Determination of Siloxanes in Biogas by Solid-phase Adsorption on Activated Carbon

Nack-joo Kim, Seung-Kyu Chun,[†,*] Daniel K. Cha,[‡] and Cheal Kim[*]

Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul 139-743, Korea
[*]E-mail: chealkim@seoultech.ac.kr
[†]Green Tech. Research Center, SUDOKWON Landfill Site Management Corp., Incheon 404-706 Korea
[*]E-mail: tocsk@naver.com
[‡]Department of Civil & Environmental Engineering, University of Delaware, Newark, DE 19716, USA

The objective of this study was to develop a simple, less time-consuming and accurate sampling technique based on solid-phase sorption with activated carbon as the sorbents. The results from solid-phase sorption techniques were compared to that from a conventional solvent impinger-based technique to confirm the efficacy of the proposed method. The laboratory results indicated that the solid-phase sorption method was suitable for the determination of siloxanes as the measured concentrations were similar to that from a solvent impinge method. The data from solid-phase sorption method showed excellent recovery and reproducibility while the sampling was less labor intensive and less time consuming than the solvent impinge method. Following the laboratory tests, the solid-phase sorption technique was successfully applied to sampling biogas from a field site. This study shows that the activated carbon-based solid-phase sorption can be a reliable and less time-consuming option for the sampling and collection of siloxanes under various different landfill conditions.

Key Words : Siloxanes, Landfill gas, Solid-phase adsorption, Activated carbon

Introduction

Landfill gas, generated by anaerobic degradation of buried waste, is composed of methane and carbon dioxide (which account for 99% of the gas) as well as trace amounts of water, sulfur, chlorine, and silicon compounds. Of the primary compounds, methane has about 25 times higher global warming potential (GWP) than that of carbon dioxide and thus has a greater impact on global warming. On the other hand, methane can be captured and used as an energy source. Hence, the transformation of methane in landfill gas into a usable resource is actively being studied worldwide in order to effectively reduce greenhouse gas emissions as well as to develop an alternative source of energy.[1-4] In Korea, landfill gas has been economically converted to energy resource by producing alternative fuels and producing electric power using steam turbine or gas engine power generation.[5]

However, the efficiency and performance of the power generation facilities are less than expected because the fuel quality is low (the methane content is only about 50% in landfill gas). In additions to decreased efficiency, other problems such as scaling and abrasive deposits were observed due to trace amounts of impurities.[6,7]

Application of landfill gas in power generation is often hindered by siloxanes, which are volatile organic compounds containing silicon, oxygen and methyl groups. The linear form is denoted as L, and the cyclic form as D. The number of silicon atoms is indicated with the subsequent numeric value. Although various types of siloxanes are found in nature, the siloxane compounds that can be readily measured are D3, D4, D5, L2, L3, L4, and L5. Among a small number of siloxanes detected in landfill sites, D4 makes up the largest portion. L2 and L3 are usually detected only in landfill gas, not in anaerobic digester gas.[8,9] These siloxane compounds are converted into silicon dioxide (SiO_2) when landfill gas is combusted and the resulting SiO_2 can deposit on the surfaces of pistons, cylinder heads, exhaustion valves, gas turbines, and other components internal combustion engines, to cause premature wear and failure of equipment.

Thus, in order to efficiently operate landfill power generation systems and transform landfill gas to more cost-effective energy resources, removal of siloxane is critical. However, a major obstacle to developing appropriate control strategies for siloxanes continues to be the difficulty in the analysis of siloxanes.[10-12]

Currently, the most common analysis for siloxanes involves capturing siloxanes in a solvent by passing gas samples through an impinger. This method allows low detection limits and a good recovery rate; however, the method requires complicated sampling protocol, including flow rate measurement and an ice bath in the field for the cooling of impinger solvent.[13]

In this study, we compared the methanol-based solvent absorption method, which is most commonly used for capturing siloxanes, and solid adsorption methods based on activated carbons to examine whether the solid adsorption method requiring a short measurement time can be applied for the accurate and reliable measurements of siloxanes in the field samples. The lab and field experiments were performed with the conventional solvent absorption method

Table 1. The types and characteristics of selected siloxanes[15]

