Comparison between Thermal Desorption Tubes and Stainless Steel Canisters Used for Measuring Volatile Organic Compounds in Petrochemical Factories

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ABSTRACT

Objective: The purpose of this study was to compare thermal desorption tubes and stainless steel canisters for measuring volatile organic compounds (VOCs) emitted from petrochemical factories.

Methods: Twelve petrochemical factories in the Mailiao Industrial Complex were recruited for conducting the measurements of VOCs. Thermal desorption tubes and 6-l specially prepared stainless steel canisters were used to simultaneously perform active sampling of environmental air samples. The sampling time of the environmental air samples was set up on 6 h close to a full work shift of the workers. A total of 94 pairwise air samples were collected by using the thermal adsorption tubes and stainless steel canisters in these 12 factories in the petrochemical industrial complex. To maximize the number of comparative data points, all the measurements from all the factories in different sampling times were lumped together to perform a linear regression analysis for each selected VOC. Pearson product-moment correlation coefficient was used to examine the correlation between the pairwise measurements of these two sampling methods. A paired *t*-test was also performed to examine whether the difference in the concentrations of each selected VOC measured by the two methods was statistically significant.

Results: The correlation coefficients of seven compounds, including acetone, *n*-hexane, benzene, toluene, 1,2-dichloroethane, 1,3-butadiene, and styrene were >0.80 indicating the two sampling methods for these VOCs' measurements had high consistency. The paired *t*-tests for the measurements of *n*-hexane, benzene, *m/p*-xylene, *o*-xylene, 1,2-dichloroethane, and 1,3-butadiene showed statistically significant difference (*P*-value < 0.05). This indicated that the two sampling methods had various degrees of systematic errors. Looking at the results of six chemicals and these systematic errors probably resulted from the differences of the detection limits in the two sampling methods for these VOCs.

Conclusions: The comparison between the concentrations of each of the 10 selected VOCs measured by the two sampling methods indicated that the thermal desorption tubes provided high accuracy and

precision measurements for acetone, benzene, and 1,3-butadiene. The accuracy and precision of using the thermal desorption tubes for measuring the VOCs can be improved due to new developments in sorbent materials, multi-sorbent designs, and thermal desorption instrumentation. More applications of thermal desorption tubes for measuring occupational and environmental hazardous agents can be anticipated.

KEYWORDS: air sampling; consistency; petrochemical factory; stainless steel canister; thermal desorption tube; volatile organic compounds

INTRODUCTION

The petrochemical industries have been developing for >35 years in Taiwan. The petrochemical industries have a major contribution to the gross domestic product of Taiwan. Most of the petrochemical factories have improved the process safety management systems to decrease potential safety risks. However, they are still facing the challenges of excessive antipollution protests and strict environmental regulations. Many hazardous chemicals are utilized in and probably emitted from the complicated processes of petrochemical factories (Yen and Horng, 2009; Chang *et al.*, 2014). Human health hazards for residents living in the vicinities of petrochemical factories in Taiwan have been reported (Yang *et al.*, 2004; Chan *et al.*, 2006; Liu *et al.*, 2008; Tsai *et al.*, 2009; Chio *et al.*, 2014). The emission of volatile organic compounds (VOCs) from petrochemical factories has raised wide public concern. However, systematic investigations on the concentration profiles of VOCs from petrochemical factories in Taiwan have rarely been carried out.

The US Environmental Protection Agency (EPA) has suggested the method (EPA Method TO-15) for determination of VOCs in air collected by specially prepared stainless steel canisters and analyzed by gas chromatography/mass spectrometry (GC/MS) (US EPA, 1999a). This method has the advantages of no pump requirement, simultaneous analyses of multiple chemicals, and allowing the detection of very low concentrations of chemicals normally above 0.5 part per billion (p.p.b.) by volume. In addition, canisters offer better recovery of ultra-volatile compounds, such as acetylene, ozone precursors, greenhouse gases, etc., which have a very low breakthrough volume on most sorbents at ambient temperature. However, the major disadvantages associated with the use of canisters include the high cost of sampling apparatus preparation and sample analysis, low resistance to dirty environments (e.g. high particulate) as well as

the bulkiness of sampling apparatus. Therefore, the stainless steel canisters were not usually used for large sample investigation.

