42. Irradiation of (*E*)-iodoenolether **4E** in CDCl₃ for 1 h under ordinary laboratory fluorescent lights gave the isomerized (*Z*)-iodoenolether **4Z**, and proton-substituted enol ethers. **4Z**: ¹H NMR (CDCl₃) δ 4.84 (t, J=5.0 Hz, 1H), 2.90-2.71 (m, 1H), 2.76 (dd, J=13, 9.6 Hz, 1H), 2.43 (d, J=13.4 Hz, 1H), 2.21 (t, J=7.1 Hz, 2H), 2.12-1.20 (m, 10H), 0.87 (t, J=7.2 Hz, 3H); ¹³C NMR (CDCl₃) δ 156.9, 88.2, 66.2, 42.6, 37.8, 34.9, 34.2, 33.0,

31.9, 24.1, 21.4, 13.9.

43. de Boer, T. J.; Backer, H. J. *Org. Synth. Coll.* 1963, *4*, 943.

44. (a) Larock, R. C.; Brown, H. C. *J. Organomet. Chem.* 1972, *36*, 1. (b) Larock, R. C.; Gupta, S. K.; Brown, H. C. *J. Am. Chem. Soc.* 1972, *94*, 4371.

45. Normant, J. F.; Chuit, C.; Cahiez, G.; Villieras, J. *Synthesis* 1974, 803.

Preconcentration of Cd by Continuous Hydroxide Precipitation-Dissolution in Atomic Emission Spectrometry

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On-line preconcentration by direct precipitation with hydroxide has been developed and applied for the analysis of Cd in Inductively Coupled Plasma Atomic Emission Spectrometry. Cadmium is continuously precipitated with hydroxide and dissolved by nitric acid in on-line mode. Currently, the enrichment factor is more than 90 times for 20.0 mL of sample and could be further increased very easily. For a large sample throughput, 1.0 mL of sample loop is used and the enrichment factor is 4.5 with the sampling speed of 15/hr. The method has been applied to the analysis of NIST reference sample and has yielded good results with the certified value.

Introduction

Cadmium has been well studied because of its high toxicity even at low concentrations.[1] Varieties of technique[2,3] to determine Cd at very low concentrations have been developed. Different species of cadmium has been separated and detected by HPLC-ICP[4,5] (High Performance Liquid Chromatography-Inductively Coupled Plasma). Also, it has often been needed to separate analytes from matrix to reduce or avoid interferences. Precipitation is a very attractive method of achieving both preconcentration and matrix separation and has been widely used in this sense.[6-8] Because of the recent development of Flow Injection Analysis (FIA), the on-line precipitation preconcentration[9-13] method has been developed and began to appear only in these days. The advantages are well discussed in other literatures.[8,13]

Most of researches[11-14] have focused on the utilization of coprecipitation because it is more efficient in collecting trace elements quantitatively. Inorganic carriers[15,16] as well as organic collectors[11,12] have been used to preconcentrate various elements. Welz et al.[11] used a "knotted" reactor instead of filter to increase sample throughput. Some of the researchers[17,18] utilized more sophisticated techniques to enhance detection limits. Nielson[18] studied the technique of on-line coprecipitation combined to hydride generation. Arsenic was first coprecipitated with hafnium. When it was dissolved in HCl, sodium tetraborate was added to generate arsenic hydride. Detection limits could be enhanced more than 30 times in Graphite Furnace Atomic Absorption Spectrometry.

Anions also could be preconcentrated and analyzed. Esmadi[19] used AgNO₃ to precipitate arsenite and cyanide

ions. After both anions were precipitated, an acid and ammonia were sent as dissolving reagents in sequence. When an acid was sent, silver arsenite was dissolved out and for ammonia, silver cyanide eluted out. The concentrations of arsenite and cyanide could be measured separately.

However, it has been a trouble to collect large amount of precipitation on a filter. Because of the back pressure at the filter region caused by the precipitates, the flow could be slowed down or even stopped. Thus, large volume of sample was difficult to be preconcentrated. Furthermore, blockage of flow frequently resulted in a poor precision. "Knotted" reactor gives less back pressure but the peak becomes broadened because of its large loop length.

