

Development and Application of an On-site Continuous VOCs Sensing Network

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Accurate sampling and analysis techniques must be established to control the emission of Volatile Organic Compounds (VOCs) and identify the performance of pollution reduction of control equipment. CSC adopts the sampling method which is approved by the Environmental Protection Agency to collect VOCs in the air and conduct offline GC/MS analysis, successfully establishing a testing laboratory that meets quality control requirements. In addition, for the purpose of conducting a long-term continuous study and controlling of VOCs in the air of the plant, we also partner with Tricorntech Corp. to develop an online and continuous monitoring system. The system includes the VOCs continuous monitoring device named as Miniaturized Total Analysis Platform (MiTAP), industrial chassis, anemometer, and real-time data collection interface. The core technology, MiTAP, integrates sampling/concentration, micro-GC, and detection modules, enabling total solution for sampling/analysis and data processing in one device. Take 10 VOCs (acetone, benzene, ethylbenzene, naphthalene, styrene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, toluene, m/p-xylene, and o-xylene) for example, the accuracy was verified by GC/MS and MiTAP concurrently, showing the R value lies between 0.899 and 0.997, which was highly correlated. Moreover, by comparing the canister sampling followed by GC/MS analysis with on-site continuous monitoring of MiTAP, the results showed that the measured concentrations and trends were fully consistent with each other. We have successfully set up eight monitoring systems at the potential VOCs emission spots since February 2016, obtaining VOCs data for each process plant. By continuously monitoring the VOCs in the plant area, it can be immediately known when abnormally excursions occur. Determination of the emission sources and possible emission sites can be made possible with the aid of the meteorological information of the anemometers as well as the concentrations of the eight VOCs. Further reduction control actions can be readily taken accordingly.

Keywords: VOCs, MiTAP, GC/MS

1. INTRODUCTION

Volatile Organic Compounds (VOCs) are carbon-based compounds that have vapor pressure to vaporize then enter the atmospheric environment⁽¹⁾. VOCs and nitrogen oxides are key ingredients in the photochemical formation and results in the formation of ozone, and other oxidants, which have great influence on atmospheric chemistry, regional air quality, and climate change^(2,3). Fugitive VOCs emission from industrial areas in Taiwan has posed growing health concerns to workers and nearby communities with chronic exposure^(4,5). The VOCs monitoring in specific industrial parks has been enforced by the Taiwan Environmental Protection Agency (EPA) as the persistent effort in VOC emission reduction. China Steel Corporation (CSC) is sited in Linhai Industry Park, where more than 30 industry sectors are located with around 500 manufacturing plants contributing to a complex mixture of various fugitive VOCs. Although the amount of fugitive VOCs emitted may be individually small, the cumulative emissions of the plants can be considerable. The exact emission source is hardly discriminated as the neighboring

plants possibly utilize similar raw materials with cross interference on the fugitive VOCs. Moreover, the emission frequency can be closely correlated with the manufacturing process, cycles, and schedules. Unexpected leakage may consequently contribute to both random and periodic sources of VOCs. It is highly desirable that the fugitive VOCs can be precisely monitored in the facility to provide valuable information to the controller for manufacturing process optimization.

The regulation, which CSC has long complied, requires VOCs collection using canisters followed by off-site analysis with gas chromatography mass spectrometry (GC/MS) in a laboratory. The GC/MS method provides accurate results on speciated VOCs analysis, allowing CSC to evaluate the nominal concentration of each compound within the production plants. However, the GC/MS analysis is time consuming, expensive to implement, and needs a specialist to perform complex system operations as well as intensive data interpretation. As a result, the standard offline lab method is limited in providing the facility controller good temporal resolution and spatial distribution of VOCs for leakage

remediation and fabrication process improvement⁽⁶⁾.