Using thermal desorption tubes with subsequent analysis by GC for measuring VOCs in ambient air was documented by the US EPA (1999b) and other organizations (Health and Safety Executive—HSE, 1993; NIOSH, 1996; ISO, 2000). This method (EPA Method TO-17) can determine VOCs at low concentrations in air samples typically 0.5–25 p.p.b. (US EPA, 1999b). It offers the major advantage of running cost reduction per analysis because of no manual sample preparation and no solvent disposal expense when compared with solvent extraction methods as well as no expensive air extraction equipment needed, larger sample volumes and less prone to irreversible contamination when compared with the EPA Method TO-15. Because of no dilution of the collected sample it greatly improves analytical sensitivity, that is, 1000-fold sensitivity enhancement versus equivalent solvent extraction procedures for VOCs (Woolfenden 2010a, b). In addition, thermal desorption tubes offer better recovery than canisters for a wider range of vapor phase organics including higher boiling VOCs, semi-VOCs, and polar compounds. Last but not least thermal desorption tubes provide the option of passive sampling. A comprehensive description of thermal desorption for GC is available for offering a complete picture of this topic (Woolfenden, 2012). In recent years, the innovation of thermal desorption technology makes the use of thermal desorption tubes an excellent choice for many air monitoring applications (Grote and Kennedy, 2002; Wu *et al.*, 2004; Lindahl *et al.*, 2009).

In order to comprehensively investigate the emission of VOCs in petrochemical factories, a large number of air samples are required to obtain accurate and precise estimation of VOCs concentrations. For the collection and analysis of many air samples, the

requirements of cost saving and easy preparation are the important points of consideration. In such a case, the thermal desorption tube is the good candidate for the requirements. Although the EPA Methods TO-15 and TO-17 were available many years ago, few studies have been conducted to examine the consistency of the concentrations of VOCs measured by using these two methods. Hayes *et al.* (2007) evaluated the performance of these two methods for soil gas measurements of petroleum-contaminated sites and concluded that Method TO-17 could provide reliable and accurate measurements for naphthalene and other light polyaromatic hydrocarbons, as well as hydrocarbons through the C_{16} range.

In this study, we are interested in evaluating whether thermal desorption tubes that are cheaper and more portable than the stainless canisters are adequate for measuring VOCs emitted from petrochemical factories. Although the methods used in this study were not exactly the same as the EPA Methods TO-15 and TO-17, the essence of the study focused on comparing thermal desorption tubes and stainless steel canisters for measuring VOCs emitted from petrochemical factories.

METHODS

Site of study

The site selected for VOCs' measurements in this study is the Mailiao Industrial Complex, which is situated on a seabed along the western coast of central Taiwan and includes two industrial zones, Mailiao and Hai Fong zones. It is the sixth Naphtha Cracking Project of Taiwan which occupies an area about 8 km long from south to north, extending more than 4 km along the coastline out toward the sea. More than 60 large-scale petrochemical factories including an industrial port, a large thermal power plant, an oil refinery plant, three naphtha cracking plants, a heavy machinery plant, a cogeneration power plant, and other petrochemical plants are built and hire ~11 000 on-site workers in the industrial complex. The chemicals either processed or produced by these petrochemical factories included ethylene, propylene, 1,3-butadiene, isobutylene, vinyl chloride monomer, chlorine, 1,2-dichloroethane, ammonia, acrylonitrile, epichlorohydrin, acetone, methyl methacrylate, acrylic acid, vinyl acetate, ethanol, butanol, 2-ethyl hexanol, ethyl acrylate,

butyl acrylate, 2-ethylhexyl acrylate, o-xylene, xylene, 2-ethyl hexanol, toluene, phenol, benzene, *p*-xylene, ethylene oxide, ethylene glycol, styrene, acetic acid, *N,N*-dimethyl formamide, cumene, and so on.

