Determination of an EPA Method 325B Uptake Rate for Chloroprene

David Berkowitz

Director - Business Development

Montrose Environmental Group

EPA Method 325B

Work practice document created to support the Refinery Sector Rule

- Promulgated in 2017

- Passive tubes to monitor benzene concentrations at refinery fencelines

- Also used to monitor benzene and other compounds at upstream oil and gas sites

    - Colorado Regulation 7

Passive sampling tube shelter

EPA Method 325B

Sorbent Selection

- Table 12.1 Validated Sorbents and Uptake Rates

  - Carbopack® X

  - Carbograph® 1 TD

  - Carbopack® B

- Choose a sorbent that is strong enough to retain compound of interest but weak enough to release for analysis

- Carbopack® X is the optimum choice for sampling 1,3-Butadiene

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 Validated Uptake Rates

EPA Method 325B

Addendum A

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 following the procedure in the Addendum. Must determine:

- Uptake rate of each compound

- Relative accuracy compared to the theoretical concentration in the chamber
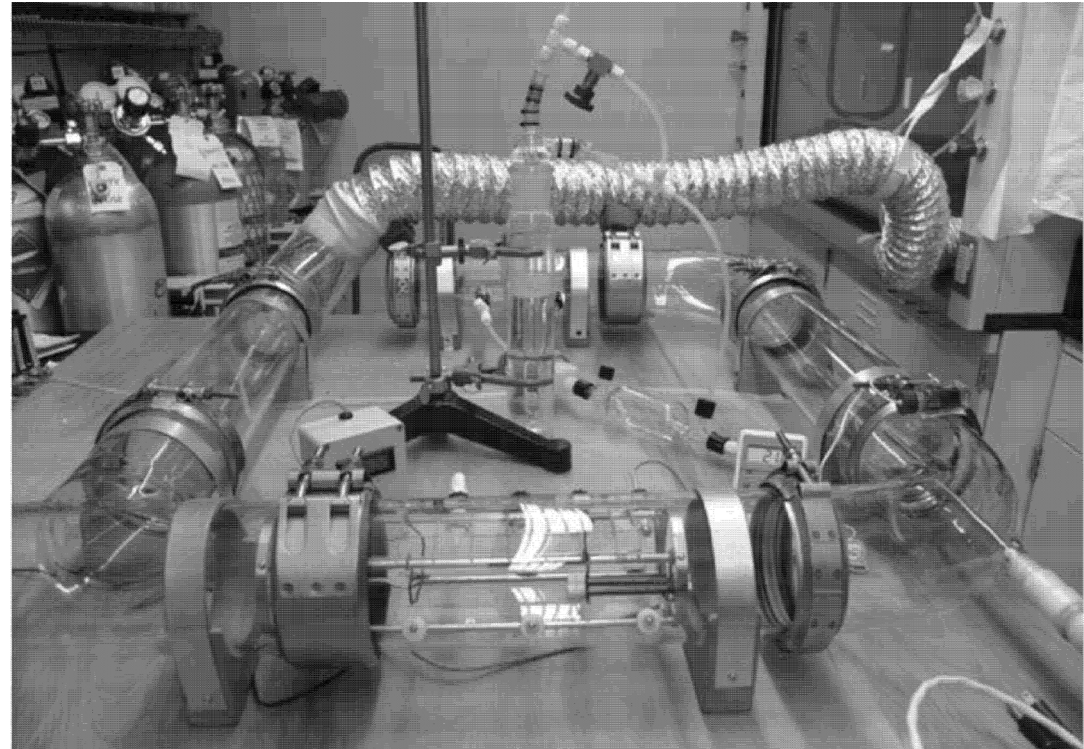
USEPA Sorbent Tube Exposure Chamber

EPA Method 325B

Addendum A

Expose sorbent tubes in test chamber

- Eight tubes at two different levels each
  - 2-5 times the detection limit
  - Middle of analysis calibration range
- Atmosphere must be between 35% to 75% RH
- Temperature must be $25 \pm 5°C$
- Uptake rate must be ≥ 0.5 mL/min

Montrose Environmental Exposure Chamber

EPA Method 325B

Addendum A

Carbopack X passive tube uptake rate studies

- Benzene & TEX – 2009 - 2015

- 1,3-Butadiene - 2017

- TO-15 list - 2017

- Chloroprene - 2021

Carbopack X sorbent tubes

Addendum A
Chloroprene Uptake Rate Study

Purchase certified gas cylinders for tube prep and analysis

- Chloroprene – 1 ppm
- Chloroprene and Benzene – 3 ppm
- Chloroprene and Benzene – 7 ppm
- Verify the cylinder concentrations match using TO-15
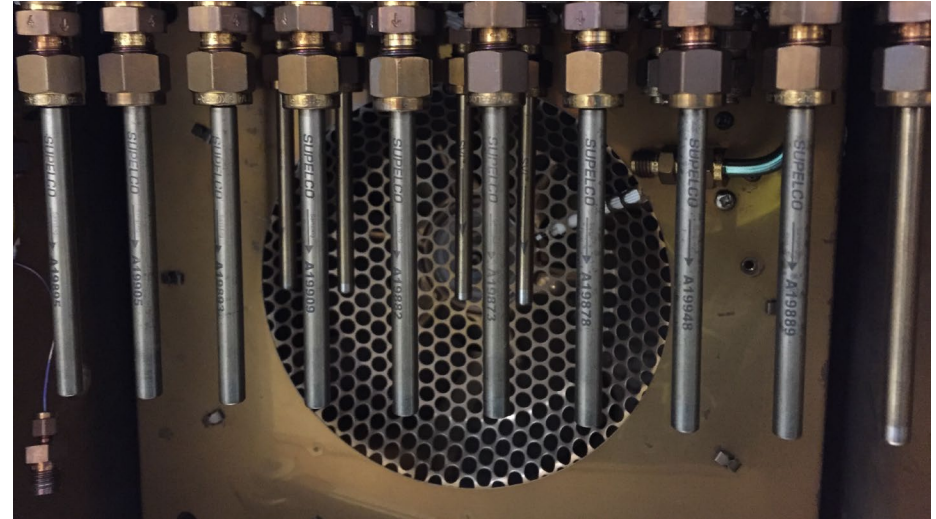

