Air Monitoring Using Passive Sampling Tubes

Presenter:

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Presentation Outline

- Introduction/Background Info
- Passive Sampling Science
- Field Work with Tubes
- Tube & Canister Comparisons
- Variation in Duplicate Tubes
- Conclusions
- Acknowledgements
- Questions?

Introduction

EPA Priority:

"We will work to mitigate [climate change] by reducing carbon pollution…from the transportation and energy sectors.

Keeping communities safe and healthy requires action to reduce risks associated with exposure to chemicals in commerce, our indoor and outdoor environments, and products and food."

Administrator McCarthy

http://www2.epa.gov/aboutepa/epas-themes-meeting-challenge-ahead

Introduction

New EPA rules and regulations are coming…

- **Proposed Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards[1]**
- **EPA Method 325A – Field deployment[2]**
- **EPA Method 325B – Lab analysis[2]**

1. http://www.epa.gov/ttn/atw/petref.html
2. http://www.epa.gov/ttn/atw/petrefine/20140515fr.pdf

Background Information

Where are the areas of concern?

- Communities bordering chemical industries.
- Communities bordering oil and gas production.
- Communities bordering oil and gas refineries.

Image Credits:
http://www.denverpost.com/ci_22680620/energy-boom-nears-colorado-cities-backlash-grows
http://tinyurl.com/pvdmcfs
http://media.nola.com/environment/photo/murphy-oil-refineryjpg-52d524b899900d7a.jpg

Background Information

Passive Sampling Science

Passive sampling based on Fick's Law of Diffusion

$$J = -D \cdot \partial\phi / \partial x$$

$$JA = U_r = -D \cdot A/L \cdot (c_i - c_o)$$

J = Diffusive flux $(mol/m^2 \cdot s)$

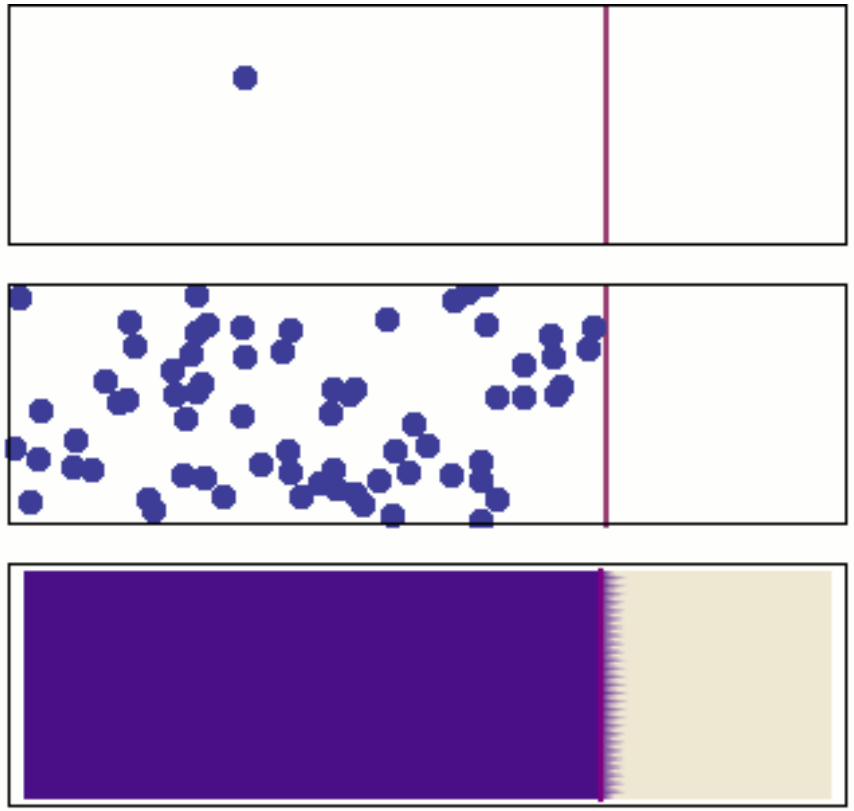
D = diffusion coefficient (m^2/s)

U_r = Uptake Rate (mol/s)

A/L = Shape parameter (m)

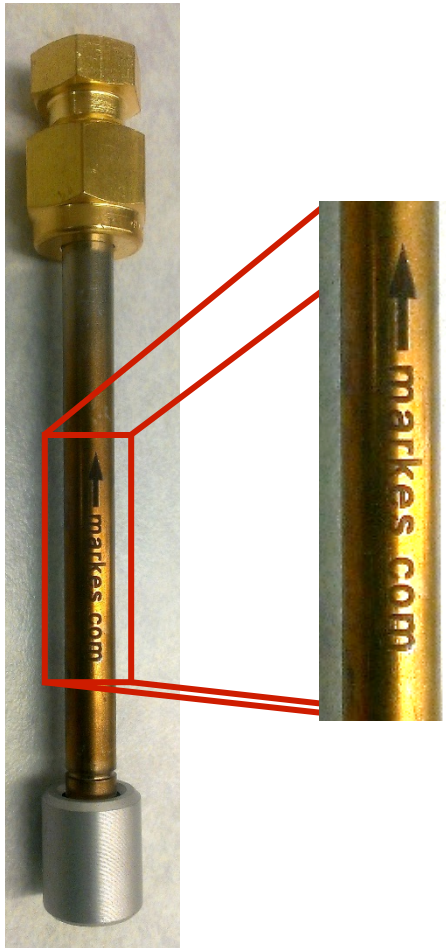
c_i = concentration at t = i (mol/m^3)

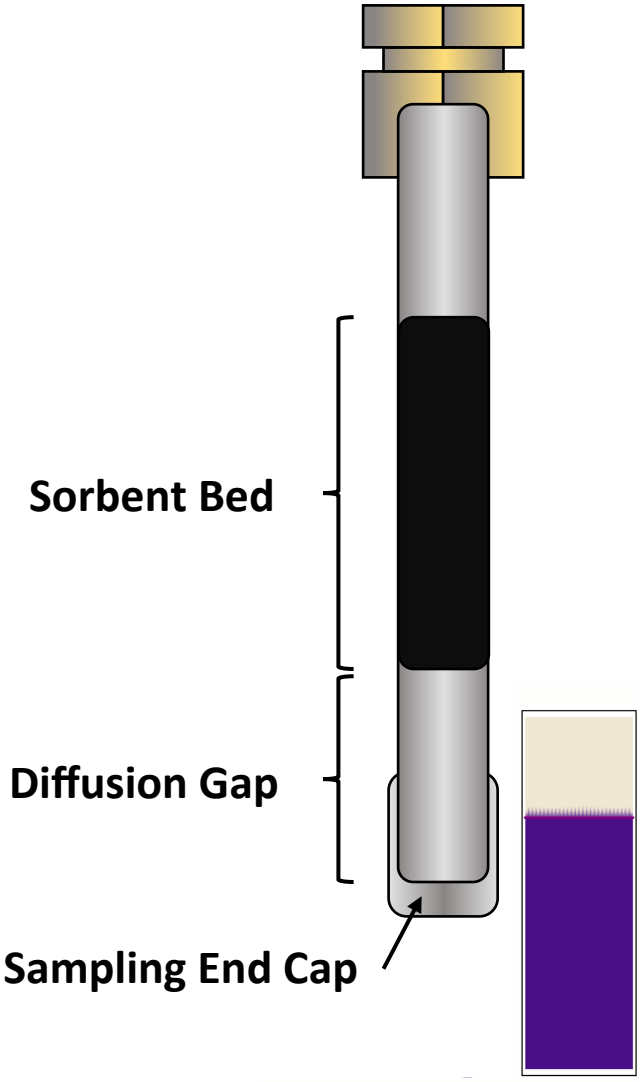
c_o = concentration at t = 0 (mol/m^3)



