

# Refinery Fenceline Monitoring – How to Comply with Method 325

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Complying with US EPA Method 325 for monitoring benzene and other volatile organic compounds (VOCs) at refinery perimeters might at first sight seem a daunting task. However, the tube-based passive samplers stipulated are long-established and well-validated, and establishing a protocol in accordance with Method 325 need not be complex. This article outlines a stepwise approach for sampler deployment, sample analysis and tube cleaning that is fully compliant with Method 325. An additional aspect discussed is automated collection of sample data, which although not required under Method 325, is recommended to ensure a robust chain of custody from field to lab, while reducing the burden of record-keeping to a minimum.

## Introduction

US EPA Method 325 has been developed to enable refineries to comply with the updated US federal regulation CFR 40, and states that monitoring of VOCs around the boundary of refineries will be compulsory from mid-2015.<sup>1</sup> This will require two-week passive (diffusive) sampling onto tubes packed with adsorbent material ('sorbent tubes'), followed by laboratory analysis to identify and quantitate the chemicals concerned.

While benzene is the primary target compound, the sampling and analysis methodology can also be used to determine other VOCs, including butadiene, toluene, ethylbenzene, xylenes and other hazardous air pollutants (HAPs).

The wording of the method itself is necessarily rather detailed, but it is important to note that the analytical methodology has been widely used for several decades for environmental monitoring. As a result, the instrumentation needed to comply with Method 325 is well-established, and a wealth of expertise is available.

This article will break down the seemingly complex requirements of Method 325 into a straightforward, four-step process (Figure 1), and highlight the key issues that should be considered in order to achieve full compliance.

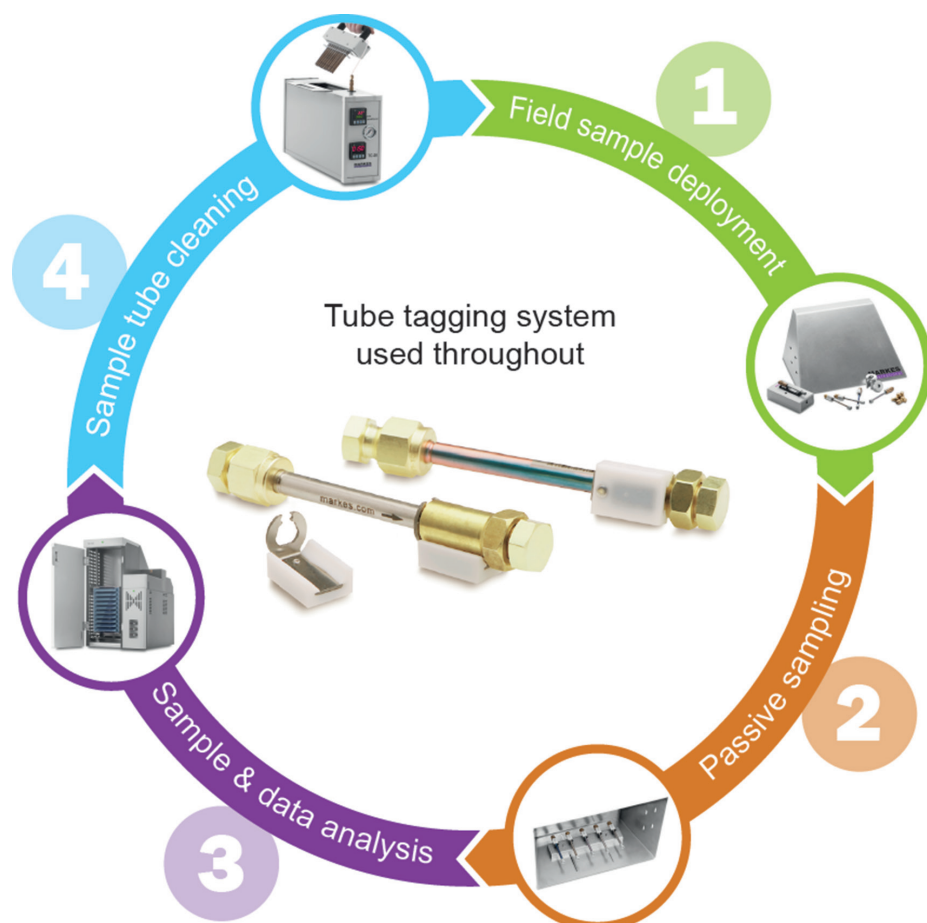


Figure 1: The stepwise sampling and analytical process enabling compliance with Method 325. See ref. 2 for a listing of the sections of Method 325 corresponding to each of the stages.

