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16. FcPP was prepared from diethyl (*p*-aminophenyl)phosphonate (2.2 g, 10 mmole), ferrocenoyl chloride (2.5 g, 10 mmole) and dry triethylamine (1.5 mL, 10 mmole) dissolved in 20 mL of dry THF. The fine yellow powder (4.2 g, 98% yield) was identified as diethyl [4-(ferrocenecarboxamido)phenyl]phosphonate by ¹H NMR. After the diethyl group of this compound was replaced by bis(trimethylsilyl), the silyl ester (0.53 g, 1 mmole) was redissolved and refluxed in 70 mL of methanol. Finally the potassium salt of [4-(ferrocenecarboxamido)phenyl]phosphonic acid was precipitated by addition of methanolic KOH solution. The precipitate was washed by neat methanol, dried under vacuum and identified by proton nmr.

Effect of Hydrochloric Acid Concentrations on the Hydride Generation Efficiencies in ICP-AES

Dong Kee Lee* and Beom Suk Choi†

*Korea Testing and Research Institute
for Chemical Industry,
Seoul 150-038, Korea

†Department of Chemistry and
Institute of Basic Sciences,
Kyung Hee University,
Yongin 449-701, Korea

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The hydride generation (HG) technique has been used extensively as a means of efficient sample introduction to improve detection limit for hydride forming elements in inductively coupled plasma (ICP)-atomic emission spectrometry (AES). The method was first described by Thompson *et al.*,¹⁻⁴ who established the best compromise conditions for the generation of hydrides from hydrochloric acid and sodium borohydride solutions. On the other hand, sodium hyd-

roxide is always used to prevent decomposition of sodium borohydride solution.⁵

The solution of pH has a significant effect on the hydride generation process, and the optimum pH regions for all hydride forming elements have been reported.¹⁻⁴ However, those are almost exclusively experimental studies. A theoretical prediction of the effect of pH on hydride generation has not yet been studied.⁶⁻⁷ In the present study, we used a continuous HG-ICP-AES system and studied the molarity relationship between reactants: acid, sodium borohydride and sodium hydroxide.

Experimental

Instrument. All measurements were carried out with a Labtam model 8440 ICP spectrometer in conjunction with a Labtam model 8440 continuous hydride generator.⁸ The experimental conditions used are summarized in Table 1. The peristaltic pumps used are the Minipuls 2 (Gilson) for the acidic sample solution and KSC 1303-P2 (Manhattan) for the basic reductant solution. The experimental errors for the measurement of the flow rates ranged 5-8%.

Reagent. All reagents were of analytical grade or higher purity, and the deionized water from Milli Q system (Millipore) was used. 1000 ppm of standard stock solutions of As(V), Bi(V), Ge(IV), Sb(V), Sn(IV) were obtained from Junsei Chemical Co. Ltd., and the diluted solution were prepared with a fixed acid solutions (0.05~4.0 M) immediately before use. Sodium borohydride solution was prepared by dissolving the powder (Aldrich) in deionized water containing 0.1% or 2.5% NaOH. The solution was filtered to eliminate turbidity and it was stable for 1 day.

Results and Discussion

In order to investigate the relationship between the concentrations of reactants, a series of analyte solutions containing different concentrations of HCl (0.05~4.0 M) were prepared. The solutions were reacted with the three cases of reduction

Table 1. Specifications and operation conditions of ICP

RF generator	27.12 MHz
RF power	1.4 kW
Observation height	6 mm above RF coil
Spectrometer	Czerny Turner type, Vacuum 1800 grooves/mm 0.01 nm/mm (2nd order)
Slit width	0.02 mm
PMT voltage	1.0 kV
Gas flow rate	Carrier 0.8 L/min Coolant 13 L/min Auxiliary 0.4 L/min
Wavelength (nm)	As 193.696 Bi 223.061 Ge 209.425 Sb 217.581 Sn 189.989

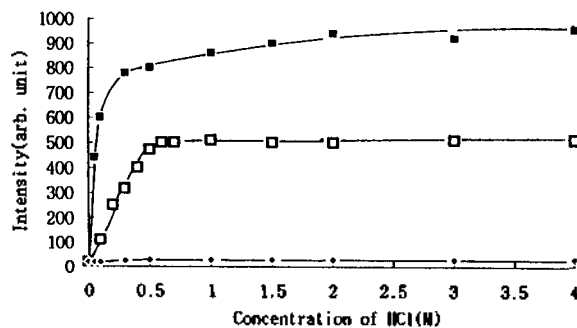


Figure 1. Effect of hydrochloric acid concentrations on the hydride efficiency of arsenic (■ 1 ppm, □ 0.5 ppm, ◆ blank). 2.5% NaBH_4 -0.1% NaOH (■), 2.5% NaBH_4 -2.5% NaOH (□).

