Sampling and Analysis of Volatile Organic Compounds Using US EPA Method 325 at Refinery Perimeters

Application Note
Environmental

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Abstract

This application note demonstrates a method-compliant solution that consists of both hardware and software packages on VOC monitoring at refinery perimeters. Procedures and results are described in each stage of the method, which includes monitoring station setup, VOC passive sampling and lab analysis.

Introduction

Petroleum refining is a major industry in the United States, where the heavier oil is processed into lighter components such as gasoline and diesel fuels. In the production process, benzene and other toxic pollutants are released from various sources, including combustion devices, production units, storage tanks and wastewater treatment units. Scientific studies have found that the acute exposure to benzene will negatively impact the development of infants and the blood system[1], whereas the chronic exposure can affect the human blood system and increase the risk of cancer[2]. In light of hazard prevention, EPA published method 325 which includes a requirement that refineries are to measure the average benzene concentration at the perimeter of the plant[3,4]. The monitoring procedure is described in the companion method 325A and 325B, starting from sampler deployment based on the geometry of the plant, followed by a 14 day passive sampling onto clean thermal desorption tubes, and finishing at a laboratory analysis by using thermal desorption as the sample introduction technique to inject target compounds into a gas chromatography / mass spectroscopy detection system. If the testing result yields a concentration of benzene above 9 mg per cubic meter over a 12 month rolling average, the method states the refinery to perform a root cause analysis.

Experiment Setup

Monitoring Station

EPA Methods 325A outlines details of sampler deployment, where monitoring stations are placed at 20° intervals beyond the fenceline boundary. For facilities with stations over 50 meters apart by following this deployment plan, additional monitoring stations are required to be added. The monitoring station deployed in this application note was manufactured by Camsco, who also provides a revolutionary fenceline monitoring software TubeTrack™ Field installed on a mobile device to assist the deployment. The monitoring station from Camsco is a weatherproof shelter that holds 4 passive sampling tubes. Each station is marked with a two-digit identification number. An optional Near Field Communication (NFC) tag is available to further streamline the information flow. The monitoring station is usually mounted on a pole as shown in Figure 1a. The TubeTrack™ Field mobile app stores the location of the station based on either the identification number or the NFC tag information and synchronize the data with other TubeTrack™ programs, including TubeTrack™ Explorer and TubeTrack™ Lab through the cloud.

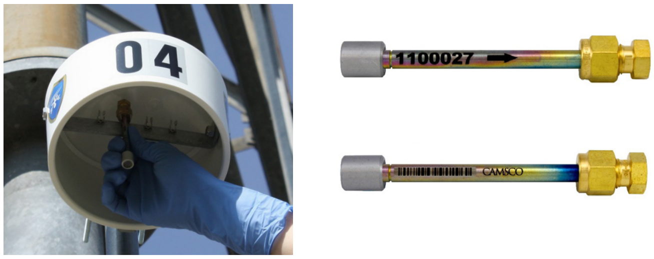


Figure 1a (left): Camsco monitoring station. Figure 1b (right): Camsco EPA 325 thermal desorption tube with diffusive cap and compression cap.

VOC Passive Sampling

Camsco EPA 325 thermal desorption tube was used as the sampling device to collect VOCs. Each tube measured ¼” outer diameter by 3.5” length and was inert coated out of 316L stainless steel. The sorbent was Carbopack X with the uptake rates well studied on various VOCs[4]. Each thermal desorption tube was uniquely identified with a human readable number as well as a scannable barcode. A directional arrow, which indicates the sampling air flow was printed on the tube to reduce operator error. Figure 1b shows a complete tube assembly ready for deployment where a diffusive sampling cap and brass compression cap were installed on the tube. To improve efficiency and reduce human errors in establishing chain of custody for field personnels, Camsco developed a sampling kit, as shown in Figure 2a, to provide all necessary equipment to complete the 14 day sampling event. Another powerful tool to achieve this goal is the TubeTrack™ Field app, where all critical data including tube ID, station location, start and stop times/dates, sample type is synchronized through the cloud (Figure 2b).

