An Investigation of Different Types of Storage Containers for Method 325

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2016 NEMC Conference
Orange County, CA - August 11, 2016

INTRODUCTION

- EPA Method 325 uses Thermal Desorption (TD) tubes to passively collect air samples along the fence line of petroleum refineries. It specifies the sampling tubes are sealed using metal long-term storage caps to prevent contamination before and after sampling.

- The method also requires the tubes to be stored in some sort of storage container.

- This research evaluates storage containers made of different materials. We investigated what VOC’s are emitted by the containers, and how effective they’re at preventing the ingress of the VOC's from external sources.

INTRODUCTION (cont.)
Excerpts from Method 325

Source: Section 4.3 of Method 325A

- "When not being used for field monitoring, the capped tubes <u>must be stored</u> in a clean, air-tight, shipping container to prevent the collection of VOCs (see Section 6.4.2 of Method 325B)."

Source: Section 6.4.2 of Method 325B

- "Storage and transportation containers. Use clean glass jars, metal cans or rigid, non-emitting polymer boxes."

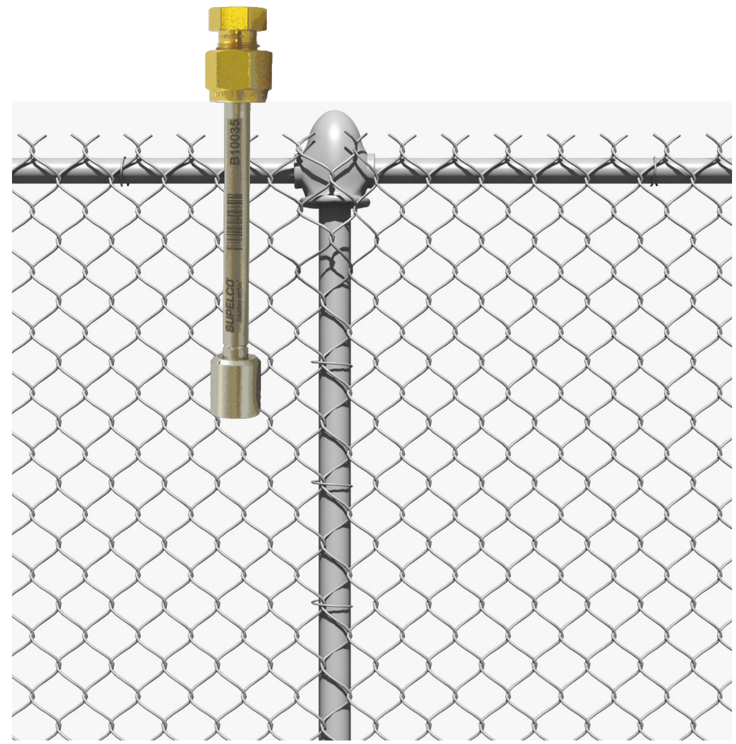
Source: Section 8.2.2 of Method 325B

- "The capped tubes <u>must be kept</u> in appropriate containers for storage and transportation."

INTRODUCTION (cont.)

What is EPA Method 325?

- A new air sampling method for monitoring the fenceline of petroleum refineries.
- It’s specific for monitoring the average air concentration of volatile organic compounds (VOC’s).
- Samples are collected by using passive sampling tubes that are strategically placed along the fenceline.
- The tubes are then sent to a laboratory to be analyzed using thermal desorption and gas chromatography.



INTRODUCTION (cont.)
Storage Times

Sampling Tubes will spend a lot of time in storage, so the secondary storage container maybe useful at maintaining sample integrity.

- Sampling tubes tubes must be used for sampling within 30 days of being conditioned.

- The tubes are deployed in the field for 14 days.

  (The long term storage cap from the sampling inlet is to be stored in the empty storage container)

- The tubes must be analyzed within 30 days.

INTRODUCTION (cont.)
What's the Difference Between the Caps?

Long Term Storage Caps
Protect the tubes from contamination before and after sampling. The seal is made using a PTFE ferrule inside the caps.

Diffusive Cap
Placed on the tube (in the field) prior to putting them in the shelter.

Analytical Caps
Seals the tubes during analysis.

Overview

- The long-term storage caps alone provide an adequate seal that prevents volatiles from entering the tubes during transport & storage… if they're properly tightened. *(They already have a >30 year track record)*

- But, people can forget to tighten one or both of the long term storage caps.

or

- If the lab chooses to refrigerate the samples, the caps can loosen, since the PTFE ferrule inside the long-term storage cap has a different thermal expansion coefficient than the stainless steel tube.

The consequence………

- If the long storage caps fail, and the wrong storage container is used - the storage container itself could be a source of contamination….

EXPERIMENTAL
Goal of the Study

- We investigated five different types of storage containers.

- The first test investigated what contaminants were emitted from each type of storage container.

- The second test investigated how effective the storage containers were at preventing the ingress of a 62-component volatile gas mix through the storage containers and into the sampling tubes.

EXPERIMENTAL (cont.)
Passive Sampling Tube used in the Study

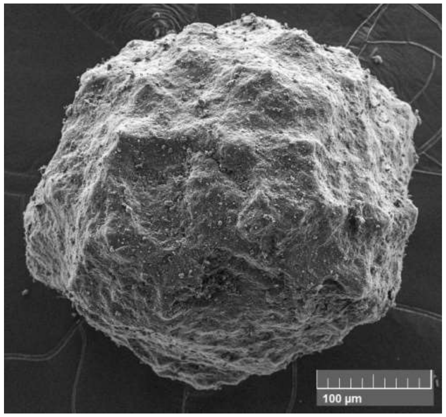
Tube Dimensions: 3.5-inches (89 mm) long x 1/4 inch (6.4 mm) O.D. x 5 mm I.D.

- Tubes were packed with Carbopack X, conditioned at 350° C with N_2 at 100 mL/min.
- Tubes were pre-tested to make sure they were free of contaminants prior to the experiments.

EXPERIMENTAL (cont.)
Adsorbent used in the Passive Sampling Tube

- **Carbopack X has the most validated uptake rates listed in the method.**
  - Hydrophobic – so very little water vapor is retained while sampling.
  - It retains & releases a wide range of volatile compounds.
  - It bridges the gap between other graphitized carbon blacks, and the stronger carbon molecular sieves adsorbents.

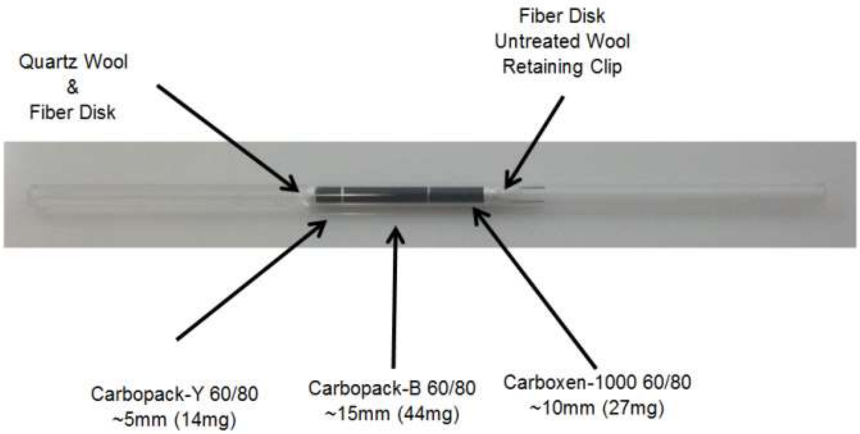
BET Surface Area	Density	Pore Diameter
240 m^2/g	**0.44 g/cc**	**100 Å**



EXPERIMENTAL (cont.)
Analytical Parameters

- Thermal Desorber: PerkinElmer TurboMatrix
- Tube Desorb: 330°C for 5 min.
- 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)