In this study, eight in-plant VOCs monitoring sites were selected around the production facilities at the boarder of CSC, forming a sensing network to monitor fugitive VOCs arisen from complex manufacturing activities simultaneously. The monitoring network allows CSC to investigate the fugitive VOCs in correlation with material/odor inventory of each plant, manufacture process, and hot spots where certain VOCs may routinely be released into the ambient. Real-time monitoring of VOCs at an unprecedented time/space scale is realized by utilizing online speciated VOCs analysis systems, MiTAP series (Miniaturized Total Analysis Platform). Designed, manufactured, sold and serviced by Tricorntech Corporation, MiTAPs are portable real-time gas analyzers detecting multiple VOCs on site and in real-time. During 2012~2014, CSC collaborated with Tricorntech and played an important part in the in-situ test. Hence, MiTAPs are suited to provide data at a resolution that may be linked with locating the emission of fugitive VOCs, exposure, and effective action plans ultimately for emission control.

2. EXPERIMENTAL METHOD

2.1 Standard VOCs analyzing methods

About 2015, we successfully established the VOCs analysis methods for ambient air quality in CSC fields. The analysis procedure is mainly followed by the Taiwan EPA Method NIEA A715.15B⁷ and USEPA Method TO-15⁽⁸⁾. Sampling and laboratory equipment for VOCs are shown in Figure 1.

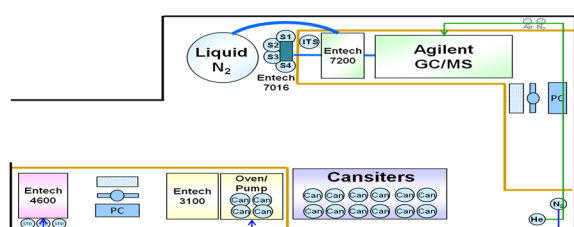


Fig.1. Sampling and laboratory equipment for VOCs.

An air sample was collected by a 6L stainless canister. The canister was cleaned before and after the sample analysis using the Canister Cleaning System (Entech 3100), which consists of a computerized control module with vacuum pumps and an oven containing a passivated manifold with fittings for connection of canisters. The control software initiates the cleaning of canisters by heating coupled with multiple pressurization/evacuation cycles. A blank sample is analyzed from each cleaning batch as a control to assure proper cleaning has been achieved. After evacuated to -30 mmHg, the sample canister is ready for collecting the air sample. For a 1-hour sample time, we need to verify that the flow controller is

correctly calibrated and set to 100 cc/min. Then, carry the canister to all the sampling sites. Open the canister valve and record its initial pressure reading on the absolute gauge. After the sample period, record the final pressure reading in psig and close the canister valve. Then take the canisters back to the laboratory for GC/MS analysis.

Analysis of target substances designated as VOCs was performed by automatic pre-concentrator system (Entech 7200) with subsequent capillary gas chromatography (GC, Agilent 7890A) coupled with a mass spectrometry detector (MS, Agilent 5975C). The GC/MS is interfaced with an Entech 7200 pre-concentrator and Entech 7016D autosampler. The Entech 7200 is designed to concentrate the VOCs which are at ppb levels in ambient air by flowing the sample through three consecutive cryogenic traps at different controlled temperatures. This results in very low detection limits not obtainable without cryogenic preconcentration. The Entech 7016D is a 16-position canister sampler interfaced with the GC/MS. The autosampler pulls 200mL of each sample into the GC/MS for analysis. There are more than 90 VOCs that could be measured in T64 VOC laboratory. The pre-concentrator instrumental settings and operating conditions are shown in Table 1 and GC/MS conditions are shown in Table 2.

