

## Semi-Automatic Hydride Generation and Atomic Absorption Determination of Bismuth with *in situ* Concentration in a Graphite Furnace

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A semi-automatic method for the determination of dissolved bismuth at parts per trillion levels is described. The method involves bismuthine generation, *in situ* collection of bismuthine in a graphite furnace, and atomic absorption detection. In order to facilitate semi-automation of bismuthine generation and separation from aqueous solution, *Gore-tex* microporous PTEE membrane is used. The absolute detection limit, taken as three times the standard deviation of the instrument noise is 2 pg. The precisions are 3.1% for 100 pg and 1.9% for 1 ng of bismuth, respectively. As many as 90 measurements can be made in an hour.

### Introduction

Hydride generation and subsequent atomic spectrometric detection method is now widely employed for trace metalloid analysis since it offers several merits. Among the merits are its simplicity, high sensitivity, and freedom from matrix interferences. Prior to their introduction to an atomizer, generating hydrides are often preconcentrated to lower detection limits. Cryogenic condensation,<sup>1-6</sup> trapping in balloon or glass container<sup>7,8</sup>, and collection in graphite furnace<sup>9-16</sup> are among the commonly used techniques for this purpose. The detection limits were further lowered by replacing conventional air-acetylene flame atomizer with more sensitive ones as argon entrained hydrogen diffusion flame, quartz cuvette atomizer, graphite furnace atomizer. Despite several inherent merits, hydride techniques are rather limitedly used for trace analysis.

One major drawback is their lengthy analysis time: it normally takes several minutes to complete a measurement. Furthermore, they often require many sample manipulations which are not only painstaking, but often make them vulnerable to contamination. To overcome this drawback, many automatic or semi-automatic hydride generators<sup>17-25</sup> have been introduced. However, automatic methods are usually less sensitive than manual primarily due to smaller volumes of sample uptake in automatic methods. Among the automatic methods, a recent one for bismuth by Yamamoto<sup>25</sup> appears to be most sensitive (0.06 ng Bi) to the authors' knowledge. However, even with this sensitive method, several types of environmental samples can not be analyzed directly.

In this paper a very sensitive and high throughput semi-automatic hydride generation and atomic absorption method for bismuth is described.

### Experimental

**Apparatus.** Bismuthine generation system for the pre-

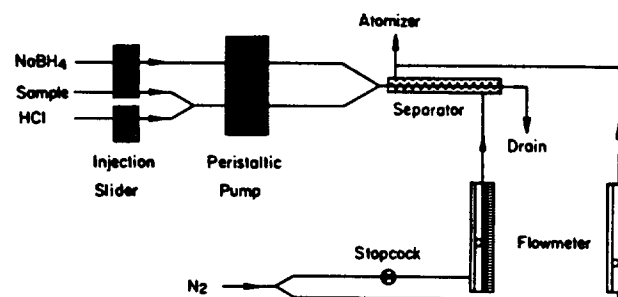


Figure 1. Flow injection manifold for HGAAS with a membrane gas/liquid separator.

sent study is comprised of a slide valve, a peristaltic pump (Bucher Instruments, USA), gas/liquid separator and two flow meters (Figure 1). In the slide valve silicon tubings for the sample and reagent solutions are pinched between a plexiglass plate and a moderately sharp steel blade. The steel blade switching is actuated by two electromagnetic solenoids of which time duration is controlled by a timer (Kun Hung Electric Co., Ltd., Korea).

The gas/liquid separator is constructed by inserting a *Gore-tex* microporous PTEE tubing (5 mm o.d., 4 mm i.d., porosity 70%, Bergohf/America Inc., USA) in a polyethylene tubing (8 mm i.d., 40 cm long). The membrane tubing is tightly connected to the reaction line from the peristaltic pump and to the drain line, respectively, with a sleeve of Teflon tape. The polyethylene tubing has two ports: one is used as an inlet of nitrogen carrier gas and the other as an outlet. Nitrogen gas carries bismuthine diffusing out of the membrane tubing to the carbon rod atomizer. The manifold has been designed to minimize the dead volumes. All components are connected with Teflon tubing (0.5 mm i.d.).