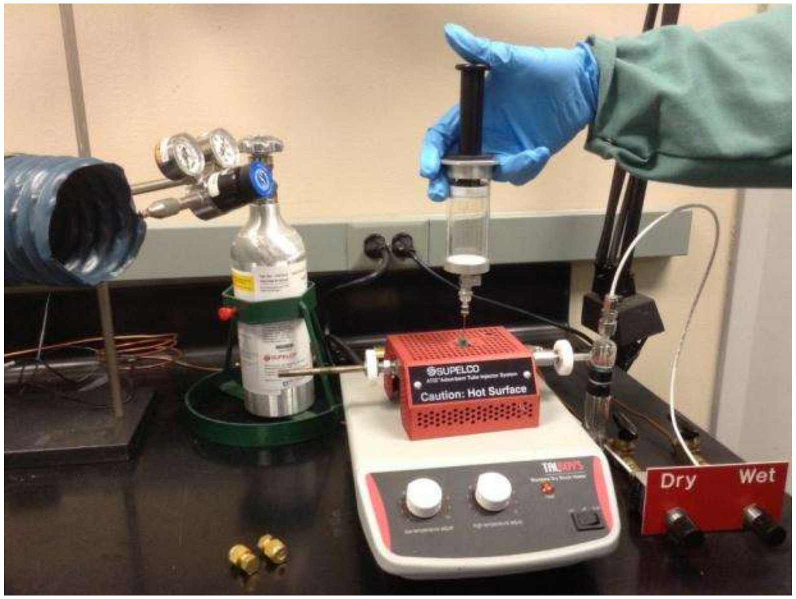
- GC/MS: Agilent 7890B / 5977A MS
- Column: Equity-1 60 M x 0.25 mm ID x 1.0 µm film (28050-U)
- 40°C for 5min,10°C/min hold for 0min 15°C/min/ to 230°C hold for 5min.
- Flow Rate: 2.0mL/min
- Scan Range: 35 to 300 amu

EXPERIMENTAL (cont.)
Components in the Gas Mix

Component	CAS#	Component	CAS#
Propylene	115-07-1	Cyclohexane	110-82-7
Halocarbon 12	75-71-8	1,2-Dichloropropane	78-87-5
Chloromethane	74-87-3	Bromodichloromethane	75-27-4
Halocarbon 114	76-14-2	Trichloroethene	79-01-6
Vinyl chloride	75-01-4	Heptane	142-82-5
1,3-Butadiene	106-99-0	4-Methyl-2-Pentanone (MIBK)	108-10-1
Bromomethane	74-83-9	cis-1,3-Dichloropropene	10061-01-5
Chloroethane	75-00-3	trans-1,3-Dichloropropene	10061-02-6
Ethanol	64-17-5	1,1,2-Trichloroethane	79-00-5
Acetone	67-64-1	Toluene	108-88-3
2-Propanol	67-63-0	2-Hexanone	591-78-6
Halocarbon 11	75-69-4	Dibromochloromethane	124-48-1
1,1-Dichloroethene	75-35-4	1,2-Dibromoethane	106-93-4
Methylene chloride	75-09-2	Tetrachloroethene	127-18-4
Halocarbon 113	76-13-1	Chlorobenzene	108-90-7
Carbon Disulfide	75-15-0	Ethylbenzene	100-41-4
trans-1,2-Dichloroethene	156-60-5	m & p-Xylene	108-38-3 & 106-42-3
1,1-Dichloroethane	75-34-3	Bromoform	75-25-2
Methyl Tertiary Butyl Ether (MTBE)	1634-04-4	Styrene	100-42-5
Vinyl Acetate	108-05-4	1,1,2,2-Tetrachloroethane	79-34-5
2-Butanone (MEK)	78-93-3	o-Xylene	95-47-6
cis-1,2-Dichloroethene	156-59-2	4-Ethyltoluene	622-96-8
Ethyl Acetate	141-78-6	1,3,5-Trimethylbenzene	108-67-8
Hexane	110-54-3	1,2,4-Trimethylbenzene	95-63-6
Chloroform	67-66-3	Benzyl Chloride	100-44-7
Tetrahydrofuran	109-99-9	1,3-Dichlorobenzene	541-73-1
1,2-Dichloroethane	107-06-2	1,4-Dichlorobenzene	106-46-7
1,1,1-Trichloroethane	71-55-6	1,2-Dichlorobenzene	95-50-1
Benzene	71-43-2	1,2,4-Trichlorobenzene	120-82-1
Carbon tetrachloride	56-23-5	Hexachlorobutadiene	87-68-3

EPA Method 325 Target Compounds

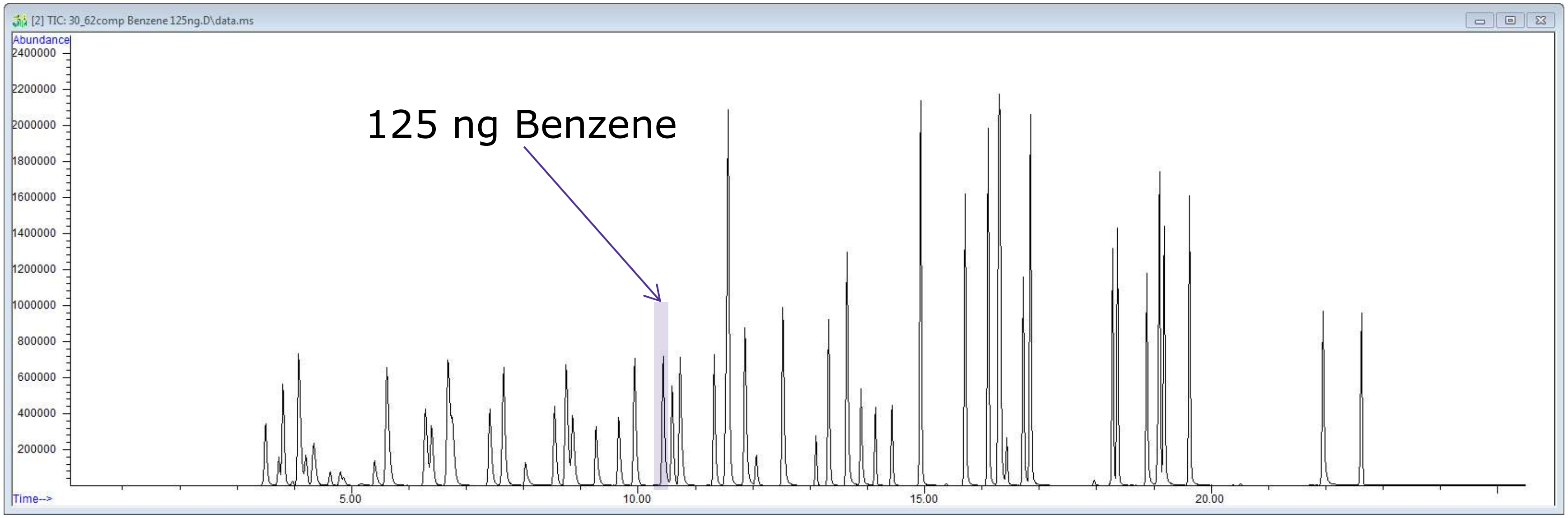
EXPERIMENTAL (cont.)
Calibration of the Analytical System



- Single-point calibration - Three Carbopack X tubes were spiked with 40 mL of the 62-component gas mix.
- The gas mix was injected into a humidified (50%RH) gas stream of N_2 which carried the components to the tube at flow rate of 50 mL/min.
- The tube remained attached to the device for 5 minutes to allow complete transfer to the sampling tube.

EXPERIMENTAL (cont.)

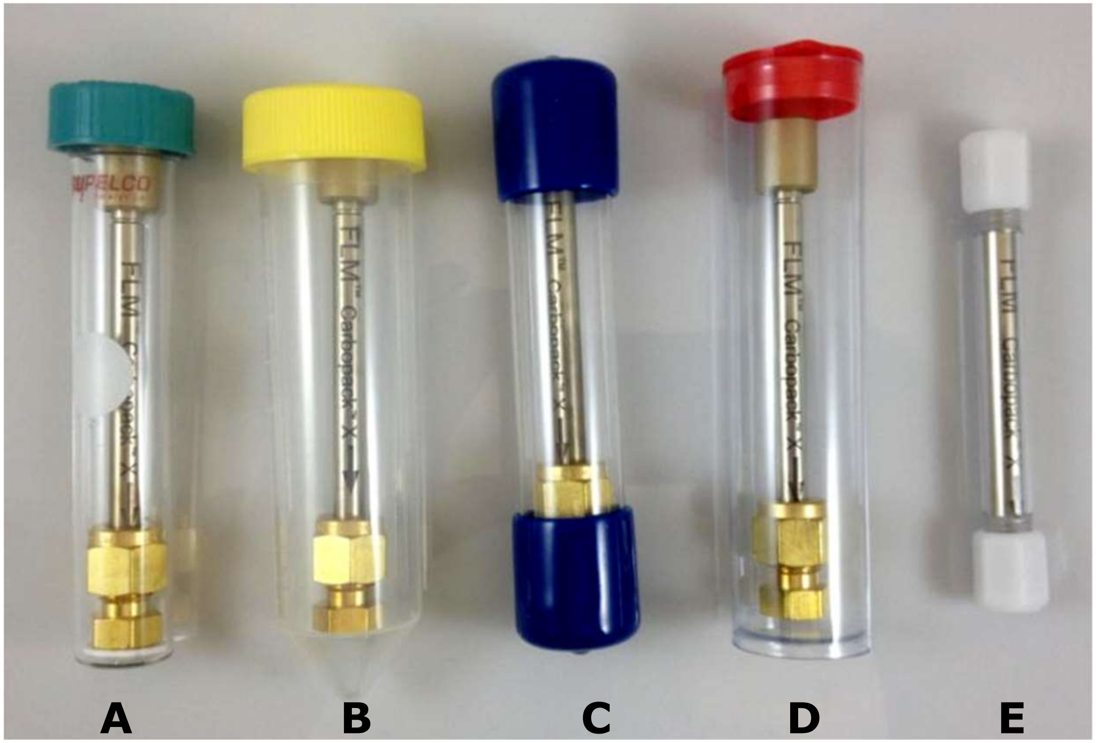
Chromatograms scaled to Benzene Action Level (Calibration from a spiked tube)



- Action Level for Benzene is 9 µg/m^3
- If we sampled an atmosphere containing 9 µg/m^3 of Benzene for 14 days, based on the published sampling rate of 0.67 mL/min there would be 125 ng of Benzene collected on tube.