Factories participating in VOCs' measurements

Twelve petrochemical factories participated in VOCs' measurements of this study including the acrylonitrile plant (AN), acrylic acid and ester plant (AA/AE), polyvinyl chloride plant (PVC), acrylonitrile-butadiene-styrene plant (PABS), utilities supply plant 3 (UR3), oil refinery ethylene plant 3 (OR3), naphtha cracking plant 1 (OL1), naphtha cracking plant 2 (OL2), naphtha cracking plant 3 (OL3), plasticizer plant (DEHP), bisphenol A plant 1 (BPA1), and the 1,4-butylene glycol plant (1,4-BG). For each factory, before taking air sampling a walkthrough survey was done to collect information on the working process and chemicals being used and emitted from the processes. In order to avoid measurements under detection limits, the sampling locations were specially targeted to the vicinities of possible emission sites of VOCs, including fugitive equipment leaks (e.g. valves, flanges, pumps, compressor seals, and other piping components), storage tanks, loading/transfer operation units, wastewater treatment units. Also, the selected sampling locations should not cause any inconvenience and safety problem for the workers in the factories.

Chemicals measured

In this study, 10 species of VOCs including acetone, *n*-hexane, benzene, toluene, *m/p*-xylene, *o*-xylene, 1,2-dichloroethane, 1,3-butadiene, ethylbenzene, and styrene in the collected samples were measured. The whole sampling duration was lasted for about 6 months. Two kinds of sampling devices, i.e. two thermal desorption tubes and a 6-l specially prepared stainless steel canister (Model 29-10622G, Entech Instruments, Inc., Simi Valley, CA, USA), were used to take environmental air samples for at least 6 h in every sampling for each factory. The adsorbents, Tenax TA (60/80mesh, Supelco, Bellefonte, PA, USA) and Carboxpack X (60/80mesh, Supelco), were packed separately into two thermal desorption tubes for sampling the compounds except 1,3-butadiene and 1,3-butadiene only, respectively. That is, the Tenax TA tubes were used to sample all compounds except butadiene and the Carboxpack X tubes were used to sample

butadiene only. These two thermal desorption tubes equipped with a calibrated sampling pump and a dual port manifold (Gilian, Sensidyne, USA) were set up at 200 ml min^{-1} to actively take a complete set of air samples. The stainless steel canister was cleaned by a canister cleaning system (3100, Entech Instruments, Inc., Simi Valley, CA, USA) and for reuse by evacuating and refilling with nitrogen multiple times to completely eliminate VOCs introduced during the previous sampling. After cleaning, canisters are finally evacuated to 10 mtorr in preparation for sampling. When the canister was opened to the atmosphere, a sample of air was drawn through a sampling train comprised of a flow controller and a critical orifice that regulated the rate and duration of sampling into the pre-evacuated and passivated canister. Theoretically, the thermal desorption tubes are cleaned in the desorption process of the thermal desorption system rendering them immediately available for resampling. In this study, after the chemical analysis of the thermal desorption tubes was finished, these tubes were cleaned according to the following procedures. The tubes were put into a tube cleaning system in batches. The tube cleaning system had a unit to heat the tubes according to the temperature program $50\text{--}150^\circ\text{C}$ at $20^\circ\text{C min}^{-1}$, $150\text{--}200^\circ\text{C}$ at 5°C min^{-1} and $200\text{--}300^\circ\text{C}$ at $20^\circ\text{C min}^{-1}$. During the heating time, purified nitrogen was introduced into each tube at the flow rate 100 ml min^{-1} to blow residual compounds out of the tube. After the cleaning, the tubes were stored in a dry cabinet with humidity control at 35% for next sampling.

A pair of thermal desorption tubes were attached side by side to a pole close to the sampling inlet of the stainless steel canister to simultaneously take an environmental air sample at the manufacturing process area of each factory. The sampling time of the environmental air samples was set up on 6 h close to a full work shift of the workers. Each factory was visited once roughly about a month, and two stainless steel canister samples and four thermal desorption tube samples (two Tenax TA tubes plus two Carboxen X tubes) were collected during each visit. All of the air samples were sent to chemical analytical laboratories immediately after sampling.

Air samples analysis

The air samples collected by the thermal desorption tubes were analyzed by using an automatic thermal

desorption system (PerkinElmer TurboMatrix ATD-50) equipped with a GC flame ionization detector (Agilent-6890, Agilent Technologies, Inc., Santa Clara, CA, USA). Two GC columns, DB-1 ($30 \text{ m} \times 0.53 \text{ mm ID}$, $1 \mu\text{m}$ capillary column), and DB-WAX ($30 \text{ m} \times 0.25 \text{ mm ID}$, $0.5 \mu\text{m}$ capillary column) were used for quantifying the 10 selected compounds of VOCs. This analytical method was developed by our laboratory with the modification of the US EPA TO-17 method on the MS detection.