Direct precipitation could be more advantageous than coprecipitation in this sense. Since no carrier is used, a large amount of sample can be preconcentrated thus increasing enrichment factor. Until now, only a few studies have been performed using direct precipitation. Valcarcel[16,18] has shown that trace amount of Pb in a rock sample can be effectively analyzed by continuous precipitation using ammonia. Our group[20,21] has recently shown that sulfide precipitation could be utilized in the analysis of tin group elements. Homogeneous precipitation of As with sulfide anion was successfully demonstrated. H₂S was generated by the hydrolysis of thioacteamide in the reaction coil. Two most common type of precipitates, sulfide and hydroxide, are very easy to use and many cations can be precipitated.

In this research, on-line direct precipitation preconcentration by forming hydroxide precipitation is demonstrated for the analysis of Cd because it can form hydroxide precipitation very easily even at low concentration levels. Oth-

er elements that form hydroxide precipitation can also be investigated and the study on the preconcentration of copper will be published separately.

Experimental

Reagent and instrument. All reagents were analytical reagent grades and doubly deionized water (Millipore Q) was used. Bicarbonate-carbonate and ammonia-ammonium buffers were used to control the pH of mixed solution to be 10. For carbonate buffer, 4.2 gr of bicarbonate and 5.0 gr of carbonate were dissolved in 0.5 liter of doubly distilled water. For ammonia buffer, 0.15 N of 0.1 L ammonia and 0.15 N nitric acid 0.05 L were mixed and the pH was adjusted at 10. The final pH was adjusted with a pH meter by adding strong acid or base. Filters were placed in the filter housing (Figure 1) and could be easily replaced. The stainless filter was the one originally used in the HPLC solvent filtering. It was grinded and shaped to fit in the housing. A membrane filter (HA type) was also used and showed good result. When the sample concentration was high (above 10 ppm), the flow could be blocked and the membrane filter was deformed because of high pressure. An ICP (Model; plasma 1000, Perkin Elmer, CT, U.S.A.) was a sequential spectrometer and its optimum instrumental conditions are listed in Table 1.

Experimental procedure. The basic experimental system was similar to the one used in the other study[20] and is shown in Figure 2. First, a small amount of acid was introduced to dissolve out any precipitates left. Secondly, fixed amount of sample was loaded to the 6-way valve by a syringe (Figure 2-A). When the valve was in "inject", as in Figure 2-B, sample was introduced to the reaction coil. At the same time, precipitant (NaOH or buffer) was introduced into the reaction coil by pump 2. All the precipitates generated were collected at the filter region. At the final step, a dissolving reagent was introduced by pump 2 to dissolve
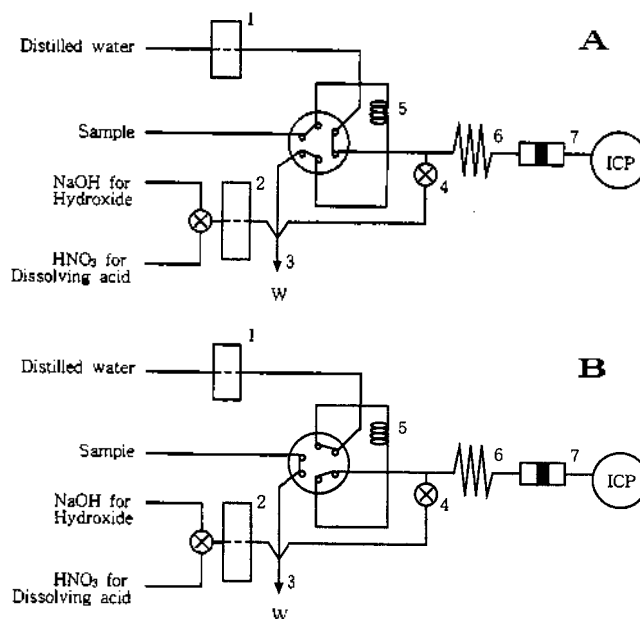

Figure 1. A schematic diagram of the filter cartridge.

