

# Passive monitoring of benzene and other hazardous air pollutants at refinery perimeters in accordance with EPA Method 325

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## Abstract

A stepwise approach for volatile organic compounds (VOCs) passive (diffusive) monitoring used in occupational hygiene/personal exposure, indoor air, and ambient air/large-scale environmental monitoring is described. By eliminating the requirement for a sampling pump, diffusive monitoring provides a simple method of collecting the large number of samples required in many air monitoring programs. A range of equipment that allows fully method-compliant deployment of tube-based passive samplers, sample analysis and tube cleaning were used. All these stages were underpinned by a radio-frequency identification tagging system to ensure a robust chain of custody from field to lab.

## Introduction

The US Environmental Protection Agency (EPA) has proposed new legislation for US petroleum refineries to control emissions from storage tanks, flares and coking units. The EPA Method 325-A and B<sup>1</sup> was proposed for passive monitoring of VOCs for fugitive and area sources. It is required to comply with the US Federal Regulation CFR 40<sup>2</sup>. Although benzene is the primary target compound of Method 325, the sampling and analysis methodology can also be used to determine other VOCs, including other hazardous air pollutants without further method development. The Method 325 provides procedures for the preparation, conditioning, blanking, and shipping of sorbent tubes prior to sample collection. When the sampled tubes reach the laboratory, they are analysed using thermal desorption–gas chromatography (TD–GC), typically with detection by mass spectrometry (MS).

Various types of diffusive sampler are available, and the decision on the type of sampler depends on the monitoring scenario. Fenceline (perimeter) monitoring data, together with additional results taken upwind/downwind of the plant and in local population centers, may simply be used to demonstrate that a particular industrial site is or is not contributing significantly to ambient hydrocarbon concentrations. Perimeter measurements can also be used in combination with wind speed/direction data to determine emission levels and distribution of emitted hydrocarbons. This work briefly introduces the diffusive sampling in practice and the analysis of diffusive samples.

## Method 325 A: Field sampling

Up to 24 monitoring locations should be distributed around the perimeter of the refinery, in a pattern that depends upon the size and shape of the site (Figure 1). Unobtrusive diffusive (passive) samplers are placed around the factory fenceline for extended time periods (e.g. 14 days) to monitor key 'criteria' pollutants such as benzene. Shelters to house the sampling tubes are mounted on 1.5–3 m poles located around the perimeter of the facility.

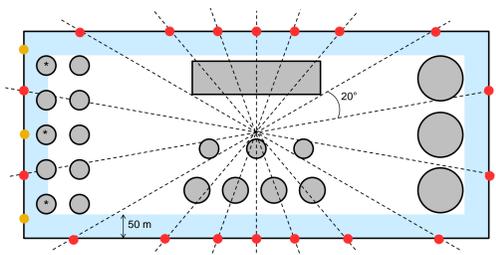


Figure 1: Example of monitoring stations on a rectangular site of 750–1500 acres. Monitoring sites (•) are placed just beyond the boundary at 20° intervals. Sources between two monitoring stations and within 50 m of the boundary (\*) require that additional monitoring stations (•) are installed.

Method 325 states the use of sorbent tubes packed with Carbograph™ 1TD, Carbopack™ B, or Carbopack X (or equivalent, i.e. Carbograph 5TD). Sorbent tubes must be cleaned ('conditioned'), and demonstrate ≤0.2 ppbv of any contaminants or interferences before use. A pre-purging of the tubes removes oxygen and prolongs their life. Field blank tubes must be deployed at the same time as the sampling tubes and must be housed in the shelter – on these tubes the long-term storage caps stay fitted to both ends.

## Method 325 B: Analysis of diffusive samples

When the sampled tubes reach the laboratory, they are analysed using thermal desorption–gas chromatography (TD–GC), typically with detection by mass spectrometry (MS). To determine the concentration of benzene, five-point calibration curves are used to calculate the mass on tube from the peak abundance. The following equation is then used to determine the airborne concentration:

$$\text{Concentration (ppm)} = \frac{\text{Mass of sample on tube (ng)}}{\text{Uptake rate (ng ppm}^{-1} \text{ min}^{-1}) \times \text{Sampling time (min)}}$$

## Experimental

Prior to analysis, the sorbent tubes are tested under stop flow conditions to ensure sample integrity and are cleaned with the Markes' TC-20™ tube conditioner that allows up to 20 industry-standard sorbent tubes to be simultaneously conditioned at elevated temperatures. The TC-20 – with versions for tagged and untagged tubes – frees up instrument time to run samples rather than condition tubes. In addition, it allows tubes to be conditioned using high-purity nitrogen, rather than the more expensive helium carrier gas. Markes' specially developed 325 tube packed with the recommended mass of Carbopack X sorbent are sent to the field in Markes' customer-labelled 325 Containers™. Sampling end time and date information is usually logged at this stage, either manually or electronically.