Fick, A. (1855). "Ueber Diffusion." Annalen der Physik 170(1): 59-86.

Passive Sampling Science

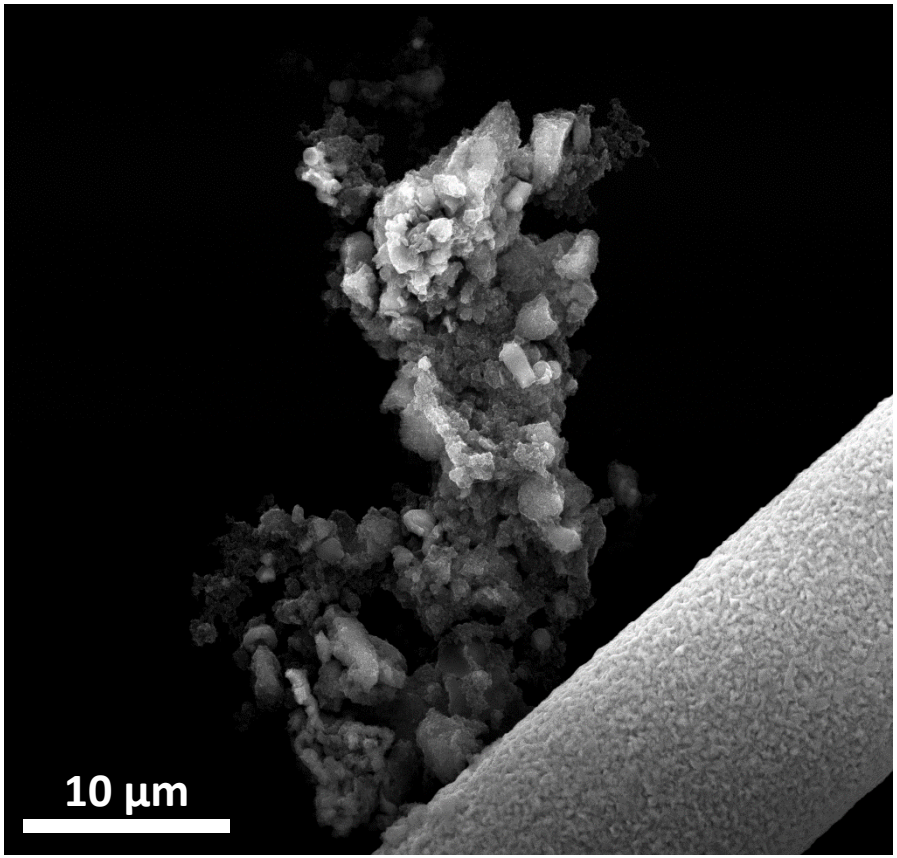


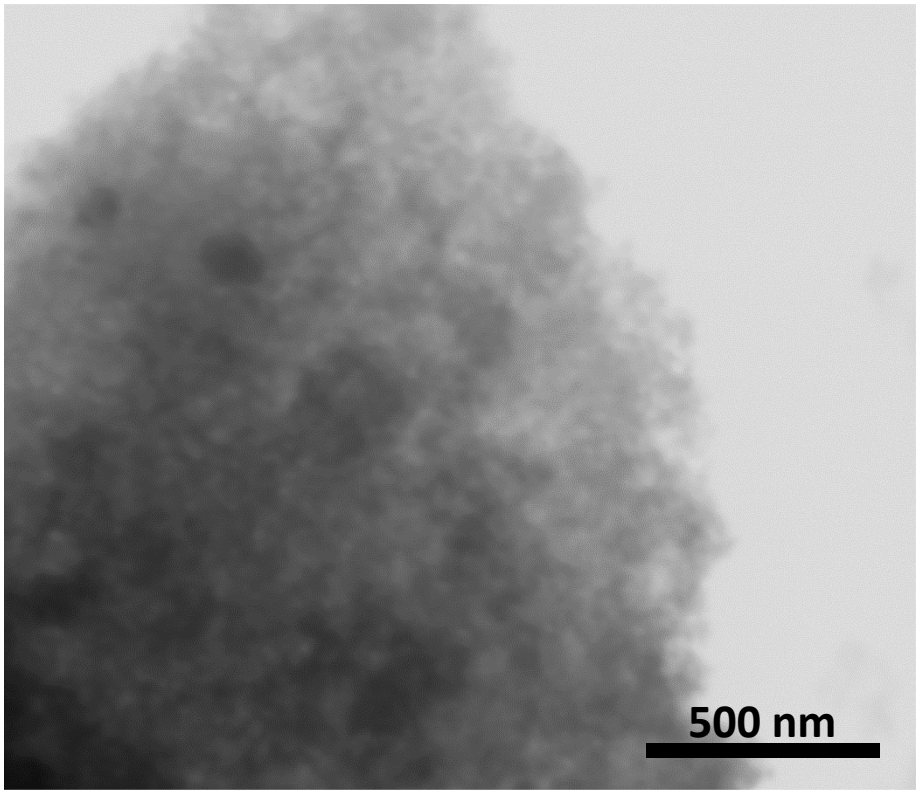


Passive Sampling Science

Compounds are effectively trapped for analysis later!