The apparatus for bismuthine collection and subsequent atomic absorption determination is the one utilized previously for bismuth by Lee<sup>9</sup>. Atomic absorption signal are

monitored on an atomic absorption spectrophotometer (Perkin-Elmer 1100 M) onto which the modified Varian-Techtron CRA-90 atomizer is mounted. Peak heights are recorded on a Perkin-Elmer Ex-800 printer. The operating parameters are: EDL Bi power output, 8 W; wavelength 223.1 nm; slit width, 0.2 nm; nitrogen carrier gas flow rate, 150 ml/min during bismuthine generation and 40 ml/min during atomization. The temperature settings of the carbon rod atomizer are: drying, 110°C for 90 sec; ashing, 400°C for 20 sec; atomizing, 1850°C for 2 sec with 800°C/sec ramping.

**Standards and Reagents.** All solutions are prepared with deionized and doubly distilled water. Bismuth stock standard [1000 mg/l Bi(NO<sub>3</sub>)<sub>3</sub>] is obtained from Junsei Chemical Co. Ltd., Japan. Working standards of lower concentrations are prepared by consecutive dilutions of the stock standard with 0.1 M HCl. High purity acids {HCl (6 M), HNO<sub>3</sub> and HOAc} are prepared by distilling reagent-grade acids in a TEFLON-still. 2% (m/v) NaBH<sub>4</sub> solution is made by dissolving reagent grade NaBH<sub>4</sub> (Alfa Chemical Co., USA) in 0.02 M NaOH and subsequently filtering it through 0.4 μm membrane filter.

**Procedure.** Prior to initial sample measurement, hydride generation system is purged with nitrogen for about one minute to remove air entrained in the system, and then rinsed with 0.1 M HCl solution for 20 seconds. By switching the slide valve to HCl stream and activating peristaltic pump, preset volumes of sample and NaBH<sub>4</sub> solutions are simultaneously introduced into the system. The hydride generated is separated from the reacted solution to the outer side of the microporous Teflon tubing by diffusing through its wall and swept to the carbon rod atomizer by the carrier gas. After 10 seconds the carrier gas flow is decreased by closing the stopcock of the main gas inlet, and then the program cycle of the atomizer is initiated. The system is rinsed with 0.1 M HCl for the next run.

**Environmental Samples.** Rain and snow samples were collected using a large laboratory-made Teflon funnel which was connected to a 500-ml Teflon bottle. The sample was acidified by adding 4 ml of purified HCl per liter of sample and then stored in polyethylene bottle until analysis.

Mussel samples were collected from July to October, 1988 along the Korean coastlines. The samples were depurated immediately after collection for 24 hr for the purpose of the complete excretion of gut contents. The samples depurated were put into polyethylene bags, frozen in dry ice and then transported to a shore-based laboratory for metal analysis. In the laboratory, the samples were thawed to room temperature, shucked with a polycarbonate knife and homogenized by a blender with polycarbonate blade to minimize contamination.

0.5 g of a freeze-dried bulk sample from 20 individuals was completely digested with 10 ml of conc. HNO<sub>3</sub> on a hot plate maintained at 120°C. The residue was redissolved in 10 ml of 1 M HNO<sub>3</sub> and stored in a cleaned polyethylene bottle for analysis.

Aerosol particles were collected on Whatman No. 41 filter papers using a high volume aerosol sampler (University of Rhode Island Model 400, USA) from October, 1988 to September, 1989 at a rocky coast of Taean Peninsula, Korea. The aerosol-loaded filter paper was cut into a 6×8 cm size with ceramic scissors and completely dissolved with a

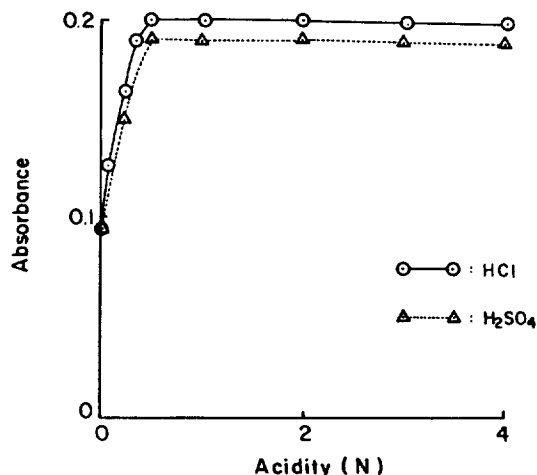


Figure 2. Effect of acid strength on bismuthine generation (0.2 ng of Bi).