Standard materials	Molecular formula	Abbreviation	MW	V.P. (mmHg, 77°F)	B.P. (°F)	Water solubility (mg/L) 77°F
Hexamethylcyclotrisiloxane	$C_6H_{18}O_3Si_3$	D3	222	10	275	1.56
Octamethylcyclotetrasiloxane	$C_8H_{24}O_4Si_4$	D4	297	1.3	348	0.056
Decamethylcyclopentasiloxane	$C_{10}H_{30}O_5Si_5$	D5	371	0.4	412	0.017
Hexamethyldisiloxane	$C_6H_{18}Si_2O$	L2, MM	162	31	224	0.93
Octamethyltrisiloxane	$C_8H_{24}Si_3O_2$	L3, MDM	236	3.9	307	0.035
Decamethyltetrasiloxane	$C_{10}H_{30}Si_4O_3$	L4, MD$_2$M	301	0.55	381	-
Dodecamethylpentasiloxane	$C_{12}H_{36}Si_5O_4$	L5, MD$_3$M	384	0.07	446	-

and the solid adsorption method using coconut-activated carbon, coal-activated carbon, and silica gel.

Experimental Method

Chemicals and Adsorbent Materials. Seven representative siloxanes typically detected in landfill gas[14] were selected as the standard siloxane materials and the compounds with at least 98% purity were obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). The list of the selected siloxanes and their chemical properties are shown in Table 1. The laboratory experiment was performed with D4, which typically accounts for the largest component of landfill gas. HPLC-grade methanol was used (99% purity) as a solvent for sampling, desorption, and analysis. The high purity nitrogen gas (Daeyoung Gas Co., Ltd., Busan, South Korea) was used as the carrier gas.

The adsorbents used in the experiment were coconut-activated carbon and coal-activated carbon (Samcheonri Activated Carbon) and silica gel (Samdeuk Chemical). Table 2 summarizes the properties of the adsorbents used in this study.
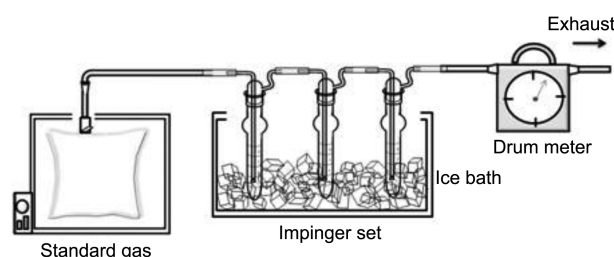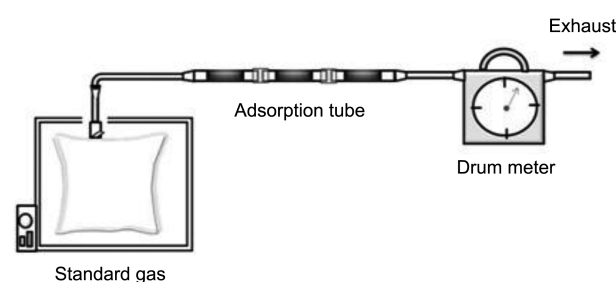
Experimental Apparatus. Octamethylcyclotetrasiloxane (D4), which is typically found in landfill gas at the highest concentration, was selected as the representative siloxane material for the laboratory experiment. The nitrogen carrier gas containing D4 concentrations of 10, 30, 50 and 100 ppb were used for the solvent absorption and the solid adsorption tests.

The schematic diagram of the solvent absorption apparatus with a series of impingers is shown in Figure 1. Solvent absorption was conducted based on the Air Toxics method[16]: 18 L of the gas sample were collected for two hours in three 6 mL impingers, containing methanol as the solvent since methanol has ideal properties for capturing siloxanes.[17]

For solid adsorption, gas samples were passed through

Figure 1. Schematic of experimental equipment for the impinger method.

