

A New On-line Coprecipitation Preconcentration Technique for Trace Metal Analysis by ICP-AES

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In a stream of water sample, trace metal ions are quantitatively coprecipitated with Indium hydroxide and filtered. The filtered precipitate is continuously dissolved in 3 M nitric acid and introduced to ICP directly. The lead, cadmium, and copper are concentrated more than 10-fold and determined with ICP-AES at a sampling frequency of 10/hour. The detection limits are 2.89, 1.43, 0.52 ppb for lead, cadmium, and copper respectively. Recoveries of lead, cadmium, and copper are 98.7, 94.3, and 104.5% respectively. The RSD values for three elements are about 3-5% currently.

Introduction

In recent years, Atomic Emission(AE) and Atomic Absorption(AA) techniques are progressing to meet the needs of ever complex samples. Especially in the areas of environmental and biological chemistry as well as in semiconductor areas, difficult situations arise often because of low concentration of analytes. Quite frequently, concentrations of analyte lie below the detection limit. Consequently, people have been using preconcentration techniques such as an evaporation method, extraction¹, coprecipitation method,²⁻⁵ and column method.⁶⁻¹⁰ The coprecipitation method has many advantages; it is a simple technique and several analytes can be concentrated simultaneously. In this method, trace amounts of analytes are precipitated and collected with a coprecipitating reagent and the enrichment factor can be greater than 100 times. Furthermore, it can be used in separating analytes from a matrix such as alkali. In the classical coprecipitation preconcentration method, hydroxide precipitations³⁻⁵ with Fe, Ga, Ce, In as well as organic reagents^{11,12} such as APDC (Ammonium Pyrrolidine Dithiocarbamate), DDTC(Diethyl Dithiocarbamate) have been used. Sung, W. S. *et al.*⁴ has used In as a collecting agent to analyze Cd, Cu, Fe, Mn, Pb, and Pd in sea waters by the floatation method. Hiraide *et al.*¹³ also analyzed Cu(II) using In as a collecting agent. However, this batch type experiment takes a long time (30 min. per sample) and contaminations from glass wares and the environment can cause errors.

On-line method is particularly attractive because it takes less time (20/hour) and is less vulnerable to contaminations because that few glasswares are used and samples are contained in a closed loop. Since flow injection technique can also be employed, only a small amount of sample can be effectively concentrated. Finally, an automation is also feasible. Bearing these in mind, scientists have begun to utilize the on-line preconcentration technique.

The most explored area in the on-line preconcentration is the column method. Chelating agent such as 8-HOQ (hydroxyquinoline) can be packed in a column and used to collect trace amounts of metal ions. The complexes can be eluted out by a dissolving reagent and the eluent can be analyzed with ICP-AES¹⁴⁻¹⁶ or AA.¹⁷ Sakamoto¹⁵ have determined trace amounts of Co(II) in sea water. Hirata *et al.*⁶ have used an ion exchange column (Muramac-1) to analyze

Cr, Ti, V, Fe, and Al with an ICP. Schuramel¹⁸ have used EDTA(Ethylenediaminetetraacetic Acid)-Cellulose to determine Cu, Fe, Zn, Cr, Ni, Mn, V in environmental samples. Sperling¹⁹ have used activated Alumined to determine Cr(II) and Cr(IV). These methods show good enrichment factor but the columns have to be prepared in each laboratory. Also, the pH should be controlled to separate elements.

In the on-line preconcentration technique using precipitation, Valcarcel²⁰ analyzed ppm level of Cu in silicate rocks by precipitating Cu with rubenic acid without any coprecipitating reagent. After the precipitates are collected, they are dissolved with an oxidant. However, if the concentration of analyte is low, a direct collection of precipitate could result in errors and consequently, the addition of collecting agent is inevitable. Currently, in the on-line coprecipitation methods, organic coprecipitant such as HMA-HMDTC(Hexamethylene Ammonium-Hexamethylene Dithiocarbamate) have been used. Welz²¹ have used a knotted tube to separate the precipitates and analyzed Cd, Co, and Ni with FAAS(Flame Atomic Absorption Spectrometry). Fang²² used the same method to analyze Ni and Cd with ETAAS(Electrothermal Atomic Absorption Spectrometry). Z. Zhuang²³ used Co-APDC as a carrier and collected the precipitates of Cd, Cu, Fe, Ni, Pb, and Zn onto the PTFE(Polytetrafluoroethylene) filter and dissolved with the mixed solution of 1:1 nitric acid and hydrogen peroxide to be analyzed with ICP-AES.

