Storage Time Study of Passive Sampling Tubes Used for EPA Method 325

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2017 NEMC Conference
Washington D.C.
August 10, 2017

What is EPA Method 325?

- New passive air sampling method for monitoring the fenceline of petroleum refineries.
- It provides the average air concentration of volatile organic compounds (VOC's), with Benzene being the target compound.
- Samples are strategically placed along the fenceline.
- After sampling the tubes are sent to a laboratory to be analyzed using thermal desorption and gas chromatography.

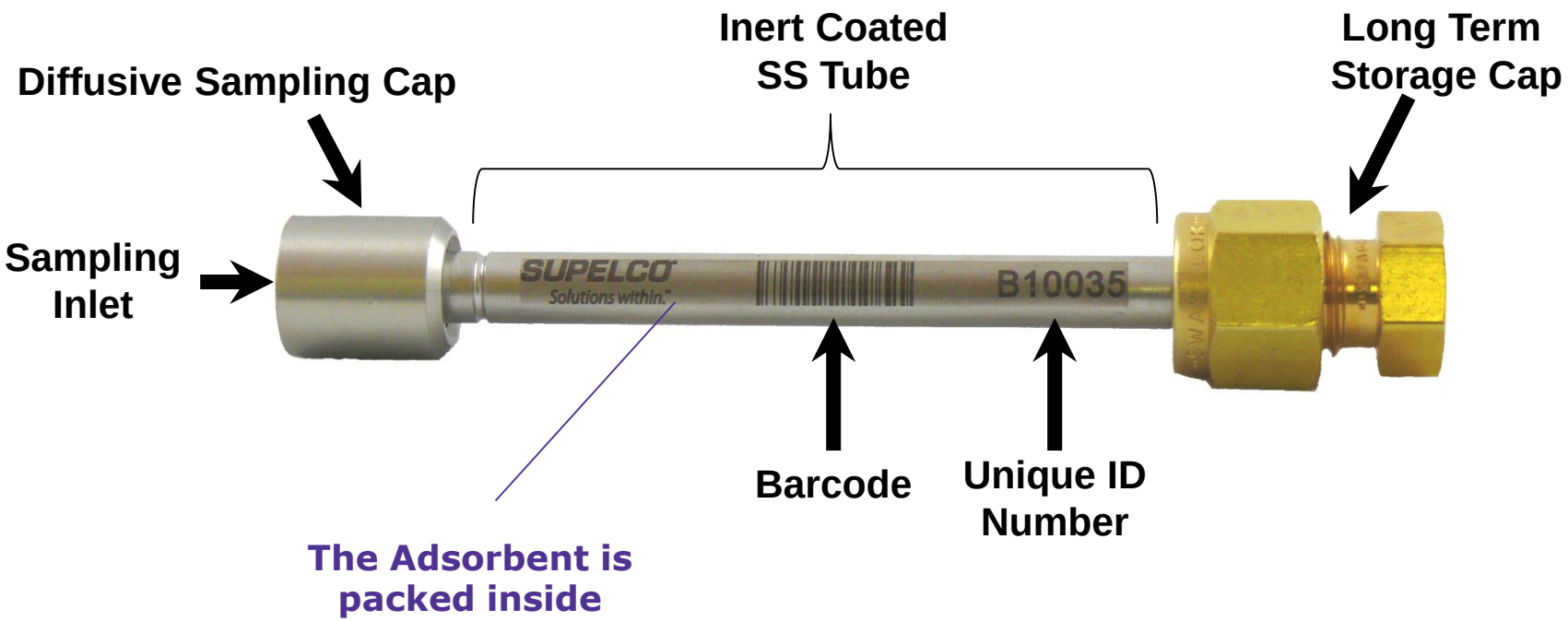
How the Samples are Taken

- Sampling shelters are permanently mounted along the fenceline of the refinery.
- The sampling tubes are placed in the shelter with the inlet pointing down.

Shelter provided courtesy of Enthalpy Analytical Inc. Durham NC

- The tubes hang in the shelter for 14-days.
- After 14-days the tubes are removed, capped, and a new set of tubes are installed in the shelter.
- Sampling takes place year round with 26 sampling events per year.

Overview of the Passive Sampling Tube

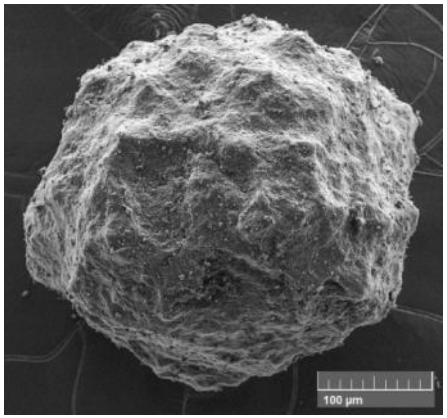


Tube Dimensions: 3.5-inches (89 mm) long x 1/4 inch (6.4 mm) O.D. x 5 mm I.D.

Carbopack X (Graphitized Carbon Black Adsorbent)

- Hydrophobic – so very little water vapor is retained while sampling.
- It retains & releases a wide range of volatile compounds.
- It bridges the gap between weaker adsorbents such as Tenax and other graphitized carbon blacks, and the stronger carbon molecular sieves.

BET Surface Area	Density	Pore Diameter
240 m^2/g	0.44 g/cc	100 Å



Allowable Storage Time & Temperatures

Method 325 specifies the sampling tubes must be analyzed within 30 days.

Or

7 days if the compounds are reactive.

Tubes can be stored at ambient temperature or refrigerated.

8.5.4 Intact tubes must be analyzed within 30 days of the end of sample collection (within one week for limonene, carene, bis-chloromethyl ether, labile sulfur or nitrogen-containing compounds, and other reactive VOCs).

Note: Ensure ambient temperatures stay below 23 °C during transportation and storage. Refrigeration is not normally required unless the samples contain reactive compounds or cannot be analyzed within 30 days. If refrigeration is used, the atmosphere inside the refrigerator must be clean and free of organic solvents.

Source: Method 325B—Volatile Organic Compounds from Fugitive and Area Sources

Objectives of this Storage Study

1. To determine sample recovery from spiked tubes after they've been in storage for 7, 14, 21 and 30 days.

2. To determine if the storage temperature affects recovery.

3. To identify other VOC's (not specified in Method 325) that store well when placed in storage. *(These compound will be candidates for future uptake rate studies)*

4. To identify which VOC's are not suitable for long term storage on Carbopack X sampling tubes.

How You Can Use this Storage Time Data

1. **If a particular compound(s) could be sampled with Carbopack X**

2. **It shows if a compound stores well on Carbopack X**

3. **You can use the data to determine a maximum storage time for a particular compound**

Overview of the Study

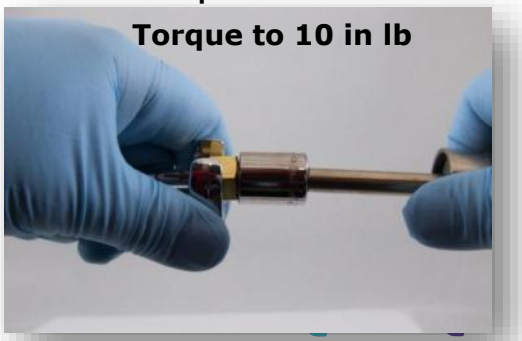
1. Condition tubes prior to spiking.
2. Spike the tubes with multi-component gas mix.
3. Sealed the tubes with long-term storage caps.
4. Placed the spiked tubes in a (clean) metal paint can for storage.
5. Place half of the tubes in the office and the other half in a refrigerator.

