

### Chromatographic Application of Microcolumns Made of Glass-Lined Stainless Steel Tubing III: Preparation of a 0.3 mm I.D. Column

Won Jo Cheong\* and Hyun Joo An

Department of Chemistry, Inha University,  
Incheon 402-751, Korea

Received January 5, 1996

Microcolumn liquid chromatography was launched by a few leading research groups<sup>1-7</sup> in late seventies, and has been continuously improved and elaborated in techniques and designs.<sup>8-20</sup> Therefore, high pressure injectors with a very small internal sample loop, detectors with a flow cell of very low volume, reliable micro-flow pumps, and appropriate fittings are now commercially available. Packed silica microcolumns (320  $\mu\text{m}$  I.D., 3-5  $\mu\text{m}$  stationary phase particles) are also commercially available. On the other hand, packed stainless steel microcolumns with I.D. less than 1 mm are not yet commercially available. The inner surface of tubing should be mirror-like to secure good packing especially for microcolumns. Packed silica capillary microcolumns are fragile even though they show good column performance. We have reported<sup>21,22</sup> preparation of 0.5 mm I.D. packed microcolumns made of glass-lined stainless steel tubing and showed that performance of glass-lined columns is better than that of plain stainless steel columns.

In this study, we prepared a 0.3 mm I.D. microcolumn using glass-lined stainless steel tubing and examined its performance. Stainless steel columns of 0.3 mm I.D. have not been reported in the literature so far. Such a small column is expected to be useful in LC/MS applications.

### Experimental

We constructed the micro-LC system by combining the appropriate components which match with the microcolumn we prepared. We used a Shimadzu (Tokyo, Japan) 10AD pump to give low flow rates (0.001-0.02 mL/min.). A Rheodyne (Cotati, USA) 7520 injector with a 0.5  $\mu\text{L}$  internal loop, and an Isco (Lincoln, USA) CV4 capillary window detector were used to minimize the extracolumn void volume. A YoungLin (Seoul, Korea) D520B computing integrator was used to produce chromatograms at 254 nm.

Methanol and water were of HPLC grade and purchased from Fisher (Pittsburg, USA) and used without further purification. *p*-Nitroaniline and propylbenzene were of reagent grade, obtained from Aldrich (Milwaukee, USA), and used as received. *N,N*-dimethyl-*o*-nitro-*p*-toluidine was synthesized in our laboratory.<sup>23</sup> Glass-lined stainless steel tubing and Adsorbosphere C18 (5  $\mu\text{m}$ ) packing material were purchased from Alltech (Deerfield, USA).

We used special techniques in preparing and installing microcolumns to minimize the extracolumn void volume since its diameter is only 0.3 mm (30 cm length) and the total mobile phase volume in the column is only 21.2  $\mu\text{L}$  assuming that the overall column porosity is 0.60. Thus, a smooth and volumeless connection of the column between

the injector and the detector is essential. First, we connected the column directly to the injector without using any connecting tubing or frit. Second, we combined a fritted silica capillary directly to the column exit with a union. We prepared the fritted silica capillary by tapping the capillary tip over silica particles (5  $\mu\text{m}$ ) on a flat surface to put a tiny amount of silica particles inside the capillary tip and by treating the tip instantly with a propane burner flame to cause sintering of the silica particles. We burned the polymer coating of the capillary 15 cm downstream from the fritted tip to produce a transparent optical window, then introduced the capillary into the UV detector cell block until the optical window reached the appropriate position. The capillary I.D. is 50  $\mu\text{m}$ . The inner capillary volume between the column exit to the optical window is only 0.3  $\mu\text{L}$ .

We used 5  $\mu\text{m}$  Adsorbosphere C18 particles as the packing material. We dried the stationary phase at 90  $^{\circ}\text{C}$  at least for 4hrs, prepared its slurry by mixing 50 mg particles with 10 mL methanol, and sonicated it for 20 min before packing. The precut tubing combined with the sintered frit capillary through a union was connected to the slurry reservoir, and the pressure of the Alltech (Deerfield, USA) slurry packer, raised to 8,000 psi instantly, and to 10,000 psi within 2-3 min, and the final pressure was maintained for 5-10 min. The reservoir and the column were vibrated during packing with a mechanical vibrator.

We chose *p*-nitroaniline, *N,N*-dimethyl-*o*-nitro-*p*-toluidine, and propylbenzene as the test solutes considering their polarity range and retention times, and prepared methanol solutions to examine the performance of the column we prepared. The eluent was 90/10 (vol%) methanol/water. We varied the eluent flow rate within 0.001-0.02 mL/min. The retention time ( $t_r$ ) and peak width at half-height ( $w_{1/2}$ ) of each solute were measured to compute the number ( $N$ ) and height equivalent ( $H$ ) of theoretical plates.