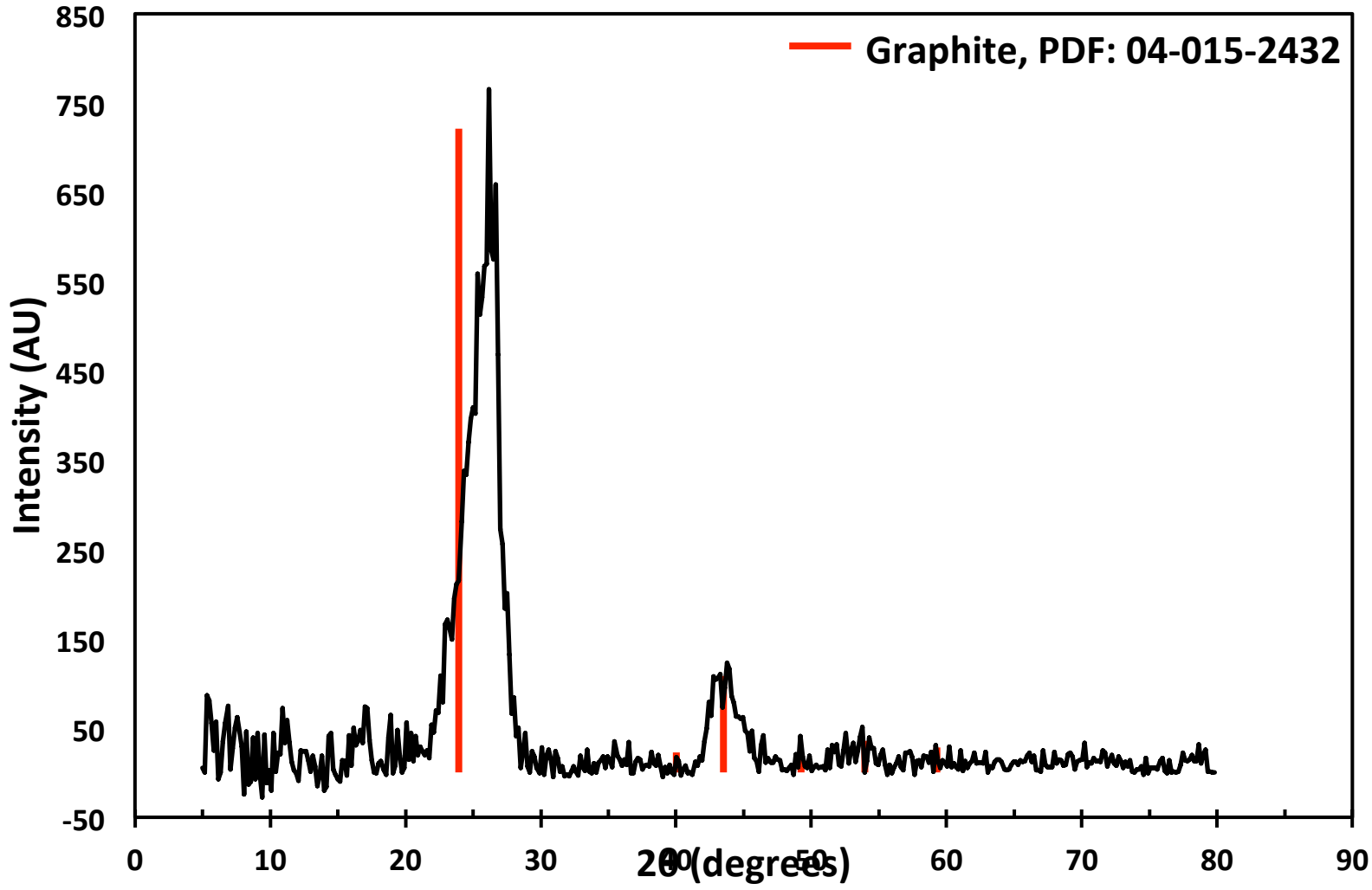
Passive Sampling Science





SEM and BF STEM images of TD tube packing material.

Passive Sampling Science



Passive Sampling Science

Common sorbent used for passive air monitoring:

Sorbent	Advertized Surface Area ($m^2 \cdot g^{-1}$)	BET Surface Area ($m^2 \cdot g^{-1}$)	Pore Size (nm)	Pore Volume ($mL \cdot g^{-1}$)
Carbograph 5	560	232.9	6 - 10	0.50
Carbopack X	240	240.1	20 - 80	0.57

Sorbent	Cu (ppm)	Cr (ppm)	Cd (ppm)	Pb (ppm)	Mn (ppm)	Ni (ppm)	V (ppm)	Zn (ppm)
Carbograph 5	0.110	0.18	ND	ND	0.10	0.18	1.90	0.41
Carbopack X	0.130	0.09	ND	ND	0.08	0.05	8.60	0.51

Mastrogiacomo *et al. Chromatographia* **2002**, 55, 345 - 348

Field Work with Tubes

Field studies performed:

- **Refinery fencelines**
- **Petroleum well pad in summer**
- **Petroleum well pad in winter**
- **Compared Carbopack X to Tenax tubes**

Field Work with Tubes

Site Wide Average Sampling Time ~ 7 days	Winter 2014 Sampling Period: 8.14 days (ppbv)	Summer 2013 Sampling Period: 6.05 days (ppbv)	Seasonal Difference (%)
Benzene	1.36	1.47	7.5
*Cyclohexane	1.85	2.52	26.6
Ethylbenzene	0.08	0.24	66.7
*Heptane	1.01	1.49	32.2
*Hexane	1.51	1.67	9.6
Toluene	2.74	3.55	22.8
1,2,4-Trimethylbenzene	<0.0074	0.42	N/A
1,3,5-Trimethylbenzene	<0.014	0.47	N/A
m- &/or p-Xylene	0.76	1.50	49.3
o-Xylene	0.10	0.35	71.4

Significant seasonal variation. Further projects underway.

Field Work with Tubes

Site A Location 1 Sampling Time ~ 7 days	Carbopack X Average N = 2 (ppbv)	Tenax TA Average N = 2 (ppbv)	Percent Difference (%)
Benzene	0.599	0.313	91.4
Toluene	0.814	0.713	14.2
m-/p-Xylene	0.474	0.583	23.0
o-Xylene	0.174	0.209	20.1

Field Work with Tubes

Site A Location 2 Sampling Time ~ 7 days	Carbopack X Average N = 2 (ppbv)	Tenax TA Average N = 2 (ppbv)	Percent Difference (%)
Benzene	0.351	0.238	47.5
Toluene	0.617	0.752	21.9
m-/p-Xylene	0.636	1.11	74.5
o-Xylene	0.163	0.244	49.7

Pay attention to application notes for sorbents!

