

Exhaled Breath Analysis for Body Burden Estimates of Aromatic Volatile Organic Compounds

Wan-Kuen Jo, Ki-Bum Song, and Chang-Mo Nam*

Department of Environmental Engineering, Kyungpook National University, Taegu, Korea
**Environmental Research Group, Korea Electric Power Research Institute(KEPRI) 103-16, Munji, Yusong, Taejon, Korea*

(Manuscript received on October 29, 1999)

The present study evaluated the body burden of aromatic VOCs in roadside and underground storekeepers. The Method Detection Limit(MDL) of the analytical system ranged from 0.2 to $0.4\mu\text{g}/\text{m}^3$ for the target VOCs. The recovery of the sampling system for the compounds was above 80%. For all the target compounds, the breath concentrations of the smokers were similar to or slightly higher than those of the nonsmokers for both the roadside and underground storekeepers. For Ethylbenzene, p-Xylene, and o-Xylene, the breath concentrations of the underground storekeepers were somewhat higher than those of the roadside storekeepers. In contrast, the breath m-xylene concentration of underground storekeepers was similar to that of roadside storekeepers. For both the roadside and underground storekeepers, the breath concentrations prior to and after work were not significantly different.

Key words : breath, Ethylbenzene, roadside and underground storekeepers, o,m,p-Xylene

1. Introduction

Breath analysis has often been used as way to determine the body burden of volatile organic compounds(VOCs) and it has proved to be a feasible, cost-effective, non-intrusive, and highly sensitive method¹⁻³⁾. Some previous research groups⁴⁻⁶⁾ have used breath analysis to determine the body burden from occupational exposure to VOCs and have found a correlation between the breath concentration of workers and the inhalation exposure(or body burden) at ppm levels. The Total Exposure Assessment Methodology(TEAM) study identified a general association between breath concentrations of various VOCs and personal activities related to environmental exposure.¹⁻³⁾ The basic principle underlying exhaled breath monitoring is that VOCs in exhaled breath are indicative of the body burden of these chemicals. This is based upon the gaseous equilibrium that exists between alveolar air and pulmonary capillary blood.⁷⁻⁸⁾ Blood only takes about 1 second to pass through the pulmonary capillaries, plus the

diffusion of respiratory gases between the alveolar and pulmonary blood is completed within 0.3 seconds.⁹⁾ Accordingly, the equilibration of VOCs between alveolar air and blood is almost instantaneous. This fact allows the results of a breath analysis, as related with the total dose in the human body, to be used as an estimate of the body burden.

In the TEAM study, breath samples were collected from subjects using a non-rebreathing two-way valve attached to a Tedlar sampling bag, with purified, humidified air being supplied from an inhalation bag. The mixed exhaled breath in the collection bag was transferred to a 5/8 in. I.D. Tenax packed trap. However, such a method is cumbersome because the device is laboratory-based and not portable. The method is also limited by a collection/recycle time of 15 to 20 minutes. As a result, this method can not be reliably employed for studying the decay of VOCs in breath, since the initial portion of decay is very rapid and the long sampling time of the device does not facilitate the separate collection of initial breath samples after exposure. Accordingly, the present study

the separate collection of initial breath samples after exposure. Accordingly, the present study constructed a portable breath-sampling system to collect mainly alveolar breath and then evaluated the body burden of aromatic VOCs in persons supposedly exposed to elevated VOC levels. The new portable breath sampling system only took 2 minutes at most to collect the alveolar samples.

2. Methods

2.1. Subjects

Two groups (smokers and nonsmokers) of five volunteers each were solicited from two occupations: underground shop keepers and roadside shop keepers. The roadside storekeepers were chosen only if their stores were located near a main street with heavy traffic. The underground storekeepers were selected only if their stores were located near an entrance/exit of the underground facility. The subjects were classified into two groups (smokers and nonsmokers) since smoking is another possible source for exposure to the target compounds. All the subjects who participated in this study were apparently healthy.