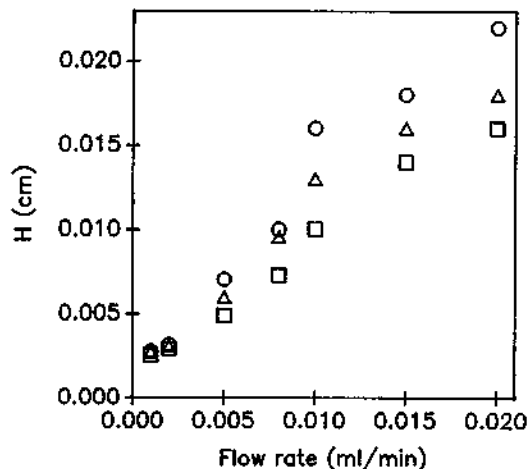
### Results and Discussion

We assembled the values of number of theoretical plates of three solutes for each flow rate in Table 1. We also plotted  $H$  vs. flow rate (Van Deemter plot) in Figure 1.  $H$  decreases monotonically as the flow rate decreases and hits the lowest value at the minimum flow rate. The numbers of theoretical

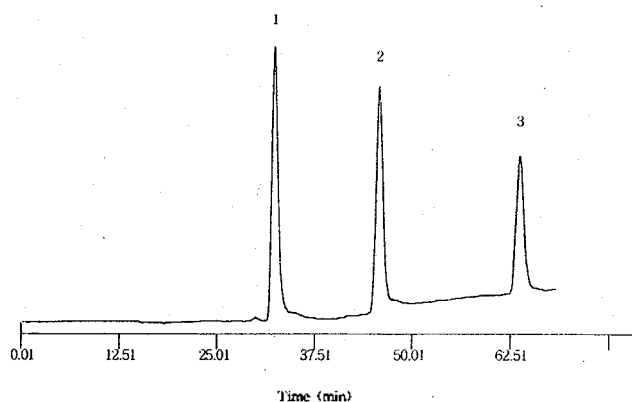
**Table 1.** Theoretical plate numbers of three test solutes measured on the glass-lined stainless steel packed microcolumn of 0.3 mm I.D. at various flow rates

Flow rates <sup>a</sup> (mL/min)	Plate numbers ( $\pm$ s.d.)		
	<i>p</i> -nitroaniline	DNT <sup>b</sup>	propylbenzene
0.001	10820 $\pm$ 325	11050 $\pm$ 442	11910 $\pm$ 357
0.002	9465 $\pm$ 130	9845 $\pm$ 197	10320 $\pm$ 309
0.005	4252 $\pm$ 412	5025 $\pm$ 302	6160 $\pm$ 308
0.008	2960 $\pm$ 154	3135 $\pm$ 188	4111 $\pm$ 285
0.01	1897 $\pm$ 19	2355 $\pm$ 24	2873 $\pm$ 57
0.015	1638 $\pm$ 33	1832 $\pm$ 37	2161 $\pm$ 24
0.02	1357 $\pm$ 27	1669 $\pm$ 17	1904 $\pm$ 57

<sup>a</sup>90/10(vol%) Methanol/water was used as the eluent. <sup>b</sup>*N,N*-dimethyl-*o*-nitro-*p*-toluidine.



**Figure 1.** Plot of HETP vs. flow rate of the eluent. ○ = *p*-nitroaniline, △ = *N,N*-dimethyl-*o*-nitro-*p*-toluidine, □ = propylbenzene.



**Figure 2.** Chromatogram of the test solutes eluted in 90/10 (vol%) methanol/water at 0.001 mL/min, and measured at 254 nm. 1 = *p*-nitroaniline, 2 = *N,N*-dimethyl-*o*-nitro-*p*-toluidine, 3 = propylbenzene.

plates are over 10,000 at the lowest flow rate. Such values are good enough for routine analyses of real samples. The chromatogram at 0.001 mL/min is, as an example, shown in Figure 2. We can expect even higher column efficiencies at flow rates less than 0.001 mL/min considering the variation trends of column efficiency with the eluent flow rate. That is promising since our ultimate goal of development of microcolumns is to construct a useful LC/MS system, and the lower the flow rate is, the more beneficial it is to maintenance of the LC/MS system.

The monotonous increasing trend of column efficiency with decreasing flow rate seems to be due to thorough elimination of extracolumn void volume. Band broadening by extracolumn void volume is greater for lower flow rates. As we mentioned before, we connected the column inlet directly to the injector without any frit, and the column outlet, to the silica capillary with a sintered frit. The volume of the silica capillary from the column exit to the optical window of the detector is only 0.3  $\mu$ L. The actual sample volume injected was less than 0.15  $\mu$ L even though the sample loop size is 0.5  $\mu$ L since we employed the "partial injection tech-

nique" by adjusting the injection time properly depending upon flow rates. Thus we successfully limited the extracolumn void volume less than 0.5  $\mu$ L in all.