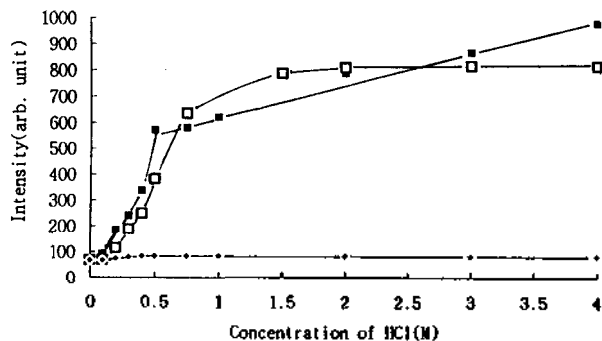


Figure 2. Effect of hydrochloric acid concentrations on the hydride efficiency of bismuth (1 ppm). Represents of the symbols are the same as those used in Figure 1.

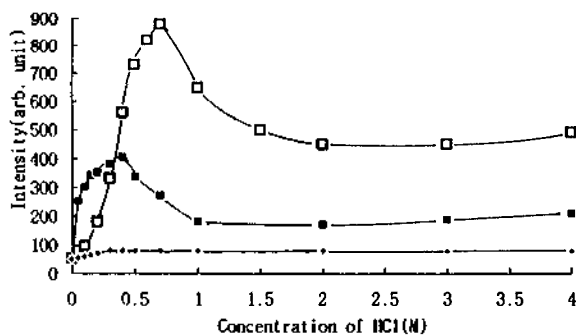


Figure 3. Effect of hydrochloric acid concentrations on the hydride efficiency of germanium (■ 0.25 ppm, □ 0.5 ppm). Represents of the symbols are the same as those used in Figure 1.

solution, 2.5% NaBH_4 -0.1% NaOH, 2.5% NaBH_4 -2.5% NaOH, and 1.0% NaBH_4 -2.5% NaOH.

The signals of arsine generated from first two reduction solutions are shown in Figure 1. At low acid concentrations, the hydride generation efficiency increases as the concentration of HCl increases and reaches maximum at about 0.3 M when 2.5% NaBH_4 -0.1% NaOH solution is employed. The maximum is increased to about 0.7 M when the concentration of reduction solution is 2.5% NaBH_4 -2.5% NaOH.

The hydride generation efficiencies of Bi, Ge, Sb and Sn by the first two reduction solutions are also shown in Figure 2~5. They show similar trends with that of the arsine except

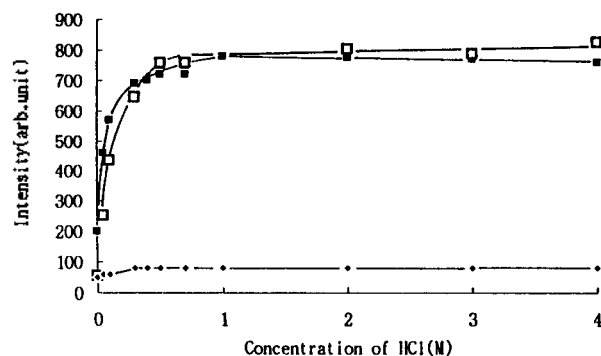


Figure 4. Effect of hydrochloric acid concentrations on the hydride efficiency of antimony (0.5 ppm). Represents of the symbols are the same as those used in Figure 1.

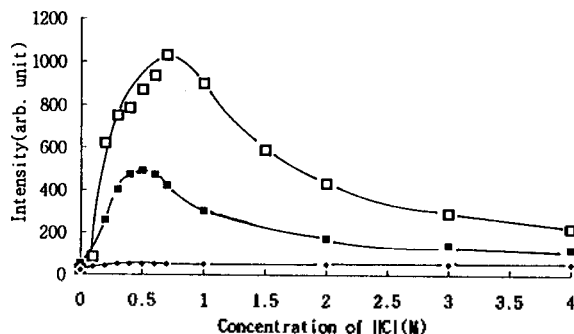


Figure 5. Effect of hydrochloric acid concentrations on the hydride efficiency of tin (■ 0.5 ppm, □ 1.0 ppm). Represents of the symbols are the same as those used in Figure 1.

that the hydride generation efficiencies of group IV elements (Ge, Sn) decrease at high concentrations of acid, and the behaviors are similar with that reported by Thompson *et al.*¹⁻⁴ Mostly, the maximum hydride generation efficiencies occur between 0.3~0.4 M HCl solution when 0.1% NaOH is used, and those are increased to 0.6~0.8 M when 2.5% NaOH is utilized. Thus, the concentration of NaOH in sodium borohydride solution seems to be important for the hydride generation process.