Table 1 Instrument conditions of Pre-concentrator

	Pre-concentrator Operating Parameters
Instrument	Entech 7200
Sample Standby Temp.	30°C
Trap Cooldown Temp.	-160°C
Sample Sweep	1 min
Sample Desorption Time	4 min
Sample Desorption Temp.	250°C
Cryo Focusing Temp.	-170°C
Cryo Inject Temp.	225°C
Trap Desorption Temp.	250°C

2.2 Novel Continuous VOCs Monitoring System-MiTAP

TricornTech MiTAP is a portable on-site continuous VOC analyzer (~19cm×26cm×35cm, W×H×D) using micro gas chromatography (micro-GC) with sub-ppbv

Table 2 Instrument conditions of GC/MS

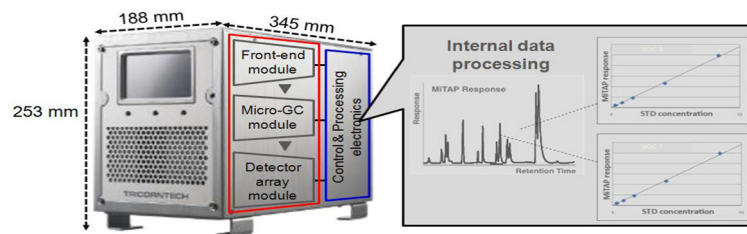
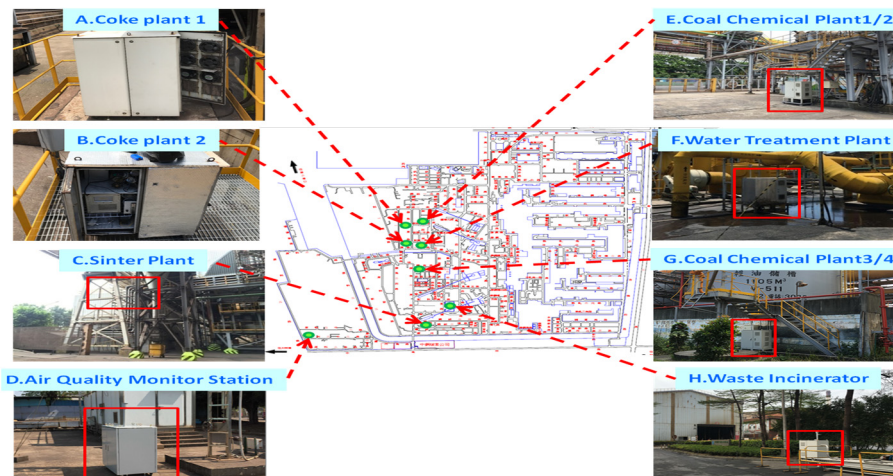
GC/MS Operating Parameters for VOCs Analysis	
Instrument	Agilent 6890GC 5975MSD
Analytical Column	DB-624 60 m × 0.25 mm, 1.8 μ m
LTM program	40°C(10.5 min)→96°C(8 min) at 6°C/min →210°C(9 min) at 12°C/min
Column flow	1.3 mL/min
Carrier gas	Helium
Scan mass range	29-265 amu

level limit of detection (LoD). As shown in Figure 2, the analyzer consists of three main gas analysis modules: front-end module, micro-GC module, and detector array module. The miniaturized front-end module provides automatic air sampling and concentration via an internal flow control pump. The collected VOCs sample is then thermally transferred and separated by the micro-GC module and the concentrations of analytes are determined by detector/sensor array module. Specific 10 VOCs such as acetone, benzene, ethylbenzene, naphthalene, styrene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, toluene, m/p-xylene, and o-xylene are individually calibrated and certified in this study. In each 60-minute

analysis cycle, the analyzer's integrated data process engine directly calculates VOC concentrations based on its calibration database. Each detected VOC result is then displayed and also recorded within the system which can be exported for further histogram analysis.

2.3 VOC sensing network in CSC

A gas sensing network approach for on-site continuous VOC monitoring was proposed and implemented in CSC, Taiwan. Eight air VOC monitoring stations were installed besides the production facilities forming a VOC sensing network as illustrated in Figure 3. Each

**Fig.2.** Illustration of portable VOC analyzer MiTAP.**Fig.3.** VOC sensing network in CSC.

VOC monitoring station was equipped with a customized MiTAP VOC analyzer, which was able to detect specific 10 compounds in each analysis. An anemometer, Young 86000, was also installed along with each VOC monitoring station to provide wind field information, such as wind speed and directions at corresponding station. Furthermore, the monitoring stations were connected to remote server and control center, which communicated and received the VOC analysis results from all VOC analyzer and anemometers.