When we use the microcolumn for a LC/MS system, we could use a silica capillary of a much smaller I.D. and improve the column efficiency by further reducing the extracolumn void volume. Employing a commercial sample injector with a tiny internal sample loop (0.06  $\mu$ L) will be helpful, too. We would expect 20,000 or so as a number of theoretical plates if we could further improve column packing technique in addition to the above modifications, which is subject to future studies.

## Conclusion

We have packed a useful glass-lined stainless steel microcolumn of 0.3 mm I.D. and 30 cm length. With the aids of a silica capillary as an optical window and a sintered silica frit inside the capillary at the end of the column, we obtained numbers of theoretical plates over 10,000 for the test solutes at the lowest mobile phase flow rate of the pump used in this study. We expect an even better column efficiency if a flow rate less than 0.001 mL/min could be used according to the trend of the Van Deemter plot. Such results encourage us to employ the rigid glass-lined stainless steel microcolumn in LC/MS applications, the ultimate goal of this study.

**Acknowledgment.** This work was supported by the Korea Science and Engineering Foundation (1995 Funds: 951-0304-033-1).

## References

1. Scott, R. P. W.; Kucera, P. J. *J. Chromatogr.* **1976**, *125*, 251.
2. Scott, R. P. W.; Kucera, P. J. *J. Chromatogr.* **1978**, *169*, 51.
3. Tsuda, T.; Novotny, M. *Anal. Chem.* **1978**, *50*, 271.
4. Tsuda, T.; Novotny, M. *Anal. Chem.* **1978**, *50*, 632.
5. Ishii, D.; Asai, K.; Hibi, K.; Jonokuchi, T.; Nagaya, M. *J. Chromatogr.* **1977**, *144*, 157.
6. Tsuda, T.; Hibi, K.; Nakanishi, T.; Takeuchi, T.; Ishii, D. *J. Chromatogr.* **1978**, *158*, 227.
7. Ishii, D.; Tsuda, T.; Takeuchi, T. *J. Chromatogr.* **1979**, *185*, 73.
8. Kucera, P. *Microcolumn High Performance Liquid Chromatography*, Ed.; Elsevier: Amsterdam, 1984.
9. Novotny, M.; Ishii, D. *Microcolumn Separations*, Eds.; Elsevier: Amsterdam, 1985.
10. Scott, R. P. W. *Small Bore Liquid Chromatography Columns*, Ed.; Wiley-Interscience: New York, 1984.
11. Novotny, M. *Anal. Chem.* **1988**, *60*, 500A.
12. Harvey, M. C.; Sterns, S. D. *J. Chromatogr.* **1983**, *21*, 473.
13. Borra, C.; Han, S. M.; Novotny, M. *J. Chromatogr.* **1987**, *385*, 75.
14. Novotny, M.; Alasabdro, M.; Konishi, M. *Anal. Chem.* **1983**, *55*, 2375.
15. Kennedy, R. T.; Jorgenson, J. W. *Anal. Chem.* **1989**, *61*, 1128.
16. Grescentini, G.; Bruner, F.; Mangani, P.; Yafeng, G. *Anal.*

*Chem.* **1988**, *60*, 1659.

17. Karlsson, K. E.; Novotny, M. *Anal. Chem.* **1988**, *60*, 1662.
18. Bauer, H. *Chromatographia* **1989**, *28*, 289.
19. Banks, J. F.; Novotny, M. *J. Microcolumn Sep.* **1990**, *2*, 84.
20. Berry, V.; Van Rossum, P.; Pretorius, V. J. *Liq. Chromatogr.* **1990**, *13*, 391.
21. Cheong, W. J.; Cha, K. W.; Choi, J. D. *J. Korean Chem. Soc. (Korean)* **1995**, *39*, 471.
22. An, H. J.; Cheong, W. J. *J. Korean Chem. Soc. (Korean)* **1995**, *39*, 863.
23. Cheong, W. J.; Chun, S. H.; Lee, G. Y. *J. Liq. Chrom. & Rel. Technol.* **1996**, *19*, 277.

