A DEVELOPMENT OF A NOVEL THERMAL DESORPTION TECHNIQUE FOR MEASUREMENT OF VOCS IN AMBIENT AIR

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Abstract : The most demanding task for the continuous and long-term on-line measurement of volatile organic compounds (VOCs) is the minimization of test sample loss and the preconcentration of the trace gases. While the cryogenic preconcentration method produces excellent chromatographic results, it requires an extremely costly liquefying apparatus and cryogens. In a conventional thermal desorption method, poor chromatographic resolution due to a large amount of elution volume for complete extraction of samples on adsorbent is the main disadvantage, causing relatively low sensitivity. In this study, a novel thermal desorption system with a special syringe pump and a peltier cooling element, which can lower sampling temperature down to -30℃, was developed for VOC preconcentration and introduction. A nafion dryer was used optionally for removing water vapor. It was concluded that this novel thermal desorption system performed equivalently to the commercially available state-of-the-art cryogenic sample preconcentration system, and revealed even better separation capability.

INTRODUCTION

Management of volatile organic compounds (VOCs) in Korea was originated from the law of atmospheric environmental conservation in 1995. More specific environmental regulation for the Yochon industrial areas commenced in 1996 and for the Ulsan/Onsan industrial complexes in 1997. Thirty one VOCs including acetaldehyde, benzene, and styrene were emitted from the plants treating petrochemicals, organic solvents, etc. were regulated because their raid vapor pressure was greater than or equal to 10.3 kpa.[1] These VOCs included a considerable amount of odorous compounds and most of the odor problems occurred because of not only one odorous compound but also many different chemical species. Therefore, it is not that easy to find a fine line between VOCs and odorous compounds from this point of view.[2] On the other hand, it is well known that VOCs are involved in photochemical reactions and result in photochemical oxidants such as ozone.

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VOCs have attracted more interests in VOC emission inventory because they were taken into account as an important factor of ozone alarm system.[3] However, the VOC on-line measurement system has not been developed domestically and has been very costly in case we introduced it from other advanced countries. Therefore, it is needed to monitor atmospheric VOCs continuously for the ozone alarm system or the performance test of ozone prediction model. That is to say, it is urgent to develop the domestic on-line measurement system. Especially, the development of a novel thermal desorption method, the core technique of the on-line system, is required at this point.

It is not easy to measure ambient VOCs because the concentration of them in the atmosphere is either the ppbv or pptv level; therefore, more systematic approaches in sampling and analysis are needed.[4~6] In general, there are two methods to collect VOCs in the atmosphere. One is to collect the samples in a vessel such as a stainless steel canister coated with an inert material.[7,8] The other is to take a sample using an adsorbent trap.[9~11] The thermal desorption units commercialized presently were equipped with an autosampler including many canisters or adsorbent traps, interfaced with the analytical instruments for a consecutive analysis.[12] In general, 6 L of a canister is used and 12 L of an air sample can be collected under pressure at 2 atm, so a continuous sampling for a long period of time is possible. However, special care such as cleaning a vessel is required when a sample is collected and analyzed using the canister. Therefore, the adsorbent trap technique for more feasible sampling and analytical approach has been studied extensively and developed worldwide since 1990's.

In the case of advanced countries, automatic tube sampling methods have been developed and used in the field. There are two types of preconcentration techniques. One is to use liquid nitrogen[13] and the other is to use a special concentration trap instead of liquid nitrogen, when the sample concentrated will be

thermally desorbed within a very short time.[14] This kind of thermal desorption system is in the commercial stage nowadays. The purpose of this study is to develop a novel thermal desorption system feasible, reproducible, and durable for VOC analysis, and to evaluate the fundamental performance of the system by comparing the present sample introduction systems.

EXPERIMENTAL

Equipment

General sample collection and introduction systems : Some difficulties in continuous and long-term on-line observation of VOC often encountered minimization of sample loss and preconcentration of test samples at the same time. Liquid nitrogen has been most frequently used in the laboratory but sometimes dangerous for the end users. The consumption amount of liquid nitrogen seems too much for continuous monitoring; therefore, it is not desirable to use liquid nitrogen in a general monitoring site. In this study, a preconcentration system with a peltier cooling element was used for sample pretreatment and introduction.