The canisters were analyzed by using GC/MS (Agilent 6890 GC and 5973 MS, Agilent Technologies, Inc.) with a pre-concentration system (Entech 7100A cryogenic sample pre-concentrator, Entech Instruments, Inc.) according to the method modified from the US EPA TO-14 method (US EPA, 1999c) to the US EPA TO-15 method (US EPA, 1999a) to measure the concentrations of 10 selected compounds of VOCs. Three GC columns, HP DB-624 ($60 \text{ m} \times 0.25 \text{ mm ID}$, capillary column), HP DB-624 ($60 \text{ m} \times 0.25 \text{ mm ID}$, capillary column), and GS-GASPRO ($60 \text{ m} \times 0.35 \text{ mm ID}$, capillary column), were used for the quantification of the 10 selected compounds of VOCs.

The quality control (QC) and quality assurance (QA) procedures in an analytical laboratory were followed. In brief, reagent blank samples were analyzed to confirm the absence of interferences. For each chemical, a set of seven concentrations of standard solutions was prepared to establish a calibration curve. The coefficient of determination of each calibration curve should meet the criteria for acceptability with a value of 0.995. The QC samples were injected after every 10 sample injections to monitor the performance of total analytical process. The coefficient of variation of the QC samples was controlled within 10%. Recoveries were evaluated by spiking a given amount of three standard samples at various concentrations (low, medium, and high concentrations) separately into the two types of thermal desorption tubes. The minimum recovery requirement of each chemical at each concentration was 80%.

When the measured concentration of the compound was below the limit of detection (LOD) of the analytical method, half of LOD was used to substitute the measured value of the compound for statistical data analysis.

Statistical analysis

To demonstrate the consistency of the concentrations of the selected VOCs measured by the thermal desorption tubes and the canisters, all the measurements from all the factories in different sampling times were lumped together to conduct a linear regression analysis for each selected VOC. The Pearson product-moment correlation coefficient was calculated to examine the measurement consistency. A paired *t*-test was performed to examine whether the difference in the concentrations of each selected VOC measured by these two sampling methods was statistically significant.

RESULTS

A total of 94 pairwise samples collected by the thermal desorption tubes and canisters were carried out in the 12 factories in the petrochemical industrial complex. Table 1 shows the descriptive statistics of VOCs' measurements taken by the thermal desorption tubes and stainless steel canisters for 10 compounds in 12 petrochemical factories. The concentration of each measured VOC in each factory was in the range of 0–85 p.p.b. The mean concentrations of the measured VOCs except acetone in the factories were <10 p.p.b. All the measured concentrations were well below the corresponding 8-h time-weighted average exposure limit of threshold limit value recommended by the American Conference of Governmental Industrial Hygienists (ACGIH, 2014). This indicated that the VOCs' emissions from the manufacturing processes were well controlled.

After excluding the missing measurements with either one of these two sampling methods, linear regression analyses for assessing the consistency of measured concentrations of VOCs between the thermal desorption tubes and the canisters were performed. The results of the linear regression analyses are presented in Table 2. The Pearson product-moment correlation coefficients of the pairwise measurements of the VOCs were in the range of 0.275–0.999. All the correlation coefficients were statistically significant (*P*-value < 0.05). This indicated that the two sampling methods provided highly correlated measurements for the selected VOCs. Figure 1 shows the scatter plot of the concentrations measured by the canisters as a function of the concentrations measured by the thermal desorption tubes for each selected VOC. All the fitted linear regression lines had positive slopes.