2.2. Sampling System

A portable breath sampling system was used to collect primarily alveolar air. The subject breathed through a new mouthpiece into a non-rebreathing two-way valve (Laerdal Medical Co.). This valve directed clean air for inhalation by the subject and then directed the exhaled breath into a temporary storage Teflon tube (1.3 cm i.d. x 760 cm). The clean air for inhalation was provided via the filtration of ambient air through charcoal purifiers. The exhaled breath was continually withdrawn onto a Tenax trap (0.64 cm-o.d. and 18 cm-length) to collect the target VOCs (Ethylbenzene, o-Xylene, m-Xylene, p-Xylene) using a personal sampling pump (A.P. Buck Inc. Model I. H). The nominal sample flow rate was 1 l/min and the sampling duration was 2 minutes. The sampling pump was calibrated by a digital flow meter prior to and following the collection of each sample. The average of these two rates was used as the sample flow rate in all volume calculations. No samples departed more than 10% from the initial

flow rate during this study. The air volumes collected were adequately large for the sensitivity of the analytical system and sufficiently small to remain below the breakthrough volumes of the target VOCs.

2.3. Analysis

The VOCs collected on the Tenax TA trap were analyzed by coupling a thermal desorption system (TDS, Tekmar Model Aerotrap 6000) to a gas chromatograph (GC, Varian 3400CX) with a flame ionization detector (FID) using a 0.53-mm-i.d. by 60-m-length DB-WAX wide-bore capillary column (J&W Scientific). Next, the adsorbent (Tenax TA) trap was thermally desorbed at 250°C for 10 minutes, and the target compounds cryofocussed at (120°C on a cryo trap (15.2-cm-length, 0.32-cm-o.d. tube packed with glass beads). The cold trap was rapidly heated to 250°C, flushed to the Cryofocussing Module (CM) of the TDS, and cooled to 120°C to refocus the target compounds. The CM was then heated to 225°C and flushed to transfer the target compounds to a GC. The initial oven temperature was set at 35°C for 5 minutes and ramped at 4°C/min to 200°C for 5 minutes. The target VOCs were identified by their retention times using GC/FID analysis. The quantitative analysis of the target compounds was performed using the calibration curves of a minimum of five concentrations.

2.4. Flash Evaporation System

A Flash Evaporation System (FES) was constructed to estimate the VOC collection efficiency of the breath sampling system. The main body of the FES consisted of a glass reactor with an injection port. The reactor was maintained at a temperature of 250°C using a heating tape connected to a variable transformer. Purified nitrogen gas was employed to transport the target VOCs injected into the port to a Tenax TA cartridge connected on line. The flow was adjusted to approximately 60 mL/min. Prior to connecting the cartridge to the line, nitrogen gas was allowed to pass through the reactor for an hour to wash out any contaminants inside the reactor. Thereafter, nitrogen gas was allowed to pass through the cartridge for 12 min to collect a volume of about

The cartridges prepared with the FES were analyzed, then these results were compared with the results obtained from direct injections into the analytical system.

2.5. Quality Control and Quality Assurance Program

The quality assurance/quality control(QA/QC) program included laboratory and field blank traps, spiked samples, and duplicate measurements of integrated samples. At the beginning of each day, a laboratory blank trap and field blank trap were both analyzed to check for any trap contamination, however, no trap contamination was identified. An external standard was analyzed daily to check the quantitative response. When the quantitative response differed more than $\pm 25\%$ from that predicted by the specified calibration equation, a new calibration equation was determined. Seven sampling traps spiked with standards were used to determine the method detection limits(MDL) of the system.

3. Results and Discussion

As shown in Table 1, the MDL ranged from 0.2 to 0.4 $\mu\text{g}/\text{m}^3$ for the target VOCs. The MDL was below the typical breath levels for the target compounds¹⁻³. Thus, it would appear that the analytical system used in the present study can be effectively applied to estimate the body burden of target compounds from typical environmental or occupational exposure. In fact, the breath levels of the target compounds measured in the present study were well above the MDLs.

Table 1. Method detection limits(MDL) and recovery of breath sampling system for five aromatic VOCs

| Compound | MDL($\mu\text{g}/\text{m}^3$) | Recovery(%) |
|--------------|---------------------------------|-------------|
| Ethylbenzene | 0.2 | 83 |
| m-Xylene | 0.3 | 87 |
| p-Xylene | 0.3 | 91 |
| o-Xylene | 0.4 | 88 |

Table 1 also shows the collection efficiency of the breath sampling system for the target compounds. The recovery of the sampling system

for the compounds was above 80%. This is within the allowable range of VOC recovery for adsorption techniques¹⁰. Accordingly, this allows the breath sampling system to be utilized in the field for the evaluation of aromatic VOC body burdens associated with potential exposure to VOCs. Therefore, the breath sampling system was applied to evaluate the exposure of roadside and underground storekeepers to aromatic VOCs.