In this report, we propose an on-line coprecipitation technique using Indium as a carrier for the first time. It is attractive because it is well known for making good hydroxide precipitates and gives a relatively simple spectral background, which is important in ICP-AES. Unlike organic precipitant, organic solvent which can be troublesome in the ICP is not necessary. As indium is precipitated, analytes will be coprecipitated in the flow. After the precipitates are collected on a filter, they are dissolved with acid and sent to ICP. As mentioned earlier, this on-line coprecipitation has many advantages and could be effective especially in the area of trace analysis.

Experiment

A schematic diagram of the experiment is shown in Figure 1. A peristaltic pump (Osmatic, Cole-Parmer) is used to send solutions of sample, buffer, and oxidant. A PTFE six-way

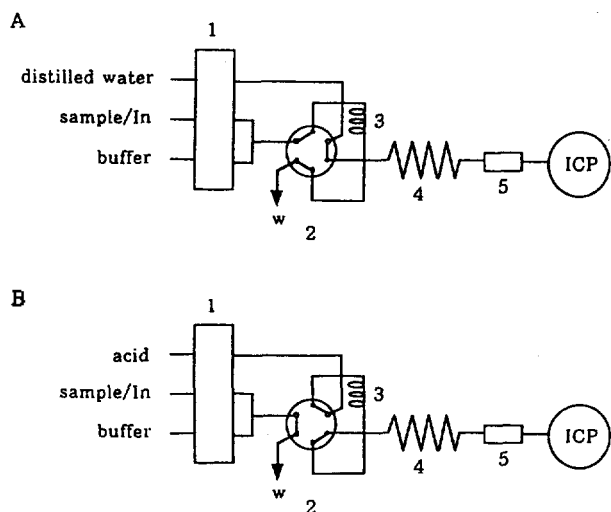


Figure 1. A schematic diagram of the on-line coprecipitation system: (A) washing of reaction coil and filter, and sample loading; (B) filtering of precipitate and precipitate dissolving; (1) peristaltic pump; (2) injection valve; (3) loading coil; (4) reaction coil; (5) filter; (w) waste.

injection valve is used to collect a fixed volume of sample. For oxidant, viton tube is used because strong acid can easily attack a normal plastic tube. The tubes are all PTFE of 0.8 mm i.d. and the filter housing has been constructed in this laboratory.

Instrument and Reagents. A sequential ICP spectrometer (Plasma 1000, Perkin Elmer) is used to determine the concentrations and the transient signal is recorded with an integrator (Spectra-Physics, U.S.A.) to measure peak area. The system is equipped with a standard cross flow nebulizer. Standard solutions are made from all 99.999% of $\text{Pb}(\text{NO}_3)_2$, CdO , and $\text{Cu}(\text{NO}_3)_2$. The buffer solution is made from 5.0 gr of NaHCO_3 and 4.2 gr Na_2CO_3 dissolved in 1 L of water. For the carrier solution, 99.9999% In metal is dissolved in conc. HNO_3 and diluted to 50 mL of 2% nitric acid. This stock solution is later diluted to a proper concentration before each use. The water used is all doubly deionized.

Experimental Procedure. The process can be divided into four steps; 1) washing 2) loading 3) collecting 4) dissolving.

1) washing: Nitric acid and water are sent to clear the loading coil, reaction coil, and filter while the valve is in the position shown in Figure 1B.

2) loading: Sample mixed with In carrier is loaded onto the loading coil while the valve is in the position shown in Figure 1A.

3) collecting: The valve is turned to send the loaded sample through the mixing coil (Figure 1B). The precipitates are collected into the filter.

4) dissolving: The precipitates collected are dissolved with acid solution and sent to the ICP.