Figure 2a (left): Camsco sampling kit. Figure 2b (right): Camsco TubeTrack™ Field mobile app to streamline the information flow.

Laboratory Analysis

Instrument

The sample introduction device was a CDS 7550S 72-position automated thermal desorber with a Camsco 1/8” x 115 mm focusing trap. A Shimadzu QP-2010 GC/MS system with GS-Tek GsBP-5MS capillary column was used as the separation and detection instrument. Experimental parameters are listed below:

7550S Thermal Desorber:
Valve oven: 220 °C
GC transfer line: 250 °C
Tube purge flow: 30 mL/min
Pre-heat time: 15 s
Tube desorber:
Rest temp.: 37 °C
Dry purge temp.: 37 °C
Dry purge time: 2 min
Desorb temp.: 315 °C
Desorb time: 8 min
Trap:
Rest temp.: 45 °C
Desorb temp.: 315 °C
Desorb time: 4 min

GC/MS:
GC conditions
Oven temp.: 50.0 °C
Injection temp.: 180 °C
Injection mode: Split
Column Flow: 1.01 ml/min
Split Ratio: 30.0
Temp. program:
50.0 °C hold 1 min
10.0 °C ramp to 100.0 °C
40.0 °C ramp to 210.0 °C
hold 1.25 min
Mass conditions
Ion Source: 200.00 °C
Interface Temp.: 250.00 °C
Start m/z: 45.00
End m/z: 350.00

Chemicals

BTEX standard was purchased from Sigma-Aldrich (part number CRM47993) with a concentration of 2000 μg/mL for each compound. Toluene-d8 were purchased from Restek and used as internal standard at the concentration of 2,500 μg/mL.

Results and Discussions

To ensure optimized performance, the GC/MS tuning was first completed based on Shimadzu’s specification. The results were listed in Table 1.

Table 1: BFB tuning results

m/z	Ref Mass	Lower Limit %	Upper Limit %	Ratio
50	95	8	40	15
75	95	30	66	39
95	95	100	100	100
96	95	5	9	6
173	174	0	2	1
174	95	50	120	64
175	174	4	9	7
176	174	93	101	94
177	176	5	9	6

The sample pathway in 7550S was inert-coated to minimize carryover as well as thermolysis at high temperatures. A system blank from a pre-conditioned thermal desorption tube was performed after the GC/MS tuning. The data shown in Figure 3 verifies the cleanness of the system.

The method detection limit (MDL) was then calculated by spiking 1 μL of BTEX standard along with 1 μL of internal standard onto 10 separate pre-conditioned thermal desorption tubes. The first row of Table 2 lists the MDL in the unit of absolute mass of each compound. By plugging in the uptake rate (U) into Equation 1, the MDL in the first row was converted to a concentration based MDL in μg/m^3, as shown in the 3rd row of Table 2.

$$C_m = \frac{m_{meas}}{U_{NTP} \times t} \times 10^6 \qquad \text{Eq 1}$$

where C_m is the concentration of target compounds in the air sampled (μg/m^3), m_{meas} is the mass of the compound as measured in the sorbent tube (μg), U_{NTP} is the sorbent based diffusive uptake rate in ambient temperature[5] (ml/min), and t is the exposure time (min).

Table 2: Method detection limits

Compound	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
MDL (ng), n=10	1.56	1.28	1.12	1.48	1.21
U_{NTP} (ml/min)	0.67	0.52	0.46	0.46	0.46
Converted MDL (µg/m^3), n=10	0.12	0.12	0.12	0.16	0.13

Figure 3 depicts an example run during the MDL test. The chromatogram shows narrow peaks with sufficient resolution for all target compounds.