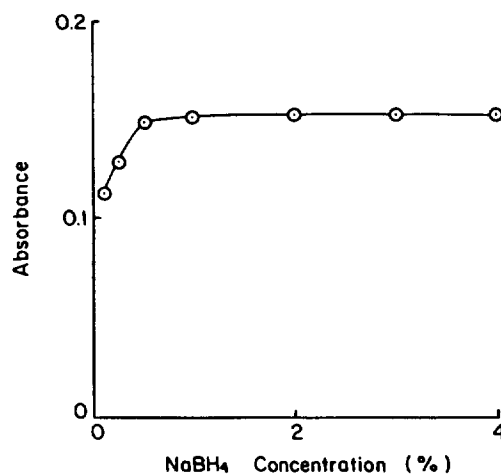


Figure 3. Effect of NaBH<sub>4</sub> concentration on bismuthine generation (0.2 ng of Bi).

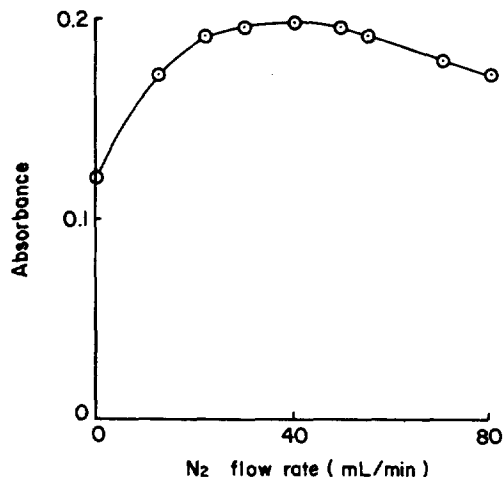
mixture of 4:2:1 of HNO<sub>3</sub>, HF, and HClO<sub>4</sub> in a high pressure Teflon bomb maintained at 170°C. The digested residue was redissolved in 25 ml of 1 M HNO<sub>3</sub>.

## Results and Discussion

### Optimization of Signal

**Reagent Concentration.** Figure 2 shows the dependency of the peak height from 0.2 ng of Bi(III) on the HCl and H<sub>2</sub>SO<sub>4</sub> concentrations. Signal increases sharply to 0.5 N and then remains constant to 4 N in both acids. These results are nearly consistent with the literature data<sup>26,27</sup>. It was also observed that when nitric acid was used, the same result as hydrochloric acid was obtained. Hydrochloric and nitric acid are preferred since they are somewhat more effective and easier to purify.

The effects of the concentration of NaBH<sub>4</sub> on the analytical response from 0.2 ng of bismuth are given in Figure 3. Absorbance remains constant when the concentration of NaBH<sub>4</sub> is higher than 0.5%. The optimum concentration of sodium borohydride was chosen 0.5% considering that dilute sodium borohydride can minimize the interferences from



**Figure 4.** Effect of sweeping gas flow rate on sensitivity (0.2 ppb Bi standards).

transition metals<sup>28</sup>.

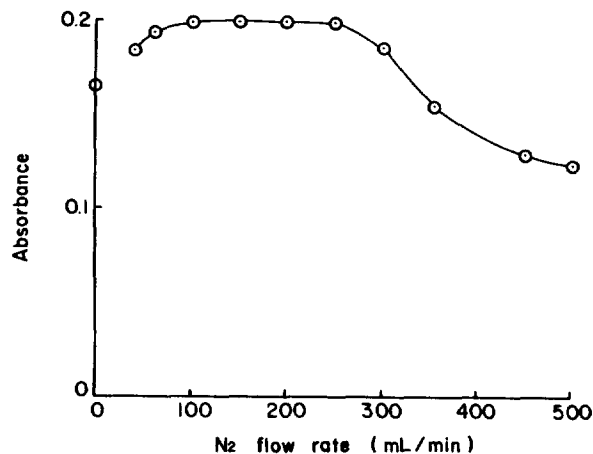
**Flow Rate of Carrier Gas.** A carrier gas stream is needed to sweep the hydride separated from the gas/liquid separator to the carbon rod atomizer. It was examined that atomic absorption sensitivity was affected by the sweeping gas flow using nitrogen gas.