Result and Discussion

The optimum conditions for the ICP-AES (Table 1) is determined to yield the best signal-to-noise ratio. Once deter-

Table 1. A Typical ICP (sequential) Operating Condition Used for the Experiment

R.F. power	: 1.12 kW
Nebulizer gas flow	: 1.3 mL/min
Auxiliary gas flow	: 1.0 mL/min
Plasma gas flow	: 15 L/min
Viewing height	: 13 mm
PMT voltage	: 700 V
Wavelength	: Pb 283.3 nm

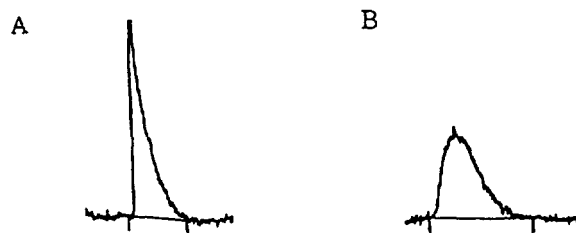


Figure 2. Comparison of peak shapes between using buffer solution (A) and NaOH solution (B).

mined for the ICP-AES, experimental optimum conditions such as the concentration of In, the type and concentration of oxidants, the flow rate of oxidant, the type of filter, the length of reaction coil, and the sample volume are decided.

Indium has been chosen as a carrier because it gives a simple spectroscopic background compared to Fe, Mg, Fe, and Ga. Also it is easy to obtain as a pure metal. The pH control has been done by $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ buffer instead of NaOH solution because the buffer can provide more constant pH condition during the precipitation thus producing more homogeneous precipitates. In Figure 2, the peak shapes from the buffer and NaOH solution are compared. The one obtained with the buffer shows a narrower peak and better reproducibility. 1 ppm Pb solution has been used throughout the experiment for the determination of the optimum experimental conditions.

The concentration of In carrier. The concentration is varied from 25 to 200 ppm and the result is shown in Figure 3. Both peak area and height are comparable in the range of 50-170 ppm. Obviously, too little In (below 50 ppm) is not enough to collect the analyte efficiently and too much In (above 170 ppm), and consequently too much precipitates, can block the flow of eluent. 50 ppm of In gives the best signal as is shown in Figure 3.

The Type and Concentration of Oxidants. 2 M HCl, 2 M H_2SO_4 , 1:1 mixed HCl and H_2SO_4 , 1:1 mixed HCl and HNO_3 , 2 M HNO_3 , 3 M HNO_3 , 4 M HNO_3 have been examined and the results are listed in Table 2. The peak areas are not much different with each other but the peak height shows that nitric acid is more favorable. It is thought that nitric acid dissolves precipitates relatively fast and produces a narrow peak width. 3 M nitric acid exhibits the best peak height and low RSD value.

Oxidant Flow Rate. The flow is varied from 1.2 mL

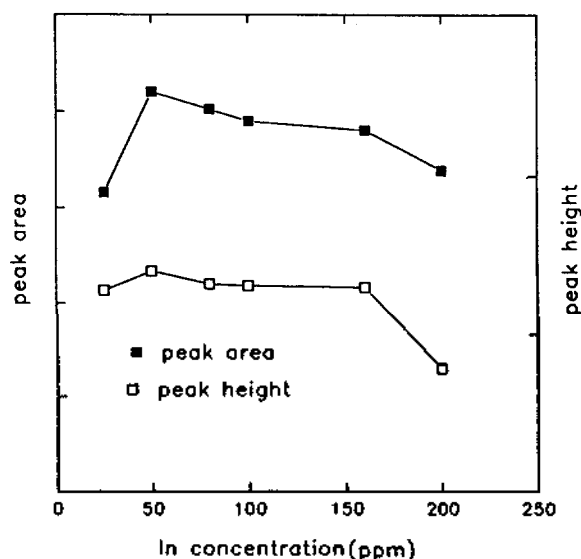


Figure 3. The effect of In concentration on the relative intensity. 1 ppm Pb solutin is used for the experiment.