However, some of the slopes, i.e. *m/p*-xylene, *o*-xylene, 1,2-dichloroethane, ethylbenzene, and styrene, of the regression lines were not close to 1.0. This signifies that the two sampling methods might not provide consistent measured concentrations of these VOCs. The results of the paired *t*-tests for examining the significance of the differences in the concentrations of selected VOCs measured by the two sampling methods are shown in Table 3. Six chemicals including *n*-hexane, benzene, *m/p*-xylene, *o*-xylene, 1,2-dichloroethane, and 1,3-butadiene showed statistically significant difference (*P*-value < 0.05) in measured concentrations. The differences of the means of the pairwise measurements for *n*-hexane, benzene, *m/p*-xylene, *o*-xylene, 1,2-dichloroethane, and 1,3-butadiene were 1.10, 0.98, 2.85, 2.53, 1.10, and 0.42 p.p.b., respectively. Apparently, the two sampling methods had various degrees of systematic errors on measuring these six chemicals. These systematic errors probably resulted from the differences of the method detection limits in the two sampling methods for the selected VOCs (Table 4). Regarding the quantification of the VOCs in the petrochemical factories, all these results clearly demonstrated that compared with the concentrations measured by the stainless steel canisters, the concentrations measured by the thermal desorption tubes could be distinguished into three categories: (i) for three chemicals including acetone, benzene, and 1,3-butadiene, the measured concentrations had high accuracy and precision; (ii) for other three chemicals including *n*-hexane, toluene, and styrene, the measured concentrations had moderate accuracy and precision; (iii) for four chemicals including *m/p*-xylene, *o*-xylene, 1,2-dichloroethane, and ethylbenzene, the measured concentrations had low accuracy and precision.

DISCUSSION

This study was the first comprehensive emission assessment of VOCs in the petrochemical factories after a large fire at the industrial complex (Shie and Chan, 2013). The repairing work of the factories including pipe replacement and maintenance was conducted during the sampling period of this study. The results of the VOCs' measurements in the 12 petrochemical factories indicated that the emission of VOCs was well controlled. Most of the time, there were only low concentrations of the VOCs emitted in to the atmosphere.

Table 1. Descriptive statistics of VOCs' concentrations measured by thermal desorption tubes and stainless steel canisters in 12 petrochemical factories

Factory	Item	Statistics	Concentration (unit: p.p.b.)									
			Acetone	n-Hexane	Benzene	Toluene	m/p-Xylene	o-Xylene	1,2-Dichlorethane	1,3-Butadiene	Ethylbenzene	Styrene
AN	T ^a (n=5)	AM	24.68	1.05	6.12	2.20	3.29	2.11	1.75	2.05	4.27	1.35
		SD	17.25	0.56	5.15	1.11	1.97	1.71	0.00	3.13	2.53	0.00
	C ^b (n=6)	AM	31.72	1.88	6.85	2.08	1.16	0.71	0.24	2.17	3.44	0.48
		SD	31.18	0.87	6.14	1.42	0.54	0.33	0.15	2.88	5.59	0.32
AA/AE	T (n=4)	AM	10.54	3.66	1.81	2.07	4.87	10.65	2.26	0.65	1.25	1.76
		SD	13.80	4.05	1.10	1.19	5.33	13.64	1.01	0.00	0.00	0.82
	C (n=8)	AM	11.68	0.84	1.87	3.65	1.65	1.45	0.18	0.03	10.20	7.78
		SD	14.74	0.89	2.19	5.88	0.98	1.12	0.15	0.00	14.82	12.44
PVC	T (n=6)	AM	84.38	9.40	1.38	6.90	8.24	1.35	5.52	0.65	1.75	1.62
		SD	84.86	16.52	0.68	12.96	14.25	0.00	6.75	0.00	0.77	0.67
	C (n=8)	AM	71.14	8.66	0.79	5.72	2.08	1.32	5.82	0.21	1.72	0.68
		SD	77.07	15.90	1.27	11.47	2.02	1.46	8.25	0.34	1.38	0.66
PABS	T (n=4)	AM	2.87	2.65	1.84	1.74	7.10	5.11	1.75	0.90	3.41	58.19
		SD	4.45	3.70	1.14	1.28	4.71	2.58	0.00	0.50	1.32	55.80
	C (n=6)	AM	1.87	0.16	0.77	1.20	2.07	2.19	0.58	0.19	3.13	38.90
		SD	4.33	0.31	1.36	1.47	2.14	2.20	0.63	0.29	2.38	70.67
UR3	T (n=11)	AM	43.50	1.74	1.43	7.46	6.05	5.40	1.75	0.98	2.31	1.23
		SD	58.67	2.49	0.80	9.81	7.94	6.19	0.00	0.71	2.84	0.24
	C (n=12)	AM	38.76	1.37	1.29	6.12	2.46	1.66	0.23	0.26	0.79	0.34
		SD	59.06	4.36	3.80	10.09	5.80	4.44	0.34	0.44	1.93	0.46