The results are shown in Figure 4 in which a broad absorbance maximum appears in the range from 100 to 250 ml/min. The absence of the sweeping gas or its low flow rate below 100 ml/min resulted in poor precision and low sensitivity owing to the incomplete sweep of the hydride generated. When the flow rate was higher than 300 ml/min, it also gave rise to low sensitivity probably due to incomplete trapping of the hydride in the porous graphite disc. On the basis of these observations, the sweeping gas flow rate is chosen to be 150 ml/min for all subsequent experiments.

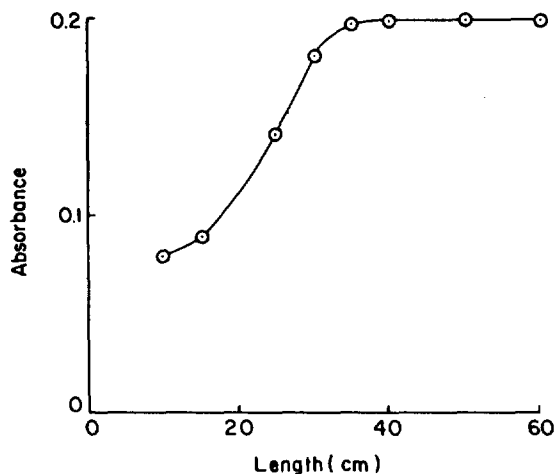
A carrier gas stream is also needed during atomization. The dependence of peak absorbance on the atomizing gas flow rate is shown in Figure 5 where 0.2 ng of bismuth in 1 ml of 0.5 M HCl is reacted with 0.5 ml of 0.5% NaBH<sub>4</sub>. There is a broad maximum in the range from 30 to 50 ml/min.

**Teflon Membrane Gas/Liquid Separator.** Gas/liquid separators with a microporous membrane have recently been examined. They include a separator with either a porous Teflon film or a porous Teflon tubing. The former was used for the determination of Hg and As by AAS.<sup>29,30</sup> The latter was used for the determination of Cl<sup>-</sup> or NH<sub>3</sub> by flow/colorimetry<sup>31</sup> or flow/fluorometry<sup>32</sup>. Compared to the membrane film separator, the membrane tubing separator provides a large surface area and therefore is suitable to separate a great amount of gas from the solution quantitatively and rapidly. In this study, the analytical performance of the membrane tubing separator as the gas/liquid separator for HGAAS is investigated.

To find the optimal length of the separator, the atomic absorption peak height of Bi standard of 0.2 ppb is measured by varying the length of the microporous Teflon tubing (4 mm i.d., 0.5 mm thick) from 10 to 60 cm (Figure 6). Increase in the length to about 35 cm greatly enhances the Bi ab-



**Figure 5.** Effect of atomizing gas flow rate on sensitivity (0.2 ppb Bi standard).



**Figure 6.** Effect of Teflon membrane (0.4 cm i.d.) length on sensitivity (0.2 ppb Bi standard).

sorption signal due to increase in the membrane surface area. It was observed that a smaller membrane in size (2 mm i.d., 0.4 mm thick), compared to a larger one at the same length, not only decreased in the absorbance but also sweated on the outer side of the membrane due to high back-pressure buildup in the line from the separator to the atomizer. Although the size effects of the membrane tubing remains to be further investigated, these observations indicate that the larger one can separate the gaseous hydride from the solution without a too high back-pressure quantitatively and rapidly. Thus, the larger Teflon membrane (0.4 cm i.d., 35 cm long) tubing is used in the subsequent experiments.