Table 2. Changes of Peak Areas and Peak Heights with Different Dissolving Solutions. 1 ppm Pb Solution is Used and the Number of Measurement is 10

Dissolving solution	Peak area (RSD %)	Peak height (RSD %)
2 M HCl	3.20 (38.6)	4.87 (21.3)
2 M H ₂ SO ₄	4.39 (27.7)	4.61 (5.50)
HCl : H ₂ SO ₄ 1 : 1 mixture	2.57 (33.1)	4.00 (12.3)
HCl : HNO ₃ 1 : 1 mixture	2.93 (19.2)	5.76 (28.2)
2 M HNO ₃	4.16 (6.73)	5.19 (21.3)
3 M HNO ₃	3.78 (14.8)	9.56 (7.87)
4 M HNO ₃	2.08 (37.1)	6.17 (19.9)

/min to 3.6 mL/min and the result is shown in Figure 4. Peak height shows the best value at around 2.0 mL/min. At the lower flow rate of oxidant, peak height is smaller even though it is expected to give higher value because the concentration will be larger. However, at the low flow rate, the nebulizer is not working in its optimum condition. At the high flow rate, the volume of oxidant is increasing for a fixed amount of precipitates thus decreasing the peak height. Another reason might be that the pressure increase could cause some precipitates pushed out of the filter. This was noticed when the background level before the peak appearance increases with a large oxidant flow. The peak area shows constant at the low flow where there is enough time of dissolving. However, at the higher flow, it is decreasing because of the same reasons mentioned for the peak height. The best speed for the oxidant is 1.8 mL/min.

Filter. 0.45 μ m HA, 0.45 μ m cellulose acetate types, and a filter paper (about 1.0 μ m) are used and the result shown in Table 3. Though it is not seen here, the result with 1.5 μ m pore size showed that the pore size was too large and resulted some leaks. The filter paper shows good results compared to 0.45 μ m membrane filters. It is physically st-

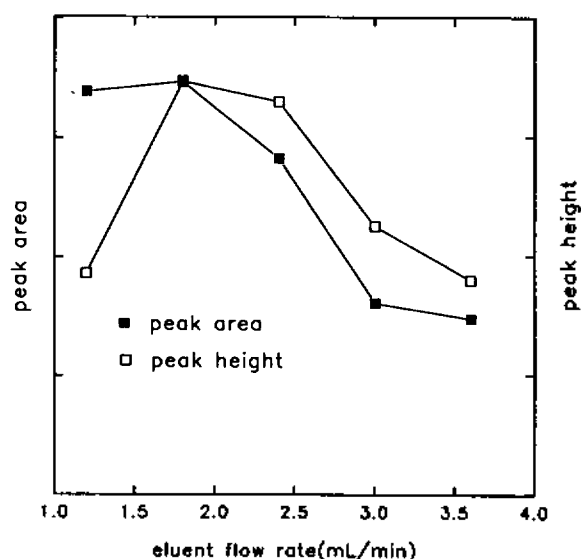


Figure 4. The effect of dissolving solution flow rate on the relative intensity.

Table 3. Changes of Peak Areas and Peak Heights with Filter Types. 1 ppm Pb Solution is Used and the Number of Measurement is 10

Filter type	Peak area (RSD %)	Peak height (RSD %)
0.45 μ m HA type	511456 (17.8)	4.83 (28.2)
0.45 μ m cellulose acetate	395965 (12.4)	4.55 (20.5)
Filter paper 1	299928 (14.0)	2.70 (10.7)
Filter paper 2	513549 (15.4)	6.61 (2.87)
Filter paper 3	487549 (14.0)	4.05 (22.7)

rong, cheap, and easy to handle. A piece of filter paper is not enough to collect precipitates quantitatively. From the Figure 5, the leak can be observed for the filter paper. To reduce the loss, three layers of filter have been employed and it begin to show the spreading of peaks due to the increase of dead volume. Thus, two filters in series shows the best results. In terms of signal, 0.45 μ m HA type filter and the filter paper are similar except the time takes about twice for the filter. In the area of precision, 0.45 μ m membrane filter is superior to paper filters about twice. Since membrane filters are physically weak, they can be easily deteriorated even at the pressure applied by the current system. Thus, the precision of membrane filter is only better with the use of support material. In overall evaluation, 0.45 μ m HA filter supported by 1.50 μ m cellulose acetate filter showed the best signal and precision and used for the experiment while filter paper showed good speed. If the pump power could be increased, 0.45 μ m filter will be even more beneficial because of more efficient collection of precipitates and good precision.

