



Passive Sorbent Uptake Development - Case Study for Chloroprene

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Fenceline Monitoring Requirement for Petroleum Refineries



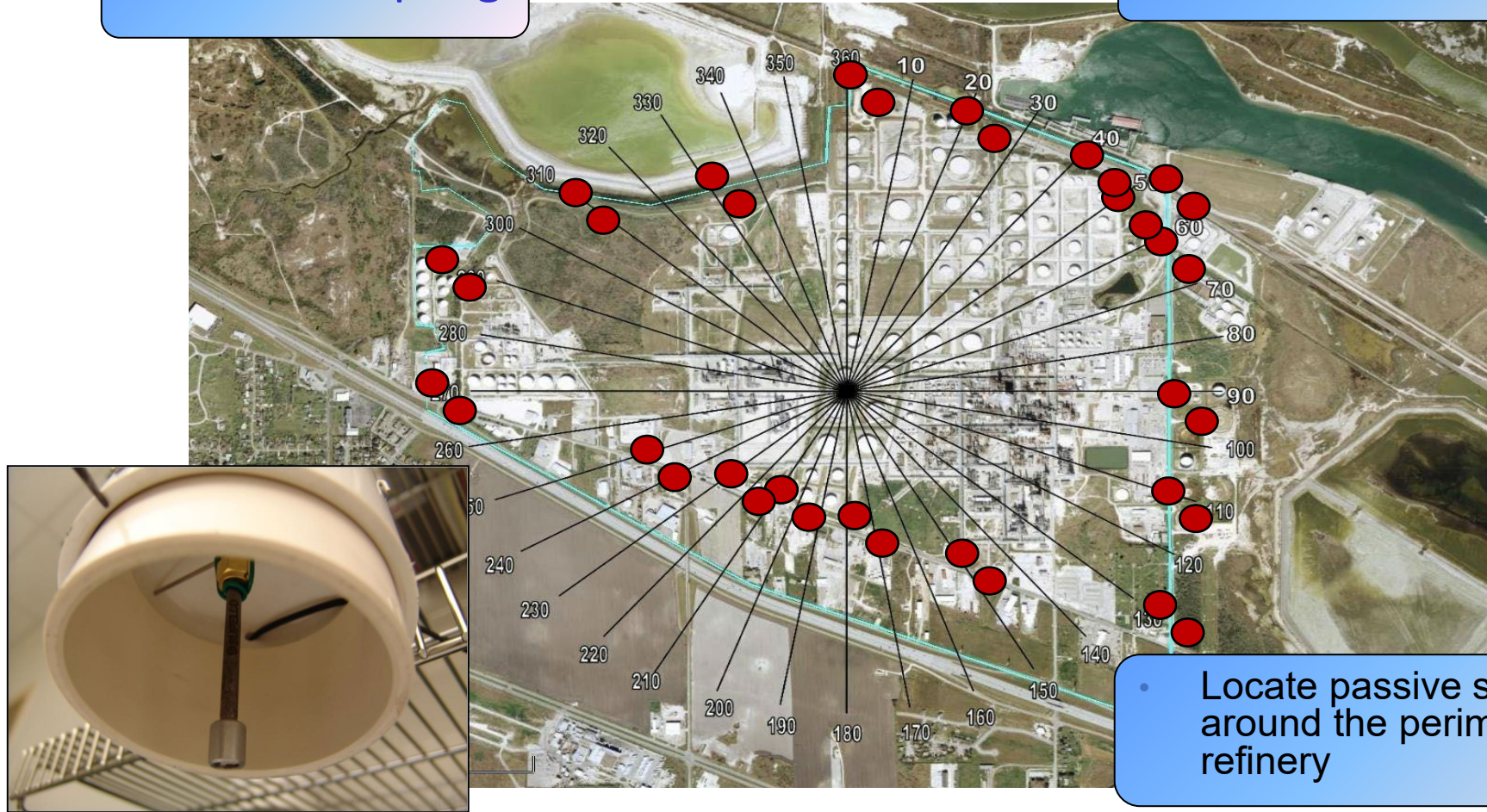
@corbis

- Fenceline Monitoring Work Practice in the Refinery NESHAP.
 - Established requirement to monitor benzene along the perimeter of US refineries.
 - Required a specific method for sampling and analysis of benzene (Methods 325A/B).
 - Reporting requirements for the monitored data.
 - Set an “action-level” at the fenceline and required analysis and corrective action when this “action-level” was exceeded.