	7 Day	14 Day	21 Day	30 Day
Ambient (Lab)	5 samples	5 samples	5 samples	5 samples
Refrigerated	5 samples	5 samples	5 samples	5 samples

6. Included field blanks, and passively collected samples inside the paint cans.

Temperatures recorded during the Study:

- **Ambient Temperature Ranged: 19° C to 28° C**
- **Refrigerator Temperature: 9° C**



VOC's in the Gas Mix

Component	CAS#
Propylene	115-07-1
Halocarbon 12	75-71-8
Chloromethane	74-87-3
Halocarbon 114	76-14-2
Vinyl chloride	75-01-4
1,3-Butadiene	**106-99-0**
Bromomethane	74-83-9
Chloroethane	75-00-3
Ethanol	64-17-5
Acetone	67-64-1
2-Propanol	67-63-0
Halocarbon 11	75-69-4
1,1-Dichloroethene	**75-35-4**
Methylene chloride	75-09-2
Halocarbon 113	76-13-1
Carbon Disulfide	75-15-0
trans-1,2-Dichloroethene	156-60-5
1,1-Dichloroethane	**75-34-3**
Methyl Tertiary Butyl Ether (MTBE)	1634-04-4
Vinyl Acetate	108-05-4
2-Butanone (MEK)	78-93-3
cis-1,2-Dichloroethene	156-59-2
Ethyl Acetate	141-78-6
Hexane	110-54-3
Chloroform	67-66-3
Tetrahydrofuran	109-99-9
1,2-Dichloroethane	**107-06-2**
1,1,1-Trichloroethane	**71-55-6**
Benzene	**71-43-2**
Carbon tetrachloride	**56-23-5**

Component	CAS#
Cyclohexane	110-82-7
1,2-Dichloropropane	**78-87-5**
Bromodichloromethane	75-27-4
Trichloroethene	**79-01-6**
Heptane	142-82-5
4-Methyl-2-Pentanone (MIBK)	108-10-1
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
1,1,2-Trichloroethane	**79-00-5**
Toluene	**108-88-3**
2-Hexanone	591-78-6
Dibromochloromethane	124-48-1
1,2-Dibromoethane	106-93-4
Tetrachloroethene	**127-18-4**
Chlorobenzene	**108-90-7**
Ethylbenzene	**100-41-4**
m & p-Xylene	**108-38-3 & 106-42-3**
Bromoform	75-25-2
Styrene	**100-42-5**
1,1,2,2-Tetrachloroethane	79-34-5
o-Xylene	**95-47-6**
4-Ethyltoluene	622-96-8
1,3,5-Trimethylbenzene	108-67-8
1,2,4-Trimethylbenzene	95-63-6
Benzyl Chloride	100-44-7
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	**106-46-7**
1,2-Dichlorobenzene	95-50-1
1,2,4-Trichlorobenzene	120-82-1
Hexachlorobutadiene	87-68-3

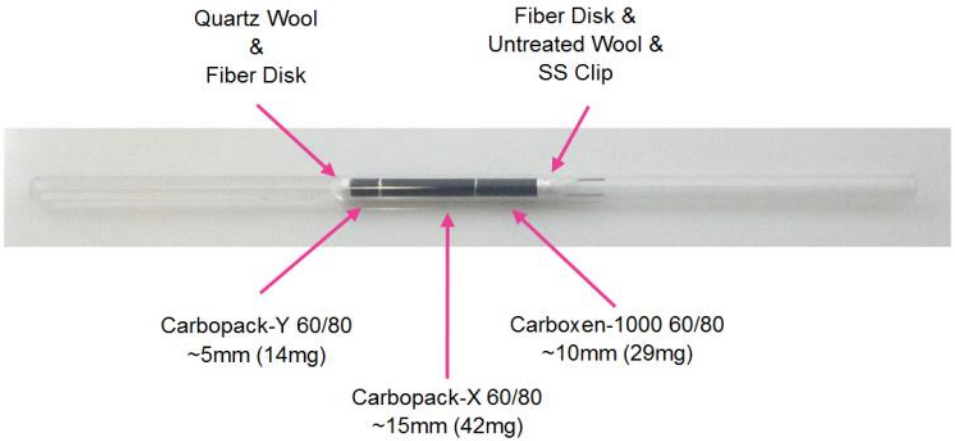
Listed in EPA Method 325

Analytical Parameters

Thermal Desorber: PerkinElmer TurboMatrix 350

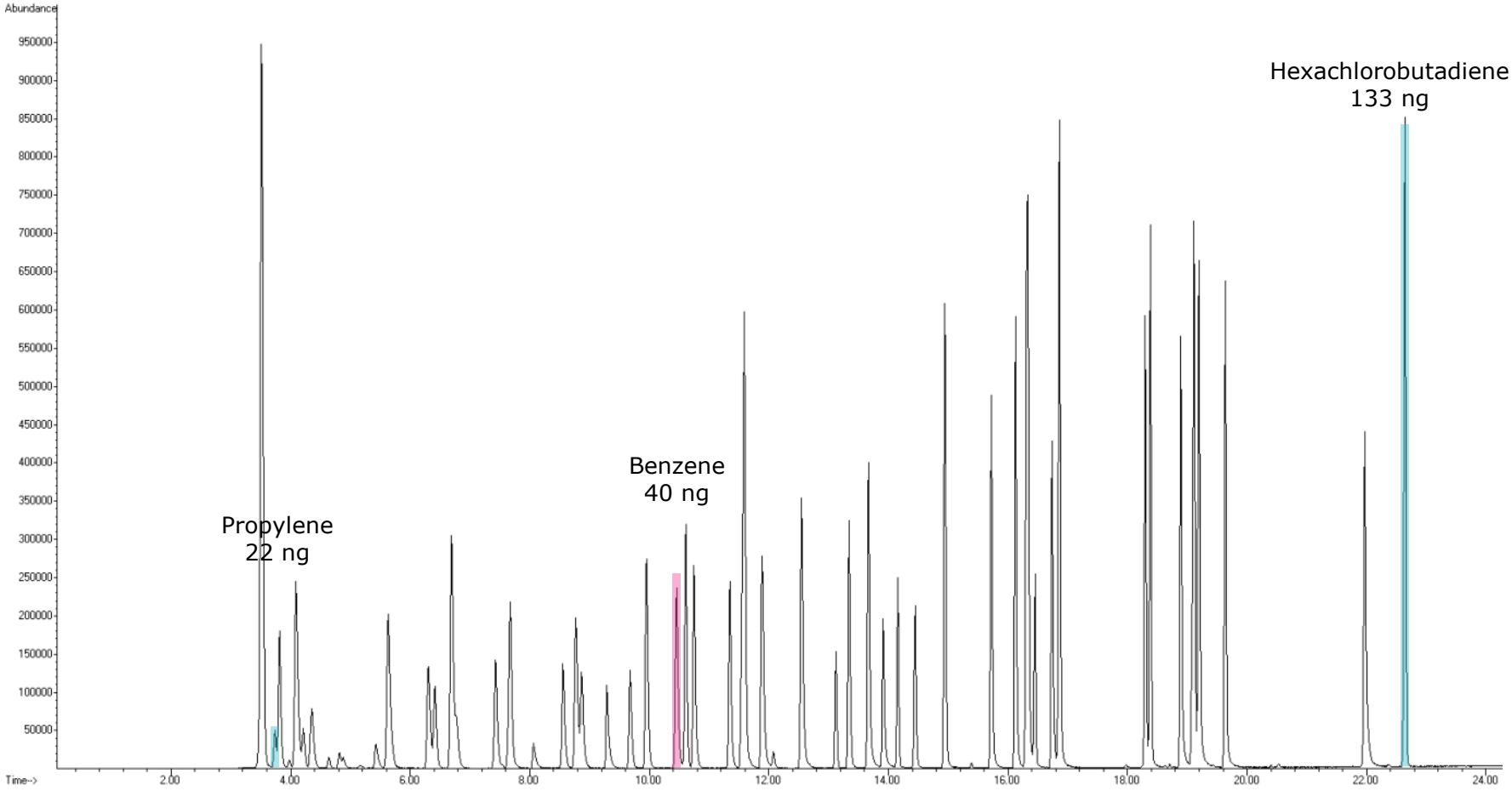
- Tube Desorb: 330°C for 5 min.
- Trap Initial: -20°C
- Trap Desorb: 330°C for 8 min.
- Valve & Transfer Line: 175°C
- Desorb Flow: 50 mL/min
- Inlet Split: OFF
- Outlet Split: 8 mL/min