Reaction Coil Length. Since the precipitation reaction takes some time, a short reaction coil is not enough. In Figure 6, it is shown that a proper distance (time) is needed for the precipitates to be made and mature. On the other

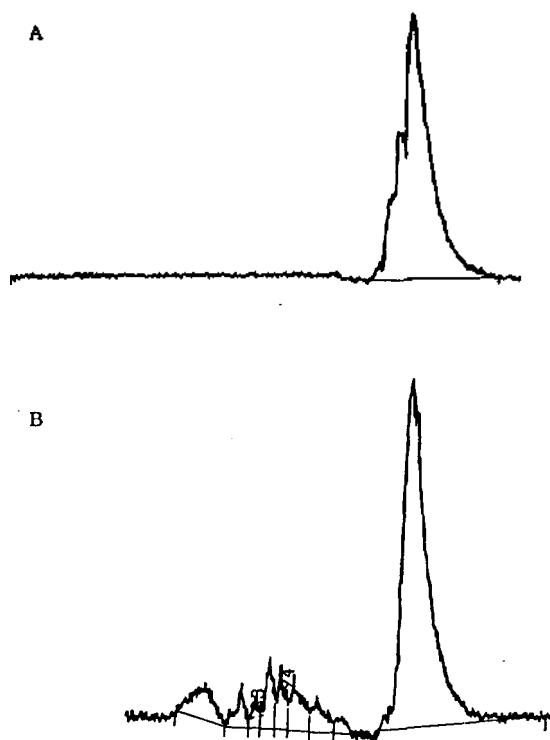


Figure 5. Comparison of peak shapes between using HA filter (A) and filter paper (B).

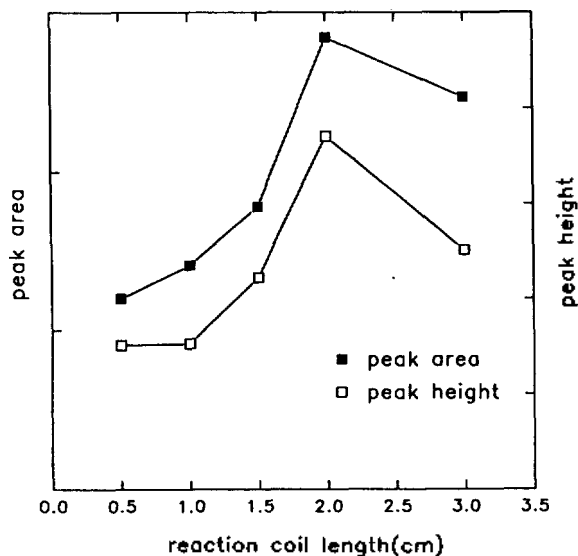


Figure 6. The effect of reaction coil length on the relative intensity.

hand if the reaction coil is too long and the precipitates stay in column too long, the longitudinal diffusion takes over and the peak spreads. Considering the peak shape and time, 2 m reaction coil was selected.

Sample Volume. Since the enrichment factor is directly proportional to the amount of sample collected, a large volume of sample should be more beneficial. In practice, too much precipitate can block the flow and the time of analysis can be increased drastically. Thus, considering the sample

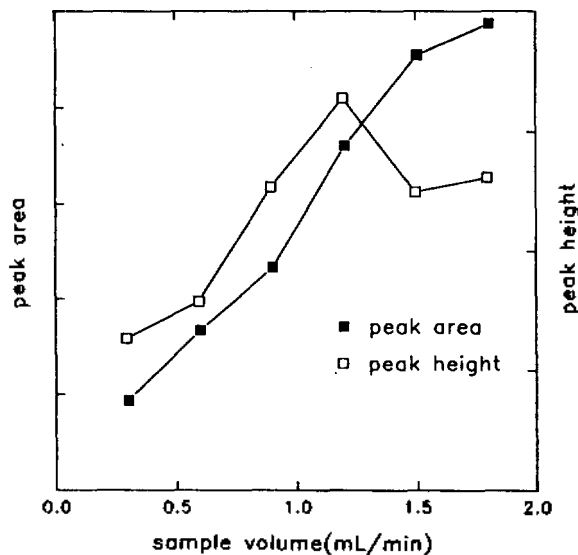


Figure 7. The effect of sample volume on the relative intensity.