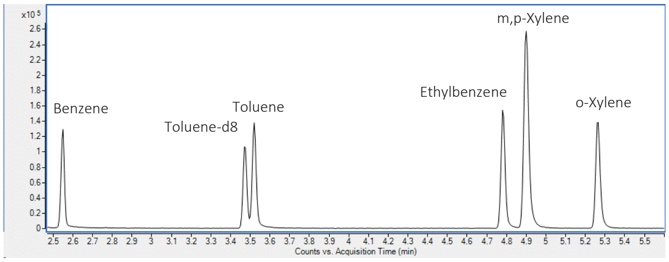


Figure 3: Chromatogram of BTEX sample with the presence of internal standard.

To ensure the efficiency of the thermal desorption system, two consecutive samples, both of which had been spiked with the same amount of 25 μL BTEX standard and were desorbed sequentially. The response from the first sample was compared to the summation of the responses from the two samples to calculate the thermal desorption efficiency. The results are listed in Table 3 and were greater than the minimum 95% requirement.

Table 3: BTEX thermal desorption efficiency from 7550S

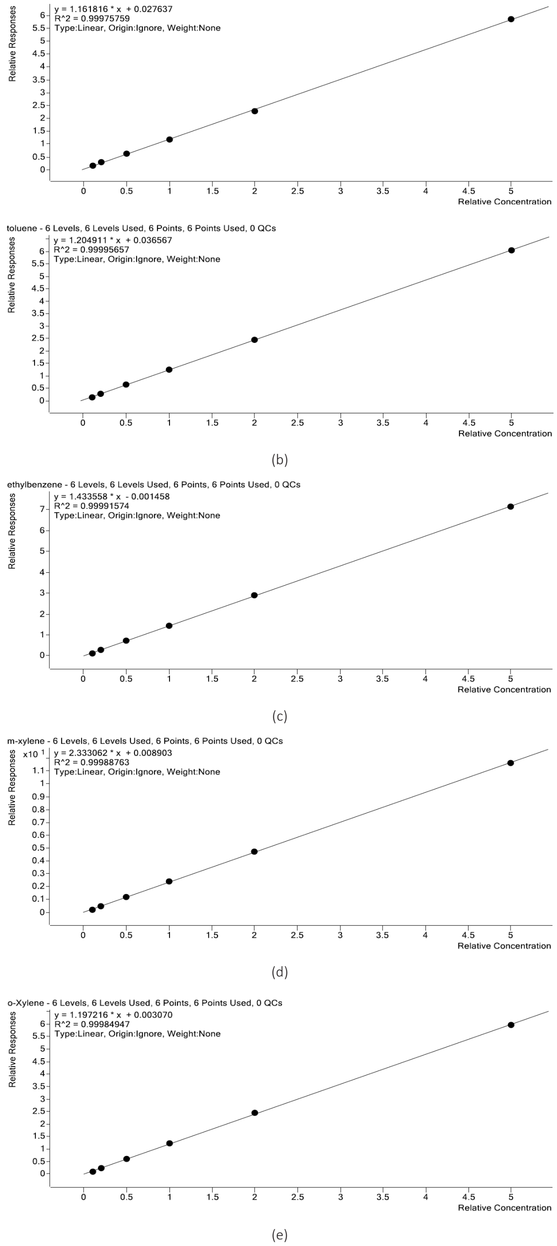
Compound	benzene	toluene	ethylbenzene	m-xylene	o-Xylene
TD efficiency	98.9%	99.2%	99.9%	99.5%	99.7%

The system was further validated by quantifying the carry over. The procedure for the test was to desorb a thermal desorption tube spiked with 25 μL of BTEX standard, and the same thermal desorption tube was immediately desorbed again to evaluate the carryover. Table 4 shows that all compounds had the carryover lower than 0.5%.

The water management function in 7550S was tested by adding 2 μL of water onto one thermal desorption tube with calibration standard spiked to mimic extremely humid samples. The dry purge was set to 100 mL/min for 10 min. The direction of the dry purge flow was in the same direction as sampling. No variation on the chromatogram was observed from the control sample that did not have water introduced, which approved this function.