Tube & Canister Comparison

Tube & Canister Comparison

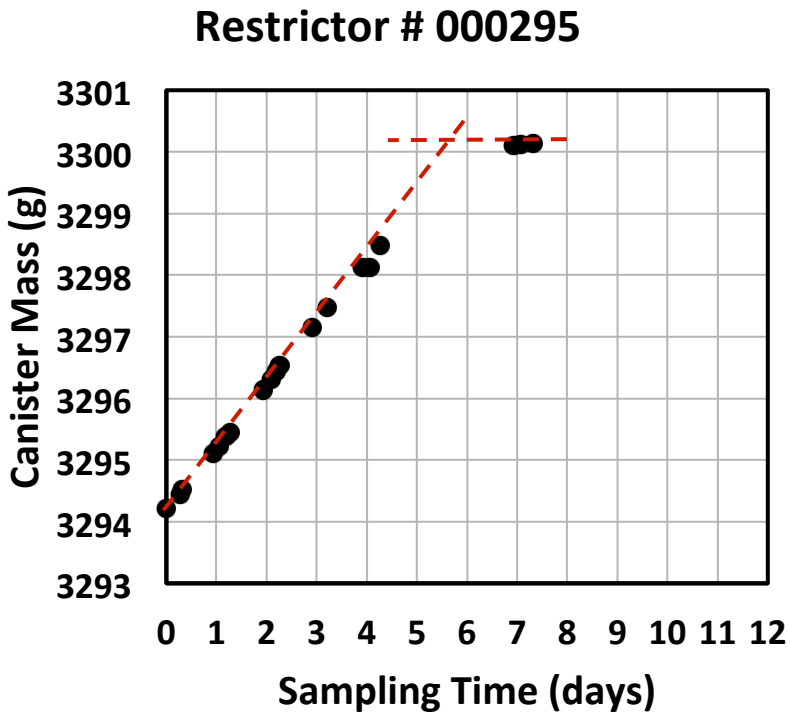
Site B Location 1 Sampling Time: 8.12 days	CpX Average N = 2 (ppbv)	Canister (ppbv)	Percent Difference (%)
Benzene	2.33	2.72	16.7
Cyclohexane	3.35	3.83	14.3
Ethylbenzene	0.152	<0.55	NA
Heptane	2.06	2.59	25.7
Hexane	3.10	3.94	27.1
Toluene	5.06	5.56	9.9
1,2,4-Trimethylbenzene	0.00935	<0.54	NA
1,3,5-Trimethylbenzene	<0.014	<0.54	NA
m- &/or p-Xylene	1.45	1.37	5.5
o-Xylene	0.191	<0.55	NA

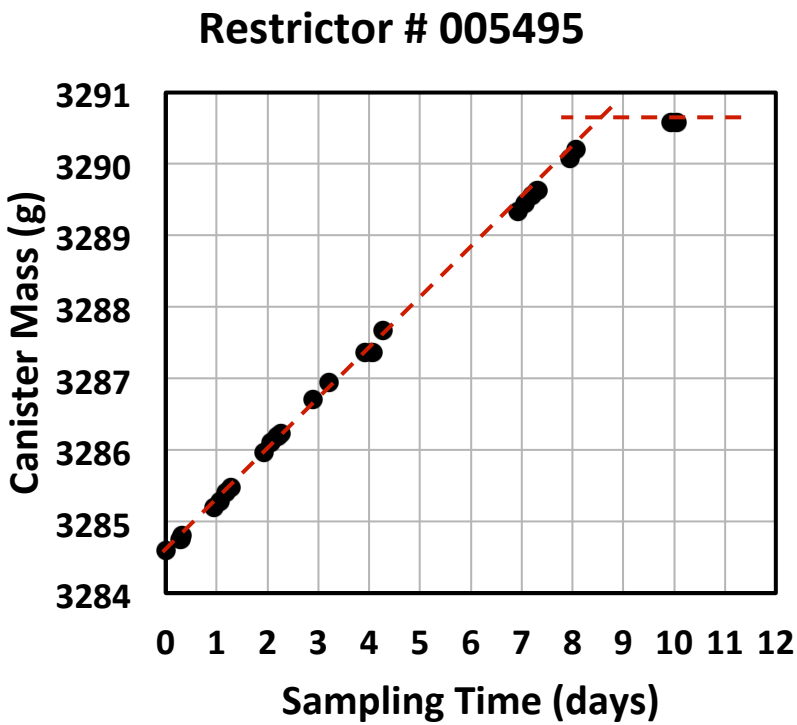
Tube & Canister Comparison

Site B Location 2 Sampling period: 7.86 days	CpX Average N = 2 (ppbv)	Canister (ppbv)	Percent Difference (%)
Benzene	5.05	5.87	16.2
Cyclohexane	2.06	1.85	11.4
Ethylbenzene	0.184	<0.54	NA
Heptane	0.887	0.980	10.5
Hexane	1.36	1.55	14.0
Toluene	6.81	7.19	5.6
1,2,4-Trimethylbenzene	<0.0076	<0.53	NA
1,3,5-Trimethylbenzene	<0.014	<0.53	NA
m- &/or p-Xylene	1.47	1.25	17.6
o-Xylene	0.204	<0.55	NA

Tubes and canisters agree within method allowable limits, ±30%.

Tube & Canister Comparison

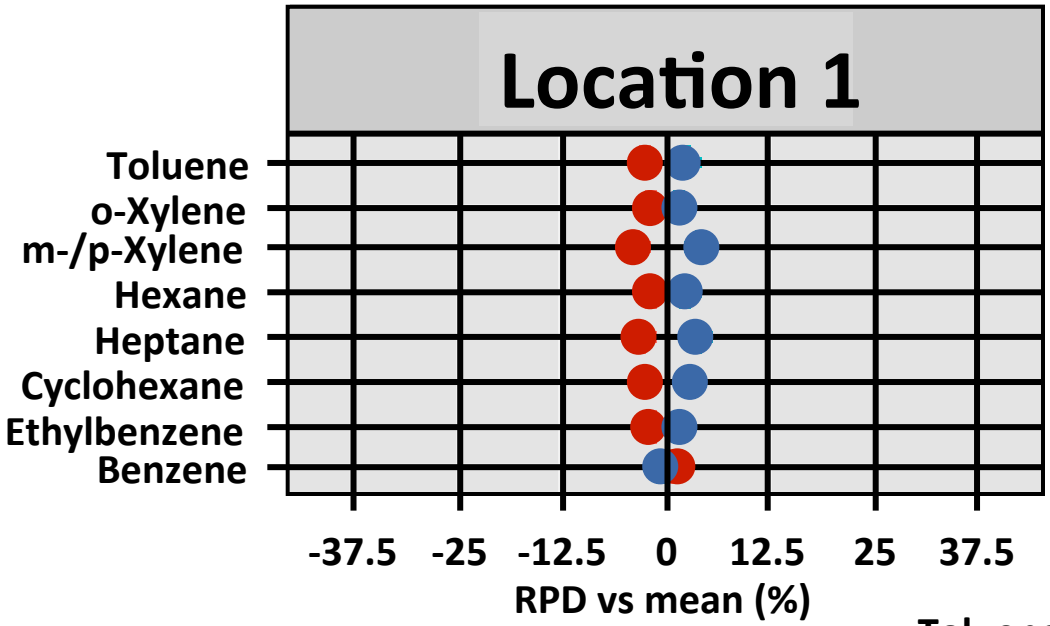




Approx. 6 days for Restrictor #000295. Approx. 8.5 days for Restrictor #005495.