Table 1. A typical Operating Condition of ICP used in the Experiment

R. F. Power	: 1.0 kW
Coolant Gas Flow L min^{-1}	: 15.0
Auxiliary Gas Flow L min^{-1}	: 1.0
Carrier Gas Flow L min^{-1}	: 1.3
Observation height mm	: 15
Wavelength nm	: 214.438

Figure 2. The on-line system of direct precipitation dissolution system for hydroxide. A; load position B; inject position 1: pump 2: pump 3: waste 4: valve 5: sample loop 6: reaction coil 7: filter

out the collected precipitates. To enhance the enrichment factor, injected sample volume could be increased. For a large volume of sample, a fixed amount of sample could be introduced by pump 1 directly. Both peak height and areas can be used to correlate signal with the sample concentration quantitatively. Peak area was measured with an integrator (Data jet, Spectra Physics, U. S. A.).

Result and Discussion

Precipitant. Several precipitants were examined to make a good cadmium hydroxide precipitate. The first type used was a strong base such as NaOH or KOH. Secondly, a buffer solution was used to provide more stable pH con-
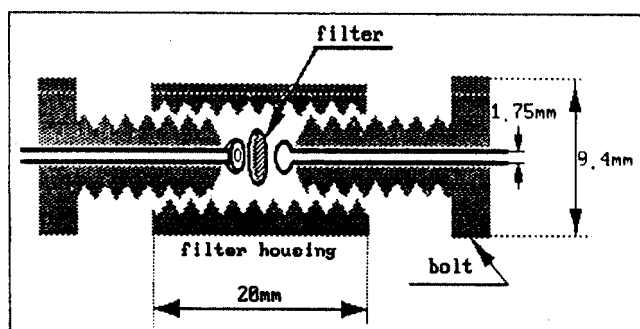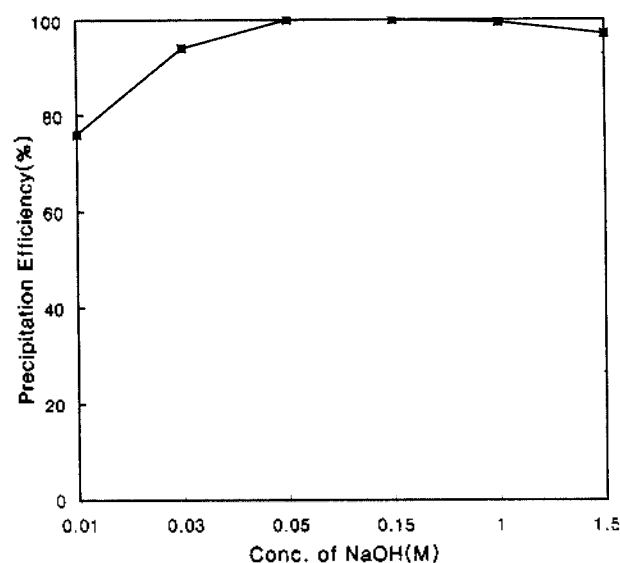

Figure 3. The relationship between the precipitation efficiency and OH concentration.

dition throughout the reaction. NaOH solution was easy to prepare and adjust pH. However, when a sample was very acidic or basic, the final pH could be different and the constant environment no longer existed. Figure 3 shows the amount of sample precipitated for different concentration of NaOH when an acidic (pH=2) sample was used. At relatively low concentration of OH⁻, the final solution could become acidic reducing the precipitate yield. Thus, it was often necessary to use higher pH solution of NaOH to make the final pH sufficiently high for acidic samples. It was required to do the opposite when a basic sample was used. A buffer was more advantageous in this aspect but should have a sufficiently high ionic strength to provide constant pH environment throughout the reaction. If pH is too low, the recovery is poor because precipitates are formed too little. In high pH, the recovery is also reduced because precipitates could be dissolved as anions. Considering the K_{sp} of $Cd(OH)_2$ is 5×10^{-15}, the theoretical concentration limit of Cd at pH 11 is 0.5 ppb.