Passive Fenceline Monitoring – EPA Method 325A/325B

Passive Sampling

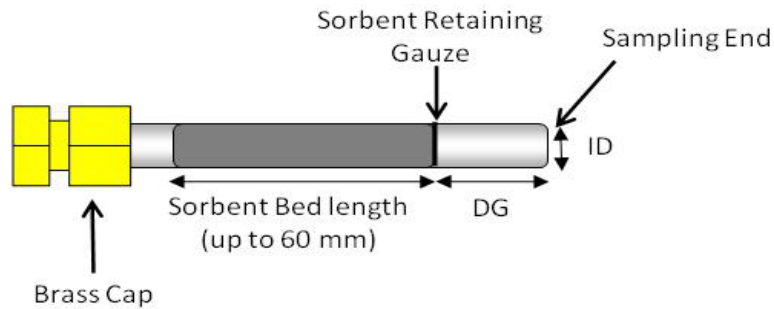
• Facility fenceline monitoring



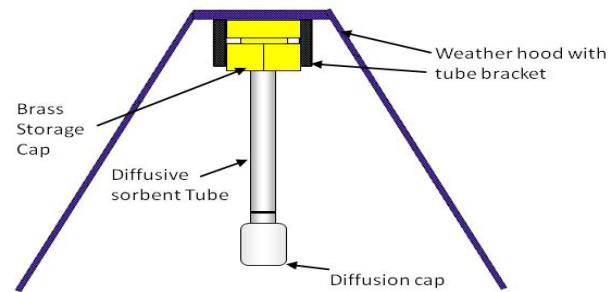
• Locate passive samplers around the perimeter of each refinery

Passive Fenceline Monitoring – EPA Method 325A/325B

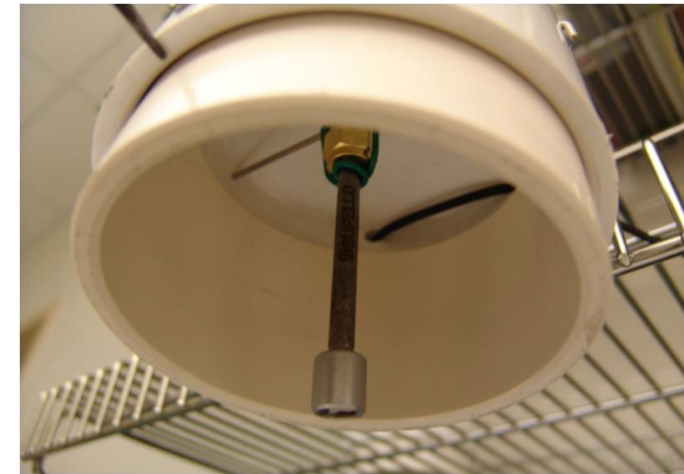
- Passive Sorbent Tube (EPA Method 325A/B)
 - Provides a single measurement for the sampling period (1 to 14 days)
 - Low cost
 - Based on an absorbing sorbent which undergoes thermal desorption and cryogenic concentration and measurement by GC/MS



Cross Section View of Passive Sorbent Tube



PS Tube Sampler

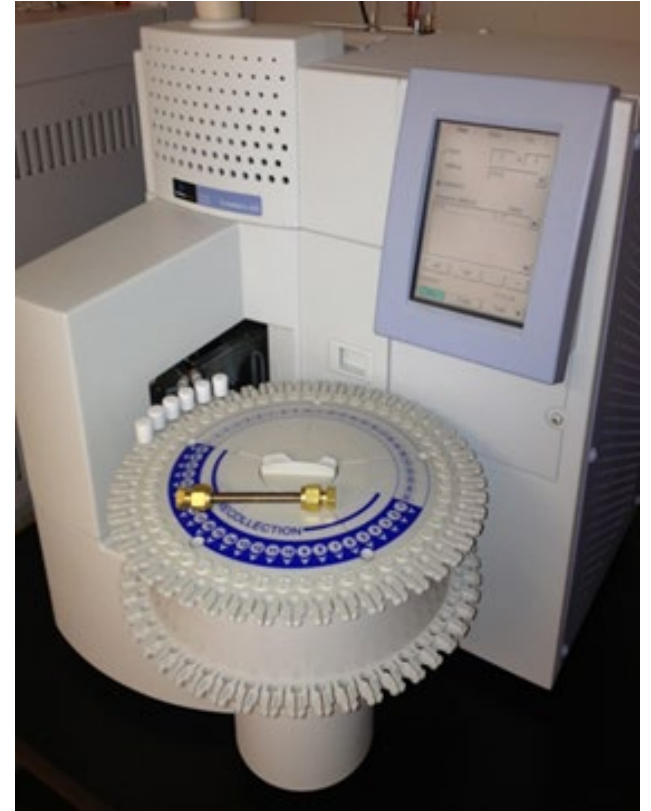


PS Sampler Example
PVC Pipe version with weatherproof hood

EPA Method 325B

Update

- Proposed rule targeted for October 2024
- Incorporate current best practices
 - Sample recollection
 - Additional sorbents
 - Additional compounds
 - Address questions surrounding tube life
 - Updates to Addendum A