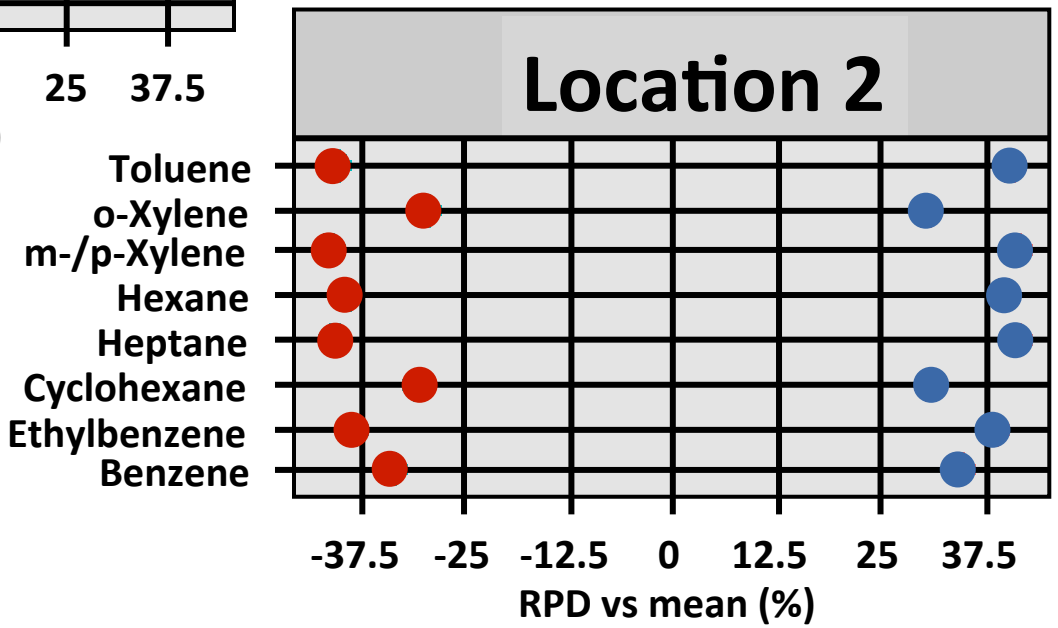
Very important to calibrate equipment before attempting field work!

Variation in Duplicate Tubes

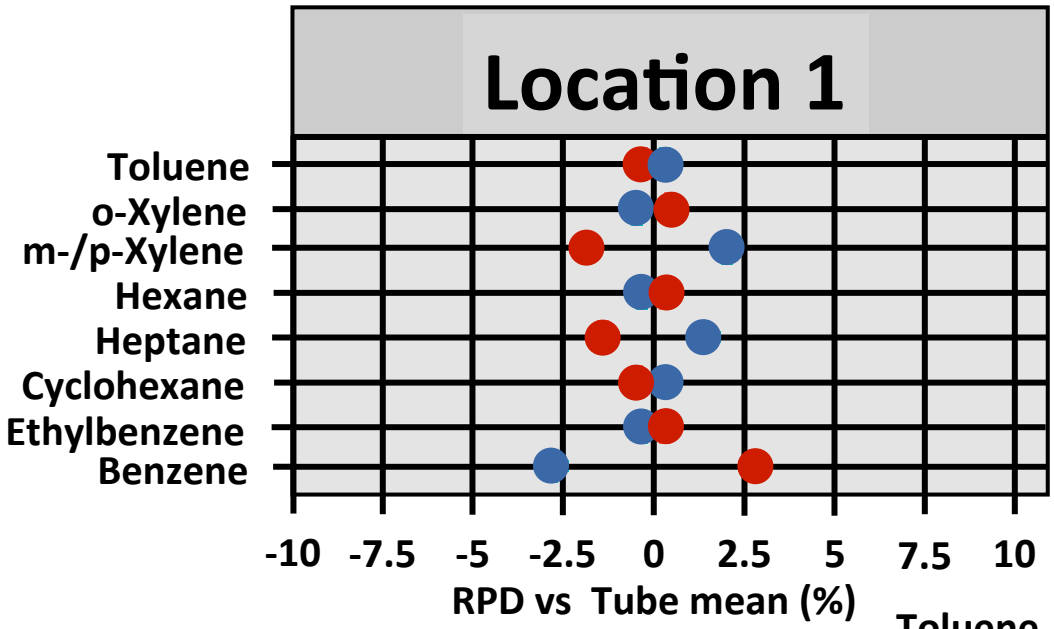


Large and small systematic variation observed for duplicate tubes.

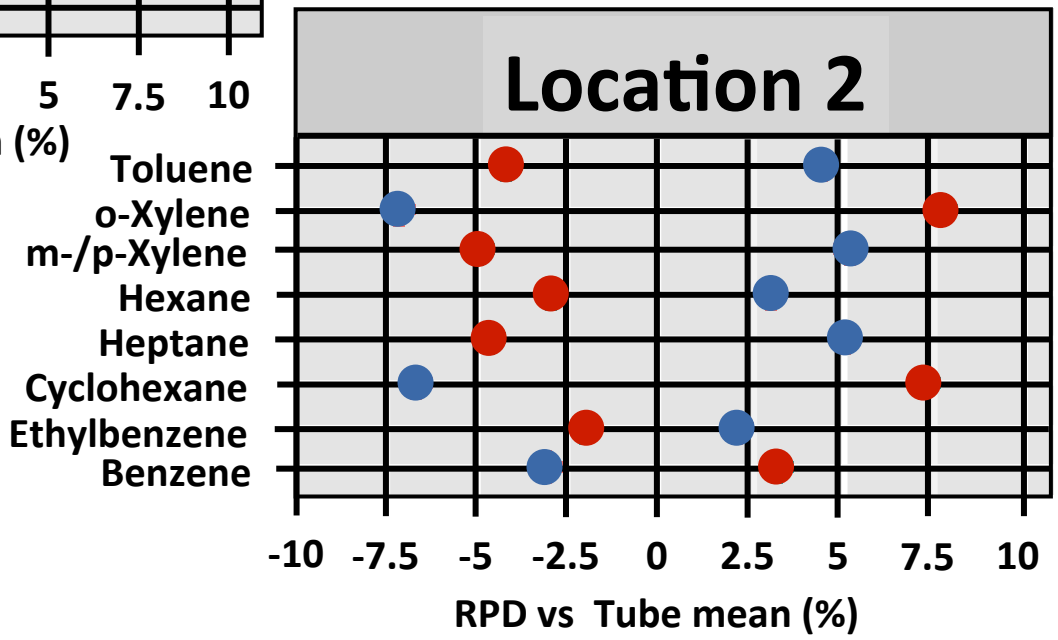
Source of systematic error is currently being investigated.