Figure 2. Schematic of experimental equipment for the solid adsorption method.

three glass tubes (7-cm length and 8 mm ID) in series, which were filled with the coconut-activated carbon, coal-activated carbon, and silica gel (Figure 2). After sampling 18 L of gas for 30 min, the captured compounds were desorbed using

Table 2. Properties of the selected adsorbents

Absorbent	Type	Size (mesh)	Bulk density (g/cc)
Coconut-activated carbon	Granule	10-25	0.43-0.48
Coal-activated carbon	Granule	10-25	0.43-0.48
Silica gel	Bead	5-10	-

Table 3. Summary of GC/MS conditions

	Conditions	
	Gas chromatograph	Agilent Technologies US/6890 GC
	Carrier gas	He
GC	Column	HP-1MS capillary (Agilent, 300 m × 250 μm × 0.25 μm)
	Flow	1 mL/min
	Inlet temp.	250 °C
	Injection	1 μL
	MS	Agilent Technologies 5973N MSD
	Ionization mode	EI
MS	Analyzer	Quadruple
	Transfer line temp	280 °C
	Modus	sim mode

methanol for the subsequent analysis.

Gas Analysis. Siloxane concentrations in the collected gas samples were determined using Agilent Technologies US/ 6890 gas chromatograph (GC) and 5973N MS detector. High-purity He gas (Daeyeong Gas Co.) was used as the carrier gas. The GC/MS conditions are summarized in Table 3.

Reproducibility and Statistical Analysis. All laboratory experiments were repeated 30 times, and statistical analysis was conducted using SPSS (v. 18.0) and SAS software.

To evaluate the reproducibility, the mean, standard deviation, relative standard deviation, and standard error were calculated with descriptive statistics. Analysis of variance was performed to determine the significance of the difference between the individual methods based on the mean values. The Tukey's HSD test was applied to determine whether two capture methods are significantly different.

Results and Discussion

Standard Materials. Each standard material was diluted stepwise, and the calibration curves were prepared in the range of 2-10 μg/mL. The correlation coefficients for each siloxane were greater than 0.99, indicating good linearity. The standard peaks of the seven selected siloxanes detected with GC/MSD are shown in Figure 3.

To evaluate the reproducibility and reliability of the sampling techniques, the method detection limit (MDL) was obtained by measuring the samples containing 2 μg/mL of each standard siloxane 10 times, and the standard deviations and the relative standard deviations were obtained by measuring the samples containing 10 μg/mL of each siloxane 10 times.[18] The results are shown in Table 4. The MDLs of the selected siloxanes were in the range of 0.88-2.46 μg/mL, and the standard deviation values were 1.1 or less, indicating good reproducibility. The relative standard deviations were less than 13% for all seven siloxanes, showing that the analytical equipment had high accuracy and precision.

The recovery rate (RR) was calculated using Eq. (1) after 2 μg/mL and 10 μg/mL samples were injected 10 times. The
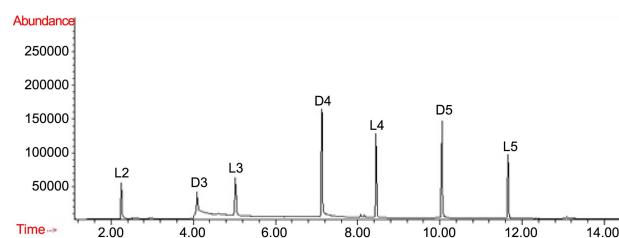
Figure 3. GC/MSD spectrum of standard siloxanes.

Table 4. Method Detection Limit, standard deviation, and RSD (%) of selected siloxanes

	L2	D3	L3	D4	L4	D5	L5
MDL (μg/mL)	2.33	2.46	1.24	0.88	1.93	1.13	2.07
SD	1.18	1.09	0.80	0.44	1.02	0.63	0.79
RSD (%)	12.93	12.07	8.54	4.54	10.18	6.35	7.90

recovery rate was high with the minimum of 92.6% and the maximum of 104.1%. The mean recovery was 98.4%.

$$\text{RR (\%)} = \frac{\text{Detected concentration}}{\text{Injected concentration}} \times 100 \qquad (1)$$

Laboratory Comparison of Inpimger and Adsorption Methods. To compare the impinger method and solid adsorption method for determining the siloxane content of landfill gas, D4 concentrations in carrier gas (nitrogen) was measured using two techniques. Table 5 shows the mean concentration of D4 along with relative standard deviation and error values obtained with each method with D4 concentrations of 10, 30, 50, and 100 ppb. The reported values are the average of 30 measurements.