(Photo of the Focusing Trap)



- GC/MS: Agilent 7890B / 5977A MS
- Column: Equity-1 (60 M x 0.25 mm ID x 1.0 µm film)
  40 °C for 5 min,10 °C/min hold for 0min 15 °C/min/ to 230° C hold for 5 min.
- Flow Rate: 2.0 mL/min
- Scan Range: 35 to 300 amu

Calibration of the Gas Mix

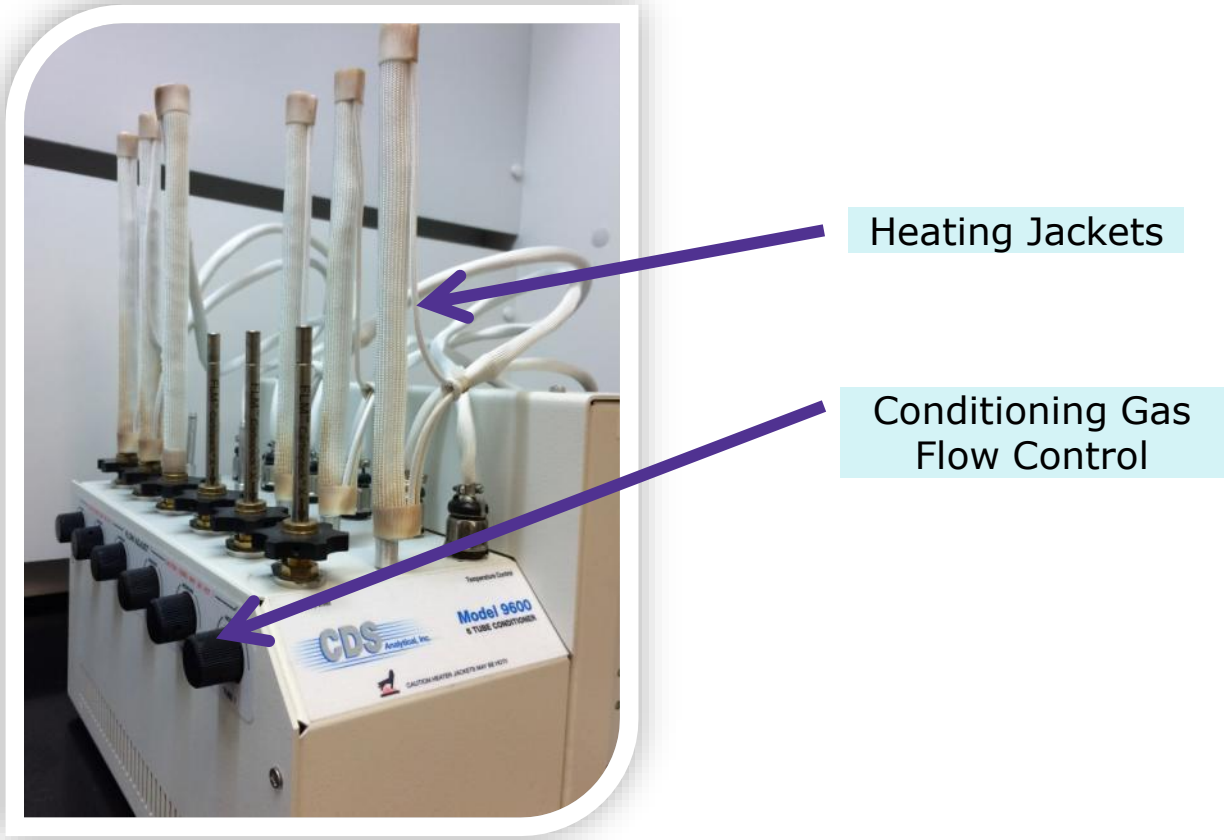


Calibration: 12.7 mL of the 62 compound gas mix at 1ppmV.

The pressure in the syringe was equalized to atmospheric pressure, prior to spiking the tubes.

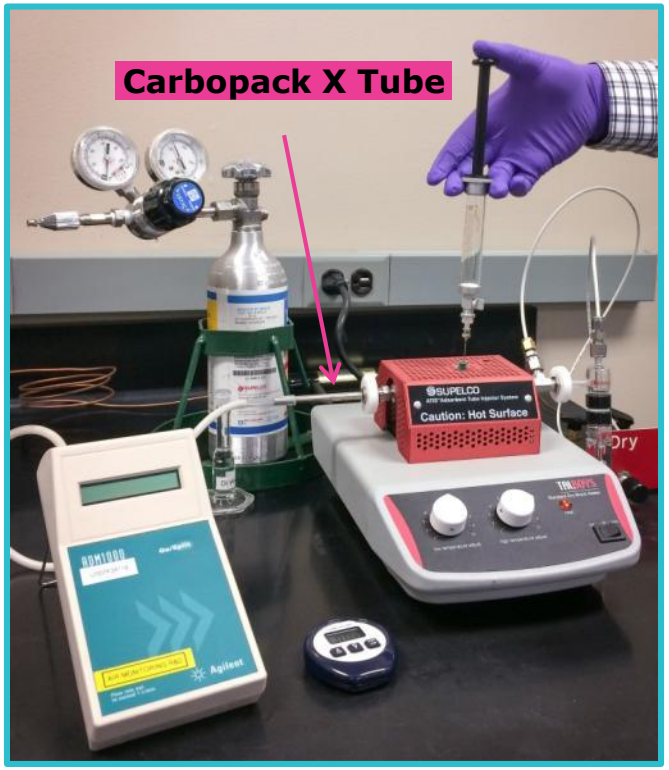
Tube Conditioning

- Tubes conditioned with a Nitrogen (100 mL/min) at 350°C for 30 minutes
- Tubes were allowed to cool to ambient temperature prior to spiking them with the gas mix.