Variation in Duplicate Tubes



Subtracting systematic error, much smaller random error remains.



Conclusions

- Significant seasonal variation observed, further studies.
- Pick appropriate sorbent for analytes.
- Canisters give comparable results, good cross check.
- Check restrictor valve calibrations.
- Investigating possible systematic error, bad tubes?
- Manufacturers should consider measuring and publishing sampling rates for their products.

Future Work:

- Investigating use of deuterated benzene and toluene as depuration compounds to study back diffusion of analytes.

Acknowledgements

- Bob Bohn
- Tam Talarski
- Jon Beihoffer
- Brad Venner
- Larry Strattan (retired)
- Jim Hoban (retired)
- NEIC Field Staff
- NEMC Organizers

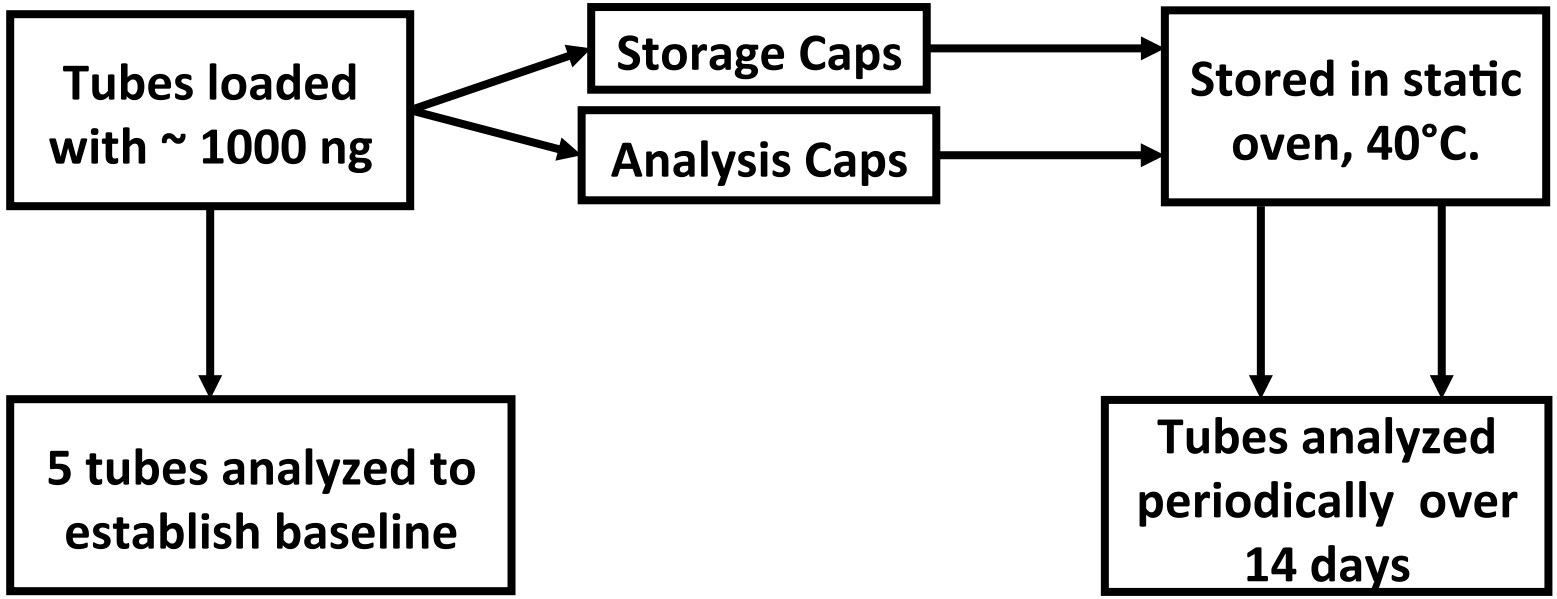
- Introduction/Background Info
- Passive Sampling Science
- Instrumentation and Equipment
- Limitations
- Field Studies
- Acknowledgements
- **Questions?**

Supporting Information

Sample Storage Testing

Supporting Information

TD Tube Storage Study:



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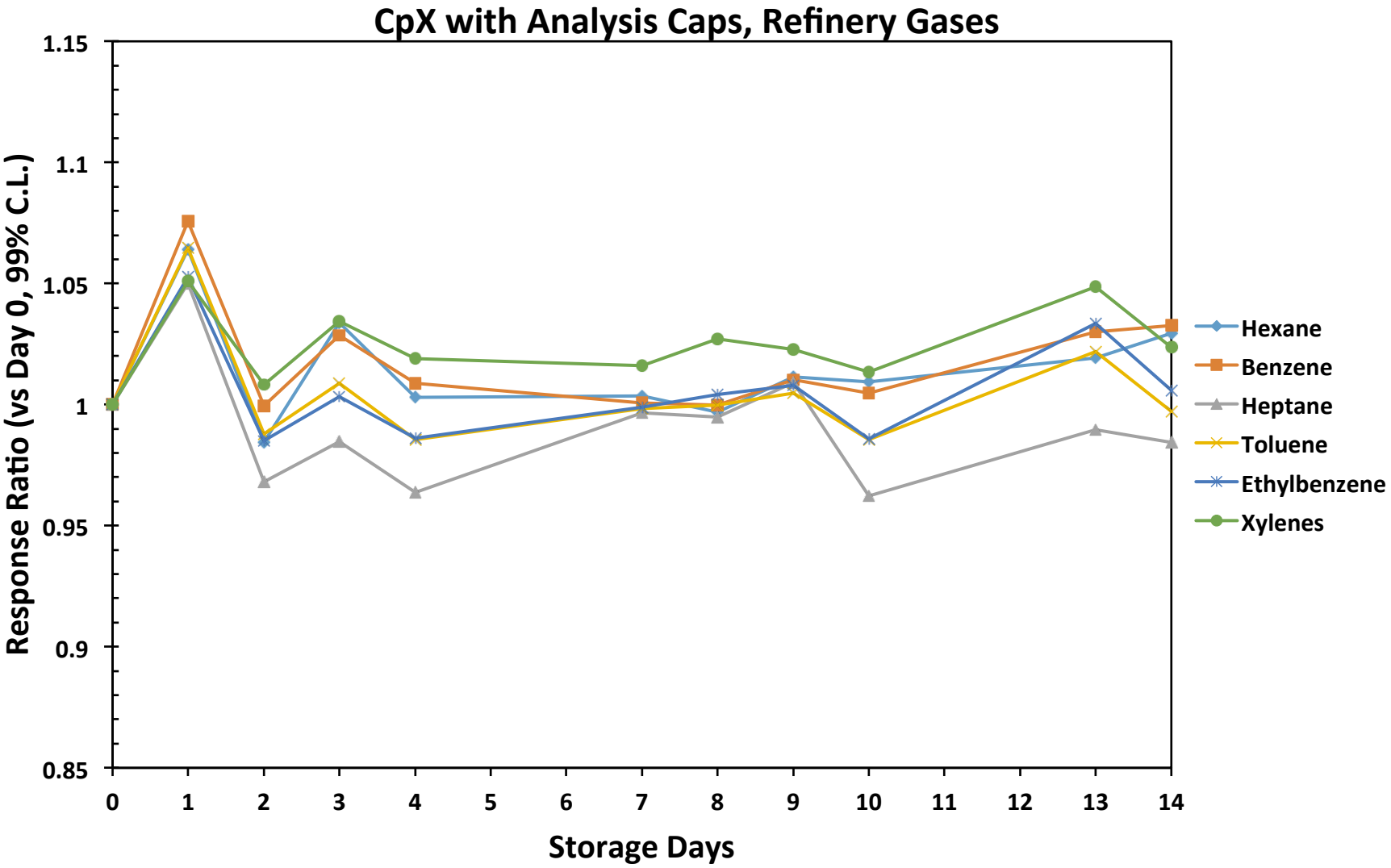