The result showed that the relative standard deviation values of the impinger and coconut data were less than 15% for all four D4 concentrations tested, showing good reproducibility. On the other hand, the relative standard deviation values obtained from the coal adsorption method ranged

Table 5. Average concentrations, relative standard deviation, and error rate of D4 in the laboratory

Concentration (mg/m³)	Parameter	Solvent absorption	Solid-phase adsorption		
		Imp[a]	Coconut[b]	Coal[c]	Sil[d]
10	Avg. (mg/m³)	8.99 ± 0.49	9.15 ± 1.29	8.07 ± 1.53	6.55 ± 2.08
	RSD (%)	5.47	14.1	19.0	31.7
	Error rate (%)	10.1	8.5	19.3	34.5
30	Avg. (mg/m³)	26.51 ± 2.89	28.43 ± 3.85	22.93 ± 6.64	16.66 ± 6.07
	RSD (%)	10.9	13.6	29.0	36. 5
	Error rate (%)	11.6	5.2	23. 6	44.5
50	Avg. (mg/m³)	46.90 ± 4.22	34.73 ± 4.83	34.64 ± 9.76	40.61 ± 14.84
	RSD (%)	8.99	13. 9	28.2	36. 6
	Error rate (%)	6.2	30.5	30.7	18. 8
100	Avg. (mg/m³)	102.82 ± 7.55	94.67 ± 9.92	85.76 ± 12.85	84.51 ± 20.83
	RSD (%)	7.35	10.5	15.0	24.6
	Error rate (%)	3.82	3.39	13.4	16.5

[a]Imp = Impinger method. [b]Coconut = Activated coconut carbon tube. [c]Coal = Activated charcoal tube. [d]Sil = Silica gel tube
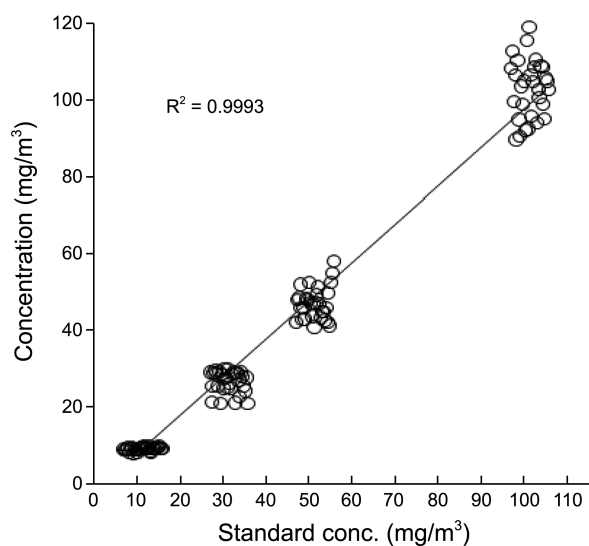
Figure 4. Concentrations of D_4 using the impinger method.

from 15 to 29%, indicating marginal reproducibility. Worst reproducibility was observed with the silica gel adsorption method as the relative standard deviation values ranged from 24.6 to 36.6%.

When 100 ppb of the standard material was used, all methods except the method using silica gel showed good reproducibility with a relative standard deviation of less than 15%.

The accuracy of the methods was compared by examining the error rate (Table 5). The solvent absorption method had error rates ranging from 3 to 12% for all four D4 concentrations. The adsorption method using coconut activated carbon exhibited comparable error rates as the solvent absorption method and substantially lower error rates than the other two adsorption methods (Table 5). This result suggests that coconut-based activated carbon may be more suitable for accurate quantification of siloxanes in gas samples. The tendencies of the capture methods for the
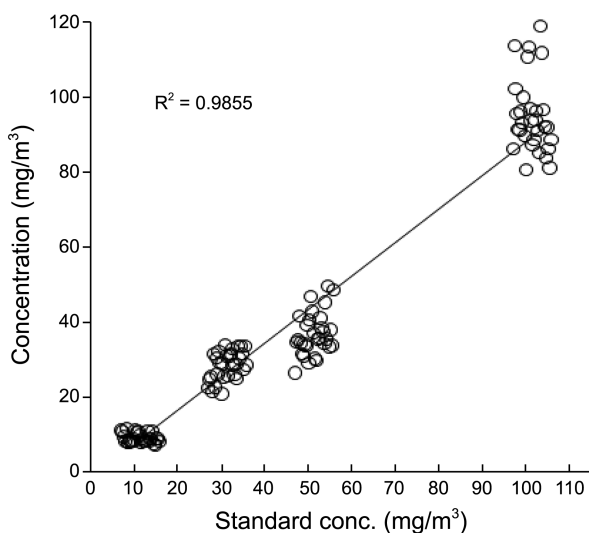

