March 2021

Fenceline Monitoring of BTEX & 1,3-Butadiene Emissions by EPA Method 325

Fugitive volatile organic compound (VOC) releases from facilities in the petroleum and petrochemical sectors may pose health and environmental risks to Canadians.

As part of the Government of Canada's Chemical Management Plan (CMP), new regulations for petroleum refineries, upgraders, and certain petrochemical facilities were promulgated November 11, 2020 to reduce the risk of exposure to humans and the environment. The SOR/2020-231 Regulations, along with the accompanying Regulatory Impact Analysis Statement, are available at the following link:

https://canadagazette.gc.ca/rp-pr/p2/2020/2020-11-11/html/sor-dors231-eng.html

The regulation came into effect January 1, 2021, and after ECCC approval of monitoring program design, monitoring must start no later than January 1, 2022, with year-round adsorbent tube deployment on a 2-week cycle.

EPA 325 Background

In May 2013, the US EPA released a proposed rule as an update to the current US "national emission standards for hazardous air pollutants for petroleum refineries" which required all refineries to monitor volatile benzene concentrations around the fenceline (perimeter) of their facilities. Benzene was selected as a representative compound to evaluate overall refinery emissions.

The proposed rule was posted to the US Federal Register on June 30, 2014 with the final rule being signed and published on September 29, 2015.

EPA Method 325 "Volatile Organic Compounds from Fugitive and Area Sources" was developed to enable refineries to comply with the updated US federal regulation 40 CFR 63.

EPA Method 325 includes two sub-parts:

» EPA 325A: Sampler Deployment and VOC Sample Collection; and
» EPA 325B: Sampler Preparation and Analysis.

These complementary methods outline the design, deployment, preparation, and analysis of a series of passive sampling sorbent tubes suspended around the refinery property line. After 2 weeks (14 days) of exposure, the passive sampling tubes are detached from the shelters, re-sealed, and sent to a laboratory for thermal desorption (TD) gas chromatography mass spectrometry (GCMS) analysis. Although benzene is the primary target compound, the sampling and analysis methodology can also be used to determine other VOCs, including 1,3-butadiene, toluene, ethylbenzene, xylenes, and other hazardous air pollutants (HAPs).

The objectives of the Canadian Regulations are to:

» reduce fugitive volatile organic compound (VOC) releases from equipment leaks at petroleum refineries and upgraders, and from petrochemical facilities that are operated in an integrated way with those facilities, in Canada;
» provide protection for human health by minimizing, to the greatest extent practicable, exposure to carcinogenic components contained in petroleum and refinery gases (PRGs);
» improve human health and environmental quality by reducing smog formation;
» promote a level playing field through nationally consistent VOC and PRG risk management measures;
» harmonize these measures, to the extent possible, with existing measures in other jurisdictions (e.g., provinces, municipalities, and the US); and
» provide regulatory certainty to the industry and other stakeholders, which will encourage them to plan and invest into the future with confidence (ECCC, Nov.2020).

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Set-Up, Application and VOC Scope

Samples are collected using a 3.5″ long x ¼″ OD stainless steel tube packed with a carbon-based adsorbent. One end of the tube is outfitted with an open mesh diffusion cap and the other end is sealed with a brass cap. The tube is positioned with the diffusion cap in a downward orientation under a protective non-VOC emitting shelter. Shelters are placed at a height of 1.5 to 2 meters above the ground on a secure pole or other suitable structure. At least one co-located duplicate sample is collected for every 10 field samples. A minimum of two unopened field blanks are collected in different shelters per sampling period to ensure sample integrity associated with shipment, collection, and storage.

Monitoring points are determined using an equal radial or linear approach, e.g. Radial: Less than 750 acres, samplers every 30 degrees based on a central emission source point (12 samples); Linear: Boundary less than 24,000 feet, a minimum of 12 sampling locations evenly spaced ±10%. Based on 26 two-week sampling events, a yearly rolling average is created which is then compared to a specified action level.

The preferred sorbent is Carbopack X, a medium/strong sorbent (for n-C3/C4 to n-C8 substances). Carbopack X is optimal for passive adsorption of the target analytes listed, including benzene and 1,3-butadiene, and is hydrophobic, minimizing moisture effects. The use of a diffusion cap and slow analyte diffusion rate (uptake rate) mitigate any extreme changes in wind vector.

Prior to use, new tubes are thermally conditioned and checked for desorption efficiency (DE). The tubes can be cleaned to low background levels, enabling target analyte detection at ppb/ppt levels. Uptake rates are based on Fick's Law of Diffusion (a compound will migrate to the surface of a sorbent at a rate dependent on: distance and area between sorbent and source, time of exposure, diffusion coefficient of the compound through air, and ambient concentration). Without an uptake rate no comparison can be made between the amount of analyte measured on the tube and the concentration at the sampling point.

Table 1. Validated Sorbents & Uptake Rates for Selected Clean Air Act Compounds
McClenny, W.A., et. al., J. Environ. Monit. 7:248-256.

Compound	Carbopack X uptake rate (mL/min)[1]
1,3-Butadiene	0.61 ± 0.11
1,1-Dichloroethene	0.57 ± 0.14
3-Chloropropene	0.51 ± 0.30
1,1-Dichloroethane	0.57 ± 0.10
1,2-Dichloroethane	0.57 ± 0.08
1,1,1-Trichloroethane	0.51 ± 0.10
Benzene	0.67 ± 0.11
1,2-Dichloropropane	0.52 ± 0.10
Trichloroethene	0.50 ± 0.05
Toluene	0.52 ± 0.14
Tetrachloroethene	0.48 ± 0.05
Chlorobenzene	0.51 ± 0.06
Ethylbenzene	0.46 ± 0.07
m,p-Xylene	0.46 ± 0.09
Styrene	0.50 ± 0.14
o-Xylene	0.46 ± 0.12
p-Dichlorobenzene	0.45 ± 0.05

[1] At 22^{o}C, 760 Torr, and 75% relative humidity

ALS Canada has been conducting this test since 2015, and has the capability and ISO 17025 accreditation to support Canada's petroleum industry in meeting these regulations.

If additional compounds to BTEX and 1,3-Butadiene are required, ALS can provide testing for a broader suite of analytes (as per Table 1) if requested.

For more information, contact the ALS environmental laboratory in Waterloo, Ontario.

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