Spiking Tubes

- The gas mix was injected into a humidified (50%RH) gas stream of N_2 that carried the VOC's to the tube at a flow rate of 50 mL/min.
- The tube remained attached to the device for 5 minutes to allow complete transfer of the gas mix to the sampling tube.



Tube Spiking Injector Parameters:

Syringe Volume of Gas: 12.7 mL

- Block temperature: 70°C
- N_2 stream humidified: 50% RH
- Total Gas Flow: 50 mL/min
  (25 mL/min dry, 25 mL/min wet)

The plunger of the syringe was slowly depressed so the total flow going through the tube did not exceed 60 mL/min.

The amount of water vapor transferred with the gas mix was 6 mg.

Calibration

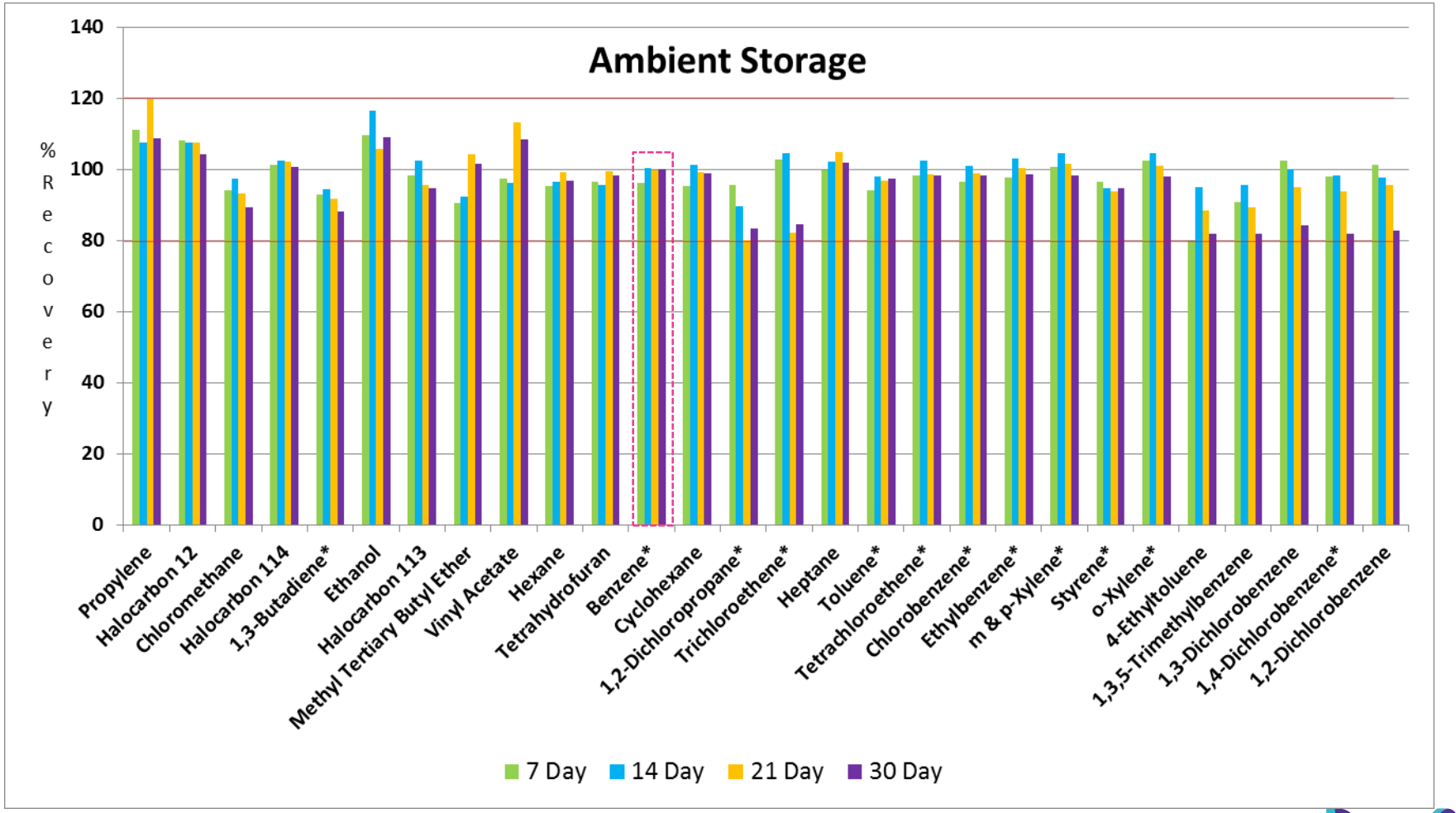
- Recoveries were calculated using a single point calibration curve.
- The same 12.7 mL volume of the gas mix was spike on three separate Carbopack X tubes, the day the analysis took place. A new calibration was carried out for each time frame.
- The average response factor from the three spikes tubes was used to calculate recovery.

Compound	ng/sample	Average Response	RSD (%)
1,3-Butadiene	27	61289	**1.6**
1,1-Dichloroethene	49	192753	**1.0**
1,1-Dichloroethane	50	207766	**0.9**
1,2-Dichloroethane	50	188488	**0.4**
1,1,1-Trichloroethane	67	272412	**1.2**
Benzene	39	341414	**1.6**
Carbon tetrachloride	77	254928	**2.2**
1,2-Dichloropropane	57	130007	**0.9**
Trichloroethene	66	273421	**0.3**
1,1,2-Trichloroethane	67	114071	**2.4**
Toluene	46	244813	**1.8**
Tetrachloroethene	83	153434	**2.3**
Chlorobenzene	56	319870	**1.1**
Ethylbenzene	53	520104	**2.0**
m & p-Xylene	107	400198	**1.7**
Styrene	52	256085	**3.0**
o-Xylene	53	201886	**1.9**
1,4-Dichlorobenzene	74	340989	**2.8**