The breath concentrations measured after work for the roadside and underground storekeepers are summarized in Table 2. The most abundant chemical was o-Xylene. The mean o-Xylene concentrations were 5.0 and 5.4 $\mu\text{g}/\text{m}^3$ for the smokers and nonsmokers in the roadside stores, respectively. For the underground storekeepers, the mean o-Xylene concentrations were 5.6 and 5.0 $\mu\text{g}/\text{m}^3$ for the smokers and nonsmokers, respectively. For all the target compounds, the breath concentrations of the smokers were similar to or slightly higher than those of the nonsmokers for both the roadside and underground storekeepers. The differences between the two groups(smokers and nonsmokers) were not statistically significant, thereby implying that smoking was not an important source for the compounds.

Table 2. Mean breath concentrations($\mu\text{g}/\text{m}^3$) of roadside storekeepers and underground storekeepers : Smokers vs. nonsmokers

| Compound | Roadside | | Underground | |
|--------------|--------------|------------------|--------------|------------------|
| | Smoker (N=5) | Non-smoker (N=5) | Smoker (N=5) | Non-smoker (N=5) |
| Ethylbenzene | 3.6(1.0)* | 3.7(1.3) | 5.6(0.8) | 5.0(2.3) |
| p-Xylene | 3.3(1.4) | 2.9(1.3) | 4.3(0.8) | 4.7(2.1) |
| m-Xylene | 2.4(1.0) | 3.1(1.0) | 3.1(1.3) | 2.8(1.4) |
| o-Xylene | 5.0(1.0) | 5.4(2.6) | 7.3(1.3) | 6.7(3.4) |

* Numbers in parenthesis represent the standard deviations.

Table 3 compares the VOC exposures between the roadside storekeepers and the underground storekeepers, using the combined breath levels of the smokers and nonsmokers. For Ethylbenzene, p-Xylene, and o-Xylene, the breath concentrations of the underground storekeepers were somewhat higher than those of the roadside storekeepers. In

of the underground storekeepers were somewhat higher than those of the roadside storekeepers. In contrast, the breath m-xylene concentration of the underground storekeepers was similar to that of the roadside storekeepers. The roadside storekeepers were expected to exhibit elevated levels of the target compounds due to the automobile emissions from the nearby roads. However, the results were the reverse of this expectation. Hence, it is suggested that this difference was due to the combination of several factors including the smoking intensity of the subjects who smoked, the meteorological conditions on the roadside and traffic density, the number of smokers besides the subject, and other indoor sources for the target compounds.

Table 3. Mean breath concentrations($\mu\text{g}/\text{m}^3$) measured after work for roadside storekeepers and underground storekeepers

| Compound | Roadside (N=10) | Underground (N=10) |
|--------------|--------------------|-----------------------|
| Ethylbenzene | 3.7(1.0) | 5.3(1.7) |
| p-Xylene | 3.1(1.3) | 4.5(1.5) |
| m-Xylene | 2.7(0.7) | 2.9(1.3) |
| o-Xylene | 5.2(1.8) | 7.0(2.5) |

* Numbers in parenthesis represent the standard deviations.

The breath concentrations measured prior to and after work are summarized by occupation in Table 4. For both the roadside and underground storekeepers, the breath concentrations were not significantly different prior to and after work. The concentration differences between the two sampling times for the two occupations primarily reflected the source strength of the corresponding workplace, including smoke. Furthermore, it was indicated that neither the roadside nor the underground storekeepers were influenced by their store activity.

Exposure to a pollutant is defined as the contact at one or more boundaries between a person and a contaminant of a specific concentration for a period of time¹¹⁾. Exposure to VOCs is a dynamic process, and the average exposure can be estimated from the average concentration encountered, amount of time spent there, and inhalation rate.

Accordingly, the breath levels of roadside and underground storekeepers will be determined based on the above three parameters that influence their exposure to aromatic VOCs.