All chromatograms are set to the same abundance for comparison.

EXPERIMENTAL (cont.)
Storage Containers Tested



A. Glass Container (PTFE liner seals like a vial).

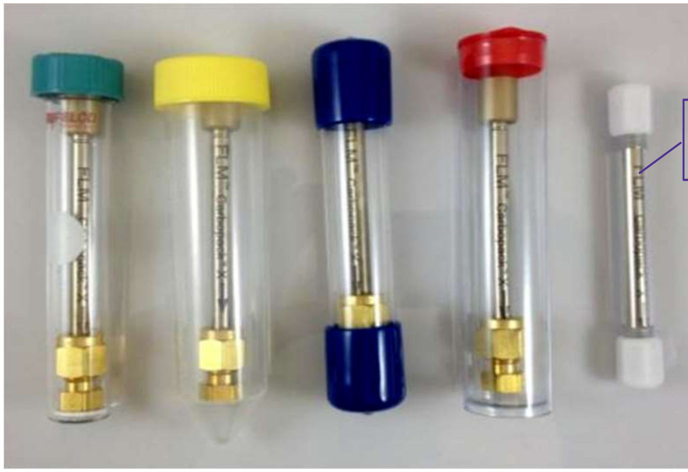
B. 50 mL Polypropylene Centrifuge Tube (Cap seals directly with the body).

C. Clear Plastic Body (Vinyl caps slip over the body).

D. Clear Plastic (PETG) Body (HDPE cap slides into the body).

E. Clear Polycarbonate (PTFE liners seal directly on the ends of the TD tube).

EXPERIMENTAL (cont.)
Preparation of Samples



See *Exception*

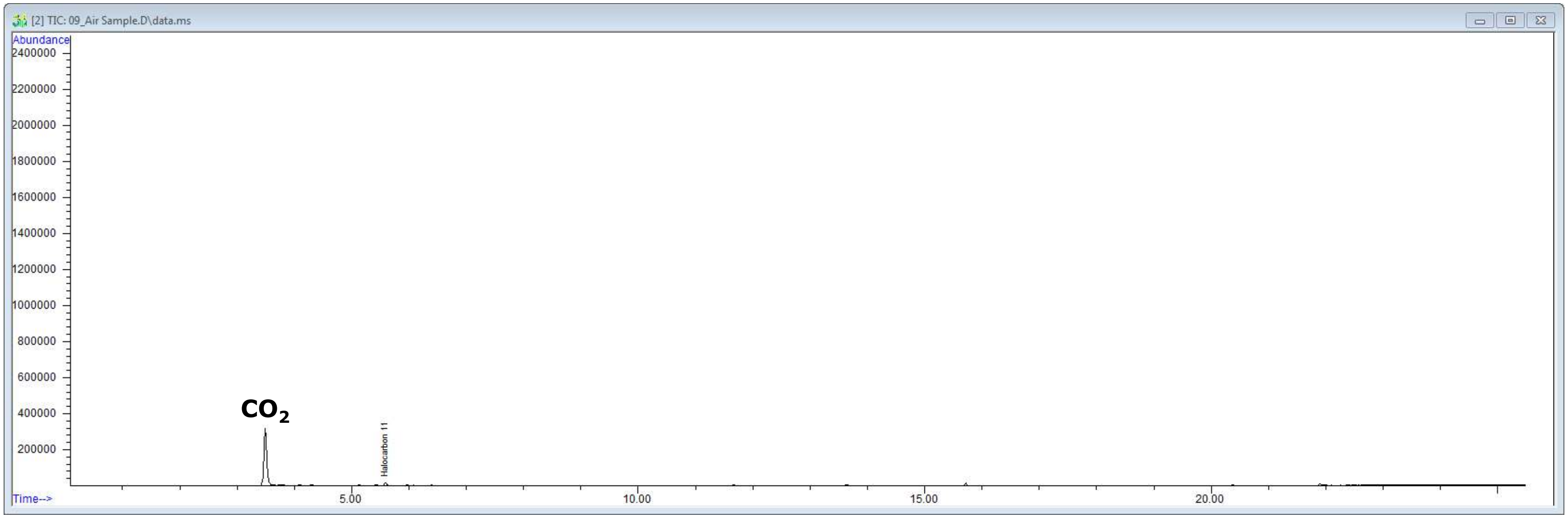
Torque Driver used to tighten Long-term Storage caps

1. Tubes were conditioned and tested to verify no contaminates were present.
2. The outlet of the tube was sealed with a brass long-term storage cap. *(tightened to 10-inches pounds).*
3. A diffusive sampling cap was placed on the inlet.
4. A single sampling tube was placed in each storage container and sealed with the storage container cap.
5. Tubes were stored at room temperature for 48 hours.

Exception: The container on the right - seals directly on the ends of tube, so the long-term storage cap & diffusive cap could not be used.

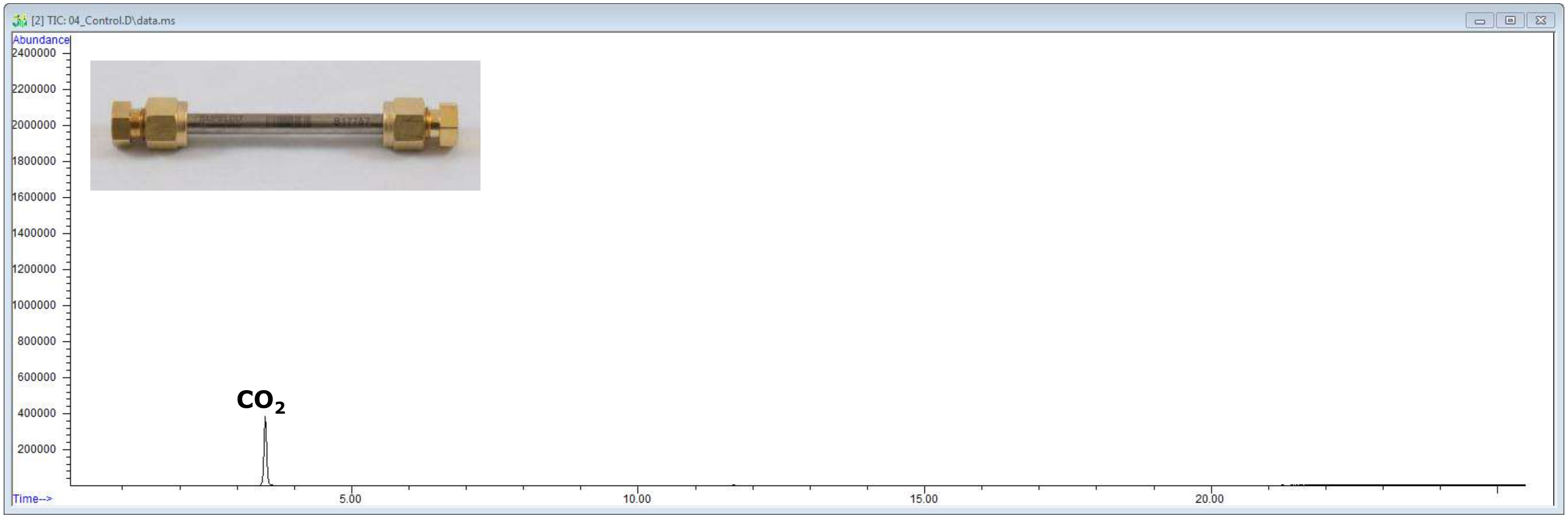
Background Emitted By The Containers

Passive air samples taken during the experiment



- 48-hours passive air sample of the R&D office area where the samples were stored
- Freon-11 was detected.