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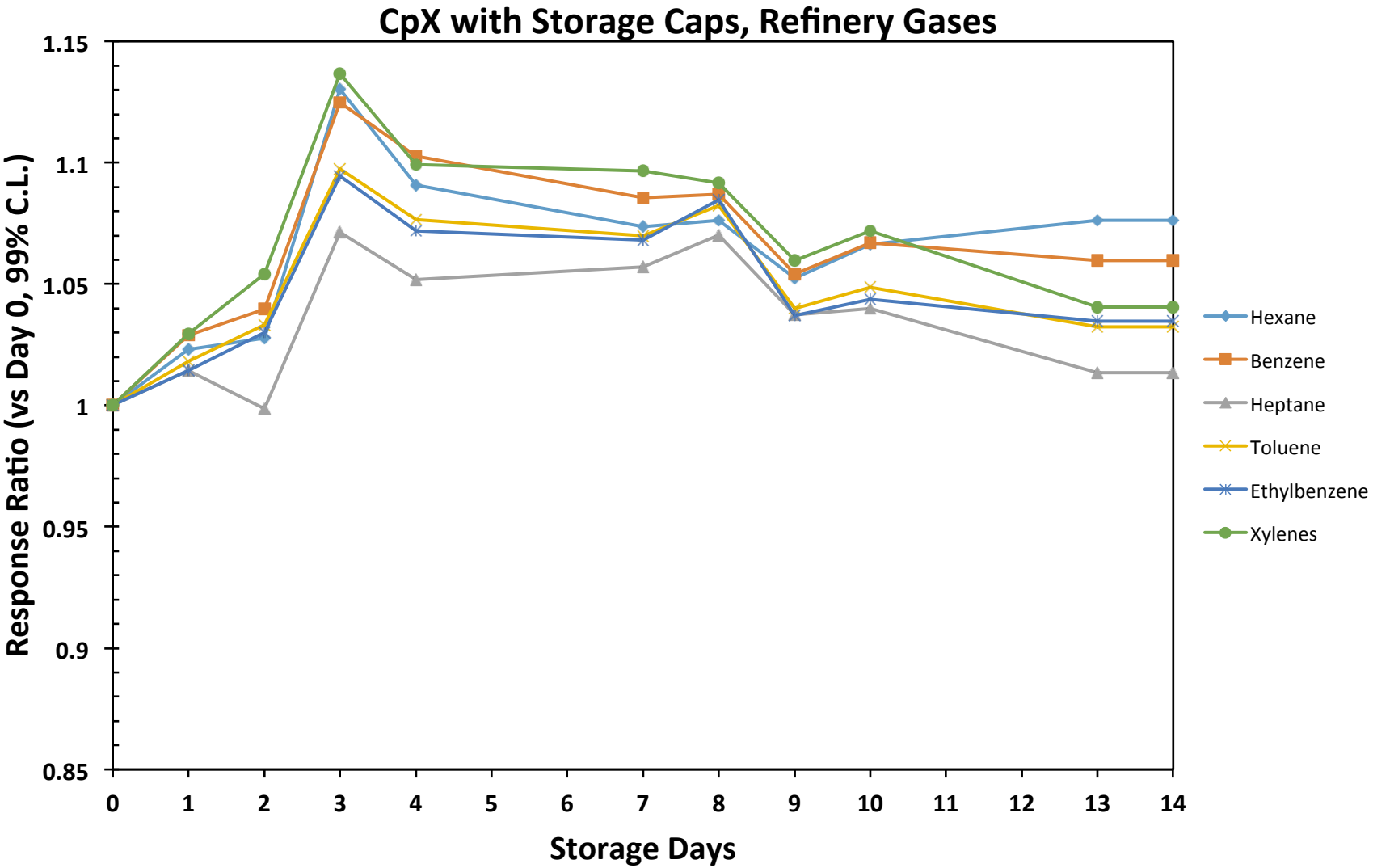

