
Figure 3. Dependency of PV quantity on the absorbance of zinc extracted from 100.00 mL of 50 ng/mL solution at pH 9. A 1.0 mL of 10% BC solution was added as a counter ion.

that more stable chelate could be formed by adding excess PV than 0.1 mL. From this result, 1.0 mL of 2% PV solution was decided to be added to 100.00 mL of real sample solution. This quantity of PV was equivalent to more than 340 times of zinc in presumably 50 ng/mL Zn(II) solution. And the Zn(II)-PV/BC chelate might more stable than other Zn(II)-chelates because its absorbance was not changed over an extended period.

The minimum quantity of BC to be needed for the synergistic extraction. As described above, Zn(II)-PV chelate ion was not efficiently extracted into MIBK because it had some negative charge. Therefore a synergistic solvent extraction was tried by forming a weakly polar complex. Generally, CTMAB (cetyltrimethyl ammonium bromide)[16] as cationic surfactant was widely used in synergistic solvent extraction. However, this surfactant was not usable in this work, because tetra alkyl ammonium iodide was precipitat-

ed. Furthermore, BC was shown the highest absorbance among six kinds of surfactant such as CTMAB, CPC (cetyl-pridinium chloride), Aliquat-336 (trioctylmethyl ammonium chloride), TOPO (tri-*n*-octylphosphine oxide), Triton X-100 and BC. For these, BC was selected as a counter ion. BC was not only a counter ion to make the chelate as the weakly polar complex, but also a cationic surfactant to help the extraction of the chelate ion. Therefore the absorbance of zinc was measured with increasing the addition of 10% BC solution (Fig. 4).

But the absorbance of zinc extracted was drastically increased by adding a very small volume of the BC solution and reached at a plateau by the addition of more than 0.02 mL. In this experiment, excess of 10% BC solution (~1.00 mL) was added to 100.00 mL sample solution because a relatively high content of zinc should be determined in water samples having a significantly different matrix. That is, such an extra amount of BC was required to make a balance with the PV for the formation the ternary complex even though the addition of extra BC caused a high background in the absorbance measurement.

The types of organic solvent for the extraction of the ternary complex Most of organic solvents used for the extraction are usually non-polar or weakly polar. The immiscible solvents with water can efficiently extract some neutral or weakly polar chemical species from an aqueous solution. But the polarity and chemical property are different from each other between solvents to react with the species specifically. The selection of a best solvent is very important to extract species.

In this work, the optimum solvent should be selected to extract the Zn(II)-PV/BC ternary complex from an aqueous solution effectively. The extraction efficiency was investigated among a number of usable solvents. That is, six kinds of solvents such as benzene, carbon tetrachloride, chloroform, MIBK, *m*-xylene and *n*-hexane were compared from each other to extract this complex. The absorbance of zinc
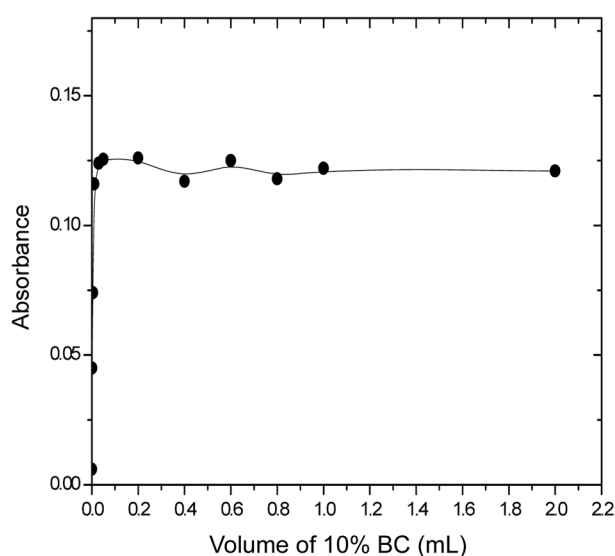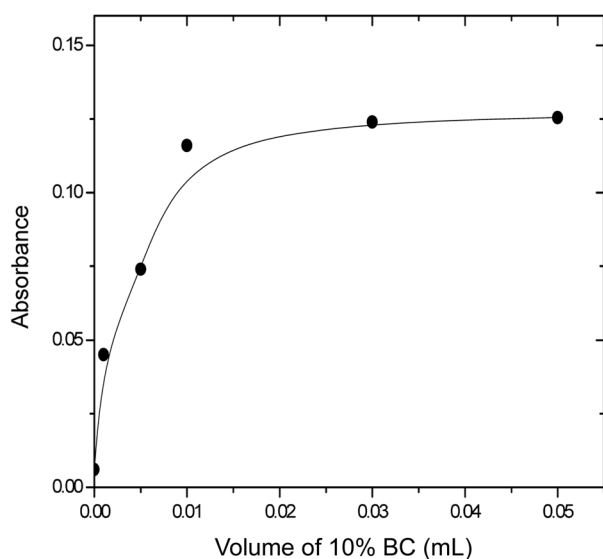
Figure 4. Absorbance Variation of zinc extracted according to the volume of 10% BC added in 100 mL of 50 ng/mL Zn(II) as a counter ion. A 1.00 mL of 1% PV was added before the BC addition.
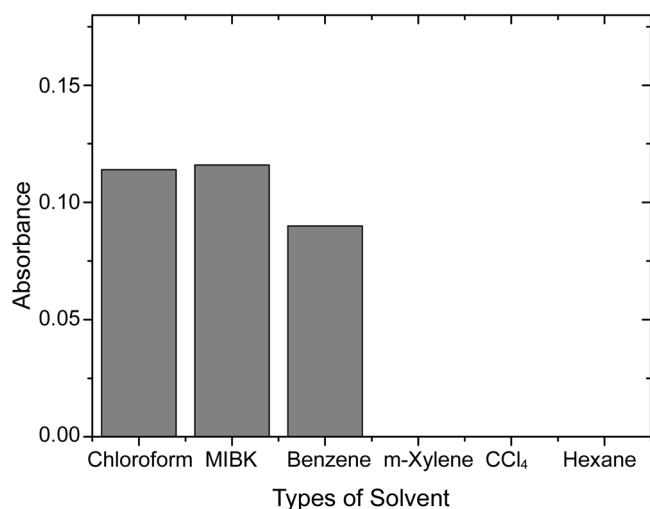
Figure 5. Extraction efficiency of ternary complex, Zn(II)-PV/BC according to the type of solvent used under the same conditions as above.