Different precipitant resulted different shapes of peaks, which suggests that precipitates formed could be different for samples and reaction conditions. As is shown in Figure 4, a sharp and tall peak was obtained with NaOH while a slightly broader one was obtained with carbonate buffer. Since buffers can provide more homogeneous environment and less of supersaturation, larger particles are expected to be formed. Consequently, they dissolve out slowly compared to the smaller particles generated under NaOH and a broader peak is obtained. However, the total amount of precipitates and area should be the same.

Peak heights and areas for different precipitants were examined and summarized in Table 2. It is shown that buffers could provide more stable condition, thus better precision (4%) in peak area measurement. It also shows that the peak area measurement is more reliable than peak height. Peak height is dependant on several factors such as rate of dissolving. When precipitates are too much loaded at the filtering region, the flow can be slow down and reduce the peak height. The nebulization efficiency also changes and
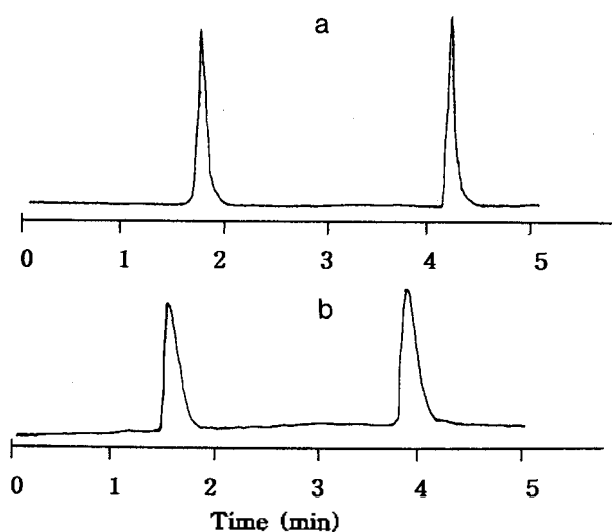

Figure 4. Comparison of peak shape of cadmium with different precipitant NaOH(a) and carbonate buffer(b). They are on the different scale. Peak height of NaOH is taller than buffer.

Table 2. Change of peak heights and peak areas with different precipitants

Precipitant	Peak Height (RSD %)	Peak Area (RSD %)	Relative Recovery
Ammonium buffer	34 mm (13)	150 mm² (4.2)	97.4%
Carbonate buffer	33 mm (12)	152 mm² (4.0)	98.7%
NaOH solution	40 mm (7.0)	154 mm² (8.8)	99.9%

ᵃ Average of five determinations concentration of cadmium; 0.30 ppm.

Table 3. Change of Peak Heights and Peak Areas with Different Dissolving Acids

Dissolving Acid	Peak Height mm (RSD %)	Peak Area mm² (RSD %)
0.5 M-HNO₃	32 (6.3)	3970 (5.0)
1.0 M-HNO₃	33 (8.7)	3925 (5.6)
0.5 M-H₂SO₄	33 (9.2)	3895 (6.4)
0.5 M-HCl	32 (8.9)	3950 (6.0)
HNO₃/H₂SO₄/HCl 1:1:1 mixture	34 (8.5)	3870 (5.4)

ᵃconcentration of cadmium; 0.30 ppm, precipitant; 0.05 M-carbonate buffer (pH=10.3).

the peak height is further reduced. Even if the flow remains constant, different particle shape and the degree of coagulation can affect the rate of dissolving. Nevertheless, peak area should remain the same unless there is a significant change in dissolving time.

Dissolving reagent. Hydroxide precipitates can be very easily dissolved in an acidic solution. In the previous study,[13] nitric acid was effective in dissolving indium hydroxide. In this research, nitric acid, sulfuric acid, hydrochlolic acid, and mixed acids were studied. As shown in Table 3, peak height and area were similar with each other. Nitric acid was chosen because it showed slightly better precision than others. Also it gives less interferences than other acids in ICP.