The Effect of Time on Recovery-Ambient Storage

VOC's with Good Recovery

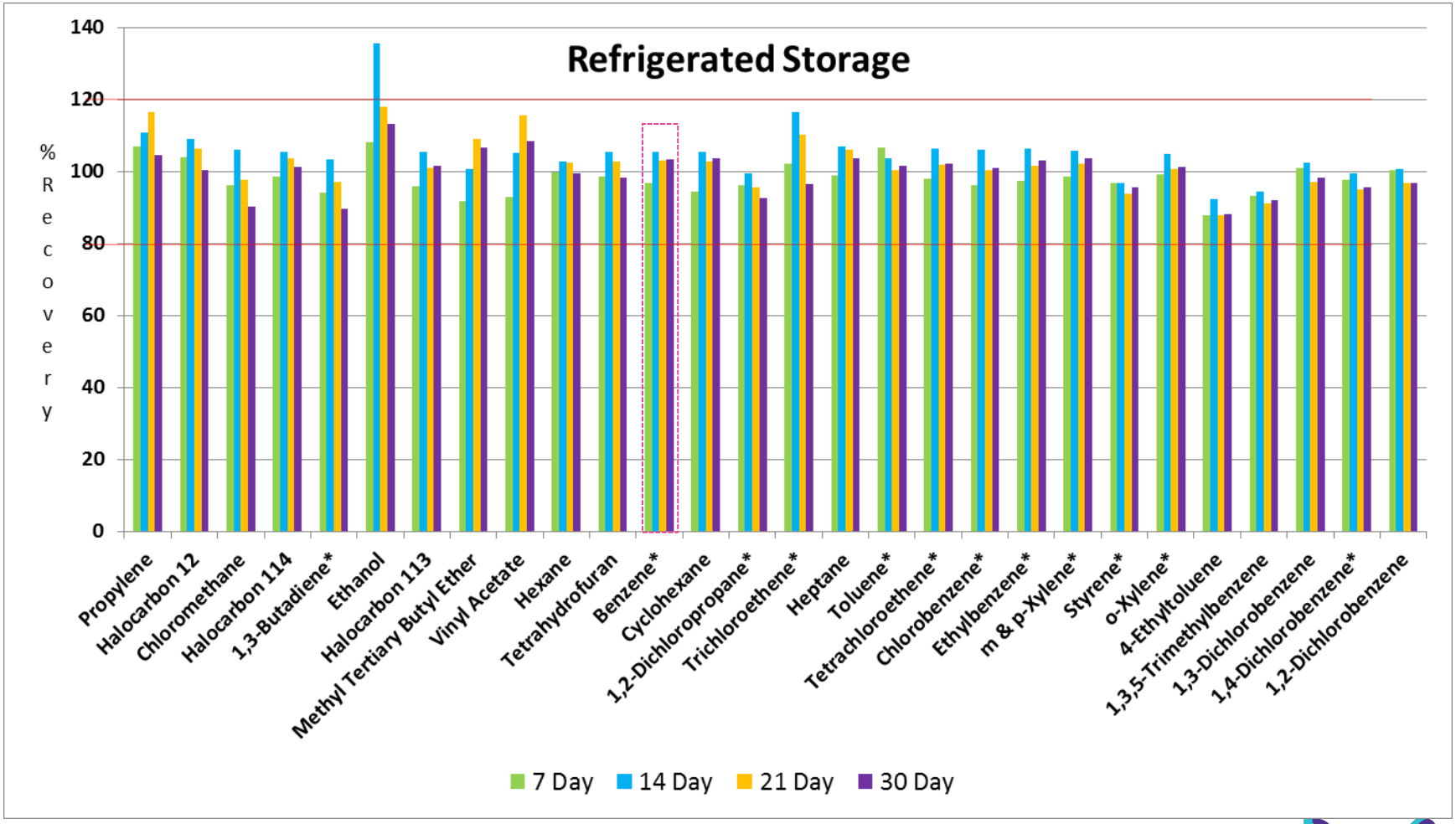
Criteria: Recovery =(80% to 120%) @ 30 Days



The Effect of Time on Recovery-Refrigerated Storage

VOC's with Good Recovery

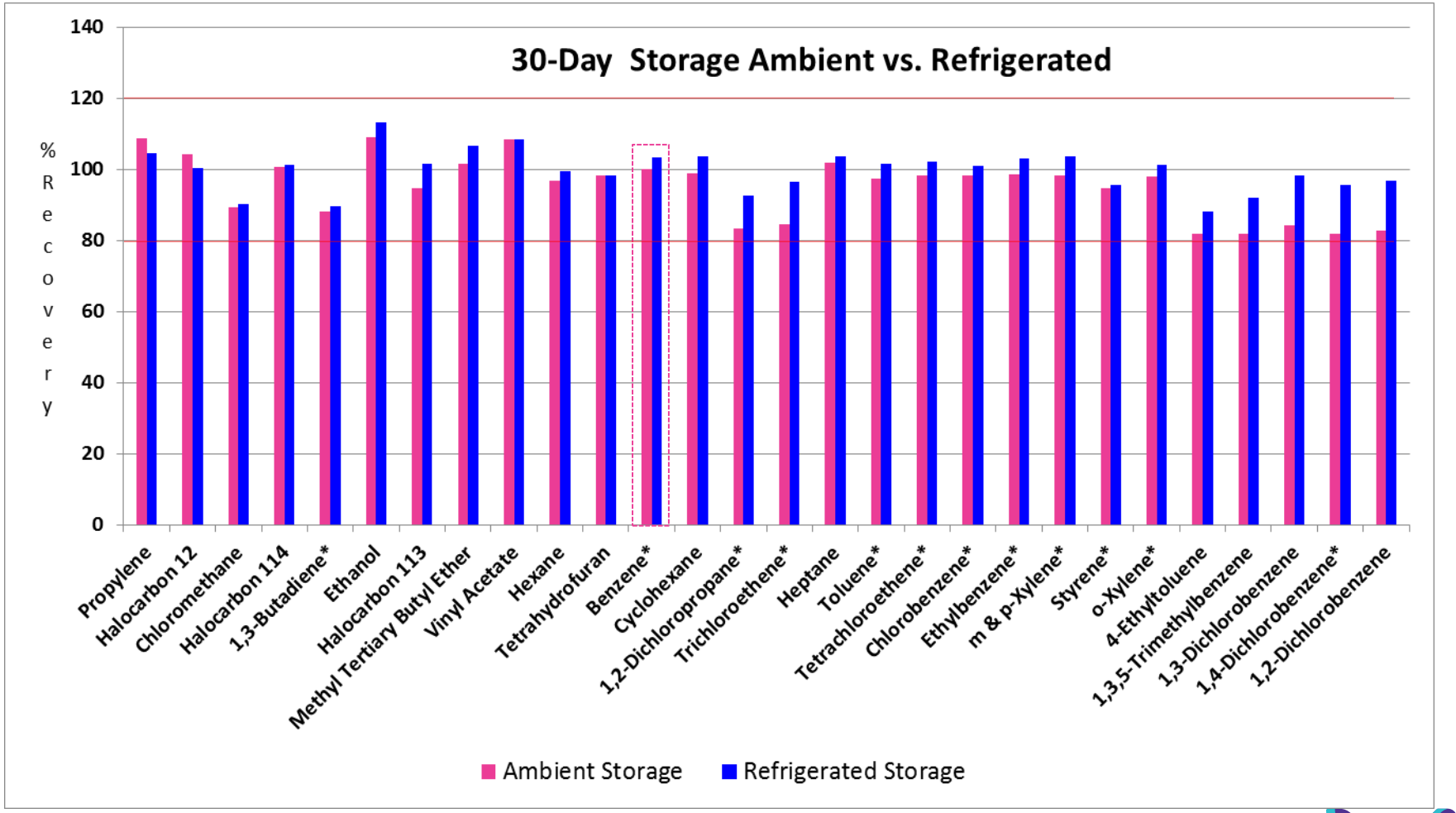
Criteria: Recovery = (80% to 120%) @ 30 Days