**Interferences.** Owing to the separation of the analyte element from the matrix constituents by volatilization in the form of the gaseous hydride, the HGAAS technique is free from spectral interferences caused by background absorption. Because of the very limited number of elements that can be volatilized by this technique, vapor-phase interferences are also very unlikely, except for mutual interferences of the hydride-forming elements<sup>33,34</sup>. It is well known, however, that a number of transition metals, mainly those of Group VIII and IB, can cause severe signal depressions in the

**Table 1.** Tolerable Limits of Co-existing Ions\*

Ion	Tolerable limit
As (III)	>50,000
Sb (III)	>50,000
Pb (II)	5,000
Te (IV)	1,000
Fe (III)	>50,000
Cu (II)	500
Co (II)	5,000
Cr (VI)	5,000

\*Tolerable limits correspond to the weight ratio of an interferent and bismuth which gives 10% negative error.

hydride generation technique, and bismuth is one of the elements that is most affected by these interferences.

The effect of interferents on the peak height in this research is assessed after a comparison of the peak with noninterferent reference neighboring peaks. In order to determine interference magnitude, we introduced the term tolerable limit corresponding to the weight ratio of an interferent and bismuth which gives 10% negative error. The tolerable limits of a various interferents are given in Table 1, which shows hydride forming element interferences as well as transition metal ones.

Among the interferents investigated in this study, copper shows the most severe interference as reported in the literature<sup>33</sup>. Various proposals have been made to reduce or eliminate transition metal interferences in the determination of hydride-forming elements, and the application of masking agents is one of them. According to the literatures<sup>35-39</sup> most of the compounds are Lewis bases which can behave as ligands. We examined the effects of various masking agents such as EDTA, thiourea, ascorbic acid, L-cystine, and L-cysteine with a view to eliminating the interfering effects of copper. Among them, L-cysteine, a first-trying masking agent to our knowledge, is the most effective in reducing interference from copper. 1% solution of L-cysteine in 4 M HCl can completely eliminate the interference from 5 ppm Cu in the determination of 0.2 ppb bismuth. Although its quantitative effects will be further investigated in the future, 1% L-cysteine solution in 4 M HCl is used only for the environmental samples encountered with any interelemental interferences.

#### Sensitivity and Detection Limit

The sensitivity of the method was about 3 pg/0.0044 Abs. of bismuth. When bismuth solution was injected directly into the graphite furnace and atomized at the same conditions, the sensitivity of 10 pg/0.0044 Abs. was obtained. The better sensitivity of the present method is probably due to higher volatility of elemental bismuth than its oxides.

The absolute detection limit, taken as three times the standard deviation of the instrument background noise, ranged from 1 to 3 pg depending on electrodeless discharge lamp intensity. This is equivalent to a concentration detection limit of 0.1 ng-0.3 ng/l for a 10 ml sample volume.

#### Precision, Accuracy and Linearity

The precision of the method was evaluated by replicate analyses of bismuth solutions containing 0.1 and 1 ng. The

**Table 2.** Results of Bismuth Analysis in USGS References Samples and Some Other Reported Values (ng/g)

Sample	This work	Reported values
W-1	0.048±0.003 (n=3)	0.046 <sup>40</sup>
G-2	0.042±0.003 (n=3)	0.035 <sup>41</sup> , 0.041 <sup>42</sup> , 0.042 <sup>9</sup>
BHVO-1	0.015±0.002 (n=4)	0.015 <sup>41,43</sup>
GSP-1	0.040±0.003 (n=4)	0.047 <sup>44</sup> , 0.032 <sup>41,45</sup> , 0.039 <sup>42</sup>

**Table 3.** Bismuth Concentrations in Rain and Snow

Sample type location	Sampling date	Concentration (pM)
Rain		
Seoul, Korea	Mar. 24, 1984	471
	May. 2, 1984	536
	Feb. 15, 1990	633
	Feb. 19, 1990	620
Cambridge, MA, USA	Feb. 24, 1984	21.3
	Feb. 28, 1984	19.8
Snow		
Youngju, Korea	Mar. 2, 1984	15.3
Seoul, Korea	Feb. 16, 1990	165

relative standard deviations of 10 replicate determinations were 3.1% for 0.1 ng and 1.9% for 1 ng of bismuth, respectively.