Automated thermal
desorber

EPA Method 325B

- Table 12.1 Validated Sorbents and Uptake Rates
 - Carbopack™ X
 - Carbograph™ 1 TD
 - Carbopack™ B
- Sorbent strength and physical characteristics must be matched to the physical properties of the compounds of interest.
- More Sorbents are needed to enable sampling of additional compounds of interest

TABLE 12.1—VALIDATED SORBENTS AND UPTAKE RATES (ML/MIN) FOR SELECTED CLEAN AIR ACT COMPOUNDS

Compound	Carbopack™ X ^a	Carbograph™1 TD	Carbopack™ B
1,1-Dichloroethene	0.57 ± 0.14	not available	not available.
3-Chloropropene	0.51 ± 0.3	not available	not available.
1,1-Dichloroethane	0.57 ± 0.1	not available	not available.
1,2-Dichloroethane	0.57 ± 0.08	not available	not available.
1,1,1-Trichloroethane	0.51 ± 0.1	not available	not available.
Benzene	0.67 ± 0.06	0.63 ± 0.07 ^b	0.63 ± 0.07 ^b .
Carbon tetrachloride	0.51 ± 0.06	not available	not available.
1,2-Dichloropropane	0.52 ± 0.1	not available	not available.
Trichloroethene	0.5 ± 0.05	not available	not available.
1,1,2-Trichloroethane	0.49 ± 0.13	not available	not available.
Toluene	0.52 ± 0.14	0.56 ± 0.06 ^c	0.56 ± 0.06 ^c .
Tetrachloroethene	0.48 ± 0.05	not available	not available.
Chlorobenzene	0.51 ± 0.06	not available	not available.
Ethylbenzene	0.46 ± 0.07	not available	0.50 ^c .
m,p-Xylene	0.46 ± 0.09	0.47 ± 0.04 ^c	0.47 ± 0.04 ^c .
Styrene	0.5 ± 0.14	not available	not available.
o-Xylene	0.46 ± 0.12	0.47 ± 0.04 ^c	0.47 ± 0.04 ^c .
p-Dichlorobenzene	0.45 ± 0.05	not available	not available.

^a Reference 3, McClenny, J. Environ. Monit. 7:248–256. Based on 24-hour duration.
^b Reference 24, BS EN 14662–4:2005 (incorporated by reference—see § 63.14). Based on 14-day duration.
^c Reference 25, ISO 16017–2:2003(E) (incorporated by reference—see § 63.14). Based on 14-day duration.

EPA Method 325B Current Validated Uptake Rates

Suggested Revisions to Method 325B

- Update Table 12-1 of Method 325B
- Carbopack X
 - Removing poor performing compounds from list – chlorinated VOCs
 - Emphasis on matching uptake rate determination duration with sampling duration
 - Updated Uptake Rates (e.g., Butadiene)

Table 13: Sampling Rates (ml/min) obtained for Carbopack X

Compound	1 week (n = 8)		2 weeks (n = 8)	
	Mean	%RSD	Mean	%RSD
1,3-Butadiene	0.54	1.6%	0.50	2.8%
Propan-2-ol	NR ¹	NR	NR	NR
Acrylonitrile	0.32	5.9%	0.32	8.9%
n-Pentane	0.55	1.7%	0.55	5.0%
1,1-Dichloroethene	0.52	7.5%	0.46	5.1%
Ethyl acetate	0.04	29.7%	0.09	19.6%
n-Hexane	0.50	2.6%	0.52	4.0%
Chloroform	0.01	19.5%	0.01	13.1%
1,2-Dichloroethane	0.10	6.3%	0.14	13.5%
1,1,1-Trichloroethane	0.41	2.1%	0.44	4.7%
Benzene	0.60	1.5%	0.60	3.5%
Carbon tetrachloride	0.22	4.7%	0.24	9.1%
Trichloroethene	0.07	15.2%	0.11	15.1%
Methyl methacrylate	0.09	43.9%	0.25	15.5%
n-Heptane	0.46	1.8%	0.47	4.0%
Toluene	0.54	1.4%	0.54	3.0%
n-Octane	0.42	1.4%	0.43	3.7%
Tetrachloroethene	0.47	1.3%	0.45	2.9%
Ethylbenzene	0.49	1.5%	0.49	3.1%
p-Xylene	0.49	1.4%	0.49	3.1%