## A Stepwise Process for Sampling and Analysis

### Step 1: Field Sample Deployment

Method 325 states that up to 24 monitoring locations should be distributed around the perimeter (fenceline) of the refinery, in a pattern that depends upon the size and shape of the site (see Figure 2). Additional monitoring stations may also be required – for example, where the regular distribution of monitoring stations does not adequately cover certain VOC emission sources, or where there are potential interfering sources such as major roads or neighbouring industrial plants.

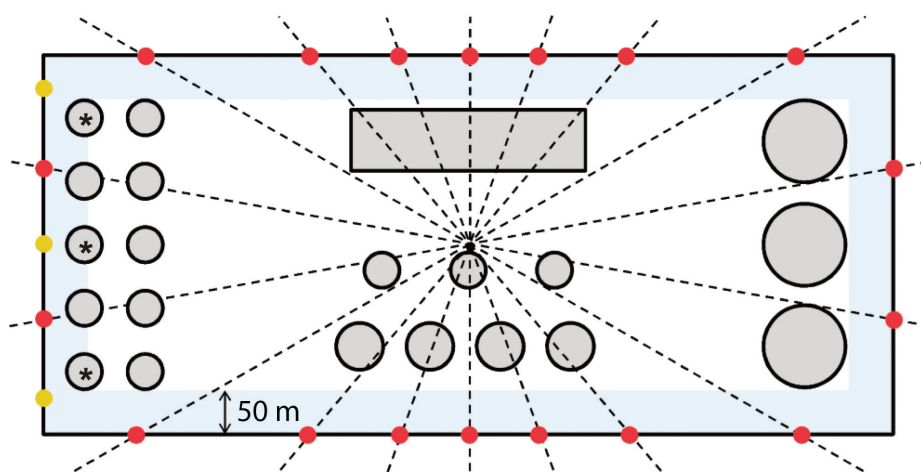


Figure 2: Example of monitoring stations on a rectangular site of 750–1500 acres containing emission sources (grey). Monitoring sites (red dots) are placed just beyond the boundary at 20° intervals. Sources between two monitoring stations and within 50 m of the boundary (\*) require that additional monitoring stations (yellow dots) are installed.<sup>2</sup>

Method 325 requires that the shelters that house the sampling tubes are mounted on 1.5–3 m poles located around the perimeter of the facility. Such shelters should obviously be weather-proof, constructed of non-emitting materials such as stainless steel, and big enough to hold samples, replicates and blanks. In accordance with standard practice in diffusive monitoring, such shelters should be positioned away from trees, walls, buildings and other large obstructions, which may cause wind funnelling or other effects that could cause local deviations in ambient air concentration. Note that during the sampling process meteorological data from the nearest available centre must also be collected.

The samplers themselves, which should be thoroughly conditioned before use (see Step 4) are fitted with a diffusive cap at the sampling end, which points down within the shelter. Doing this not only prevents particles from entering, but also eliminates air turbulence inside the tube, ensuring that the rate of adsorption of air pollutants (the 'uptake rate'<sup>3</sup>) stays constant.

### Step 2: Passive Sampling

The sampling protocol stipulated in Method 325 uses 3½-inch by ¼-inch stainless steel tubes packed with a single bed of adsorbent material ('sorbent'). Sorbents called medium-strength graphitised carbon blacks are the most appropriate sorbents for refinery monitoring, being able to trap benzene and as well as a range of other relevant compounds, including butadiene, toluene, ethylbenzene and the xylenes.