First of all, this kind of sample concentration system, so called thermal desorption system, should be able to couple the ambient air sample, standard sample, bag, canister, and adsorbent trap etc. as seen in Figure 1. Various types of sample introduction parts and cryogenic preconcentration system were hooked up with multiple selective valves.

Cryogenic preconcentration and sample introduction system : In the beginning of this research, it was planned to include a system module using liquid nitrogen, as shown in Figure 2, in order that the end user can operate the system more selectively. However, using a liquid nitrogen module in a real field is almost of no use and a loop injection module can be easily replaced instead; therefore, the module
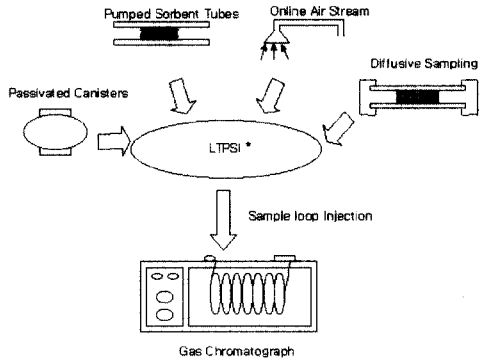
Figure 1. A concept diagram of a sample introduction system.

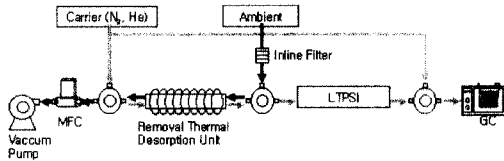*LTPSI denotes low temperature preconcentration and sample injection

Figure 2. A concept diagram of a partial on-line measurement system.

Figure 3. A schematic diagram of a novel thermal desorber and GC system.

using liquid nitrogen was excluded in this work. As shown in Figure 3, a gaseous sample injection system for a field measurement consists of 3 major parts: nafion dryer (optional), peltier cooler (optional), and a loop injection system. A loop injection system, the core part of this study, is composed of a special syringe and a sample loop. A special syringe was applied to this research based on the principle of the reverse working of a commercial syringe pump. When a VOC sample is thermally desorbed, the special syringe stores and mixes it temporarily, and then distributes the sample to the various volumes of loops hooked up with different detectors, such as FID, FPD, TCD, etc. Tenax-TA was used as the adsorbent of VOC. It is known that Tenax-TA has a weak adsorbing force at the ambient temperature but reveals much stronger force and easier desorbing characteristics at lower temperature.[15~19]

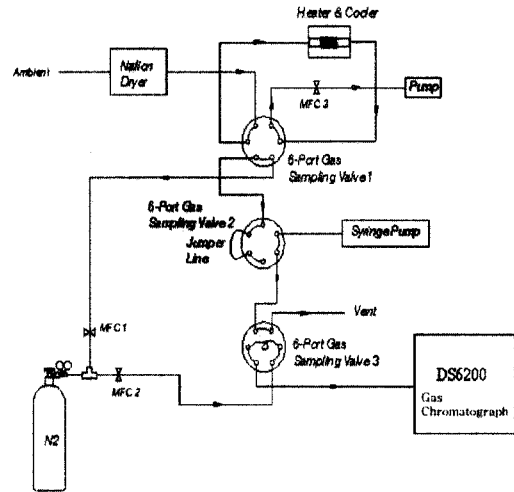## Experimental Set-up

A novel and unique gaseous sample injection

apparatus for a gas chromatography was developed. This instrument, more specifically, includes units of (1) an electronically cooled apparatus for lowering temperature to concentrate the gaseous samples in adsorbent, (2) a heating mechanism for adsorbent in a tube for thermal desorption with desorbing gas, (3) a temporary reservoir (heated syringe glass in a withdrawal syringe pump) for thermally desorbed VOCs from adsorbent tube, and (4) a sample loop. In this instrument, the chemicals on electronically cooled adsorbents are thermally desorbed and transferred to a temporary reservoir, which is a glass syringe in a syringe pump. As withdrawing speed of syringe pump is equally matched with elution volume rate of desorbing gas into the adsorbent tube, the complete desorption can be achieved in a pressure close to ambient pressure with less than 5 mL of elution volume. However, in conventional thermal desorber, high pressure desorption is required for direct capillary column injection. The low pressure desorption in our invention grants higher desorption efficiency in relatively low temperature and low elution volume, which insures the better analytical capability for thermally fragile compounds. Gaseous samples are transferred to a fixed volume (about 0.5 mL) sample loop