Control – Long Term Storage on Both Ends (No Storage Container)

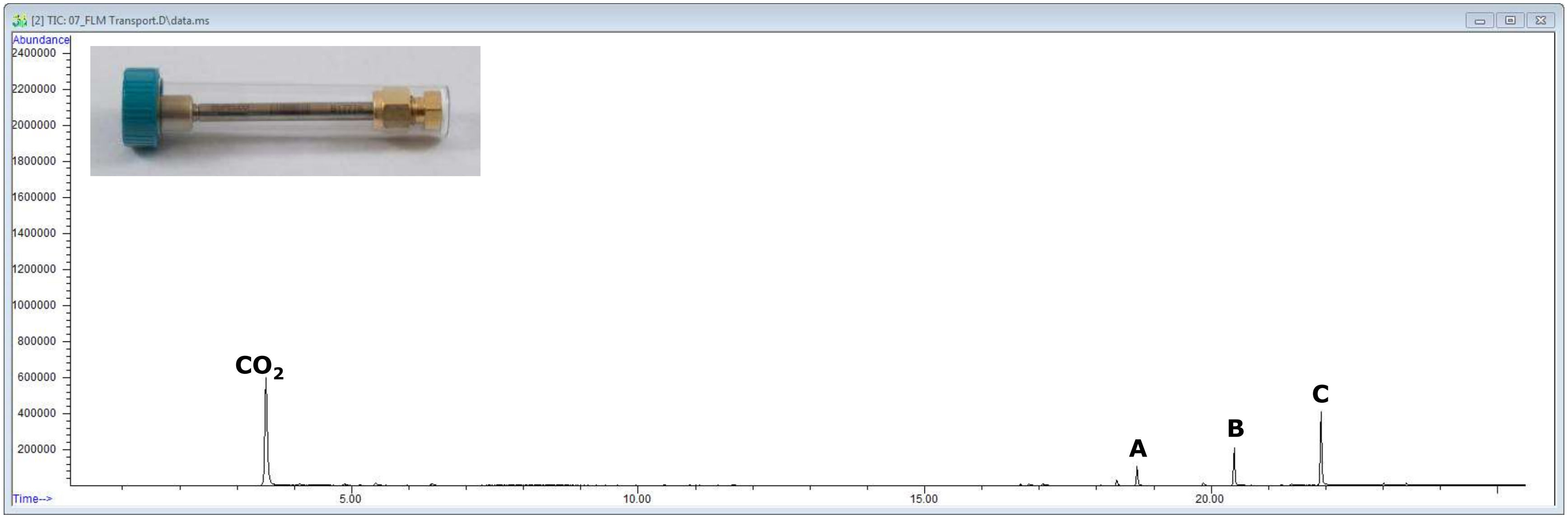


- Control Sample: Carbopack-X tube with Long-Term Storage Caps on each of the tube.

No contaminates were detected

None Detected

Glass Storage Container



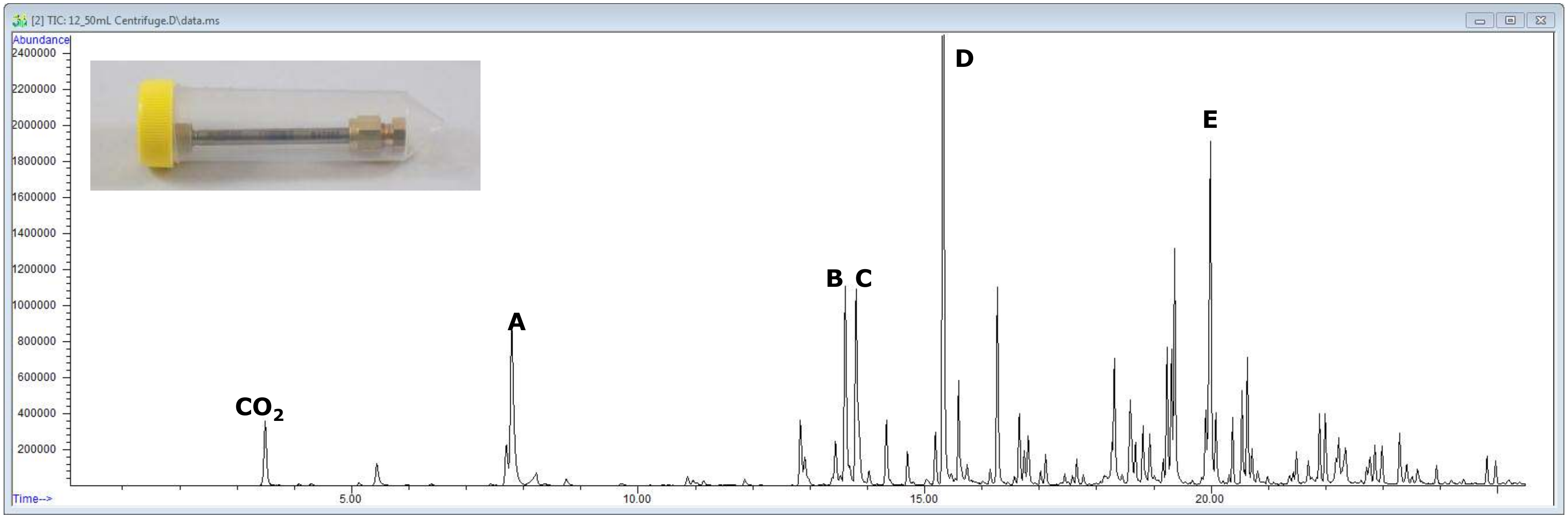
Top contaminates detected based on NIST library match

A	Octanal
B	Nonanal
C	Decanal

Calibrated VOC's identified

Ethanol	10ng
Acetone	7ng

50 mL Plastic Centrifuge Tube



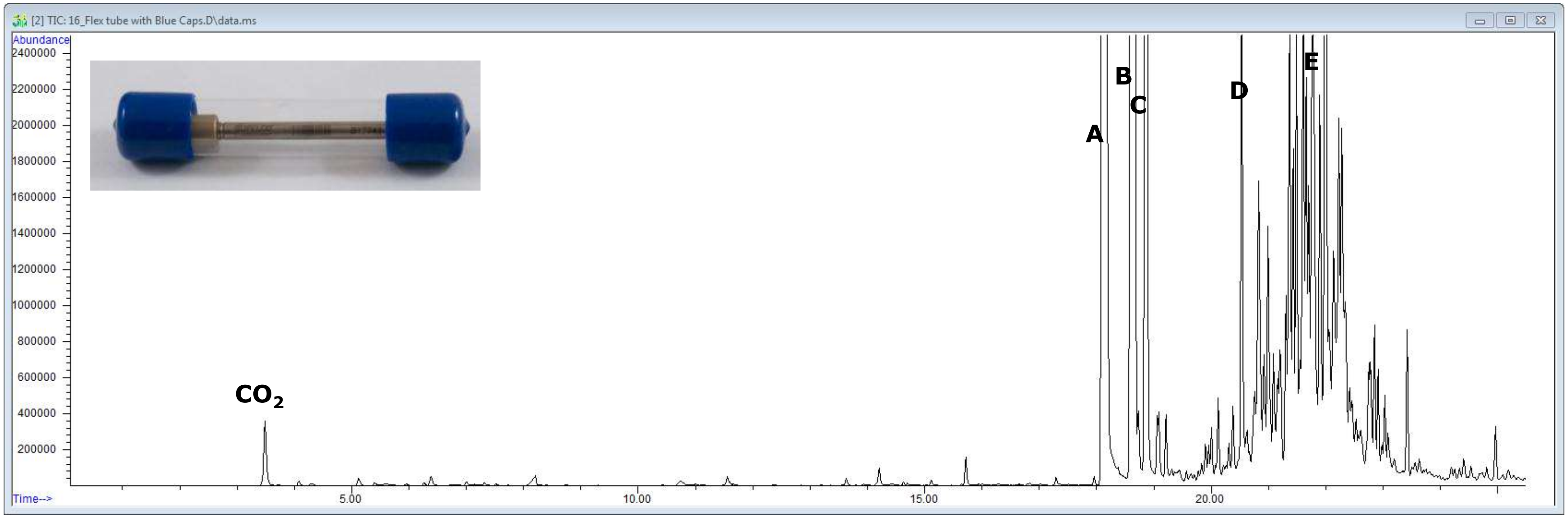
Top contaminates detected based on NIST library match

A	2-Methylpentane
B	2,3,3-Trimethylpentane
C	4-Methylheptane
D	2,4-Dimethylheptane
E	5-Methylundecane

Calibrated VOC's identified

Acetone	31ng
Vinyl Acetate	205ng
2-Butanone	48ng
Hexane	7ng
Heptane	5ng
4-Methyl-2-Pentanone (MIBK)	45ng
2-Hexanone	180ng