¹ NR = no result obtained

HSE Uptake Rate Test Report Number HG/2022/16

Suggested Revisions to Method 325B

- Update Table 12-1 of Method 325B
- New Sorbent Types
 - Carbograph 5TD – good for chlorinated VOCs
 - Updated Uptake Rates (e.g., Butadiene)
 - Carbograph 1TD
 - Carbopack B
 - Emphasis on matching uptake rate determination duration with sampling duration

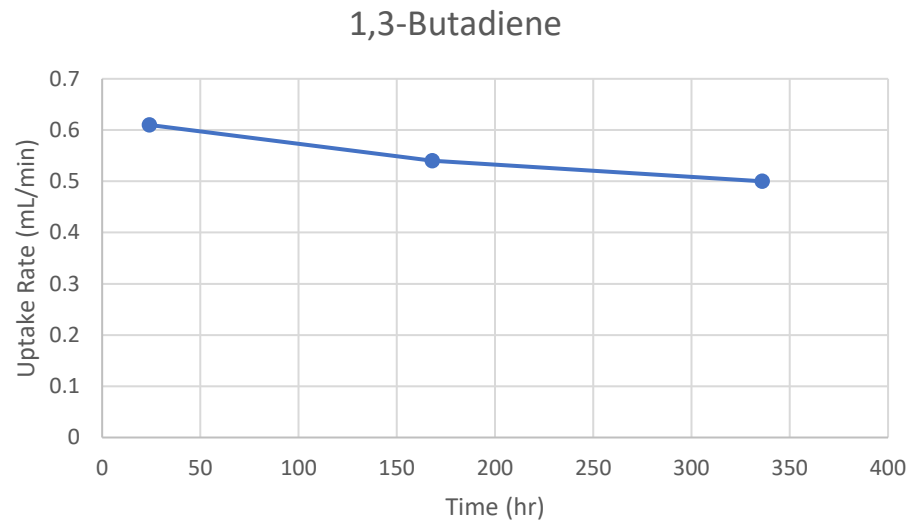
Table 12: Sampling Rates (ml/min) obtained for Carbograph 5TD

Compound	1 week (n = 8)		2 weeks (n = 8)	
	Mean	%RSD	Mean	%RSD
1,3-Butadiene	0.49	2.2%	0.48	4.0%
Propan-2-ol	0.63	1.2%	0.54	2.7%
Acrylonitrile	0.54	2.0%	0.39	3.3%
n-Pentane	0.64	2.0%	0.67	2.6%
1,1-Dichloroethene	0.49	1.7%	0.43	3.2%
Ethyl acetate	1.03	2.5%	1.06	3.2%
n-Hexane	0.56	1.6%	0.58	2.7%
Chloroform	0.55	1.3%	0.51	2.7%
1,2-Dichloroethane	0.61	1.6%	0.58	2.6%
1,1,1-Trichloroethane	0.54	1.7%	0.53	2.5%
Benzene	0.64	1.1%	0.63	2.8%
Carbon tetrachloride	0.56	1.5%	0.51	2.6%
Trichloroethene	0.56	1.3%	0.52	3.1%
Methyl methacrylate	0.89	1.3%	0.91	2.5%
n-Heptane	0.52	1.5%	0.54	2.7%
Toluene	0.57	1.3%	0.56	2.7%
n-Octane	0.47	1.7%	0.49	2.9%
Tetrachloroethene	0.52	1.4%	0.47	3.2%
Ethylbenzene	0.52	1.3%	0.51	2.7%
p-Xylene	0.52	1.3%	0.51	2.7%

HSE Uptake Rate Test Report Number HG/2022/16

1,3-Butadiene Uptake Rate Over Time

Carbopack X			
Compound: 1,3- Butadiene	24 hour	7-day	14-day
McClenny, W.A., K.D. Oliver, H.H. Jacumin, Jr., E.H. Daughtrey, Jr., D.A. Whitaker. 2005. 24 h diffusive sampling of toxic VOCs in air onto Carbopack™ X solid adsorbent followed by thermal desorption/GC/MS analysis—laboratory studies. J. Environ. Monit. 7:248-256	0.61		
N.A.Martin,P.Duckworth,M.H.Henderson,D.J.Marlowand B. A. Goody, Determination of 7- and 14-day 1,3-butadiene diffusive uptake rates for sorbent Carbopack X in Perkin Elmer type axial samplers, The Diffusive Monitor, Issue 14, December 2004.		0.56	0.46
Veronica Brown, HSE Uptake Rate Test Report Number HG/2022/16		0.54	0.5



EPA Method 325B

Addendum A to Method 325B

- New VOCs to be measured by Methods 325A and 325B must be evaluated by exposing the selected sorbent tube to a known concentration of the target compound(s) in an exposure chamber
- Chamber atmosphere concentration must be measured to verify concentrations of the target compounds
- Sorbent tubes are analyzed by EPA Method 325B and compared to reference value.