hooked up with a 6-way valve by operating a syringe pump. After loading the loop with the sample, it is switched to the injection position and directly injected to a GC column. This injection time is fast enough (less than a few hundred milli seconds) to produce uncompromising high resolution chromatography especially even in very small bore capillary columns. Exactly same sample volume of injection also yields excellent reproducibility in quantitative analysis.[6,20]

RESULTS AND DISCUSSION

Breakthrough and Recovery Experiments

It is known that the breakthrough volumes of Tenax for the 54 VOCs were over 4 liters with a flow-rate of 50 mL/min at an ambient temperature (20℃). Particularly, an adequate adsorption capacity for most VOCs (heavier than C_4) can be achieved with Tenax at cooled collection tube temperatures. No breakthrough on tested collection adsorbents was observed for BTEX (Benzene, Toluene, Ethylbenzene, m,p-Xylene, o-Xylene) compounds in a Peltier cooled collection tube at -30℃.[21,22] The recoveries of the laboratory check standards were always close to 100% for the BTEX by comparison with a direct injection of the liquid standards onto the capillary column. It was found that 2 minutes were sufficient to desorb all the BTEX compounds at 250℃.

Calibration and Detection Limit Experiments

Quantitative calibration of the developed thermal desorption systems was accomplished by using liquid BTEX, n-Hexane standards (Aldrich, purity > 95%) and static dilution bottles (#14-2080, Tekmar, Cincinnati, OH, USA). Each VOC standard was diluted from 6 to 60 ng with a series of static dilution bottles filled with ultra pure nitrogen. These standard materials in static bottles were compared and checked with known and certified standard materials of Photochemical Assesment Monitor-
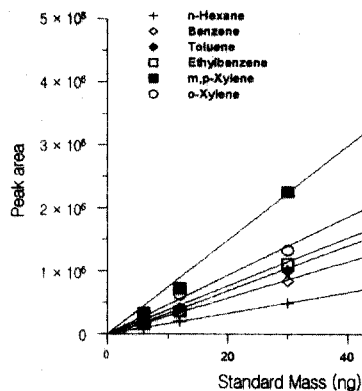

Figure 4. A quantitative result of several VOCs including BTEX.

ing Stations (PAMS) (1.15 ppm Std., Matheson, USA). The calibration curves for n-Hexane, benzene, and toluene were linear over the range from 6 to 60 ng ($r^2 > 0.999$); however, the other VOCs showed relatively low linearity ($r^2 > 0.995$). It was suggested that sample loss should occur because transfer line and six-port valves were not heated during analysis. More heavy compounds showed more manifest low linearity as seen in Figure 4. The detection limits of BTEX and n-Hexane for GC-FID with the developed thermal desorption system ranged from 0.5 to 2 ng (std. dev. ×3).

Reproducibility Experiment

Figure 5(a) shows the results of single run for 30 mL of PAMS (1.15 ppm Std., Matheson, USA) standard by developed thermal desorption syringe injector and GC-FID (Donam, Korea). The analysis was performed on a 60 m column (0.32 mm × Film Thickness 1.8 μm DB-VRX) using 2.4 mL/min carrier gas flow rate of ultra pure nitrogen. The chromatographic elution was temperature programmed as follows: isothermal at 30℃ for 12 min, then to 200℃ at a rate of 5℃/min, then an isothermal hold at 200℃ for 14 min.