The Effect of Temperature on Recovery

Ambient vs. Refrigerated VOC's with Good Recovery

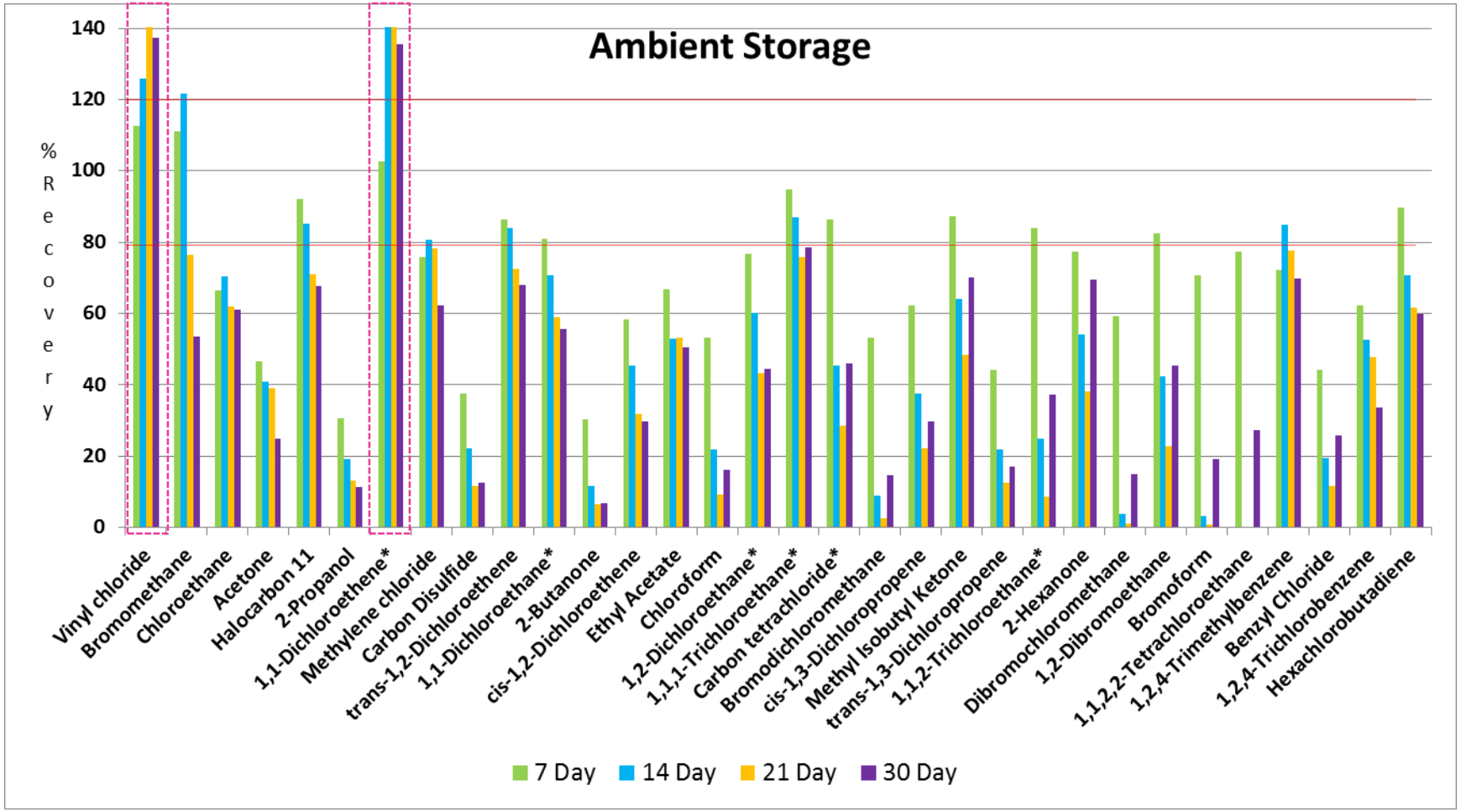
Criteria: Recovery = (80% to 120%)



The Effect of Time on Recovery-Ambient Storage

VOC's with Poor Recovery

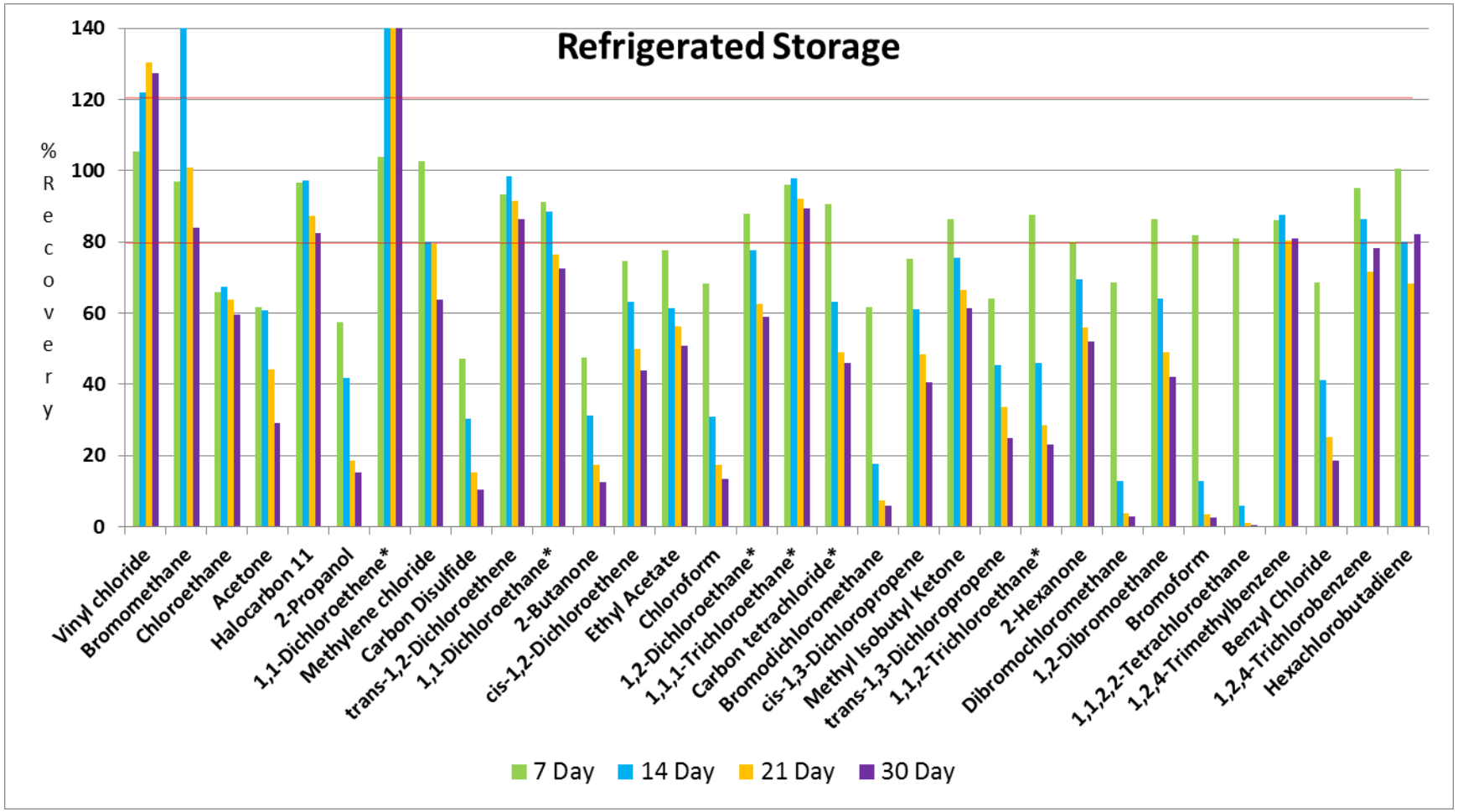
Criteria: Recovery = <80% or >120% @ 30 Days