Once in the field, the clean, conditioned and capped sorbent tubes are allowed to equilibrate at ambient temperature before removal from the storage container, to minimise risk of condensation. The storage cap at the sampling end of the tube is then removed and replaced with a diffusion cap. Field blank tubes must be deployed at the same time as the sampling tubes, and on these tubes the

long-term storage caps stay fitted to both ends.

Sampling end time and date information is usually logged at this stage, either manually or electronically. The majority of sampling tubes are now etched with unique numerical identifiers or barcodes, minimising the chance of a mix-up. However, this still presents a considerable record-keeping burden and the risk of human error, so refineries wanting to minimise costs in this regard might want to consider tube-tagging systems. These use robust radio-frequency identification tags that are attached to each tube and used to enter information such as sampling location, sampling start and finish times, sorbent type, date of packing, and number of analytical cycles. Such technology 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.

If more than one sampler is being used at a given monitoring station, they should all be deployed in quick succession, so they effectively have the same start time. Sampling is carried out for a minimum of 14 days, during which time gaseous VOCs migrate into the air gap inside the tube, and adsorb onto the sorbent (Figure 3). At the end of the sampling period, the diffusion caps are removed from the sample tubes and replaced with the long-term storage caps, ready for transport to the analytical laboratory.

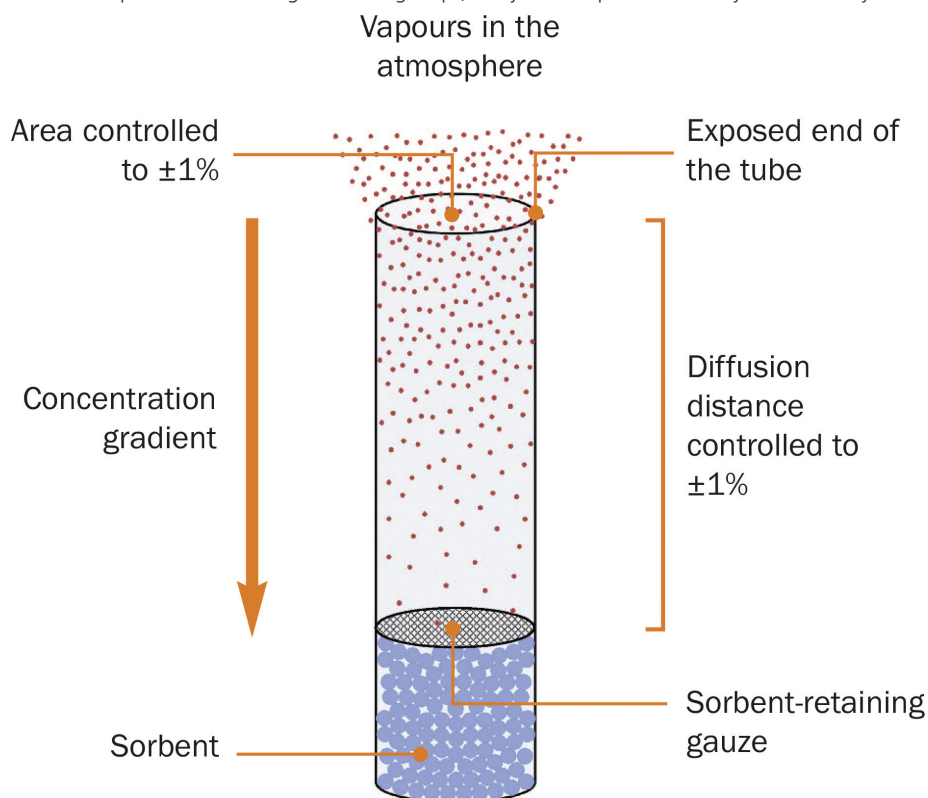


Figure 3: Schematic showing axial diffusive sampling on sorbent tubes.

### Step 3: Sample & Data Analysis

When the sampled tubes reach the laboratory, they are analysed using the well-established technique of thermal desorption–gas chromatography (TD–GC), typically with detection by mass spectrometry (MS).

Thermal desorption instruments from Markes International operate by heating the tube to transfer the volatile compounds to another, narrower tube. This too is heated rapidly to inject the compounds onto the GC column. This efficient two-stage desorption process results in a narrow band of vapour, optimising concentration enhancement and analytical sensitivity.