Table 4. The Optimum Condition Used for the On-line Coprecipitation Preconcentration System

Indium concentration	: 50 ppm
Dissolving solution	: 3 M HNO ₃
Flow rate of dissolving solution	: 1.8 mL/min
Filter type	: HA membrane filter with a support
Reaction coil length	: 2 m
Sample volume	: 1.2 mL

throughput and the enrichment factor, there is an optimum sample volume to concentrate. The peak height and area increase with the sample volume from 0.3 mL to 1.2 mL as expected and they are shown in Figure 7. When the sample volume is larger than 1.2 mL, the peak height begins to decrease because the precipitates are too much to be dissolved at once and they block the flows. Consequently, the oxidant flow rate decreases below the optimum nebulizer flow rate. In other words, the amount of sample sent to ICP per unit time, and the peak height, is decreased. However, the total amount of precipitate, and the peak area, will be proportional to the sample volume only as is shown in Figure 7. The time of analysis begins to increase sharply after 1.2 mL/min because of the restrained flow. Currently, at this system, the optimum sample volume is 1.2 mL. Of course, this value can be easily varied with the pump and filter size etc. The optimum condition for the experiment is summarized in Table 4.

A sample was prepared by mixing Pb, Cd, and Cu to be from .044 to .176 ppm and analyzed with ICP at the optimum condition obtained and the result is shown in Table 5. 7 to 13 times of the enrichment factor is acquired. The RSD values are around 3-6%. Real samples of drinking water and rain have been analyzed and shown in Table 6. It is demonstrated here that even for the low concentrations of Pb in drinking and stream waters, ICP-AES can be successfully

Table 5. Performance of On-line Coprecipitation Preconcentration for ICP

	Wavelength (nm)	Sample conc. (ppm)	Enrichment factor	Detection limit (ppb)	RSD (%)	Recovery (%)
Pb	283.3	0.100	12.9	2.89	5.89	98.7
Cd	214.4	0.176	8.10	1.43	2.91	94.3
Cu	324.7	0.044	7.10	0.52	3.43	104.5

Table 6. Comparison of Standard Addition with Calibration Curve Methods for the Determination of Pb, Cd, Cu in Environmental Samples by On-line Coprecipitation Preconcentration

		Drinking water ^a	Tap water ^b	Stream water ^c	Rain water ^d
Cu	Calibration curve (ppb)	13.4	9.26	6.26	41.5
	Standard addition (ppb)	13.8 ± 1.08	7.79 ± 0.10	7.79 ± 1.04	49.0 ± 8.23
Pb	Standard addition (ppb)	9.47 ± 2.74	9.00 ± 1.13	9.16 ± 0.82	96.7 ± 5.24
Cd	Standard addition (ppb)	3.17 ± 0.41	6.34 ± 0.72	6.34 ± 1.36	10.2 ± 0.42

^aThe cafeteria in Korea National University of Education. ^b3rd college of KNUE. ^cMee-ho river in Chung-buk. ^d1994. 3. 4.

applied. The results are obtained using the standard addition method. The calibration method and the standard method are compared with each other for Cu ion. The results of drinking water show somewhat high values. The samples are collected differently *i.e.*, the very first batch from a faucet that has not been used for a long period has been collected rather than a middle batch of a water line constantly being used. For a simple matrix of drinking water, the results agree with each other well while tap and rain water show some differences. For the stream water, the values are quite different. It is suspected that in the stream water, a lot of interfering species such as humic acid and pulvic acid could cause serious errors²³ in determining trace level of metal ions. In a sample of complex matrix, the standard addition method is more recommended.