Reaction Time (Length of the reaction coil). The reaction time was controlled by the length of the reaction coil. If it is too short, colloidal particles are formed and wouldn't be collected at the filter. If precipitates are well matured, they will be collected well but it will take more time to dissolve. Thus the peak height will be decreased at a large reaction time (long reaction coil). In Figure 5, the relationship between reaction coil length and signal is shown. When the reaction coil length was longer than 2.0 m, or 50 seconds of reaction time, peak height began to decrease as explained above. However, peak area was increasing until 3.0 m and showed a slight decrease at 4.0 m. Total amount of precipitate collected can be increasing with the reaction time until the reaction is completed and colloidal particles gathered with each other.

Precision shows the best value at 2.0 m. For a short length, reaction was not completed and showed worse values as expected. However, RSD increased at a long reaction coil length also. When the coil was too long, peak gets broadened and the measurement of peak area could become less accurate. The nature of peak commands that a sharp one produces better precision in area measurement because of the uncertainty at the bottom of a peak.
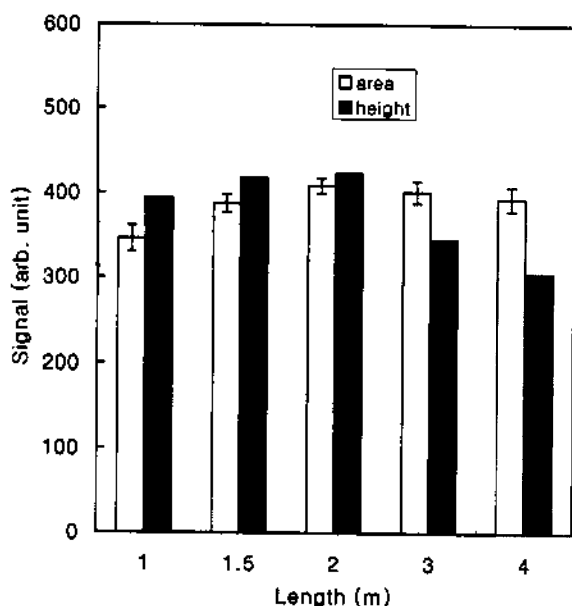
On-Line Precipitation of Cd by Hydroxide Precipitation

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Figure 5. Changes of signal and precision with the reaction time (reaction coil length).

Figure 6. Calibration curve of cadmium with on-line precipitation dissolution system.

Filter type. A stainless filter (0.45 μm) showed good rigidity and recovery rate (more than 98%). Membrane filters (0.45 μm) showed even better recovery rate (100%) probably because of the well regulated pore size. Precision was similar with each other. Paper filters showed worst recovery rate (less than 70%) and precision because of large pore size (10 μm). After several runs, a membrane filter showed a sharp decrease in precision due to deformation caused by the high pressure applied to it. Thus, it was necessary to replace a membrane filter after 5 runs. In previous study of sulfide precipitation, a stainless filter showed poor precision compared to a membrane. Unlike to sulfide precipitate, hydroxide precipitate showed similar performance and a stainless filter was chosen because of conveniency. In this experiment, a paper filter was placed before the stainless filter.

Calibration curve and analysis of real sample. Optimum conditions were determined for Cd and summarized in Table 4. Using this condition, a calibration curve was obtained and shown in Figure 6. From 0.03 ppm to 3.0 ppm, successive dilution was made from the 1,000 ppm stock solution. The slope was 156.76 and the intercept was − 5034 and r value was 0.9999. From 10 ppb and lower concentration, precision became significantly worse (20% or higher RSD) and was avoided in the Figure. For 3 ppm or higher concentrations, the curve began to show bending downward.