There are no certified standards for bismuth in aqueous solutions or natural waters, making the direct evaluation of accuracy impossible at this time. When known amounts of bismuth were spiked into seawater or river water and then analyzed, quantitative recoveries were obtained. Four United States Geological Survey (USGS) rock standards were totally digested with a mixture of HNO<sub>3</sub>-HClO<sub>4</sub>-HF acid and analyzed by the present method. The results are summarized in Table 2 along with the values reported by other workers. The results are in good agreement with the reported values, indicating the accuracy of the present method.

The calibration curve was linear in the range of 0.01-1 ng of bismuth ( $r=0.998$ ,  $n=5$ ), corresponding to a linear range of two orders of magnitude.

#### Application to Environmental Sample Analysis

**Rain and Snow.** Aliquots of the acidified rain and snow waters were used for the determination of bismuth at the optimum conditions previously stated. The blank values of bismuth in purified concentrated hydrochloric acid were found to be negligible. The results are summarized in Table 3. Bismuth concentrations in rain and snow waters in Seoul are significantly higher than in other areas reflecting high degree of air pollution in Seoul. Reportedly, bismuth is largely introduced into the atmosphere through anthropogenic processes<sup>46</sup>. Also, those in recent rain and snow waters are comparatively higher.

**Mussels.** Bismuth concentrations in the soft parts of

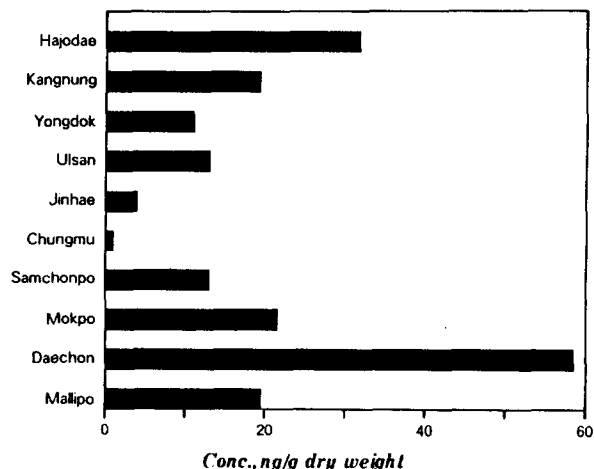


Figure 7. Bismuth concentrations in the soft parts of mussels collected along the Korean coastlines.

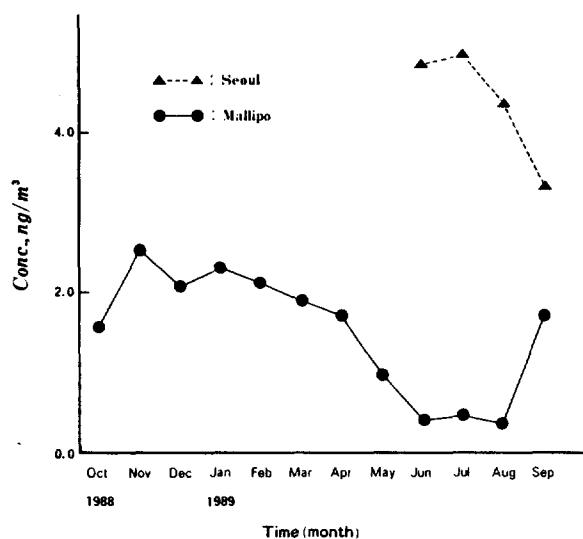


Figure 8. Temporal variation of bismuth concentrations in Seoul and Mallipo aerosols.

mussels along the Korean coastlines are shown in Figure 7. *M. Coruscus* mussel species are dominant in the East and West Coasts, while *M. edulis* species in the South Coast. Interestingly bismuth levels are much higher in *M. Coruscus* species than *M. edulis* species. It is not clear whether this comes from species difference or difference in bismuth levels in seawater.

**Aerosol Samples.** Aliquots of the solution of digested aerosol samples are used for the determination of bismuth at the optimum conditions. The blank values of bismuth in the acids used for digestion were found to be negligible. The matrix interferences were also found to be negligible using the standard additions technique.