Clear Plastic Tube with Vinyl Blue Caps



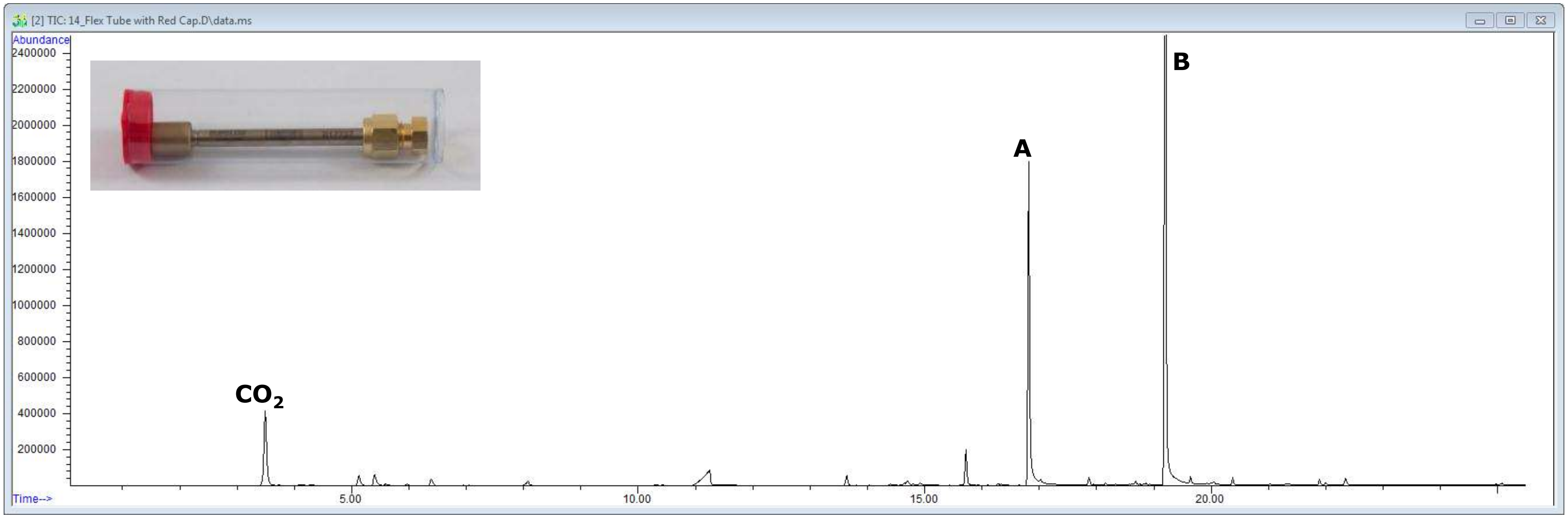
Top contaminates detected based on NIST library match

A	Phenol
B	2-Propanol, 1-(2-methoxy-1-methylethoxy)
C	2-Propanol, 1-(2-methoxypropoxy)
D	Undecane
E	Dodecane

Calibrated VOC's identified

Acetone	11ng
Methylene Chloride	23ng
2-Butanone	36ng
Benzyl Chloride	30ng

Clear Plastic Tube with Red Cap



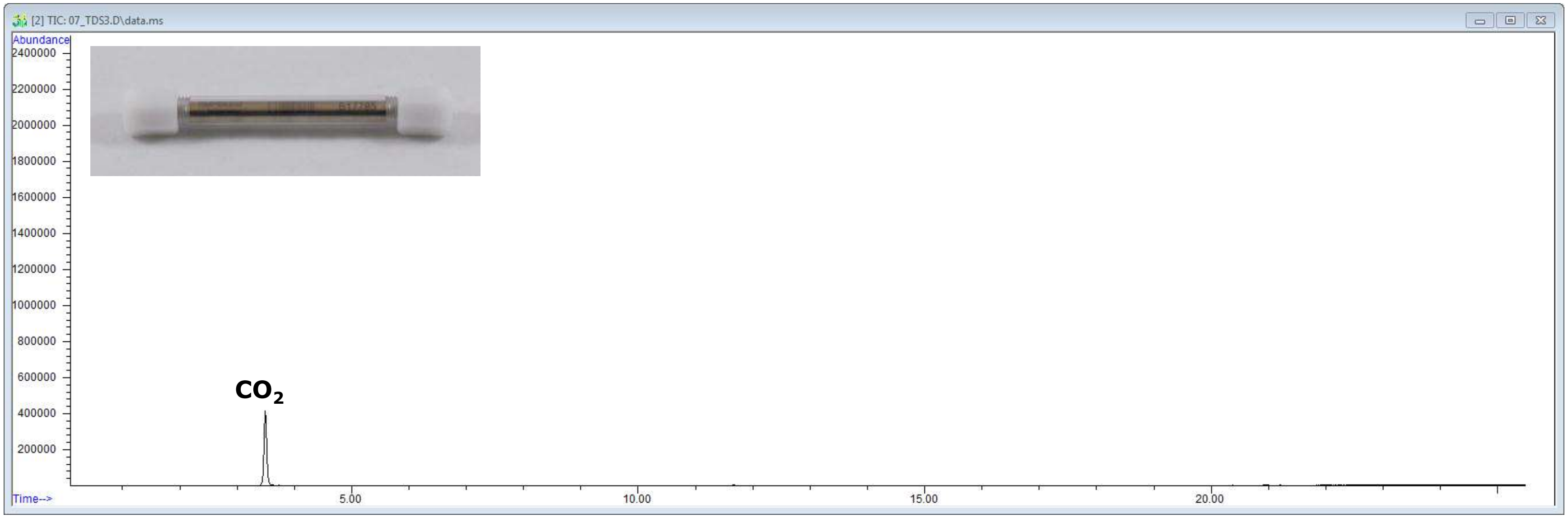
Top contaminates detected based on NIST library match

A	2-Butoxyethanol
B	2-Ethyl-1-hexanol

Calibrated VOC's identified

Acetone	42ng
Methylene Chloride	17ng
2-Butanone	11ng

Clear Plastic Tube with White Caps and PTFE Liners



Top contaminates detected based on NIST library match

None Detected

Calibrated VOC's identified

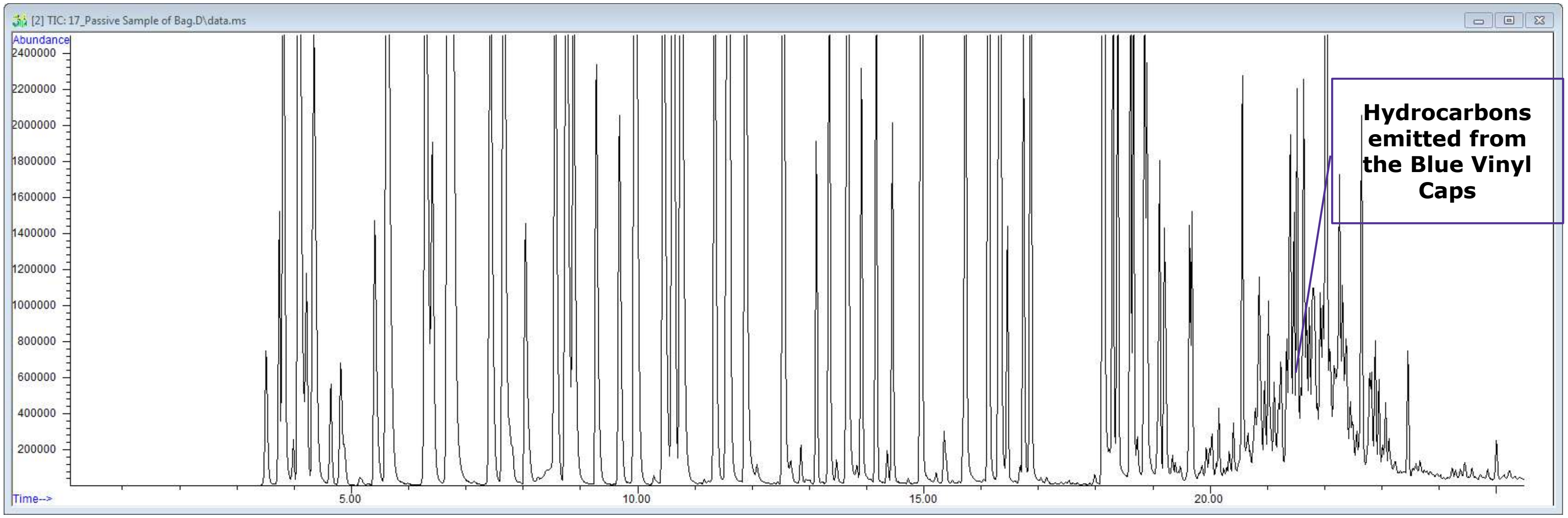
None Detected

How Effective the Storage Container Are At Preventing The Ingress Of The VOC's

Testing the storage containers ability to keep volatiles from migrating into the containers