After thorough system validations, calibration curves were drawn. Six levels of BTEX standards at the concentration of 5 ng, 10 ng, 25 ng, 50 ng, 100 ng, and 250 ng for each compound, along with toluene-d8 internal standard at a fixed 50 ng concentration were spiked onto six thermal desorption tubes respectively. The first point of calibration was picked based on EPA 325B guidance as the first calibration point shall be within five folds of the system MDL. Figure 4 showed the calibration curves along with the regression coefficients, which were all higher than 0.999 within the calibration range.

325B guidance as no more than five times the MDL. Figure showed the calibration data and all the regression coefficients are higher than 0.999 within the calibration range.



(b)

(c)

(d)

(e)

Figure 4: Calibration curves for BTEX: (a) benzene; (b) toluene; (c) ethylbenzene; (d) m,p-xylene; (e) o-xylene

Field samples from 3 monitoring stations were collected and analyzed. The sampling data was directly obtained from the TubeTrack™ Lab application, which is synchronized with the TubeTrack™ Field mobile app. These tubes were deployed on May 26, 2020 at three stations, named 01A, 01, and 02, and harvested on June 9, 2020 after 14 days of sampling. The average temperature during the collection period was documented by the software as 299.9 K, which was used to convert the effective concentration[6] based on Equation 2. Table 4 summarizes the data for all field samples.

$$C_C = \frac{m_{meas} \times 10^6}{U_{NTP} \times \left(\frac{t_{ss}}{298}\right)^{\frac{1}{2}} \times t} \qquad \text{Eq. 2}$$

where C_c is the concentration of target compound at normal ambient temperature, t_{ss} is the average temperature during the collection period at the sampling site (K), and the U_{NTP} is the sorbent based diffusive update rate for each compound (ml/min)

Table 4: BTEX concentration after conversion

Tube ID	Site	Sample type	Benzene	Toluene	Ethyl toluene	m,p-Xylene	o-Xylene
1150749	01	field blank	<MDL	<MDL	<MDL	<MDL	<MDL
1150745	01	field sample	0.52	2.41	0.30	0.34	0.23
1150621	01A	field sample	0.54	2.61	0.27	0.29	0.18
1150617	01A	duplicate	0.52	2.57	0.25	0.24	0.16
1150528	02	field sample	0.53	2.42	0.30	0.38	0.26

Figure 5 shows a chromatogram from Tube ID 1150528. No BTEX compounds were detected on the field blank tube beyond system MDL, which validates the seal of the compression cap during sampling and transportation. For three field samples, the benzene levels are at least an order of magnitude less than the EPA action limit of 9 $\mu g/m^3$. This data was uploaded by the TubeTrack™ Lab (Figure 6a) application, and is available for reviewing through the TubeTrack™ Explorer (Figure 6b) software.

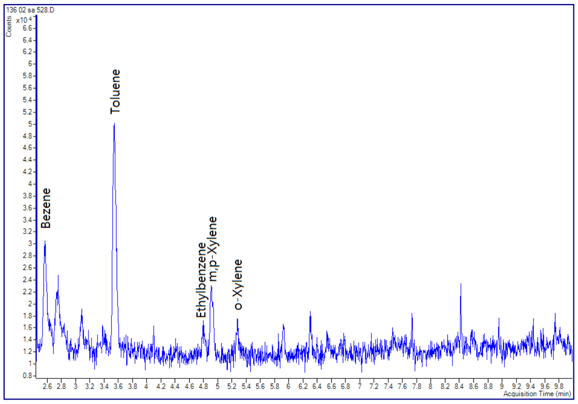
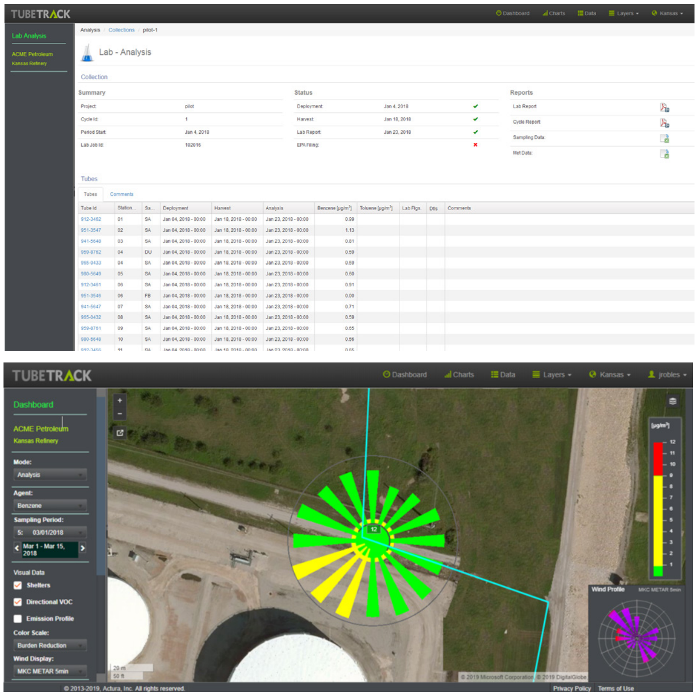