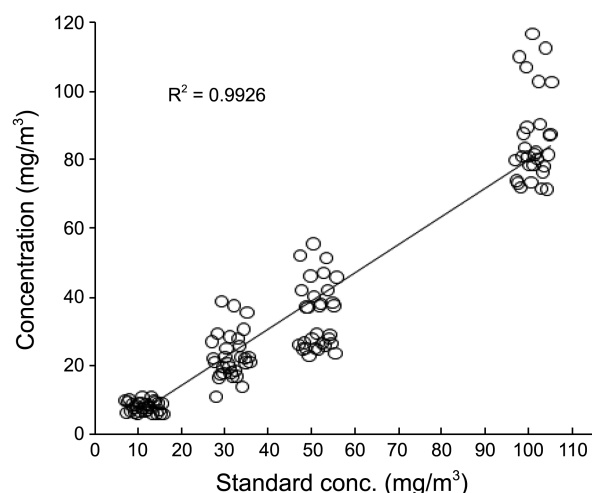**Figure 5.** Concentrations of D_4 using the coconut carbon tube.

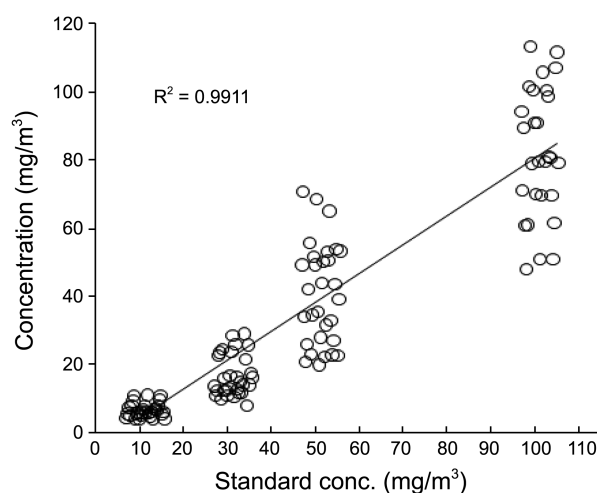**Figure 6.** Concentrations of D_4 using the activated charcoal tube.

Figure 7. Concentrations of D_4 using the silica gel tube.

results from the laboratory experiment is shown in Figures 4, 5, 6, and 7.

Siloxane Measurement of Landfill Gas from a Field Site. To examine whether the solid adsorption method can be applied for the accurate and reliable measurements of siloxanes in the field samples, siloxane measurements were carried out using the landfill gas from the A-site under the same conditions as those of the laboratory experiment. Table 6 shows the pertinent information of the target landfill site.

Table 7 shows the average siloxane concentrations of 20 measurements of biogas from the landfill site for each method. The mean concentrations obtained from two solid-phase adsorption method (coconut and coal) compared well to the concentrations obtained by solvent absorption method.

Table 6. Pertinent data of landfill site

Landfill operation (year)	Landfill depth (m)	Landfill capacity (ton)	Landfill gas composition (%)			
			CH_4	CO_2	O_2	N_2
2000-2003	20	1,253,412	51.4	49.0	0	0

Table 7. Comparison of siloxane concentration values obtained from different methods

Sampling method	Solvent absorption	Solid-phase adsorption		
	Imp[a]	Coconut[b]	Coal[c]	Sil[d]
Average Concentration (mg/Nm³)	8.91 ± 1.26	7.91 ± 1.86	7.67 ± 2.12	5.54 ± 2.53
RSD (%)	14.16	23.56	27.60	45.64

[a]Imp = Impinger method. [b]Coconut = Activated coconut carbon tube. [c]Coal = Activated charcoal tube. [d]Sil = Silica gel tube.

Table 8. Significance verification of D4 in the field

	Imp-Coco	Imp-Coal	Imp-Silica
p-value	0.615	0.435	0.001

The value obtained using the silica gel was substantially lower than the other three methods. The relative standard deviations of the methods using the impinger, coconut, coal, and silica gel were 14.16, 23.56, 27.60, and 45.64, respectively. The tendency was very similar to that of the laboratory result.