### The Catalytic Reactions of CO and H<sub>2</sub>O over New Amorphous Ternary Metal Chalcogens

Sung Han Lee\*, Jin Seung Jung\*<sup>†</sup>, Da Woon Jung,  
Seog Gu Kang<sup>†</sup>, and Hyun Hak Kim<sup>†</sup>

*Department of Chemistry, Yonsei University,  
Wonju 220-710, Korea*

<sup>†</sup>*Department of Chemistry, Kangnung National University,  
Kangnung 210-320, Korea*

*Received January 23, 1996*

The water gas shift reaction, the reaction of water vapor and carbon monoxide to produce carbon dioxide and hydrogen, has been studied by many investigators for the past several years because of its industrial importance. The water gas shift reaction can be used to increase the hydrogen content of synthesis gas with various H<sub>2</sub>/CO ratios appropriate to the production of methane, methanol, higher hydrocarbons or alcohols,<sup>1,2</sup> which is believed to be the most important use of the reaction. Metal oxide systems such as Cr<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, CoO/Al<sub>2</sub>O<sub>3</sub>, and MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> are known as good catalysts for the reaction. The purpose of this work is to proceed with studies of synthesis, physical characterization, and catalytic activities of novel ternary metal chalcogens prepared by using the Zintl phase as a precursor. As reported in the previous papers,<sup>3,4</sup> ternary metal chalcogens prepared from a simple metathesis reaction between a Zintl phase materials and a divalent transition metal halide have an amorphous structure because of the rapid precipitation of the intermetallic products. No results have been reported for the catalytic activity of Zintl phase compounds so far. In this work, we prepared three amorphous ternary metal chalcogens such as Ni<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, Cr<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, and Mn<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub>, and examined their catalytic activities for the water gas shift reaction in a single-pass flow reactor, in which appreciable catalytic activities of the amorphous chalcogens were observed. This paper reports on the catalytic activity of amorphous ternary metal chalcogens for the first time.

### Experimental

Preparation and sample manipulations were performed under an argon-filled glovebox containing less than 1 ppm of oxygen. The ternary Zintl material K<sub>3</sub>SbTe<sub>3</sub> was prepared as described previously.<sup>5,6</sup> M<sub>3</sub>(SbTe<sub>3</sub>)<sub>2</sub> (M=Ni, Cr, Mn) compounds were prepared by the reaction of an aqueous solution of K<sub>3</sub>SbTe<sub>3</sub> and MCl<sub>2</sub>. A stoichiometric quantity of K<sub>3</sub>SbTe<sub>3</sub> solution (50 mL, 0.03 M) was added slowly while stirring the metal chloride solution (20 mL, 0.05 M). A precipitate was immediately formed, which was then separated by solution filtration, washed with deionized water and acetone, and dried overnight under vacuum. To investigate the electrical properties of the compounds, the electrical conductivity was measured on pressed pellets over the temperature range 30-300 K using a van der Pauw four-probe method.<sup>7</sup> The current was supplied by a Keithley model 224 programmable current source and voltage drop across the sample was measured using a Keithley model 181 digital nanovoltmeter. Catalytic activity of the specimens was tested in a conventional single-pass flow reactor operated at atmospheric pressure. The reactor was made of alumina tubing with 1.2 cm o.d. and 30 cm length. The catalyst was held in the middle of the reactor and the section beyond the catalyst bed in the reactor was filled with alumina beads to reduce the free space. The purity of carbon monoxide was greater than 99.99 % and water vapor was produced from deionized water pumped into the reactor by a Union syringe injection pump; the lines from the exit of the syringe up to the inlet of the reactor were heated at 200 °C. The range of reaction temperature explored was 600-800 °C and the major products were CO<sub>2</sub>, H<sub>2</sub>, and O<sub>2</sub>. Blank runs were performed over inert alumina beads in the absence of catalyst and approximately 2% conversion of CO to CO<sub>2</sub> was obtained in the reaction temperature range. Gas analyses were performed by on-line gas chromatography using a thermal conductivity detector and a mass spectrometer detector, and gas compositions were calculated using external standard mixtures prepared by KSRI. A cold trap was placed at the reactor exit to remove water vapor from the gaseous mixture. Following conditions were used to compare the activity of the catalysts: atmospheric pressure, a 0.3 g sample loading of catalyst, P<sub>CO</sub>=0.19 atm, P<sub>H<sub>2</sub>O</sub>=0.81 atm, a feed flow rate at ambient conditions of 23.2 mL/min. The conversion of carbon monoxide to carbon dioxide was typically compared after 3 hrs time-on-stream. No appreciable decrease in catalytic activity were observed over extended period of 48 hrs. The details of equipments are described in the previous paper.<sup>8</sup>

### Results and Discussion

It has been known that amorphous materials are often vastly different from those of their crystalline counterparts in the physical properties and find use in a variety of applications such as ionic conductor, photosensor, electronic switching material, and catalyst.<sup>9</sup> Most amorphous solids are prepared by rapid thermal quenching, pyrolytic, or sputtering techniques. Also, chemical methods involving rapid precipitation produce noncrystalline solids in certain types of mate-