When abnormal VOC concentration triggers the present threshold, the control center can determine and take action such as alarming or sending out an email to person in charge.

3. RESULTS AND DISCUSSION

3.1 GC/MS vs. MiTAP comparison

In order to check the accuracy of MiTAP analysis, we need to compare and contrast with the MiTAP data. Specific VOCs were collected into canisters in fields and are measured by MiTAP and GC/MS at the same time. Figure 4 shows the correlation between MiTAP and GC/MS for the acetone, benzene, ethylbenzene, naphthalene, styrene, toluene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, m/p-xylene, and o-xylene. All compounds have R-value between 0.899 to 0.997. Overall, the data shows high correlation (> 0.8) between the MiTAP and the conventional GC/MS analyses for all the

VOCs. The correlation data presented in this work demonstrates that the accuracy is acceptable.

Both systems Canister+GC/MS and MiTAP were conducted to measure toluene and benzene in the field test, and the results demonstrated high correlation in both systems as shown in Figure 5. It shows that the concentrations of the two systems are consistent and reliable.

3.2 On-site continuous VOC monitoring

The proposed VOC monitoring network has been operated continuously for more than two years with around 100,000 VOC data sets collected. Figure 6 shows the total VOC concentrations detected by MiTAP analyzers at all eight stations last year (2017~2018). The average total VOC concentrations are 17.9, 20.2, 7.1, 16.7, 8.9, 9.0, 15.8 and 15.1 ppb for A to H stations, respectively. The highest concentration was in Station B (coke plant 2) and the lowest concentration was in Station C (sinter plant). Furthermore, Station D (air quality monitoring station) located at CSC south-west border showed the higher VOC concentrations could be influenced by external pollution sources by the wind field. The reason why Station D is different from others will be discussed in the next section.