was measured in the back-extracted solutions to select the optimum solvent (Fig. 5).

As shown in the figure, chloroform and MIBK provided much higher absorbances than other solvents. Such phenomena could be explained as follows. The ternary complex, Zn(II)-PV/BC, had a weak polarity so that it could be much efficiently extracted into these solvents of a weak polarity compared to non-polar solvents such as carbon tetrachloride, *m*-xylene and n-hexane. Due to the high toxicity of chloroform, MIBK was selected as a good solvent among the solvents tested for extraction. In addition, MIBK was efficient for the back extraction.

A chemical species in an aqueous solution should be contacted with an organic solvent for a long time for the effective extraction. Therefore the sample solution was thoroughly shaken in a separatory funnel together with a

solvent. In this experiment, the funnel was shaken in a mechanical shaker for 30 minutes for the extraction of ternary complex and for 10 minutes for the back extraction. And the funnel was stood for 40 and 30 minutes after the extraction and back extraction, respectively. Such conditions were optimized by measuring the absorbance of zinc back extracted.

In this case, the back extraction of the ternary complex from MIBK was done to eliminate some backgrounds in the absorbance measurement by a flame AAS. A nitric acid showed a higher absorbance than those of other acids such as HCl, CH_3COOH and H_2SO_4. The concentration of HNO_3 was adjusted to 1.0 mol/L.

Interferences of concomitant elements. The interference of concomitant elements can be thought to be very important in the extraction if they form some complexes with a given ligand competitively. But the interference is not so serious in the measurement of AAS absorbance because AAS measurement is very selective toward elements. Usually the former interference can be overcome by adding an excess amount of the ligand. In this case, the addition of much ligand may cause something problems in a phase separation as well as in the absorbance measurement.