Figure 5: Chromatogram of tube ID 1150528

Field precision was calculated from comparing sample tube 1150621 to its duplicate sample 1150617. The calculated field precision is listed in Table 5 for each compound. The result showed that the precision for all compounds were under the required criteria of 30%.

Table 5: Data on field precision

	Benzene	Toluene	Ethyl toluene	m,p-Xylene	o-Xylene
Field precision	3.5%	1.7%	6.2%	18.5%	15.8%



Summary

Project: pilot
Cycle Id: 1
Period Start: Jan 4, 2018
Lab Job Id: 102016

Status

Deployment: Jan 4, 2018 ✓
Harvest: Jan 18, 2018 ✓
Lab Report: Jan 23, 2018 ✓
EPA Filing: ✗

Reports

Lab Report
Cycle Report
Sampling Data
Met Data

Tube Id	Station...	Sa...	Deployment	Harvest	Analysis	Benzene [µg/m³]	Toluene [µg/m³]	Lab Flgs.	Dtls	Comments
912-3462	01	SA	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.99				
951-3547	02	SA	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	1.13				
941-5648	03	SA	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.81				
959-8762	04	DU	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.59				
965-0433	04	SA	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.59				
980-5649	05	SA	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.60				
912-3461	06	SA	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.91				
951-3546	06	FB	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.00				
941-5647	07	SA	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.71				
965-0432	08	SA	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.59				
959-8761	09	SA	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.65				
980-5648	10	SA	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.56				
912-3456	11	SA	Jan 04, 2018 - 00:00	Jan 18, 2018 - 00:00	Jan 23, 2018 - 00:00	0.65				

Mode: Analysis
Agent: Benzene
Sampling Period: 5: 03/01/2018
Mar 1 - Mar 15, 2018
Visual Data
☑ Shelters
☑ Directional VOC
☐ Emission Profile
Color Scale: Burden Reduction
Wind Display: MKC METAR 5min

Figure 6a (top): TubeTrack™ Lab user interface. Figure 6b (bottom): TubeTrack™ Explorer user interface

Conclusions

This application note has showcased a complete solution that consists of innovative hardware and software from Camsco and CDS Analytical to comply with EPA 325 method. These technologies combined streamline compliance efforts and improve data collection, analysis, and accuracy.

References:

1. California OEHHA. "Technical Support Document for Noncancer RELs." Appendix D at 182
2. ATSDR. "Toxicological Profile for Benzene." U.S. Department of Health and Human Services. August 2007. at 23-24
3. 40 CFR § 63.658 - Fenceline monitoring provisions
4. Method 325B—Volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis
5. McClenny, William A., et al. "24 h diffusive sampling of toxic VOCs in air onto Carbopack X solid adsorbent followed by thermal desorption/GC/MS analysis—laboratory studies." Journal of Environmental Monitoring 7.3 (2005): 248-256.
6. Heidi C. Hayes, Patching the Holes in the Fenceline - Updates to EPA 325 Requirements, Eurofins Air Toxics