Table 1. Continued

Factory	Item	Statistics	Concentration (unit: p.p.b.)									
			Acetone	n-Hexane	Benzene	Toluene	m/p-Xylene	o-Xylene	1,2-Dichlorethane	1,3-Butadiene	Ethylbenzene	Styrene
OR3	T	AM	34.17	3.28	4.20	1.10	3.54	1.35	1.75	0.80	1.69	1.35
	(n = 6)	SD	21.64	5.61	6.81	0.00	4.53	0.00	0.00	0.36	0.88	0.00
	C	AM	31.23	0.69	3.27	0.91	1.15	0.76	0.32	0.52	0.68	0.15
	(n = 8)	SD	45.04	0.48	4.40	0.55	0.40	0.94	0.29	0.73	0.88	0.09
OL1	T	AM	29.28	2.32	10.73	3.78	3.89	2.14	1.75	5.14	2.41	2.09
	(n = 6)	SD	9.90	1.48	10.92	3.44	2.77	1.94	0.00	6.57	1.56	0.86
	C	AM	27.40	2.09	11.74	3.47	2.41	1.55	0.47	5.67	2.70	1.78
	(n = 6)	SD	23.08	2.81	10.92	3.10	1.63	1.37	0.24	7.13	2.56	2.06
OL2	T	AM	28.43	1.11	11.49	1.70	4.42	2.83	1.75	3.55	1.25	1.35
	(n = 6)	SD	28.62	0.76	16.68	0.93	4.35	2.86	0.00	5.91	0.00	0.00
	C	AM	27.11	1.15	15.18	5.64	3.26	1.52	0.51	5.32	1.18	1.83
	(n = 8)	SD	31.97	1.01	18.83	5.34	2.28	1.40	0.62	4.94	1.30	3.37
OL3	T	AM	47.62	3.06	43.42	5.68	3.24	3.22	1.75	2.95	1.71	2.56
	(n = 7)	SD	48.45	2.56	72.65	9.81	3.07	3.81	0.00	3.56	1.04	2.01
	C	AM	45.06	1.96	37.09	7.02	1.47	1.06	0.67	2.22	0.94	1.93
	(n = 8)	SD	58.92	2.54	67.56	10.37	1.54	1.35	0.80	2.54	1.35	3.43
DEHP	T	AM	32.15	2.41	2.04	5.57	5.04	7.96	1.76	64.24	1.25	1.35
	(n = 6)	SD	43.16	1.93	2.19	7.19	8.59	11.93	0.01	130.74	0.00	0.00
	C	AM	36.14	0.78	1.05	1.86	1.90	2.14	0.17	40.31	0.98	0.77
	(n = 8)	SD	47.04	1.39	2.01	2.69	1.61	2.06	0.13	105.48	1.26	0.53

Table 1. Continued

Factory	Item	Statistics	Concentration (unit: p.p.b.)									
			Acetone	n-Hexane	Benzene	Toluene	m/p-Xylene	o-Xylene	1,2-Dichlorethane	1,3-Butadiene	Ethylbenzene	Styrene
BPAI	T (n = 4)	AM	20.45	0.80	1.55	1.10	2.70	2.98	2.27	19.68	7.58	1.84
		SD	24.38	0.00	1.20	0.00	2.90	2.43	1.05	34.00	7.35	0.97
	C (n = 8)	AM	46.49	0.65	1.12	1.57	1.84	0.84	1.65	13.28	2.95	0.19
		SD	53.63	0.60	0.94	2.32	2.04	1.12	1.78	24.66	4.68	0.11
1,4-BG	T (n = 5)	AM	16.67	1.14	5.48	1.32	3.22	1.35	3.94	7.50	1.89	1.35
		SD	17.87	0.47	3.17	0.50	3.56	0.00	3.45	7.74	1.42	0.00
	C (n = 8)	AM	21.03	0.70	3.53	1.31	1.18	2.54	1.52	6.69	0.65	0.29
		SD	16.92	0.55	2.56	0.61	0.64	3.39	2.18	7.29	0.33	0.14
Total	T (n = 70)	AM	34.35	2.73	8.25	3.90	4.73	3.82	2.29	8.12	2.44	3.54
		SD	46.06	5.51	25.40	6.74	6.29	5.80	2.32	37.13	2.75	12.80
	C (n = 94)	AM	33.51	1.75	6.84	3.57	1.91	1.48	1.03	6.38	2.33	3.83
		SD	46.16	5.23	22.11	6.43	2.50	2.21	2.87	31.87	5.32	19.27

^aT represents the measurements taken by thermal desorption tubes.^bC represents the measurements taken by canisters.^cThe samples were not analyzed for the chemicals.