The Effect of Time on Recovery-Refrigerated Storage

VOC's with Poor Recovery

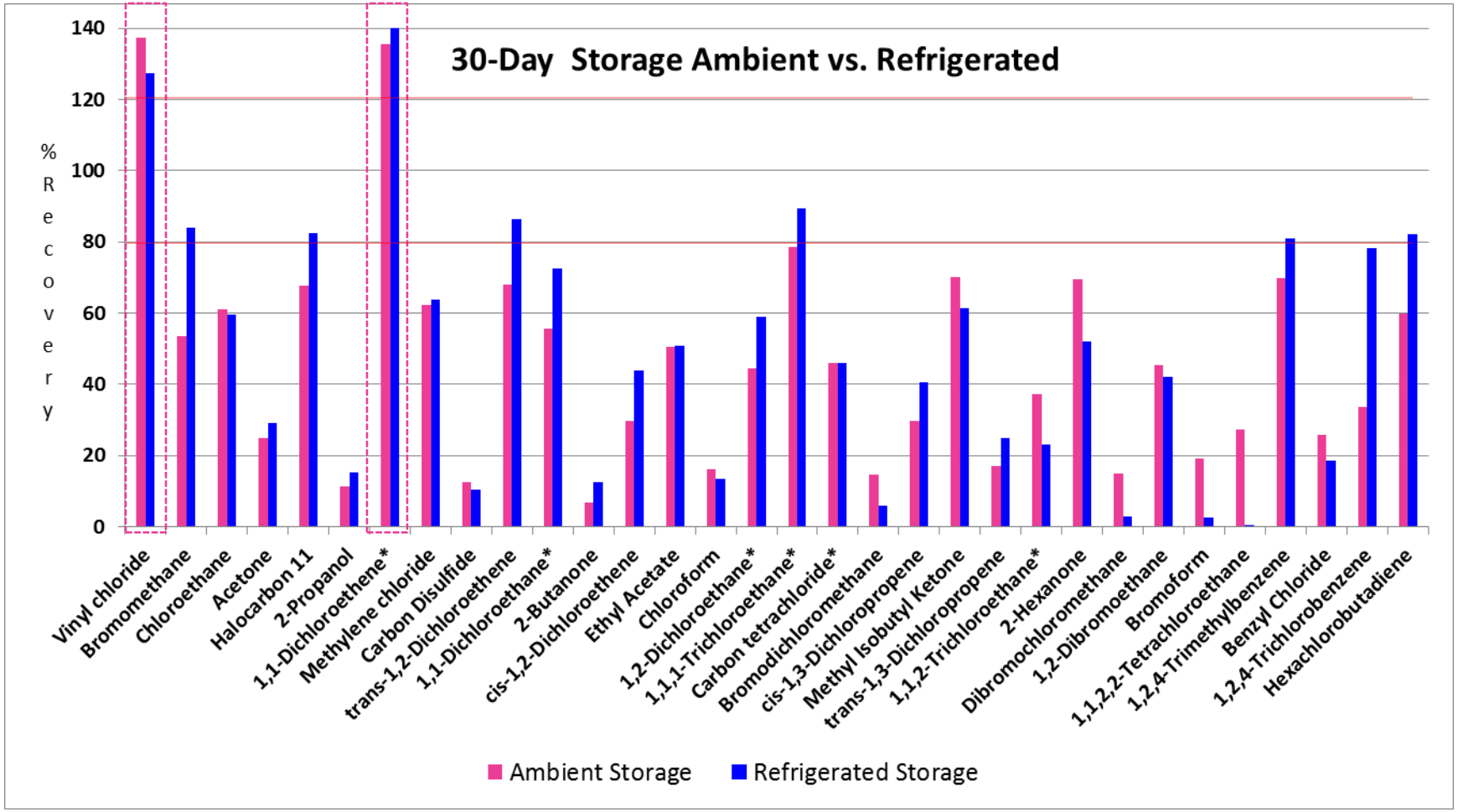
Criteria: Recovery = <80% or >120% @ 30 Days



The Effect of Temperature on Recovery

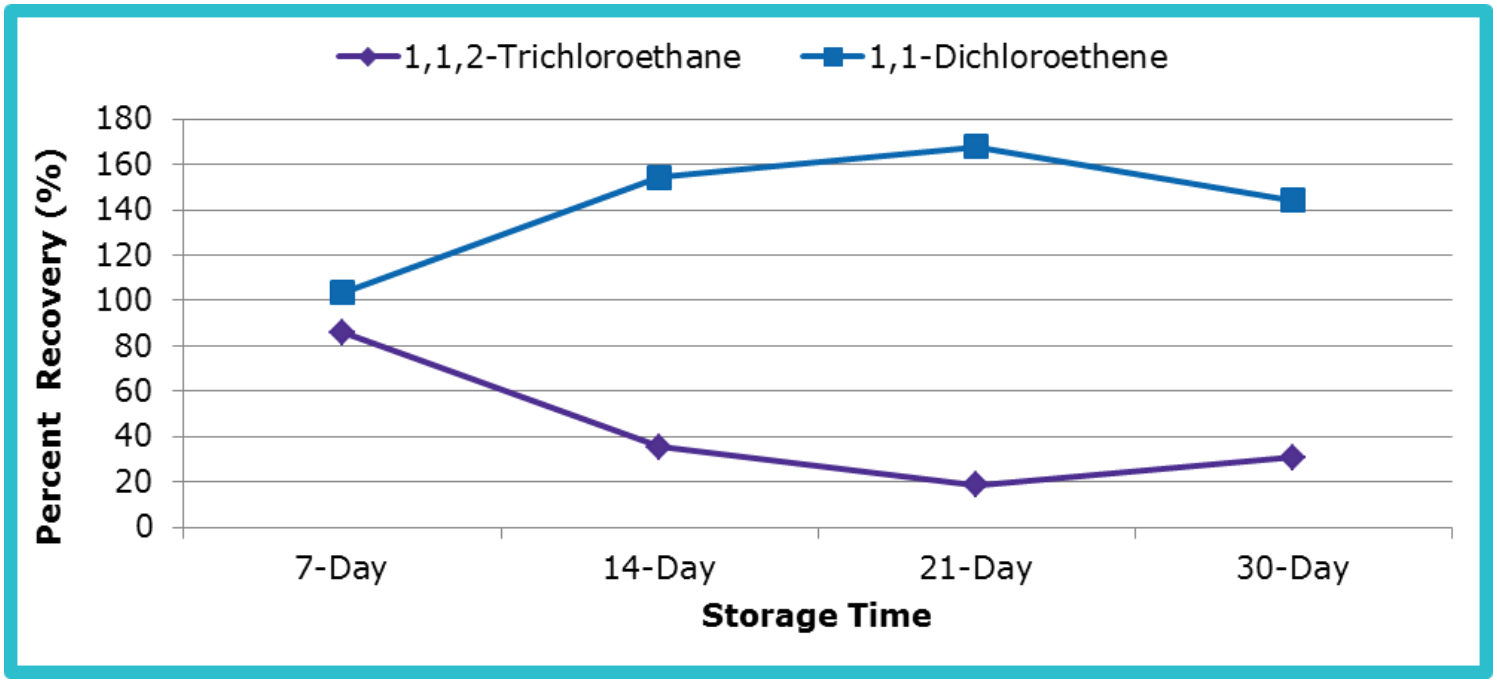
Comparison - VOC's with Poor Recovery

Criteria: Recovery = <80% or >120



Dehydrochlorination of 1,1,2-Trichloroethane ?