3.3 Case study for abnormal results

Table 3 lists the interested VOCs detected by

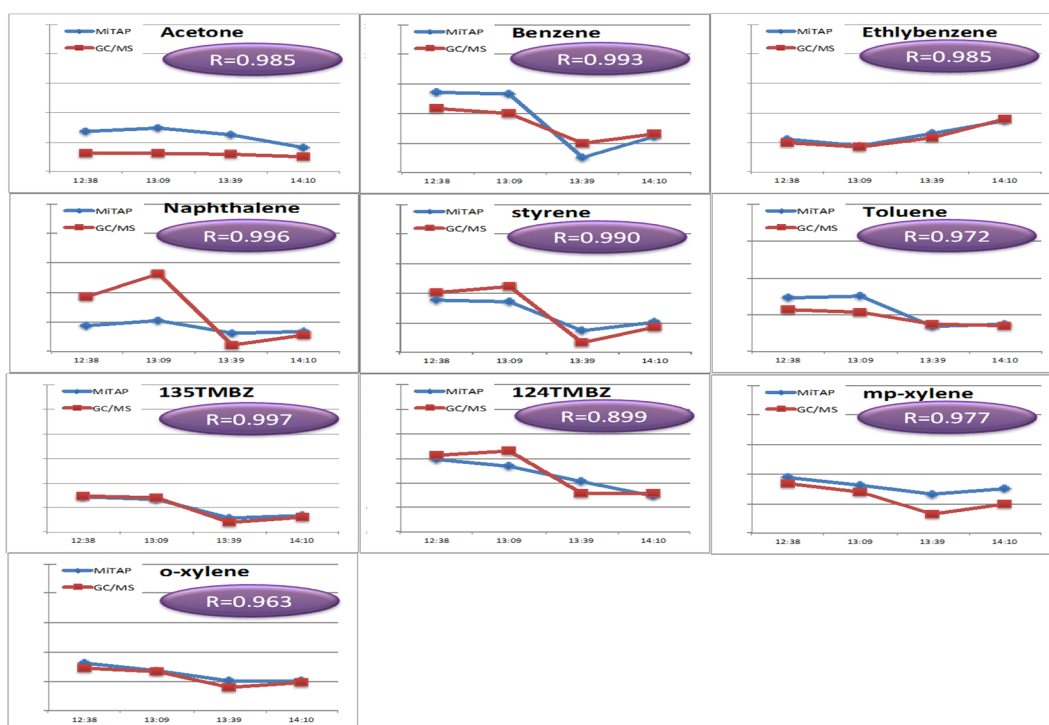


Fig.4. Analysis correlation between MiTAP and GC/MS.

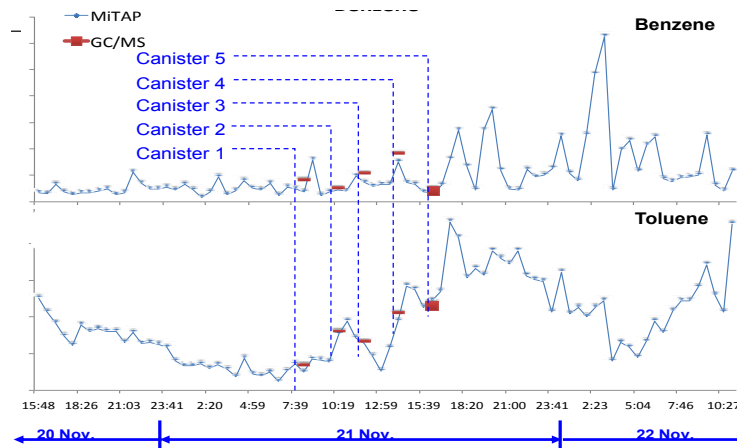


Fig.5. Comparison of “Canister+GC/MS” vs. “MiTAP only” analysis data.

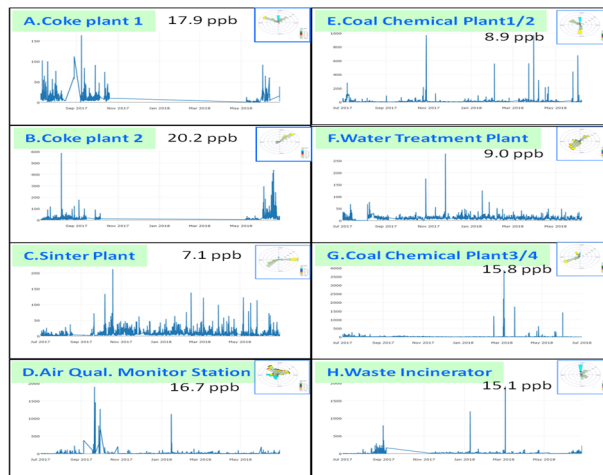


Fig.6. 2017~2018 Total VOC monitoring results at 8 stations in CSC.

Table 3 VOCs of interest detected by MiTAP analyzers at stations D, E, and F. Unit in ppbv

		Acetone	Ethylbenzene	Styrene	Toluene	m/p-xylene	o-xylene
Station D	Max	41.9	20.4	34.6	55.2	21.4	17.9
	Min	0.6	2.6	0.2	12.8	2.0	0
	Ave.	8.8	9.5	11.1	23.7	9.9	7.3
Station E	Max	8.6	5.1	1.8	16.1	14.4	5.4
	Min	2.2	0	0.1	2.2	0.6	0.3
	Ave.	4.3	0.2	0.4	5.6	2.0	0.9
Station F	Max	44.9	12.4	4.2	13.6	43.6	17.2
	Min	1.5	0	0.1	1.3	0	0
	Ave.	4.7	0.5	0.6	4.1	3.3	1.0

MiTAP at Stations D, E and F. The VOCs are at low levels (< 5 ppbv for toluene) at Stations E and F near the coal chemical plant. Station D is located at the southwest boundary of the plant away from the manufacturing

facilities, and the detected VOC concentration is significantly higher (> 30 ppbv for toluene) than Station E and F. Figure 7 shows that the toluene concentrations of Station E and F were at regular fluctuation cycle (<1 ppbv

~ 10 ppbv) during the daytime, which was closely related to the production activity of CSC. Nevertheless, the toluene at Station D has a significant higher concentration without any correlation with the toluene concentration at Stations E and F, which appeared that the VOCs should not be from CSC production activity.