The large number of samples required by Method 325 means that automated analysis is all but essential, but fortunately instruments are available that can run 100 sample tubes in succession, reducing running costs and allowing unattended operation over entire weekends.

To determine the concentration of benzene, five-point calibration curves are used to calculate the mass on tube from the peak abundance, with a simple equation then being used to determine the airborne concentration.<sup>4</sup>

While the primary objective of Method 325 is to quantify the level of benzene, the sampling and analytical techniques described above also allow the simultaneous analysis of a wide range of compounds using the same workflow, without additional effort or cost (Figure 4).

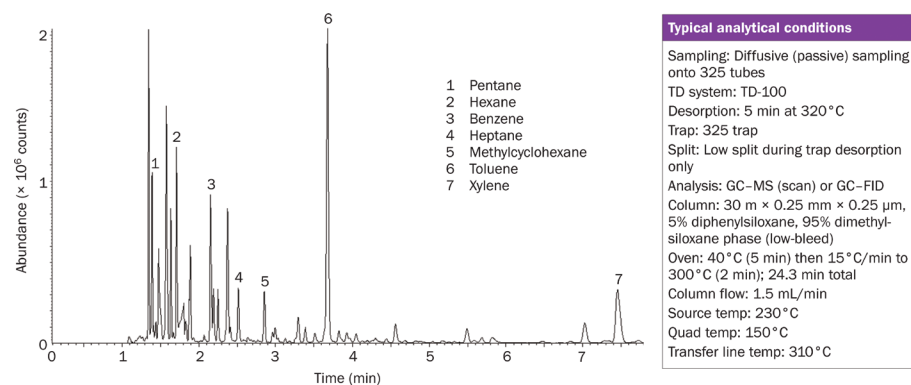


Figure 4: The results of two-week passive sampling of contaminated air around a refinery perimeter, with analysis by TD–GC–MS, showing the detection of a number of hazardous VOCs, including benzene, toluene and xylene.

### Step 4: Sample Tube Cleaning

Method 325 states that sorbent tubes must be cleaned ('conditioned'), and demonstrate  $\leq 0.2$  ppbv of any contaminants or interferences before use. This can be done on the analytical instrument, but a better solution is to use a dedicated instrument able to condition multiple tubes at once, at elevated temperatures. Using such a system frees up instrument time to run samples rather than condition tubes, providing a rapid return on investment. In addition, it allows tubes to be conditioned using high-purity nitrogen, rather than the more expensive helium carrier gas.

### Conclusions

This article has shown that, although the requirements of US EPA Method 325 might at first sight seem complex, the technologies to comply with it are readily available and well-validated. The straightforward four-step protocol we have outlined here will enable refineries to achieve full compliance with the method, with all equipment described being available directly from Markes International.

Markes International has extensive experience of consulting on standard/regulatory methodology in the USA and worldwide, which places us in a very good position to advise refineries and contract laboratories on the best way to comply with Method 325.

### References

1. US federal regulation CFR 40, Annex A of Part 63: Petroleum refinery sector risk and technology review and new source performance standards.
2. Federal Register Vol. 79, No. 125, Appendix A to Part 63 [AMENDED], pages 37046–37074, <https://www.federalregister.gov/articles/2014/06/30/2014-12167/petroleum-refinery-sector-risk-and-technology-review-and-new-source-performance-standards>  
Field sample deployment: See Part A, section 6.3 (page 37048).  
Passive sampling: See Part A, section 8.5 (page 37052).  
Sample & data analysis: See Part B, section 4 (page 37056).  
Sample tube cleaning: See Part B, section 6.2 (page 37057) and section 9.2 (page 37059).  
Tube transport (to field or laboratory): See Part B, section 6.4.2 (page 37057).
3. Widespread use of diffusive sampling over many years has resulted in a large number of published uptake rates, meaning that new users do not need to determine them experimentally. See Markes International's Application Note 001, <http://www.markes.com/Resources/Application-notes/Technical-support.aspx>.
4. For more details of these calculations, please see Markes International's Application Note 114, <http://www.markes.com/Resources/Application-notes/Environmental.aspx>.