Certified calibration cylinders

Addendum A
Chloroprene Uptake Rate Study

Chloroprene Uptake Rate Study

- Prepared sorbent tubes

  - Carbopack X tubes

  - Selected at random from inventory of ~9,000 tubes

  - Conditioned per Standard Operating Procedures

  - Blank analysis to confirm cleanliness
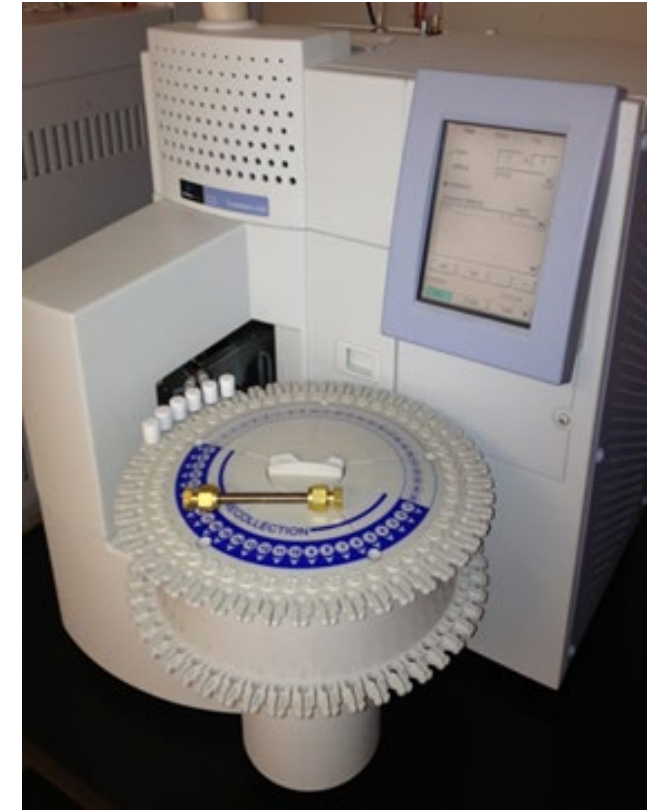

Passive tube conditioning oven

Addendum A
Chloroprene Uptake Rate Study

- Determine spiking levels

  - Mid (CCV) level at ~2.5 ppb for 14 days

  - Low Level

    - Spike and analyze 7 tubes to determine the MDL

    - Calculate the concentration 2-5 times the MDL using an estimated uptake rate of 0.5 mL/min

Automated thermal desorber

Addendum A
Chloroprene Uptake Rate Study

Chamber conditions

- Target of 80 degrees F

- Relative humidity

  - Low level – 70%

  - Mid Level – 50%

TEMPERATURE AND RH CONDITIONS

Activity	Temperature	Relative Humidity	Calculated Relative Humidity	RH Bias (Criteria ± 10% RPD)
CCV (High Level)	78.0	69.8	66.5	2.43
URC (Low Level)	80.0	49.9	52.4	-2.31

Addendum A
Chloroprene Uptake Rate Study

Atmosphere concentrations

- Benzene added as a surrogate

- Verified by TO-15 sample collected during the experiment

		CHAMBER BIAS		
Activity	Compound	Theoretical Chamber Concentration (ppbv)	TO-15 Measured Concertation (ppbv)	Bias (Criteria ± 30% RPD)
CCV (High Level)	Chloroprene	33.8	38.4	12.8
CCV (High Level)	Benzene	33.8	39.5	15.6
URC (Low Level)	Chloroprene	1.24	1.33	7.00
URC (Low Level)	Benzene	1.24	1.51	19.6

Addendum A
Chloroprene Uptake Rate Study

Precision

- Twelve replicates at each level

- Relative Percent Difference <±20%

  - High level

    - Benzene – 3.6%

    - Chloroprene – 4.7%

  - Low level

    - Benzene – 11.2%

    - Chloroprene – 7.2%

Addendum A

Chloroprene Uptake Rate Study

Uptake Study Results

- Calculate uptake rate of benzene to validate chloroprene results

- Benzene uptake rate acceptable within ±15%

- Use the average of the two levels

SURROGATE UPTAKE RESULTS

Activity	Compound	Calculated Uptake Rate (ml/min)	Acceptance (Criteria 0.57-0.77)
CCV (High Level)	Chloroprene	0.55	NA
CCV (High Level)	Benzene	0.58	Pass
URC (Low Level)	Chloroprene	0.57	NA
URC (Low Level)	Benzene	0.67	Pass

Addendum A
Chloroprene Uptake Rate Study

Uptake Study Results

- Relative standard deviation

  - Benzene 2.0%

  - Chloroprene 2.1%

- Relative Accuracy – must be ±10% at the 95% confidence limit

  - Benzene 8.2%

  - Chloroprene 0.5%

Questions?

David Berkowitz

Director   - Business Development
Montrose Environmental Group

dberkowitz@montrose-env.com