Among 55 compounds listed in PAMS standard, 47 compounds could be identified clearly and quantified in a chromatogram. Total ion chromatogram with a cryogenic thermal desorption system (Entech, USA) with GC-
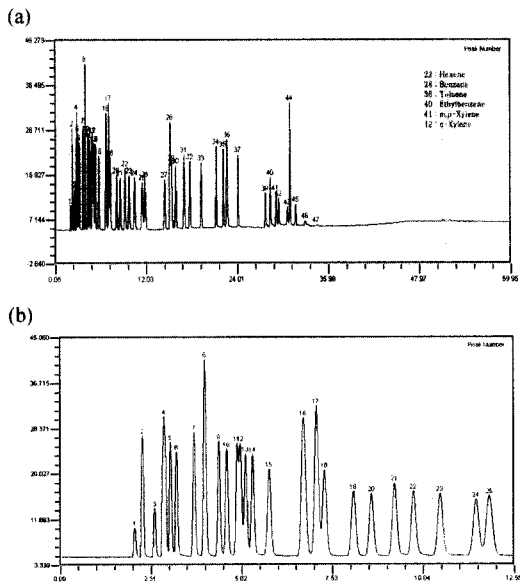
(a)

(b)

Figure 5. An example chromatogram of ozone precursors. (a) depicts a total analysis time and (b) describes a magnified chromatogram during the initial 12 minutes of run.

MS(HP5973 MSD) running with the same chromatographic operational conditions could only resolve and identify only 47 peaks with the same standard, too. In this respect, our thermal desorption system performed equivalently to the commercially available state-of-the-art cryogenic sample preconcentration system. In order to separate all 55 compounds, the different configurations of columns are recommended, particularly two column system with a PLOT column.[23]

Reproducibility was determined with triplicate runs of 30 ng BTEX and n-Hexane standards (Figure 6). Although the relative standard deviations of triplicate run of n-Hexane, Benzene, and Toluene were better than 2%, those of Ethylbenzene and Xylene were approximately 5%. The large uncertainty in higher molecular weight compounds is not clear at this stage. However, as the relative standard deviation of tested compounds were better than 5%, the developed system maintained appropriate reproducibility overall.
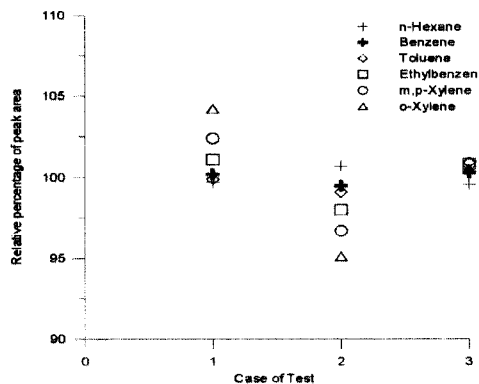

Figure 6. A result of some reproducibility tests through replicate analysis; This result was obtained from a relative comparison based on an average of three replicates.

As the injected volume from the loop is relatively small compared to the flow rate of carrier gas (larger than 3 mL/min) to the GC, a short time is required for a complete injection to the GC column in order to ensure the greatly improved peak separation and prevent a tailing phenomenon when analyzing the sample gases in the gas analyzing apparatus. An injection of precisely same volume from fixed volume loop (20 mL) to produce superior reproducibility is needed in GC analysis. With our invention, we can significantly improve the degree of peak separation and reproducibility in gaseous sample analysis with GC.

Blank Test

A chromatogram of a blank right after the injection of 15 mL of 1.15 ppm VOC standard is shown in Figure 7. Cleaning up adsorbents, sample transfer lines, the syringe, and a sample loop was sufficiently enough to get blank levels close to the level of detection limit for most of VOCs.

Application to Ambient Air Samples

In order to provide basis for an accurate concentration determination of VOCs in air, four different institutions, Dongshin University, Hankook University of Foreign Studies, Or-
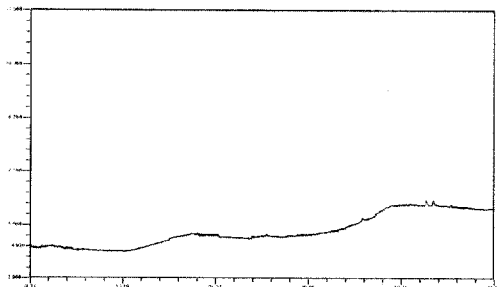
Figure 7. A chromatogram of a blank sample obtained right after the injection of standard sample in Figure 4.