Figure 8 shows the monthly variation of bismuth concentrations in aerosol samples from Mallipo and Seoul. Elevated levels in Seoul reflects more contamination of the area and lower values in summer are probably due to increased washout by rain.

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## The Salt Effect on The Nucleophilic Substitution Reaction

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The nucleophilic substitution reactions of *p*-substituted benzenesulfonyl chlorides with *p*-substituted anilines were carried out in 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol and 2-propanol mixtures. The salt effect was observed to be inhibited by the reaction of 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol with nucleophiles. To investigate the effectiveness of the salt for the nucleophilic substitution reaction the relative salt effect was determined. According to the comparison with the inhibitive salt effect and the substituent effects for the substrates and nucleophiles, the reactions were predicted to be controlled by the salt effect more than substituent effect in HFP-PrOH mixtures.

### Introduction

The factors underlying ionizing power and nucleophilicity of solvents involved in  $S_N2$  reactions have long held the interest of mechanistic chemists.<sup>1</sup> These solvent effects on nucleophilic substitution reactions have presented as linear free energy relationships (LFER) as a major tool studying.<sup>2</sup>

In the discussion thus far, an attempt has been made to understand nucleophilicity by use of relatively well understood model reactions,<sup>3</sup> or by use of reaction conditions that reduce the number of variables affecting nucleophilicity.<sup>4</sup>

However, it seems now clear that the failure of nucleophilic substitution reactions from the use of LFER in unsuitable solvent systems such as poly fluorinated alcohols as which are well known to have a highly ionizing power and very poor nucleophilic assistant properties.<sup>4</sup>

An anomalous behavior, mainly from Schleyer *et al.*<sup>5</sup> proved that solvolysis of primary and simple secondary substrates involved nucleophilic solvent assistance (*ks*). Moreover, the magnitude of *ks* is significant, even in the case of weakly nucleophilic media such as 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol (HFP).<sup>6</sup> Conductibility studies carried out on various electrolytes in HFP show that their solvating ability is strong towards anions and weak towards cations.<sup>7</sup>

In the study of the evaluation of the anomalous medium effect, McManus<sup>8</sup> *et al.* showed that the binary solvent mixtures of HFP and 1, 3-propane-dithiol (PDT) were nonlinear with solvent nucleophilicity dropping off at high HFP concentrations. Nevertheless, HFP-PDT mixtures were surprisingly, 3 to 4 orders of magnitude more nucleophilic than HFP-H<sub>2</sub>O mixtures although pure PDT is estimated to be only 2.5

orders of magnitude more nucleophilic than pure water.

To explain these observations, they suggest that, at high concentrations of electrophilic solvents, hydrogen bonding to the oxygen or sulfur atom in the more nucleophilic solvent molecules reduces the nucleophilicity of these solvents.

Nucleophilic substitution reaction of arenesulfonyl halides with anilines are thought to have important effects upon substrate reactivity in highly ionizing power solvents as HFP or its mixtures.

A much discussed question arising in the direct displacement process concerns the timing of bond formation and breakage, that is, whether the rate determining step corresponds to a transition state or intermediate in the reaction of arenesulfonyl halides with aniline or pyridines.<sup>9</sup> For the reactions of arenesulfonyl chlorides with pyridine bases, Rogne<sup>10</sup> concluded that the amines function reveals as nucleophilic catalysts. But King *et al.*<sup>11</sup> observed a different kind in the reaction of 1-alkenyl arylsulfonyl chloride with pyridine. In this case the nucleophilic attacks the vinyllogous carbon to form the cationic sulfene which on subsequent reaction gives either the betylate or the simple overall substitution product.

Until it has been studied thoroughly for the nucleophilic substitution reaction of arenesulfonyl chloride with various bases, any conclusion is unjustified. One of the most interesting challenges for us is the design of reaction patterns that are catalytically controlled through noncovalent interactions in the reaction of arenesulfonyl chloride with *p*-substituted anilines. Control in a catalytic system should be limited by the relative rates of the catalyzed reaction such as in highly ionizing power solvent as HFP, and the uncatalyzed