USEPA Sorbent Tube Exposure Chamber

EPA Method 325B

Addendum A to Method 325B

- Expose sorbent tubes in test chamber
- Minimum of eight tubes at two different levels each
 - Bottom of calibration range
 - Middle of analysis calibration range
- Atmosphere must be between 35% to 75% RH
- Temperature must be $25 \pm 5^{\circ}\text{C}$
- Uptake rate must be $\geq 0.5 \text{ mL/min}$



Sorbent tubes in exposure chamber

Chloroprene 24-hour Uptake Rate Study

- Initial study conducted on Carbopack X in 2021
 - Twelve sample tubes exposed at two different levels
 - Atmosphere concentrations
 - 33.8 ppbv
 - 1.24 ppbv
 - Atmospheric moistures
 - ~70% RH
 - ~50% RH
 - Chamber temperature: ~26°C
- Average calculated uptake rate: 0.56 mL/min



Thermal desorption tubes

Chloroprene 24-hour Uptake Rate Study

- 2024 study performed on Carbopack X
 - Eleven sample tubes exposed at a mid-level
 - Atmosphere concentration: 35.6 ppbv
 - Atmospheric moistures ~60% RH
 - Chamber temperature: ~26°C
- Calculated uptake rate: 0.51 mL/min



Chloroprene 7-day Uptake Rate Study

- 2024 study performed on Carbopack X
 - Included back-diffusion/concentration pulsing
 - Eleven sample tubes exposed at a mid-level for 24-hr
 - Deployed at zero concentration for 6-days
 - Atmospheric moisture: ~65% RH
 - Average temperature: ~21°C
- Average calculated uptake rate: 0.45 mL/min



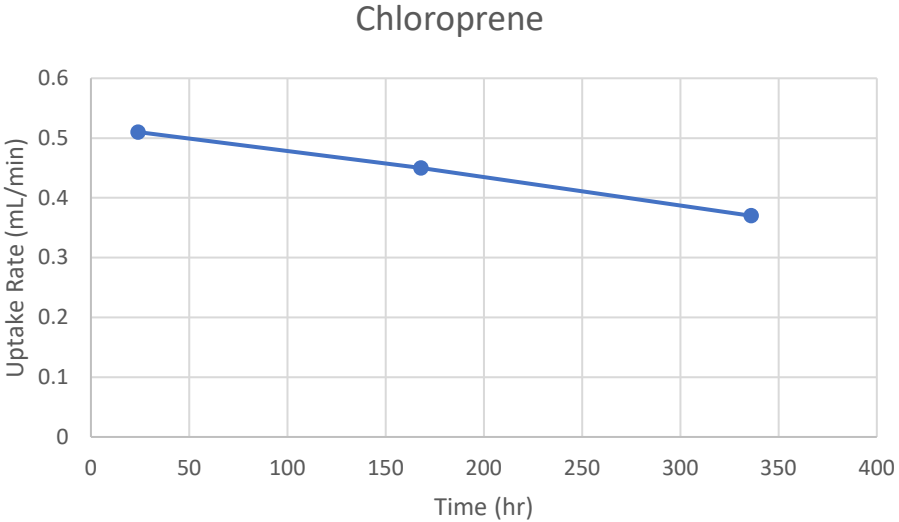
Chloroprene 14-day Uptake Rate Study

- 2024 study performed on Carbopack X
 - Eleven sample tubes exposed at 1.37 ppbv
 - Atmospheric moisture: ~60% RH
 - Chamber temperature: ~26°C
- Calculated uptake rate: 0.37 mL/min



Chloroprene Uptake Rate Over Time

Carbopack X			
Compound: Chloroprene	24 hour	7-day	14-day
EPA Chloroprene Uptake Rate Study 2021	0.56		
EPA Chloroprene Uptake Rate Study 2024	0.51	0.34	0.37
EPA Chloroprene Uptake Rate Study 2024 - Pulsed concentration		0.45	





Thank You and Questions?

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