Conclusion

The on-line preconcentration method using In as a coprecipitating agent has been developed first and successfully applied to ICP-AES to determine such low concentrations of trace metals that can not be measured directly. This method is simple, fast and free of contamination. Furthermore, several elements can be preconcentrated at the same time. Since it can employ the flow-injection technique, a small amount of sample can be preconcentrated as well. However, the current enrichment factor does not exceed 15 times, though in theory, several hundreds times is possible. The present experimental system has limitations in the pump and filter. As the sample volume increases, the amount of precipitates increase also. The back pressure builds up at the filter and blocks the flows and consequently, the sample throughput decreases. To alleviate the back pressure problem, a high pressure pump combined with a larger filter could be used. Preliminary data in our laboratory reveal that peaks are eluted in shorter time with better precision with a HPLC pump. Of course by sacrificing the sample throughput, the enrichment factor can be increased.

Another area to be improved is nebulizer and spray chamber. To increase the enrichment factor, a smaller spray

chamber is necessary. The current spray chamber has a large dead volume and enlarge the peak width and lower the peak height. Ultrasonic nebulizer is expected to give high signal due to increased sample throughput and reduced dead volume. Another approach that can enhance the enrichment factor is the direct precipitation. Since only analytes will be precipitated and collected, a lot less pressure will be built up, which means that the sample volume and consequently the enrichment factor could be increased. This experiment is under investigation in our research laboratory.

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Multidimensional Frictional Coupling Effect in the Photoisomerization of *trans*-Stilbene

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A model based on two coupled generalized Langevin equations is proposed to investigate the *trans*-stilbene photoisomerization dynamics. In this model, a system which has two independent coordinates is considered and these two system coordinates are coupled to the same harmonic bath. The direct coupling between the system coordinates is assumed negligible and these two coordinates influence each other through the frictional coupling mediated by solvent molecules. From the Hamiltonian which is equivalent to the coupled generalized Langevin equations, we obtain the transition state theory rate constants of the stilbene photoisomerization. The rates obtained from this model are compared to experimental results in *n*-alkane solvents.

Introduction

The photoisomerization of *trans*-stilbene has attracted considerable experimental¹⁻⁸ and theoretical⁹⁻¹² interests due to the fact that it provides a practical testing ground for theories of activated barrier crossing processes occurring in solution. In theoretical approaches to barrier crossing,¹³⁻¹⁵ the dependence of reaction rate on solvent friction can be considered to have two phases. At very low friction the rate of energy accumulation in the reaction coordinate may be rate-limiting and the reaction rate will increase with increasing friction. At high friction regime the frictional effects resulting from multiple barrier crossing and recrossing begin to dominate and the reaction rate begins to decrease with increasing friction. Therefore a peak known as the Kramers turnover should exist in the variation of rate with friction. In the low viscosity regime there has been an effort to detect this maximum, and it has been only observed in pressurized gases but has not been observed in low viscosity liquid.^{5,16}

The experimental situation of stilbene isomerization in alkane or alcohol solvent corresponds to high friction regime of Kramers theory. In this regime, there have been attempts to explain the effect of the medium on the isomerization rate in terms of the Kramers theory since Hochstrasser's initial application.^{1,17} The Kramers theory is based on the concept of a Brownian particle escaping over a one-dimen-

sional potential energy barrier along a potential energy curve that is piecewise parabolic. For the application to the *trans*-stilbene isomerization, the Kramers equation for the rate constant gives

$$k_{iso} = (\omega/2\pi)(\beta/2\omega') \{ [1 + (2\omega'/\beta)^2]^{1/2} - 1 \} e^{-E_b/kT} \quad (1)$$

where E_b is the barrier height, ω and ω' are the frequencies of the initial well and the curvature at the top of the barrier, respectively, and β is the reduced friction coefficient. Kramers' theory does not have the correct curvature necessary to describe the experimental results. It was found that the experimental results could be fitted very well to a viscosity dependence of the following form^{2,3}

$$k_{iso} = \frac{A}{\eta^\alpha} \exp(-E_b/kT) \quad (2)$$

where η is the solvent viscosity, A is a viscosity-independent constant, and the activation energy E_b is obtained by isoviscosity plots where the temperature is changed but the viscosity is held constant through the use of different solvents. The value of the empirical exponent α is typically between zero and unity.

Possible factors that result in the deviation from Kramers' theory are non-Markovian effects,^{14,15,18} complicated interrelation between the microscopic friction and macroscopic visco-