Table 2. Simple linear regression analyses of 10 VOCs' concentration measured by pairwise samples in 12 factories

Chemical	N	Linear regression				
		Pearson correlation coefficients (<i>r</i>)	Slope	P-value	R ²	Adjusted R ²
Acetone	69	0.992	1.024	0.000	0.984	0.984
<i>n</i> -Hexane	69	0.891	0.904	0.000	0.794	0.790
Benzene	69	0.997	0.972	0.000	0.993	0.993
Toluene	69	0.865	0.915	0.000	0.747	0.744
<i>m/p</i> -Xylene	69	0.489	0.212	0.000	0.240	0.228
<i>o</i> -Xylene	69	0.373	0.140	0.001	0.139	0.127
1,2-Dichloroethane	69	0.867	1.227	0.000	0.752	0.749
1,3-Butadiene	66	0.999	1.010	0.000	0.998	0.998
Ethylbenzene	57	0.275	0.655	0.037	0.075	0.059
Styrene	57	0.974	1.852	0.000	0.949	0.948

In this study, the measurements of some VOCs taken by thermal desorption tubes were highly correlated with those taken by stainless steel canisters. Comparing the cost and portability of using thermal desorption tubes and stainless steel canisters for VOCs' sampling and analysis, the thermal desorption tubes have the advantage of serving as routine exposure sampling devices for occupational exposure assessment. In addition, the thermal desorption tubes can reduce the usage of organic solvents for sample desorption and have much lower LODs in comparison with charcoal or silica gel tubes traditionally used in occupational and environmental measurements. Although various degrees of systematic errors for different compounds are shown in this study, more applications of thermal desorption tubes for measuring occupational and environmental hazardous agents are anticipated due to their convenient and easy usage.

Due to the complexity and variability of VOCs in air, it is difficult to find a sampling approach suitable for every monitoring scenario. In this study, we assumed that the canisters were gold standard air samplers and provided the most accurate data. However, some studies indicated that the canister sampling might not provide quantitatively accurate results for some high

reaction, polar or higher boiling compounds due to the problems of sample stability, recovery, uncleanliness, as well as the effect of temperature and moisture (Coutant, 1992; Batterman *et al.*, 1998; Daughtrey *et al.*, 2001; Hayes *et al.*, 2007). In this study, Table 1 shows negative biases for the canisters, that is, higher concentrations measured by the thermal desorption tubes than the canisters, for several compounds, e.g. for the xylenes. This could be expected under some monitoring and analytical conditions due to incomplete recovery from the canisters. Therefore, the low correlations for the xylenes observed in Table 2 might not be related to the bad performance of the thermal desorption tubes but the incomplete recovery from the canisters.

The flow rate of active sampling used for thermal desorption tubes was suggested at a constant 5–200 ml min⁻¹ (optimum is 50 ml min⁻¹) (US EPA, 1999b; Woolfenden *et al.*, 2010a). In this study, the high end of the flow rate range was used to increase the collection of VOCs. However, this high flow rate might result in the issue of sampling breakthrough of VOCs. If a lower flow rate had been used in this study, better results might have been observed in this study. Therefore, to reduce the error of VOCs measurement

of using thermal desorption tubes, the sampling flow rate should be set up at a value close to the optimal setting.