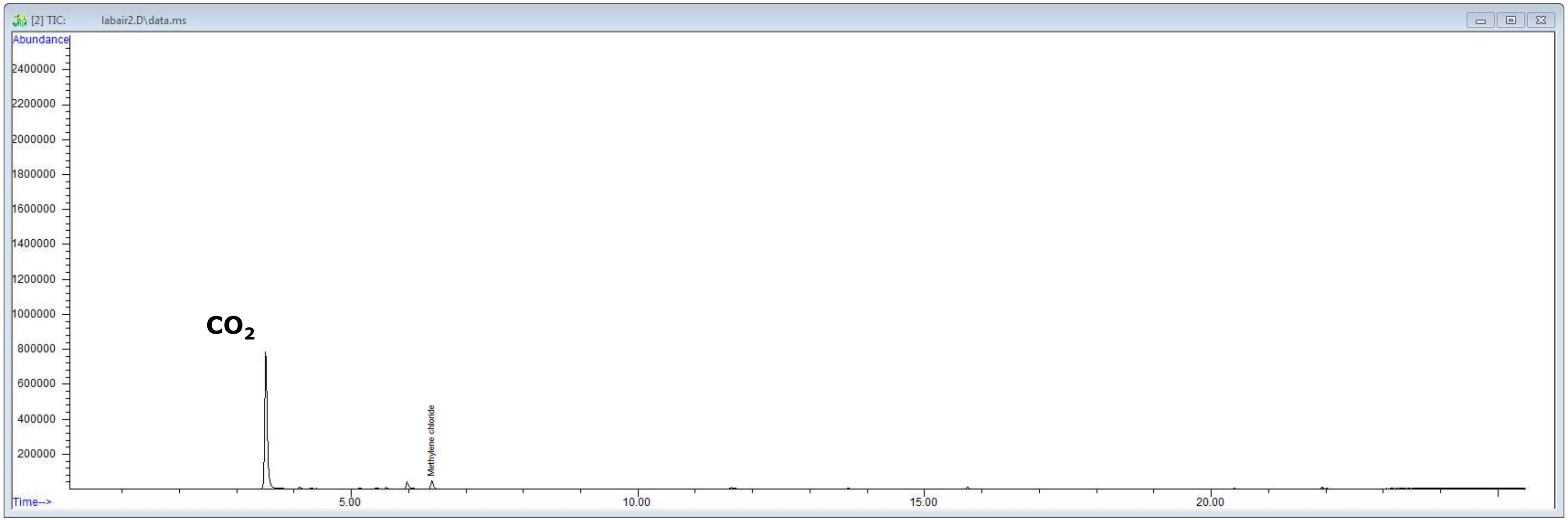
- 2-Liter Tedlar sampling bag was cut open and the samples placed inside.
- The corner was resealed and the bag was filled with a 62-component volatile gas mix *(each component 1 ppmv).*
- The storage containers remained in the bag for 48-hours.

Passive Air Sample inside the Tedlar Bag



- Passive air sample of the contents in the bag.

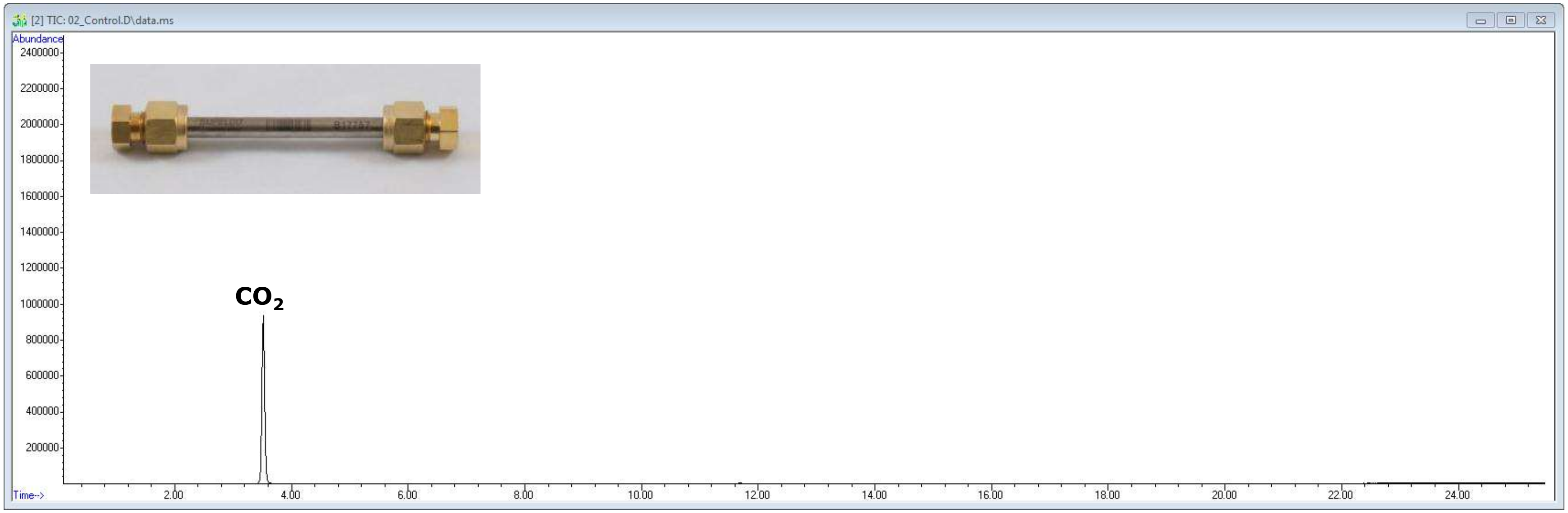
Passive Air Sample of the Laboratory



- 48-hours passive air sample of the R&D Laboratory where the samples were stored .
- Acetonitrile and Methylene Chloride was detected.

Results - Ingress of VOC's into the Storage Containers

Control – Long Term Storage on Both Ends (No Storage Container)

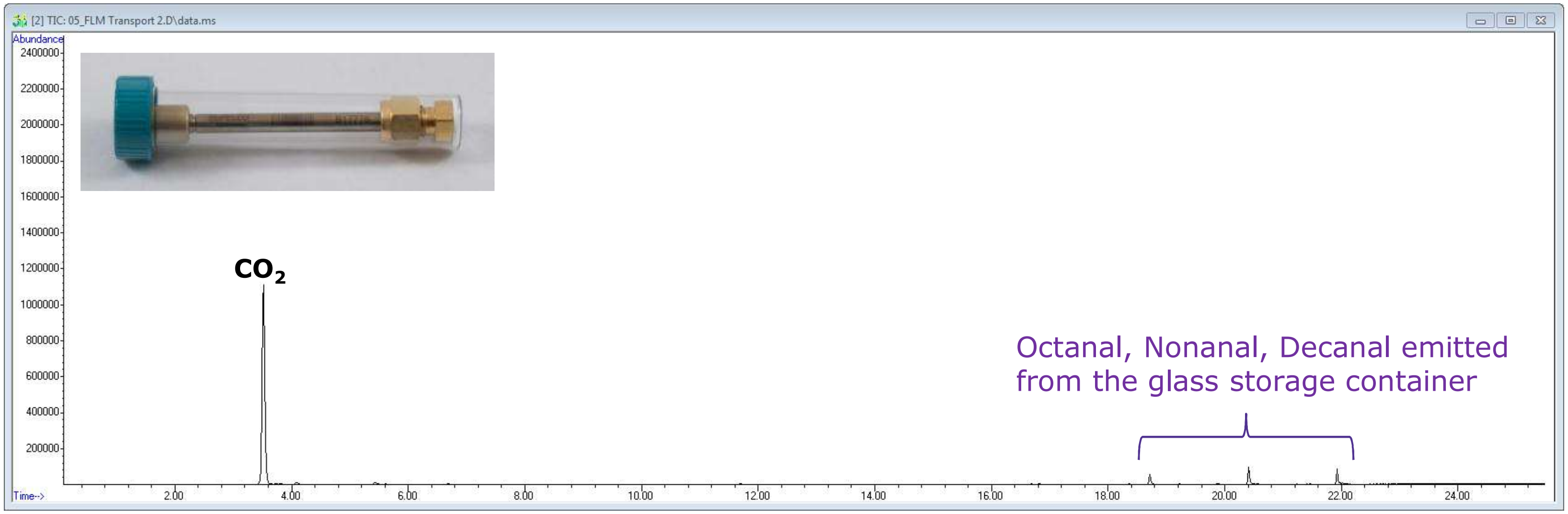


- Control Sample: Carbopack-X tube with Long-Term Storage Caps on each of the tube.