Table 4. Optimum Experimental Conditions Used in the Continuous Precipitation Dissolution Study

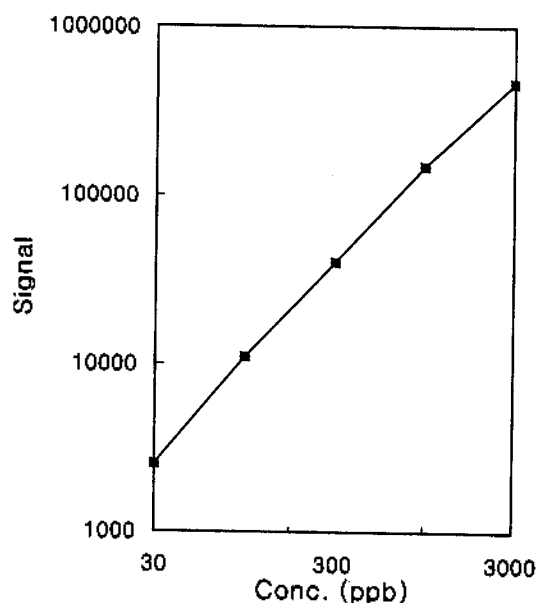| Precipitant	carbonate buffer (pH=10.3)
Filter	stainless steel+paper
Flow rate of cadmium solution	1.2 mL/min
Flow rate of precipitant	1.0 mL/min
Dissolving acid	0.5 M-HNO₃
Reaction coil length	2.0 m
Sample loading volume	1.0-20.0 mL

The enrichment factor can be increased by increasing sample volume. For 1.0 mL of sample loop, the enrichment factor was 4.5 times with the sample speed of 15/hr. The enrichment factor is defined as the ratio of peak area obtained with precipitation dissolution system to the one without precipitation based on the same peak width (Full width at Half Maximum). For 3.0 mL of sample loop, the signal area increased exactly 3 times to that of 1.0 mL and the enrichment factor increased 13.5 times with the speed of 5/hr. The area increased 20 times when 20 mL sample was used (2/hr). The enrichment factor calculated is 90 times. If speed is sacrificed, enrichment factor can be even further increased. In Figure 7, the excellent linear relationship between peak area with the sample volume concentrated is shown. Peak height shows some degree of linearity but is less accurate than peak area.

To examine the accuracy of this technique, a standard sample of NIST-SRM 1566 (Oyster tissue) was analyzed.
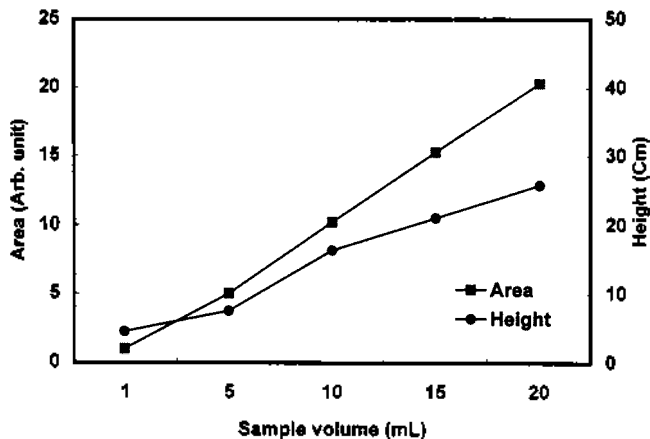

Figure 7. Relationship of peak area and peak height with the sample volume concentrated. 0.5 ppm Cd was used under the optimized condition.

Sample (1.00 gr) was dissolved and diluted to 100 mL. The final concentration of Cd in solution was adjusted to be 35 ppb. Standard addition method was used rather than the calibration method because it suffered less of matrix interferences and gave better accuracy.[13] The result obtained was 3.7±0.3 ppm which agreed well with the certified value of 3.5±0.4 ppm. To apply this technique to other elements comfortably, further studies on interferences and analytical performances should be done, which are under investigation in our laboratory.

In conclusion, it is demonstrated that on-line direct precipitation preconcentration using hydroxide as a precipitant is feasible to enhance the detection limit of Cd in atomic spectrometry. It is simple, fast, yet efficient for the preconcentration of trace elements and can be applied to other techniques than ICP as well. By selecting a proper precipitant, applications can be extended to specific elements as well as multi-elemental preconcentration.