In order to investigate the molarity relationship between HCl in analyte and NaOH in reductant solution, the increased millimoles of the two reagents are compared. The experimentally observed flow rates of the acidic analyte and basic reductant solutions are 1.6 and 1.0 mL/min, respectively. Since the HCl concentration to reach the maximum efficiency for As is increased from 0.3 M (for 0.1% NaOH) to 0.7 M (for 2.5% NaOH), the difference of the millimole for HCl is roughly 0.64 mmol/min [$0.4 \text{ mol/L} \times 1.6 \text{ mL/min}$]. On the other hand, the difference of the millimole for NaOH is 0.6 mmol/min [$0.6 \text{ mol/L} (=2.4\%) \times 1.0 \text{ mL/min}$]. The two values are roughly identical considering the error from measuring the flow rates of the solutions. The differences of the HCl concentration to reach the maximum efficiencies for the other four elements are also ranged between 0.3~0.4 M, which are roughly the same as arsenic. Therefore, in all cases the following molarity relationship between the two reactants may be observed.

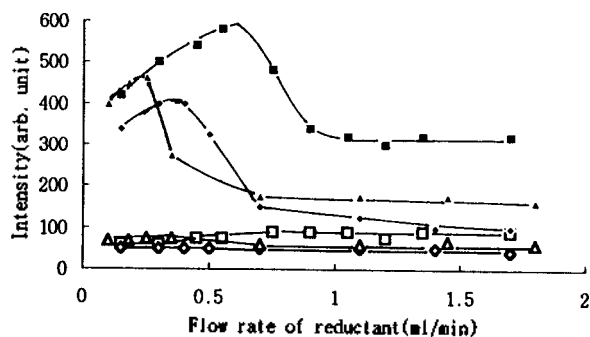


Figure 6. Effect of flow rate of the reduction solution on the hydride efficiency of arsenic. The concentration and flow rate of HCl solution are 0.5 M and 0.8 mL/min. 2.5% NaBH₄-2.5% NaOH (▲), 2.5% NaBH₄-0.1% NaOH (■), 1.0% NaBH₄-2.5% NaOH (◆). Open symbols are the background signals.

Table 2. The comparison of amounts of the reagents at the turnover points for generation of arsene

No	Reductant Solution			Acid Solution	
	NaBH ₄ (M)	NaOH (M)	flow rate (mL/min)	total amounts (mmol/min)	amount (mmol/min)
1	0.66	0.625	0.24	0.31	0.40
2	0.66	0.025	0.58	0.40	0.40
3	0.264	0.625	0.36	0.32	0.40

No. 1: 2.5%(0.66 M) NaBH₄+2.5%(0.625 M) NaOH; No. 2: 2.5% NaBH₄+0.1%(0.025 M) NaOH; No. 3: 1.0%(0.264 M) NaBH₄+2.5% NaOH. Flow rate of acidic (0.5 M HCl) arsenic solution is 0.8 mL/min.

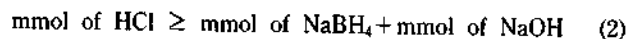
increased mmol of HCl \approx increased mmol of NaOH (1)

It has been reported that NaOH is used as a stabilizing agent for sodium borohydride solution and the amount of NaOH added depends on workers' preference.⁵ However, present work shows that concentration of NaOH is important and the amount of NaOH in the reductant solution should be carefully controlled.

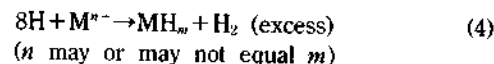
Maximum hydride generation efficiency of arsenic is retained at high concentrations of HCl as shown in Figure 1. Thus, there should be a turnover point at which maximum hydride generation occurs, when an acidic arsenic solution is reacted with basic reductants with increasing flow rates. The three turnover points of the arsine obtained from the reaction of fixed amount of acid (0.5 M \times 0.8 mL/min) with three different reductants are shown in Figure 6. The turnover point obtained from the reduction solution of 2.5% NaBH₄-2.5% NaOH is observed approximately at 0.24 mL/min, and

the points are increased to about 0.58 and 0.36 mL/min when the concentrations of reductant solutions are 2.5% NaBH₄-0.1% NaOH and 1.0% NaBH₄-2.5% NaOH. The millimoles of acid are also dependent on NaBH₄ concentration. At the same NaOH concentration (2.5%), the higher concentration of NaBH₄ required lower flowrate of the reductant solution.

Table 2 shows the comparison of the calculated amounts of acid and reductants at three turnover points. In all cases, the millimoles of acids are roughly same or slightly larger than that of reductants (Eq. 2).



The present work can make two conclusions. The amount of NaOH in the reductant solution is important and the neutralization of NaOH by HCl is preferential reaction for hydride generation. And the maximum hydride generation efficiencies of the hydride forming elements can be achieved when the millimoles of acid begin to exceed the sum of the millimoles of NaBH₄ and NaOH. But, the reason why the hydride generation efficiencies of the group IV elements (Ge, Sn) are suppressed at highly acidic solutions should be further studied. Eq. (2) partially supports the hydride generation mechanism that the hydride is generated by the reaction of element (Mⁿ⁺) with nascent hydrogen, produced by the 1 to 1 reaction of acid and sodium borohydride.



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