Compound that migrated past the Long Term Storage Caps

None Detected

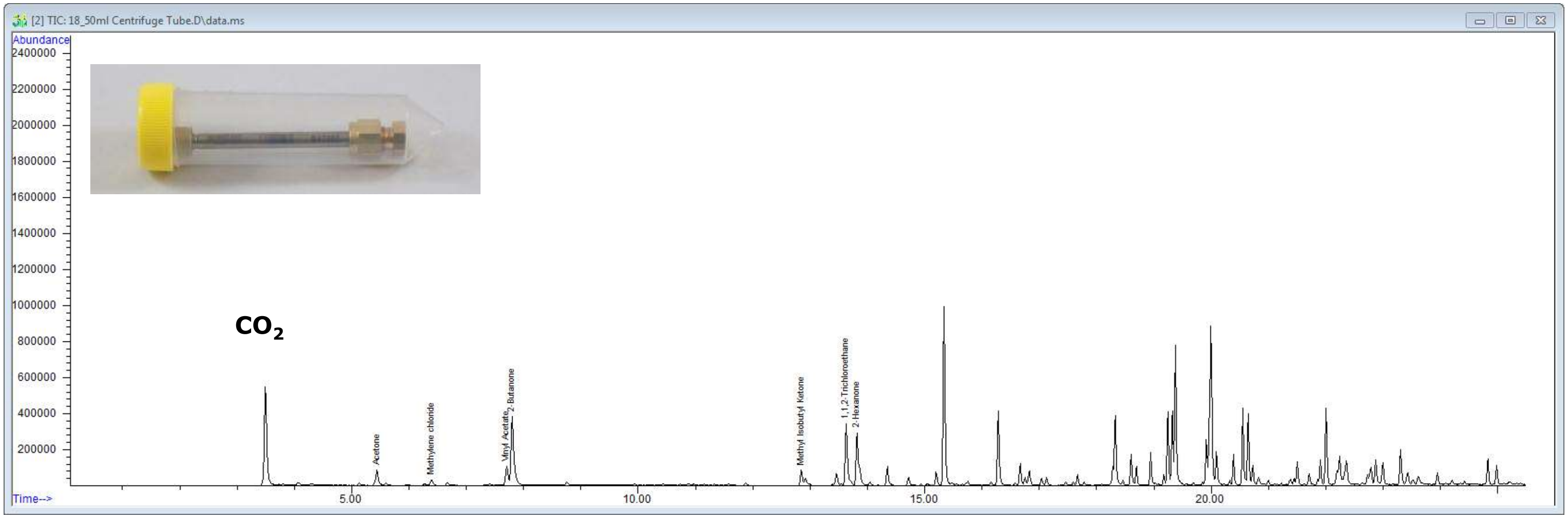
Glass Storage Container



Compound that migrated inside the container

None Detected

50 mL Plastic Centrifuge Tube

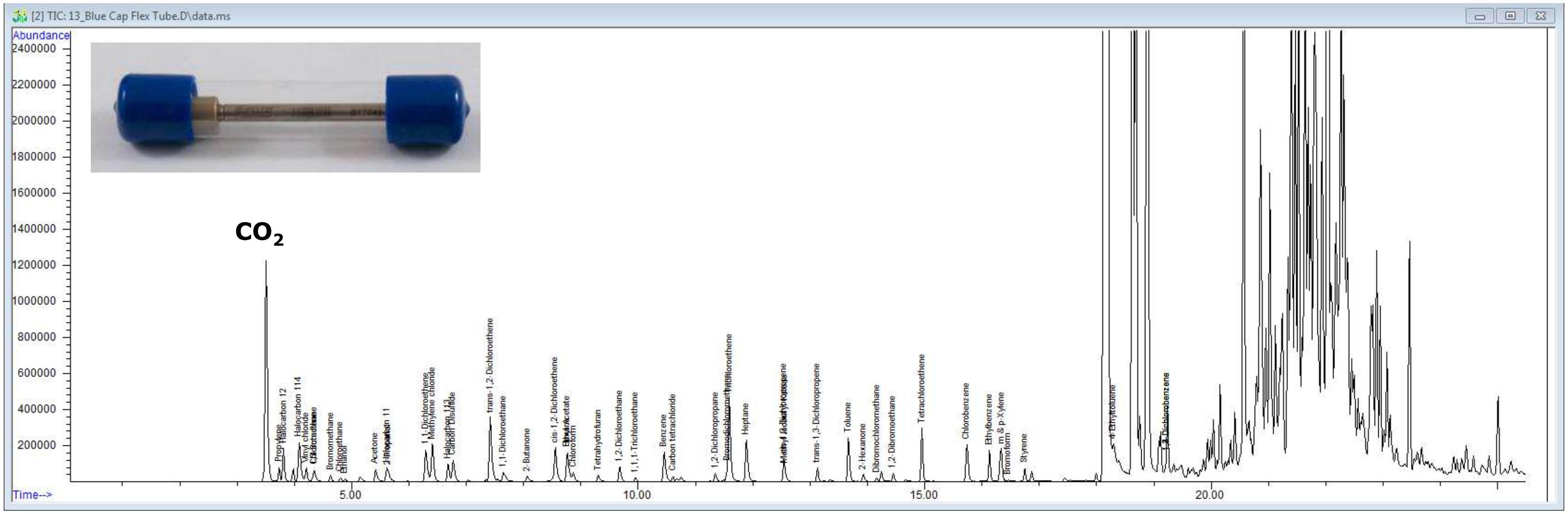


Compound that migrated inside the container

Acetone	**22ng**
Methylene chloride	**12ng**
Vinyl Acetate	**88ng**
2-Butanone (MEK)	**150ng**
4-Methyl-2-Pentanone (MIBK)	**10ng**
1,1,2-Trichloroethane	**5ng**
2-Hexanone	**48ng**

Results - Ingress of VOC's into the Storage Containers

Clear Plastic Tube with Vinyl Blue Caps

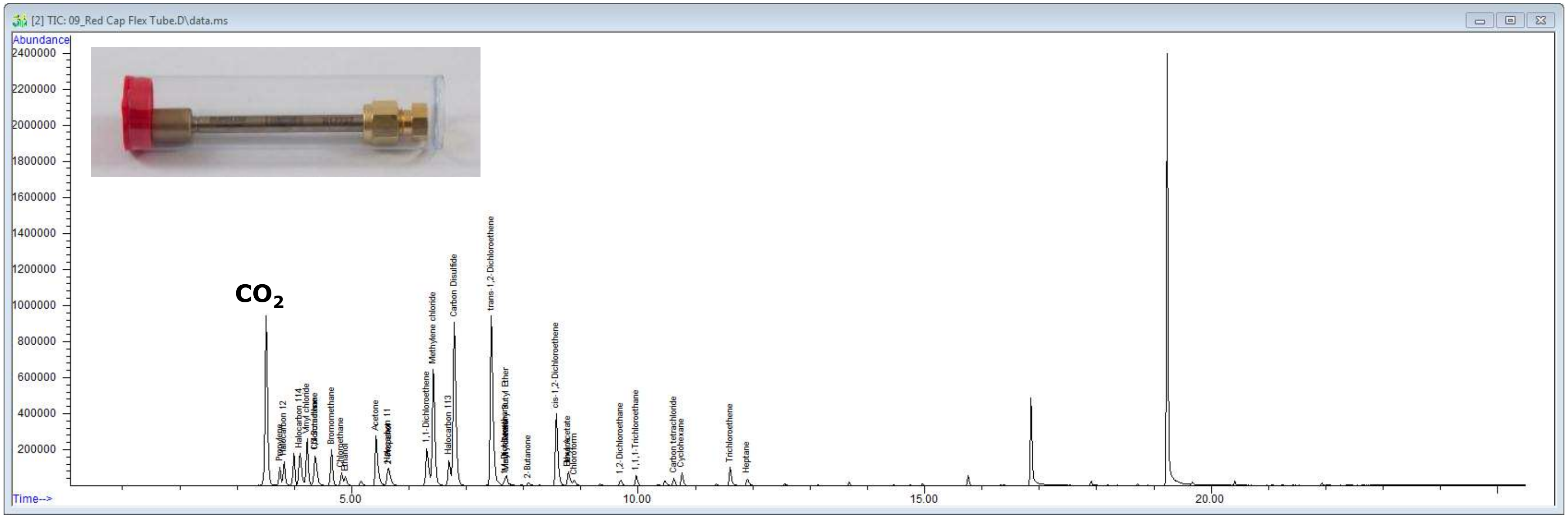


Compounds that migrated inside the container:

Propylene	26ng	2-Butanone (MEK)	25ng	2-Hexanone	11ng
Halocarbon 12	50ng	cis-1,2-Dichloroethene	59ng	Dibromochloromethane	15ng
Chloromethane	20ng	Ethyl Acetate	32ng	1,2-Dibromoethane	29ng
Halocarbon 114	62ng	Hexane	25ng	Tetrachloroethene	39ng
Vinyl chloride	39ng	Chloroform	19ng	Chlorobenzene	20ng
1,3-Butadiene	24ng	Tetrahydrofuran	11ng	Ethylbenzene	28ng
Bromomethane	57ng	1,2-Dichloroethane	31ng	m & p-Xylene	24ng
Chloroethane	24ng	1,1,1-Trichloroethane	5ng	Bromoform	6ng
Ethanol	21ng	Benzene	29ng	Styrene	10ng
Acetone	40ng	Carbon tetrachloride	9ng	1,1,2,2-Tetrachloroethane	N.D.
2-Propanol	7ng	Cyclohexane	N.D..	o-Xylene	N.D.
Halocarbon 11	27ng	1,2-Dichloropropane	11ng	4-Ethyltoluene	9ng
1,1-Dichloroethene	45ng	Bromodichloromethane	25ng	1,3,5-Trimethylbenzene	N.D.
Methylene chloride	78ng	Trichloroethene	49ng	1,2,4-Trimethylbenzene	N.D.
Halocarbon 113	27ng	Heptane	38ng	Benzyl Chloride	N.D.
Carbon Disulfide	61ng	4-Methyl-2-Pentanone	6ng	1,3-Dichlorobenzene	6ng
trans-1,2-Dichloroethene	108ng	cis-1,3-Dichloropropene	52ng	1,4-Dichlorobenzene	7ng
1,1-Dichloroethane	21ng	trans-1,3-Dichloropropene	53ng	1,2-Dichlorobenzene	7ng
Methyl Tertiary Butyl Ether	N.D.	1,1,2-Trichloroethane	N.D.	1,2,4-Trichlorobenzene	N.D.
Vinyl Acetate	N.D.	Toluene	27ng	Hexachlorobutadiene	N.D.

Results - Ingress of VOC's into the Storage Containers

Clear Plastic Tube with Red Cap

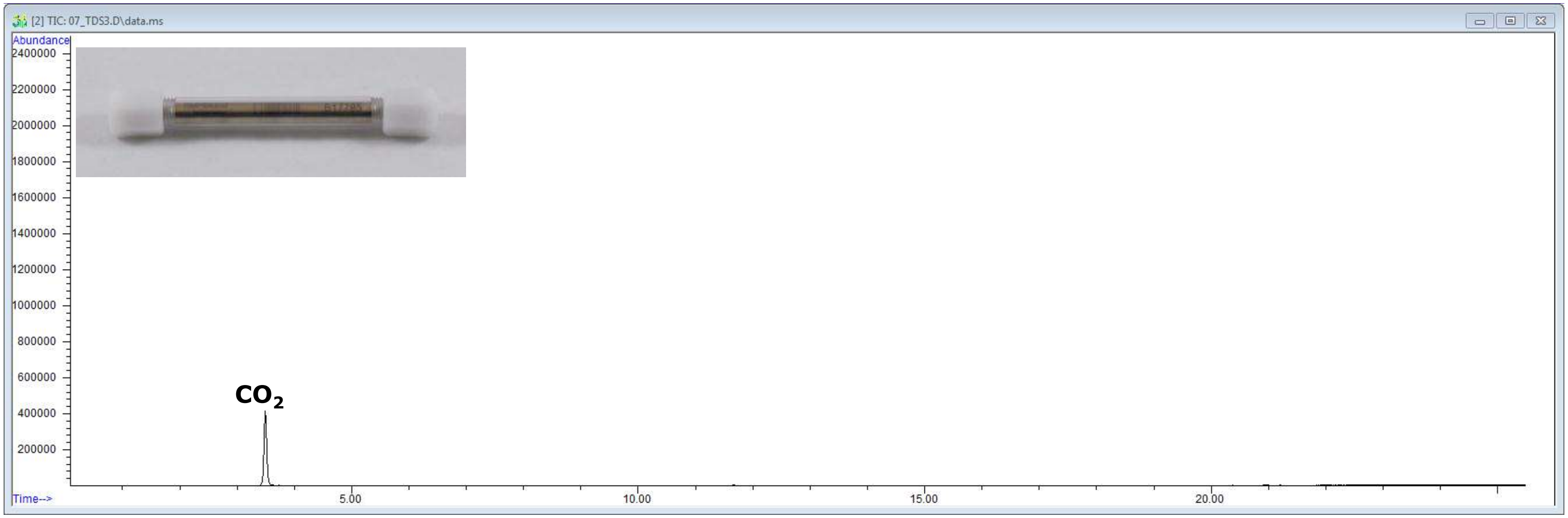


Compounds that migrated inside the container:

Propylene	36ng	2-Butanone (MEK)	14ng	2-Hexanone	N.D.
Halocarbon 12	42ng	cis-1,2-Dichloroethene	131ng	Dibromochloromethane	N.D.
Chloromethane	62ng	Ethyl Acetate	14ng	1,2-Dibromoethane	N.D.
Halocarbon 114	55ng	Hexane	11ng	Tetrachloroethene	N.D.
Vinyl chloride	150ng	Chloroform	12ng	Chlorobenzene	N.D.
1,3-Butadiene	74ng	Tetrahydrofuran	N.D.	Ethylbenzene	N.D.
Bromomethane	358ng	1,2-Dichloroethane	13ng	m & p-Xylene	N.D
Chloroethane	86ng	1,1,1-Trichloroethane	14ng	Bromoform	N.D.
Ethanol	80ng	Benzene	N.D.	Styrene	N.D.
Acetone	169ng	Carbon tetrachloride	9ng	1,1,2,2-Tetrachloroethane	N.D.
2-Propanol	34ng	Cyclohexane	15ng	o-Xylene	N.D.
Halocarbon 11	7ng	1,2-Dichloropropane	N.D.	4-Ethyltoluene	N.D.
1,1-Dichloroethene	65ng	Bromodichloromethane	N.D.	1,3,5-Trimethylbenzene	N.D.
Methylene chloride	250ng	Trichloroethene	11ng	1,2,4-Trimethylbenzene	N.D.
Halocarbon 113	42ng	Heptane	6ng	Benzyl Chloride	N.D.
Carbon Disulfide	502ng	4-Methyl-2-Pentanone (MIBK)	N.D.	1,3-Dichlorobenzene	N.D.
trans-1,2-Dichloroethene	313ng	cis-1,3-Dichloropropene	N.D.	1,4-Dichlorobenzene	N.D.
1,1-Dichloroethane	11ng	trans-1,3-Dichloropropene	N.D.	1,2-Dichlorobenzene	N.D.
Methyl Tertiary Butyl Ether	12ng	1,1,2-Trichloroethane	N.D.	1,2,4-Trichlorobenzene	N.D.
Vinyl Acetate	14ng	Toluene	N.D.	Hexachlorobutadiene	N.D.

Results - Ingress of VOC's into the Storage Containers

Clear Plastic Tube with White Caps and PTFE Liners



Compound that migrated inside the container

None Detected

Readability of Barcode through the Containers

	Quick to Read	Slow to Read	Unable to Read
	√		
		√	
	√		
	√		
	√		

Source: www.cognex.com

Tubes don't need to be removed from the storage container

Conclusion

- The long term storage caps alone will protect the tubes from volatiles during storage. A well written SOP for tightening the long term storage caps will assure the best integrity for the sample.

- The chosen storage container should not be a source of contamination, since it’s supposed to be a second layer of protection.

- The glass and plastic storage containers that used a PTFE liner emitted low levels of background, and prevented volatiles from reaching the sampling tubes.

- The laboratory should conduct a through evaluation of any storage container they plan to use.

References

- Method 325a - Volatile Organic Compounds from Fugitive and Area Sources: Sampler Deployment and VOC Sample Collection
- https://www3.epa.gov/ttnemc01/promgate/m-325a.pdf

- Method 325B - Volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis
- https://www3.epa.gov/ttnemc01/promgate/m-325b.pdf

Questions For You ?

- Does the industry need a storage container designed for a single tube?

Or

- Can a storage container be designed to hold more than one tube at a time? Can it also include the field blanks and duplicates samples?

Thank You

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