Figure 8. Representative chromatograms of four field samples at the Hadaewon-dong site of Seongnam from August 15th, 2001 to August 16th, 2001.

ganic Analysis Group of Korean Research Institute of Standards and Science, University of Ulsan, participated in simultaneous measurements of several VOC species under the experimental scheme of the Measurement and Analysis Division (MAD) of the Korea Society for Atmospheric Environment (KOSAE). Laboratory measurements using a certified VOC standard were also combined in this campaign. Two types of experiments were undertaken by collecting and analyzing ambient air samples from the 7th floor of Natural Science Building, Han Yang University, during two day periods of late May 1998. The first type of experiment was carried out as five consecutive experiments at two hour intervals by two institutions including Hankook University of Foreign Studies, which applied this novel thermal desorption system to the ambient air sample. On the other hand, the second type of experiment was performed as 2 to 10 hr sampling by three different institutions including the above University. The data obtained from different types of experiments were examined using various statistical approaches. In general, the results of these experiments indicated that the VOC data produced by the four Korean institutions be fairly agreeable.[20]

Continuous measurement of the ambient air samples was carried out for 24 hours at an 1 hour cycle using the developed system from August 15th, 2001 to August 16th, 2001 in the urban atmosphere of Seongnam. The air samples were withdrawn from outside of a
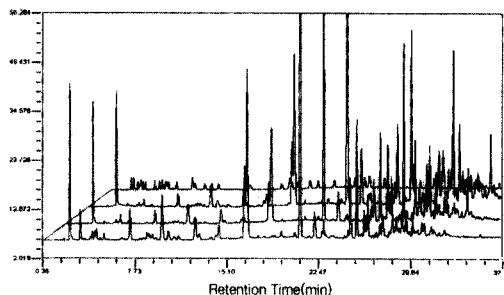
building window through the 1/4 inch PTFE tube to cooled adsorption tube at a flow rate of 50 mL/ min for one hour, prior to sample desorption and injection. Figure 8 shows the representative chromatograms for the VOCs in the atmosphere which were obtained using this developed system. As shown in the figure, the chromatogram peaks showed good separations, and also good resolution and sensitivity were preserved for the repeated measurements.

CONCLUSIONS

In order to improve the facility of VOC analysis, the pretreatment technique for GC and GC/MSD analysis of a minute quantity of gaseous compounds, was studied. In the process of measurement, gaseous samples were transferred to a fixed volume (about 0.5 mL) sample loop in a 6-way valve by using a syringe pump. After loading the loop with sample, it was switched to the injection position and directly injected to GC column. The injection time was fast enough (less than a few hundred milli seconds) to produce uncompromising high resolution chromatography especially even in very small bore capillary columns. The exact same sample volume of injection also yielded excellent reproducibility in quantitative analysis. It was also approved from a separate comparison study with a US brand desorber that this novel thermal desorption system performed equiva-

lently to the commercially available state-of-the-art cryogenic sample preconcentration system, and revealed even better separation capability.