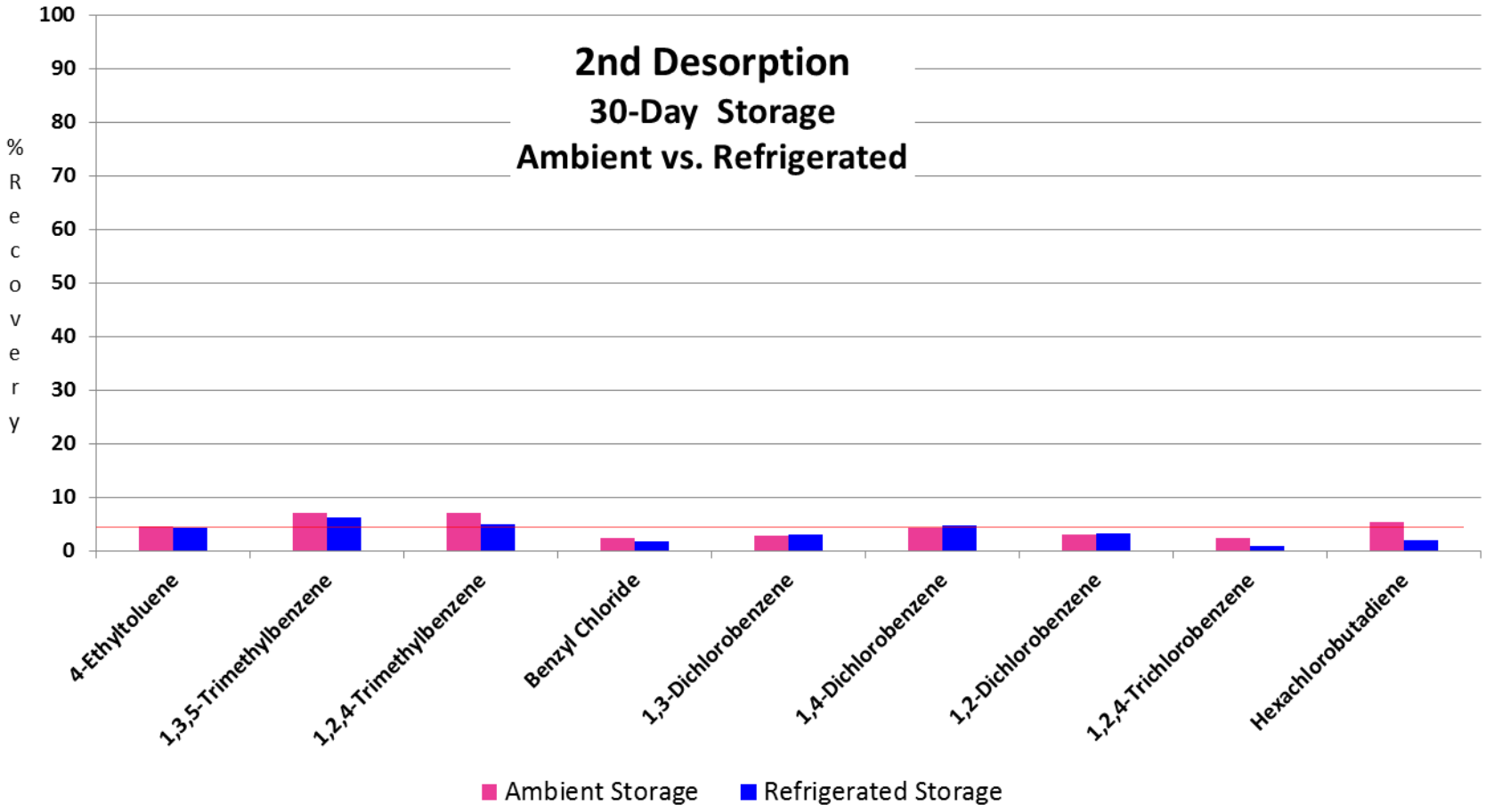
As the recovery of 1,1,2-Trichloroethane decreases, the recovery of 1,1-Dichloroethene increases.



Additional research is needed to prove this!

Carryover (Re-desorption of the Tube)

Criteria: Recovery >5%



Discussion

- Sampling tubes were desorbed for 5 minutes at 330°C. Increasing the desorption time may reduce carryover and improve the recovery values of the high molecular weight compounds.

- The abnormal high recoveries of Vinyl chloride and 1,1-Dichloroethene, appears to be caused by a breakdown of larger molecular weight chlorinated compounds over time. Spiking the tube with individual compounds would help in determining which compounds are breaking down over time.

Resent Study Published by the U.S. EPA

ELSEVIER

Atmospheric Environment

Volume 163, August 2017, Pages 99-106

Sample integrity evaluation and EPA method 325B interlaboratory comparison for select volatile organic compounds collected diffusively on Carbopack X sorbent tubes

Karen D. Oliver [a], Tamira A. Cousett [b], Donald A. Whitaker [a], Luther A. Smith [c], Shaibal Mukerjee [a], Casson Stallings [d], Eben D. Thoma [e], Lillian Alston [f], Maribel Colon [a], Tai Wu [e], Stacy Henkle [b]

The U.S. EPA study concluded…Benzene, Toluene, Tetrachloroethene, Ethylbenzene, m&p-Xylene, Styrene, and o-Xylene are stable for up 6 months when tubes were refrigerated.

Conclusions

- The storage temperature does not have a significant impact on recovery.
- Recoveries of 90% or better were obtained for Benzene and the other aromatics compounds with tubes stored for 30 days.
- 1,3-Butadiene stores well on the sampling tubes for 30 days.
- The recovery of all the brominated VOC's dropped below 80% after 14 days of storage, so storage time needs to limited to 7 days
- The abnormal high recoveries of Vinyl chloride and 1,1-Dichloroethene are most likely caused by a breakdown of larger molecular weight chlorinated compounds.
- There are a number of other compounds that store well on Carbopack X, which warrants future research studies to determine the passive sampling rates for these compounds.
- The parameters we used to spike the tubes allowed us to assess the ability of Carbopack X to retain the compounds over time. These findings provides us with a direction for future research.

thank you

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