References

1. Robards, K.; Worsfold, P. *Analyst* **1991**, *116*, 549.
2. Goenaga, I. H.; Fernandez Sanchez, M. L.; Sanz-Medel, A. *J. Anal. At. Spectrom.* **1996**, *11*, 571.
3. Sanz-Medel, A.: Valdes-Hevia, M. C.; Bordel, N., Fernandez, M. R. *Anal. Chem.* **1995**, *67*, 2216.
4. Olayinka, K. O.; Haswell, S. J.; Grzeskowiak, R. J. *J. Anal. At. Spectrom.* **1986**, *1*, 299.
5. Olayinka, K. O.; Haswell, S. J.; Grzeskowiak, R. J. *J. Anal. At. Spectrom.* **1989**, *4*, 171.
6. Hiraide, M.; Ito, T.; Baba, M.; Kawaguchi, H.; Mizuike, A. *Anal. Chem.* **1980**, *52*, 804.
7. Hudnic, V.; Gomiŝĉek, S.; Gorenc, B. *Analytica Chimica Acta* **1978**, *98*, 39.
8. Kim, Y. S.; Jung, Y. J.; Choi, H. S. *Bull. Korean Chem. Soc.* **1998**, *19*, 50.
9. Valcárcel, M.; Gallego, M. *Trends in Anal. Chem.* **1997**, *16*, 36.
10. Tyson, J. F.; Adeeyinwo, C. E.; Bysouth, S. R. *J. of Anal. At. Spectrom.* **1989**, *4*, 191
11. Welz, B.; Xu, Shukun; Sperling, M. *Applied Spectroscopy* **1991**, *45*, 1433.
12. Fang, Z.; Dong, L. *J. of Anal. At. Spectrom.* **1992**, *7*, 439.
13. Park, K. H.; Pak, Y.-N. *Bull. Korean Chem. Soc.* **1995**, *16*, 422.
14. Zhuang, Z.; Wang, X.; Yang, P.; Yang, C.; Huang, B. *J. of Anal. At. Spectrom.* **1994**, *9*, 779.
15. Martinez, P.; Gallego, M.; Valcárcel, M. *Analyst* **1987**, *112*, 1233.
16. Santelli, Ricardo E.; Gallego, M.; Valcárcel, M. *Anal. Chem.* **1989**, *61*, 1427.
17. Goenaga, I. H.; Fernandez Sanchez, M. L.; Sanz-Medel, A. *J. Anal. At. Spectrom.* **1997**, *12*, 1333.
18. Nielsen, S.; Sloth, Jens J.; Hansen Elo H. *Talanta* **1996**, *43*, 867.
19. Esmadi, Fatima T. *Microchemical Journal* **1996**, *54*, 154.
20. Cho, Y.; Pak, Y-N. *Anal Sci.* **1997**, *13*, 41.
21. Cho, Y.; Yeon, P. H.; Pak, Y-N. in submission to *Bull. Korean Chem. Soc.*

Synthesis and Structure Identification of ABCH Type Calix[4]arenes: Two Step Synthesis of Asymmetrically Substituted Calix[4]arenes from Monoalkylcalix[4]arenes

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Several ABCH type chiral calix[4]arenes were prepared from monoalkyl calix[4]arenes by treating with various acyl halide, followed by reacting with benzoyl chloride in pyridine. These asymmetrically substituted ABCH type calix[4]arenes are obtained as racemates mixture which are confirmed by the chiral shift reagent in ¹H NMR spectra. The molecular and crystal structure of 5-nitro-26-allyloxy-25-benzoyloxy-28-isobutyryloxy-27-hydroxycalix[4]arene **8a** has been determined by the X-ray diffraction method. Two independent enantiomeric molecules are crystallized in a 1:1 racemate mixture. They are in the partial cone conformation in which the benzoyloxy phenyl group is down. There is a bifurcated intramolecular hydrogen bonding involving three functional groups in each molecule.

Introduction

Calixarenes are cavity containing metacyclophanes which are currently utilized as a versatile host molecules.[1-3] One of

the most important aspect about host-guest chemistry is molecular recognition.[4,5] Like chiral cyclodextrines, calixarenes are expected to have similar chiral recognition ability because molecular structure of calixarenes could allow the