Figure 8 illustrates the wind field observed by Stations D, E and F at the same period. It can be seen that both the wind directions were from the northeast at Station E and F. On the contrary, the wind direction of Station D was mainly from the west and southwest. Therefore, the high VOC concentrations detected by station D should come from the southwest region outside CSC.

4. CONCLUSIONS

VOCs emission is becoming a serious problem in many industrial plants. This study establishes two technologies of monitoring VOCs in CSC. First, we use vacuumed canister to collect air samples, and then follow by

off-site analysis with GC/MS in the laboratory. The GC/MS method provides accurate results on speciated VOCs analysis. The method allows evaluating the nominal concentration of each compound within the production plants. Second, a VOC detection network includes MiTAP collaborated with Tricorntech, which links with the emission locations, exposure, and control actions. We can obtain VOC emission information immediately. Besides, the server will notify the corresponding person by e-mail and determine the possible emission source according to wind direction and concentration distribution when an abnormal high concentration event occurs.

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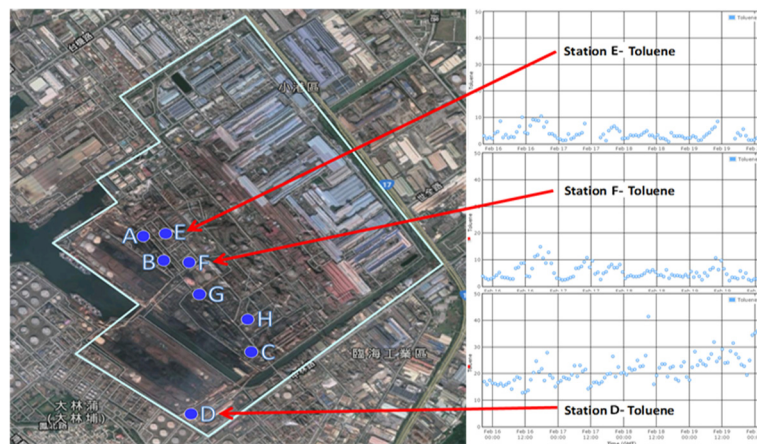


Fig.7. Illustration of toluene concentration trend observed by on-site monitoring stations.

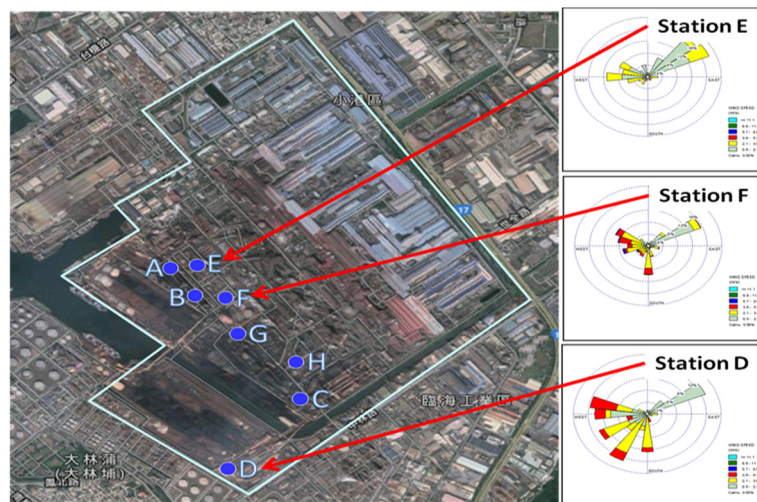


Fig.8. Wind fields observed at the stations.

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