## References

1. U.S. Environmental Protection Agency - New and Revised 40 CFR Part 63, Appendix A, Test Methods: Proposed 325A and 325B for Passive Fenceline Monitoring for Fugitive and Area Sources. March 2015.
2. U.S. Code of Federal Regulations (CFR). Title 40: Protection of Environment.

## Experimental - continuation

Markes' tubes are all etched with a unique ID number in barcode and numerical format for tracking of sample information. However, when handling the large number of tubes required by Method 325, Markes' patented TubeTAG™ system is recommended. This prevents manual transcription errors, and optimizes the audit trail. Robust radio-frequency identification (RFID) tags are fitted to the tubes, and a portable TAGSCRIBE™ unit is used to enter information such as sampling location, sampling start and finish times, sorbent type, date of packing, and number of analytical cycles. This information is then logged by the thermal desorption system and the information added to the reports. By doing this, TubeTAG allows the development of a robust 'chain of custody' from field to lab, ensures a verifiable method for audit trails, and enhances the general QC of sorbent tubes.

The unobtrusive diffusive samplers are placed in the local to be monitored and robust, non-emitting, weather-proof shelters (325 Field Station™ from Markes) capable of housing five sorbent tubes (suitable for samples, replicates and blanks) are used.

After sampling the tubes are sealed to avoid contamination and/or analyte loss and transported to the lab. Long-term storage caps are used to seal blank and sampled tubes throughout transport and storage. However, immediately before analysis they are replaced with Markes' push-on DiffLok™ caps, which protect the tubes while they are on the thermal desorber autosampler. The patented diffusion-locking technology in DiffLok caps eliminates the need for uncapping within the instrument, by allowing gas to flow through the tube when pressure is applied, while also minimizing the risk of sample loss or contaminant ingress.

The thermal desorber used is the Markes' TD-100™ (Figure 2) which operates by desorbing the sample from the tube and transferring it to a focusing (cold) trap, and desorbing it from the trap and injecting it onto the GC column. This efficient two-stage desorption process results in a narrow band of vapour, optimising concentration enhancement and analytical sensitivity.

- TD-100 has the capacity to run 100 sample tubes automatically **without the need for liquid cryogen**, reducing running costs and allowing unattended operation over entire weekends.
- Stringent leak-testing and **automatic addition** of internal standards onto each sample tube on the TD-100 ensures sample and analytical integrity.
- A (patented) ability of the TD-100 to quantitatively re-collect the split portion of samples onto a fresh sorbent tube enables **repeat analysis** of thermal desorption samples, facilitating simple and reliable repeat analysis and validation of analyte recovery.



Figure 2. Markes' TD-100 system, for automatic analysis of up to 100 sorbent tubes.



## Result

While the primary objective of Method 325 is to quantify the level of benzene, the sampling and analytical techniques described here also allow the simultaneous analysis of a wide range of compounds using the same workflow, without additional effort or cost. A representative TD–GC–MS analysis of contaminated refinery fenceline air, using two-week passive sampling, is shown in Figure 3. Note in particular the detection of benzene, toluene and xylene.

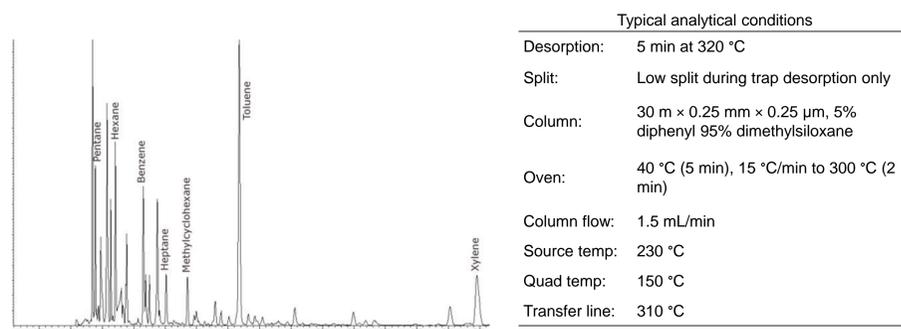


Figure 3. Two-week diffusive sampling around a refinery perimeter.

## Conclusion

Passive sampling has been well-validated for ambient air – as demonstrated by its stipulation in ISO 16017-2, ASTM D6196 and EN 14662-4, and implementation in the new Method 325 parts A and B. It is a robust method, because changes in ambient conditions (temperature, wind speed, humidity, interferences) have minimal impacts on uptake rates. It is also low-cost, because samplers can be re-used more than 50 times, and are inexpensive to buy and transport. Finally, passive sampling is versatile, because sorbent tubes can be used for pumped or passive sampling, and offer quantitative sampling and release of compounds over a wide volatility range.

Markes International provides the full range of tubes, accessories and instrumentation to comply with the Method 325, as well as complete and compliant solution packages.