Therefore, the interferences of various elemental ions were investigated in this process for the determination of Zn(II) in water samples (Fig. 6). Regrettable small interferences of Mg(II), Ca(II) and Cd(II) were occurred in given solution as in Figure 6, but the interferences were gradually increased with the increase of the concentration of Al(III), Hg(II), Ni(II) and Mn(IV). Such interferences might be due to the formation of relatively stable chelates in a aqueous solution under given conditions. Other elements were known to be present in our water samples at the level of ignorable content for the extraction of zinc by the proposed procedure here, but Mn(IV) could be not ignored in sea water because the content was high to interfere with zinc extraction.
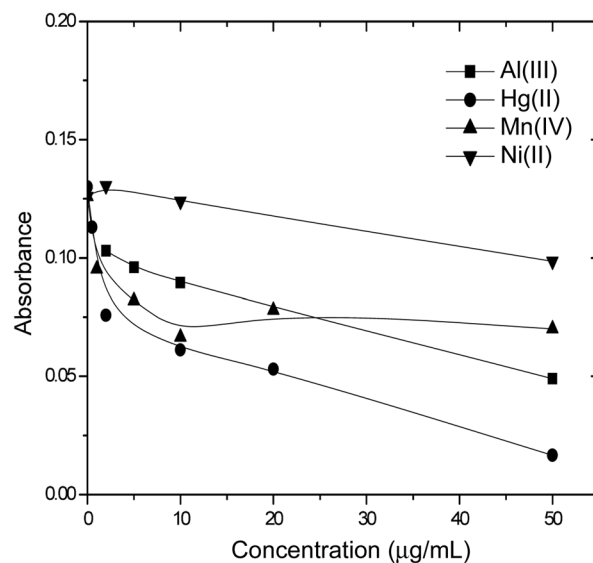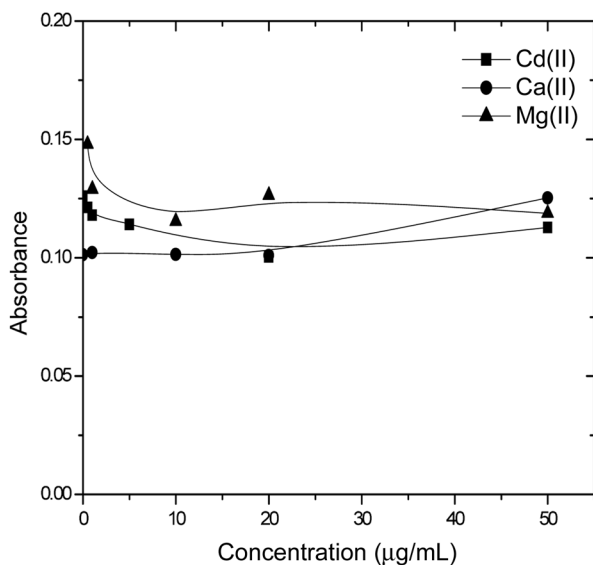
Figure 6. Interference effects of various elemental ions on the extraction and determination of Zn(II) in water samples under given conditions above.

Table 2. Analytical results of real water samples (ng/mL)

Samples	Spiked	Founded	Recovered	Recovery (%)	RSD (%)
Dalbang-dam water	0	12.72			3.09
	15	28.33	15.61	104.1	1.26
Laboratory tap water	0	15.01			5.87
	15	29.00	13.99	93.3	2.45
Jungnajin seawater	0	51.00			5.16
	50	90.18	43.28	86.58	5.00

*RSD values were calculated from five times of measurements.

Probably this interference was caused by the competition reaction to PV with zinc. Therefore the interference could be eliminated by adding much PV. Therefore, 1.0 mL of 2% PV solution was added to 100.00 mL of real sample solutions.

Calibration for the application to real samples. The procedure proposed here was applied to three kinds of real water samples. A series of the standard solutions was prepared to make a calibration curve. The content of Zn(II) was 10 to 400 ng/mL in the standard solutions. The standard solutions were treated with the proposed procedure. And the absorbance of zinc back extracted was measured in each solution to prepare the calibration curve. The curve had a good linearity of 0.9979 r^2 value, the slope of 1.790 and the intercept of 0.007.

The analytical result of zinc in three kinds of water samples was shown in Table 2. The contents were much high compared to the normally expected values. But it could be imagined that the extraordinary results were due to the regional nature of the sampling area because the area was positioned around calcium mine of high zinc. And also there were several cement factories that were known to exhaust some waste of high metals. The dam water was polluted by the waste to cause the high zinc. And the high content of zinc in a laboratory tap water was due to the 1 : 1 mixed water of city supplied water and underground water by the administrator of it. Especially high zinc in the seawater sample was expected to be caused by sampling the water from inside breakwater.

As shown in Table 2, the proposed method could be known to be a precise procedure for the trace content of zinc from less than 6% RSD. In addition, a recovery test was performed by determining the spiked concentration in the samples in which given amount of zinc was added. The recovery values of 86.58-104.1% could make this procedure a relatively reliable method.

Conclusion

The trace amount of zinc was determined by a solvent extraction. At first, a ternary complex of Zn(II)-PV/BC was formed by adding the PV and BC into the pH adjusted sample solution of ionic strength 0.1. The complex was extracted into MIBK and back extracted in 1 mole/L nitric acid to measure the AAS absorbance.

1. The solution pH was optimized at 9 and the pH was adjusted with carbonate buffer solution.

2. The ternary complex of Zn(II)-PV/BC was formed by adding excess amount of 2% PV 1.0 mL and 10% BC 1.0 mL to be extracted MIBK selected as the best solvent.

3. The interferences of Ca(II), Mg(II) and Cu(II) were not shown in the extraction and Al(III), Hg(II), Ni(II) and Mn(IV) could be ignored because of the too low concentration to interfere with. The interference of Mn(IV) could be eliminated by adding much excess of ligand and counter ion.

4. A linear calibration curve of 0.9979 r^2 linearity could be obtained to determine the zinc content in water samples. The proposed method here was evaluated to be producible and reliable with the recovery value of 86.58-104.1% and RSD of less than 6%.

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