ACKNOWLEDGEMENT

REFERENCES

1. Choi, H. J., "Preional Air Quality Management Polices and Prospects in Korea," *Proceedings of 30th Meeting of KOSAE,* pp. 41~43 (2000).
2. Rafson, J. H., Odor and VOC Control Handbook, Mcgraw-Hill, New York, (1998).
3. Ministry of Environment, Environmental White Paper, Chapter 3 (2001).
4. Paek, S. O., "Sampling and Analytical Methods for the Determination of Volatile Organic Compounds in Ambient Air," *J. KAPRA*, 12(1), 1~13 (1996).
5. Kim, M. G., Park, C. O., Kwon, Y. J., Lee, Y. K., and Lee, D. W., "Variations of Concentration Levels of Volatile Organic Compounds in the Indoor Air due to Floor Waxing," *KOSAE's Regular Conference,* 11, 253~254 (1998).
6. Heo, G. S. and Kim, B. J., "Development of VOC CRM and Interlaboratory comparison of VOC Analysis between Domestic Analytical Labs(I)," *J. KAPRA,* 13, 221~229 (1998).
7. McClenny, W. A., Pleil, J. D., Evans, G. F., Oliver, K. D., Holdrene, M. W., and Winberry, W. T., "Canister-Based Method for Monitoring Toxic VOCs in Ambient Air," *Air & Waste Management Association,* 41, 1308~1318 (1991).
8. Sin, D. W., Wong, Y. C., Sham, W. C., and Wang, D., "Development of an analytical technique and stability technique and stability evaluation of 143 C3-C12 volatile organic compounds in Summa canisters by gas chromatography-mass spectrometry," *The Analyst,* 126(3), 310~321 (2001).
9. Riggin, R. M. and Markle, R. A., Comparison of Solid Adsorbent Sampling Techniques for Volatile Organic Compounds in Ambient Air, EPA/600/S4-85/077 (1986).
10. Pollack, A. J. and Holdren, M. W., "Multiadsorbent Preconcentration and Gas Chromatographic Analysis of Air Toxics with an Automated Collection/Analytical System," *Air & Waste Management Association,* 41, 1213~1217 (1991).
11. Kim, J-C, "Factors controlling natural VOC emissions in a southeastern US pine forest," *Atmos. Environ.,* 35, 3279~3292 (2001).
12. Woolfenden, E. A., Broadway, G. M., Higham, P., and Seeley, I., Alternative on-line and sorbent tube-based sampling procedures for 24-hr air pollution profiling, Perkin Elmer Inc. (1994).
13. Shepson, P. B., Kseindienst, T. E., and McElhoe H. B., "A Cryogenic Trap/Porous Polymer Sampling Techniques for the Quantitative Determination of Ambient Volatile Organic Compound Concentrations," *Atmos. Environ.,* 21, 579~587 (1987).
14. Namiesnik, J., Torres, L., Kozlowski, E., and Mathieu, J., "Evaluation of the suitability of selected porous polymers for preconcentration of volatile organic compounds," *J. Chromatography,* 208, 239~252 (1981).
15. Senum, G. I., "Theoretical Collection Efficiencies of Adsorbent Samplers," *Environ. Sci. Technol.,* 15, 1073~1075 (1981).
16. Harris, J. C., Miseo, E. V., and Piecewicz, J. F., Further Characterization of Sorbents for Environmental Sampling, EPA-600/57-82-052 (1982).
17. MacLeod, G. and Ames, J. M., Comparative Assessment of the Artifact Background on Thermal Desorption of Tenax-

GC and Tenax-TA, Elsevier Sci. Publishers B.V. (1986).

18. Rothweiler, H., Wager, P. A., and Schsatter C., "Comparison of Tenax-TA and Carbotrap for Sampling and Analysis of Volatile Organic Compounds in Air," *Atmos. Environ.,* **25B**, 231~235 (1991).

19. Cao, X-L and Hewitt, C. N., "Thermal Desorption Efficiencies for Different Adsorbate/Adsorbent Systems typically used in Air Monitoring Programs," *Chemosphere,* **27**, 695~705 (1993).

20. Kim, K-H, Kim, J-C, Lee, G., Heo, G. S., and Lee., B-K, "Interlaboratory Study of Sampling and Analysis Techniques for Ambient VOCs under Field Conditions," *J. KOSAE,* **16**, 685~691 (2000).

21. Walling, J. F., Berkley, F. E., Swanson, D. H., and Toth, F. J., Sampling Air for Gaseous Organic Chemicals Using Solid Adsorbents, Application to Tenax. EPA-600/S4-82-059 (1982).

22. Bertman, S. B., Martin, P, B., and Roberts, J. M., "Automated Cryogenic Trapping Technique for Capillary GC Analysis of Atmospheric Trace Compounds Requiring No Expendable Cryogens : Application to the Measurement of Organic Nitrates," *Anal. Chem.,* **65**, 2944~2946 (1993).

23. Paek, S. O., "Sampling and Analytical Methods for the Determination of Volatile Organic Compounds in Ambient Air," *J. KAPRA,* **12**(1), 1~13 (1996).