Table 8 compares the solvent absorption method with each of the solid adsorption methods under the significance level condition ($\alpha = 0.05$). The adsorption methods using coconut and coal had p-values of 0.615 and 0.435, respectively, indicating that the results from the two methods are the same as that of the solvent absorption method.

Conclusions

The following conclusions are based on the experimental results obtained with the laboratory samples containing standard siloxanes and actual landfill gas samples:

1. The reproducibility and accuracy of the laboratory results indicated that solvent absorption was the best method with a mean relative standard deviation of 8.18% and a mean error rate of 7.94%. The solid adsorption method using activated coconut carbon also showed good results with a mean relative standard deviation of 12.99% and a mean error rate of 11.92%.

2. The measurement of siloxanes in the actual landfill gas samples showed that the solid adsorption method using activated coconut carbon had the lowest relative error rate of 11.22%.

3. Solid adsorption method has comparable reproducibility and recovery rate as solvent absorption method in quantifying siloxanes in landfill gas while requiring shorter collection period and simpler apparatus and equipment.

References

1. Hagmann, M.; Heimbrand, E.; Hentschel, P. *Seventh International Waste Management and Landfill Symposium*; Determination of Siloxanes in Biogas from Landfills and Sewage Treatment Plants, Cagliari, Italy, Proceeding Sardinia 99, 1999; pp 4-8.
2. Shin, H.-C.; Park, J.-W.; Park, K.; Song, H.-C. *Environmental Pollution* **2002**, *119*, 227-236.
3. Hayes, H. C.; Graening, G. J.; Saeed, S.; Kao, S. *SWANA 26th Annual Landfill Gas Symposium*; A Summary of Available Analytical Methods for the Determination of Siloxanes in Biogas, Tampa, Florida, US, 2003.
4. Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts, R.; Fahey, D. W.; Haywood, J.; Lean, J.; Lowe, D. C.; Myhre, G.; Nganga, J.; Prinn, R.; Raga, G.; Schulz, M.; Van Dorland, R. The Physical Science Basis. Changes in Atmospheric Constituents and in Radiative Forcing. *Cambridge University Press*; Cambridge, 2007.
5. Kim, N. J.; Choi, J. M.; Ji, E. J. *Korea Society of Environmental Engineers*; 2007; pp 27-41.
6. Schweigkofler, M.; Niessner, R. *Environ. Sci. Technol.* **1999**, *33*, 3680-3685.
7. Wheless, E.; Pierce, J. *SWANA 27th Annual Landfill Gas Symposium*; Siloxanes in Landfill and Digester Gas Update, San Antonio, Texas, US, 2004.
8. Raf, D.; Lise, A.; Jan, B. *Energy Conversion and Management* **2006**, *47*(1314), 1711-1722.
9. Lehmannm, R. G.; Miller, J. R.; Kozerski, G. E. *Chemosphere* **2000**, *41*, 743-749.
10. Deed, C.; Gronow, J.; Rosevear, A.; Bralthwaite, P.; Smith, R.; Stanley, P. E. A. *Scottish Environment Protection Agency*, 2004.
11. Takuwa, Y.; Matsumoto, T.; Oshita, K.; Takaoka, M.; Morisawa, S.; Takeda, N. *Special Feature on APLAS Sapporo 2008, J. Mater Cycle Waste Man 11*, 2009; p 305.
12. Rasi, S. *Dissertation*; Jyvaskyla University: 2009; p 135.
13. Nordic Council of Ministers, *TemaNord 593*, 2005; p 93.
14. Takuwa, Y.; Matsumoto, T.; Oshita, K.; Takaoka, M.; Morisawa, S.; Takeda, N. *Special Feature on APLAS Sapporo 2008, J. Mater Cycle Waste Man 11*, 2009; p 305-311.
15. Popat, S. C.; Deshusses, M. A. *Environ. Sci. Technol.* **2008**, *42*, 8510-8515.
16. Air Toxics Ltd. *In the Air* **2002**, *7*, 1-3.
17. Park, T.-J.; Yang, S.-H.; Lee, Y.-M.; Kim, H.-S. *Journal of the Korean Society of Precision Engineering* **2001**, *18*, 110-115.
18. ACIL Environmental Services Section Technical Committee. *ACIL Environmental Services Section Technical Committee*; Revision 6.0, 2006.