Recent developments in thermal desorption tube sorbents enable collection of VOCs over a wide volatile range. In addition, the designs of multi-bed sorbent tubes have improved the recovery of many volatile compounds to be quantitatively sampled and analyzed. New technical advances in thermal desorption instrumentation, including sample recollection, cryo-trapping system, electrically cooled sorbent trapping, etc., make a great improvement in analytical accuracy and flexibility for commonly encountered compounds in occupational and general environments. All these can effectively lower the detection limits of thermal

desorption tube method for quantifying VOCs to achieve the levels of comparable to those of the stainless steel canister method. Thus, the reduction of the systematic errors of the thermal desorption tube method observed in this study becomes possible. The accuracy and precision of the thermal desorption tube method for measuring certain VOCs can be improved. It is possible to anticipate that the thermal desorption tube method provides the same quality data as the stainless steel canister method.

CONCLUSION

Based on the results of VOCs' measurements from both thermal desorption tubes and stainless steel canisters in 12 petrochemical factories at the

Figure 1 Scatter plots and regression lines of VOCs' concentrations measured by two sampling methods.

Table 3. Paired *t*-test of 10 VOCs' concentrations measured by pairwise samples in 12 factories

Chemical	Sample size	Thermal adsorption tube		Canister		Paired <i>t</i> -test			
	<i>N</i>	Mean ($\bar{X}_t$)	SD (S_t)	Mean ($\bar{X}_c$)	SD (S_c)	Mean _{diff} ($\bar{X}_d$)	SD (S_d)	<i>t</i>	<i>P</i> -value
Acetone	70	34.35	46.06	32.98	47.56	1.36	6.08	1.88	0.065
<i>n</i> -Hexane	70	2.73	5.51	1.63	5.59	1.10	2.59	3.54	0.001*
Benzene	70	8.25	25.40	7.27	24.79	0.98	2.13	3.86	0.000*
Toluene	70	3.90	6.74	3.92	7.14	0.03	5.63	-0.01	0.973
<i>m/p</i> -Xylene	70	4.73	6.29	1.88	2.72	2.85	5.50	4.33	0.000*
<i>o</i> -Xylene	70	3.83	5.80	1.29	2.18	2.53	5.38	3.94	0.000*
1,2-Dichloroethane	70	2.29	2.32	1.19	3.29	1.10	1.72	5.34	0.000*
1,3-Butadiene	67	8.12	37.13	7.70	37.53	0.42	1.67	2.04	0.045*
Ethylbenzene	58	2.44	2.75	2.72	6.56	-0.28	6.38	-0.33	0.742
Styrene	58	3.53	12.80	4.90	24.32	-1.37	12.20	-0.86	0.396

**P*-value < 0.05.

Mailiao Industrial Complex, the emission of VOCs was well controlled. Most of the time, the work environment of the petrochemical factories only had low

concentrations of the measured VOCs. The comparison between the concentrations of each of the 10 selected VOCs measured by the two sampling

Table 4. Method detection limits of VOCs measured by thermal desorption tubes and stainless steel canisters

Chemical	Method detection limits (p.p.b.)	
	Stainless steel canisters	Thermal desorption tubes
Acetone	0.200	0.500
<i>n</i> -Hexane	0.076	0.500
Benzene	0.049	0.500
Toluene	0.066	1.000
<i>m/p</i> -Xylene	0.089	0.500
<i>o</i> -Xylene	0.115	0.500
1,2-Dichloroethane	0.150	3.520
1,3-Butadiene	0.054	1.300
Ethylbenzene	0.075	2.500
Styrene	0.204	2.700

methods, the concentrations of acetone, benzene, and 1,3-butadiene measured by the thermal desorption tubes had high accuracy and precision; those of *n*-hexane, toluene, and styrene had moderate accuracy and precision; those of *m/p*-xylene, *o*-xylene, 1,2-dichloroethane, and ethylbenzene had low accuracy and precision. New developments in thermal desorption tube sorbents and the designs of multi-bed sorbent tubes enable collection of VOCs over a wide volatile range and improve the detection limits of thermal desorption tubes for quantifying many volatile compounds. Furthermore, the analytical detector used for thermal desorption tubes can be changed to a better detector like the MS used for the canister analysis. Thus, the reduction of the systematic errors of measuring the VOCs by using the thermal desorption tubes observed in this study becomes possible. The accuracy and precision of using the thermal desorption tubes for measuring the VOCs can be improved. It is possible to anticipate that the use of thermal desorption tubes for measuring the VOCs can provide accurate and precise measurement data. More applications of thermal desorption tubes for measuring occupational and environmental hazardous agents can be expected.

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