Table 4. Mean breath concentrations($\mu\text{g}/\text{m}^3$) measured prior to and after work for roadside storekeepers and underground storekeepers

| Compound | Roadside | | Underground | |
|--------------|--------------------|-----------------|--------------------|-----------------|
| | Prior to (N=10) | After (N=10) | Prior to (N=10) | After (N=10) |
| Ethylbenzene | 5.2(1.9)* | 5.3(1.7) | 4.7(1.2) | 4.6(1.2) |
| p-Xylene | 4.4(1.6) | 4.5(1.5) | 3.5(1.6) | 3.9(1.6) |
| m-Xylene | 2.9(1.4) | 2.9(1.3) | 2.2(1.2) | 2.5(1.6) |
| o-Xylene | 6.7(3.0) | 7.0(2.5) | 5.5(3.1) | 6.6(5.3) |

* Numbers in parenthesis represent the standard deviations.

4. Summary and Conclusions

The breath sampling system constructed in this study was successfully utilized to evaluate the exposure of roadside and underground storekeepers to VOCs. The MDL ranged from 0.2 to 0.4 $\mu\text{g}/\text{m}^3$ for the target VOCs, which was below the typical breath levels for the target compounds. The recovery of the sampling system for the compounds was above 80%, which is within the allowable range of VOC recovery for adsorption techniques. The differences between the two groups (smokers and nonsmokers) were not statistically significant. Accordingly, it would appear that the breath concentration difference between the roadside and underground storekeepers for some target compounds was due to a combination of several factors. It was also found that neither the roadside nor the underground storekeepers were influenced by their store activities.

References

- [1] Pellizzari, E. D., K. Perritt, T. D. Hartwell, L. C. Michael, R. Whitmore, R. W. Handy, D. Smith, and H. Zelon, 1987a, Total Exposure Assessment Methodology (TEAM) Study : Elizabeth and Bayonne, New Jersey ; Devils Lake, North Dakota ; and Green-

- Agency. EPA 600/6-87/002b. NTIS #PB 88-100078.
- [2] Pellizzari, E. D., K. Perritt, T. D. Hartwell, L. C. Michael, R. Whitmore, R. W. Handy, D. Smith, and H. Zelon, 1987b, Total Exposure Assessment Methodology (TEAM) Study : Selected Communities in Northern and Southern California. Vol. III Washington, DC : United States Environmental Protection Agency. EPA 600/6-87/002c. NTIS #PB 88-100086.
- [3] Wallace, L., W. Nelson, R. Ziegenfus, E. Pellizzari, L. Michael, R. Whitmore, H. Zelon, T. Hartwell, and R. Perritt, 1991, The Los Angeles TEAM Study : Personal Exposures, Indoor-Outdoor Air Concentrations, and Breath Concentrations of 25 Volatile Organic Compounds, *J. of Exposure Analysis and Environmental Epidemiology*, 1(2), 157~192.
- [4] Monster, A., W. Regouin-Peeters, A. Van Schjndel and J. Van Der Tuin, 1983, Biological monitoring of occupational exposure to Tetrachloroethene, *Scand. J. Work Environ. Health*, 273~281.
- [5] Benoit, F. M., W. R. Davidson, A. M Lovett, S. Nacson and A. NGO, 1985, Breath analysis by API/MS-Human exposure to volatile organic solvents, *Int. Arch. Occup. Environ. Health* 55, 113~120.
- [6] Brugnone, F. L. Perbellin, G. B. Faccini, B. Danzi, G. Maranelli, L. Romeo, M. Gobbi and A. Zedde, 1989, Benzene in the blood and breath of normal and occupationally exposed workers, *Am. J. Ind. Med.* 16, 385~399.
- [7] Wilson, H. K., 1986, Breath Analysis : Physiological basis and sampling techniques, *Scand. J. Work Environ. Health*, 12, 174~192.
- [8] Brown, W. D., J. V. Setzer, R.B. Dick, F. C. Phipps and L. K. Lowry, 1987, Body burden profiles of single and mixed solvent exposures, *J. Occupational Medicine*, 29, 877~883.
- [9] Cotes, J.E. 1979, Lung Function : Assessment and application in medicine, Blackwell Scientific Publications, Oxford.
- [10] Riggan, R. M. and R. A. Markle, 1986, Comparison of solid adsorbent sampling techniques for volatile organic compounds in ambient air, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, United States Environmental Protection Agency.
- [11] Liroy, P. J., 1990, Assessing total human exposures to contaminants, *Environ. Sci. Technol.* 24, 938~945.