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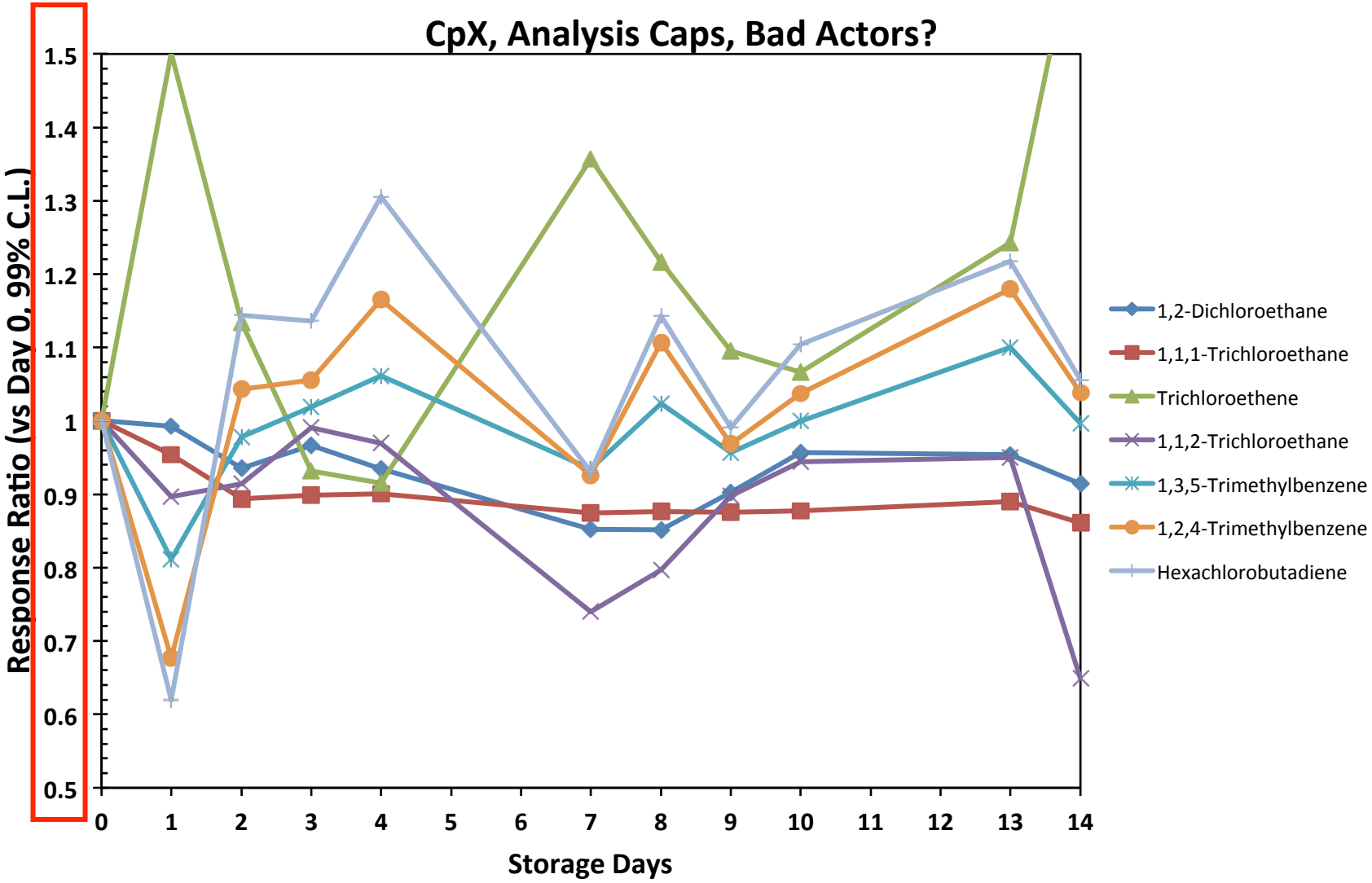

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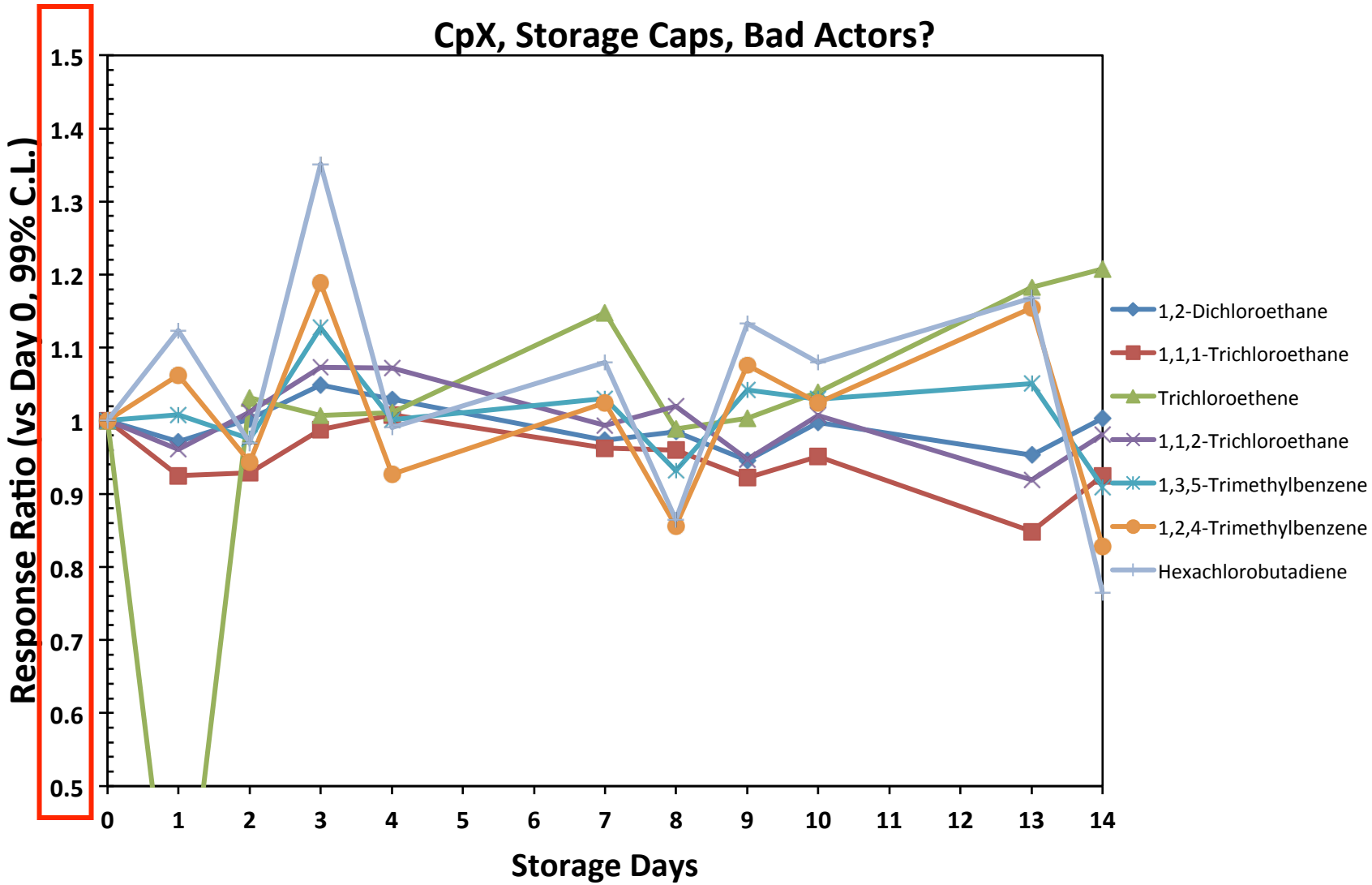

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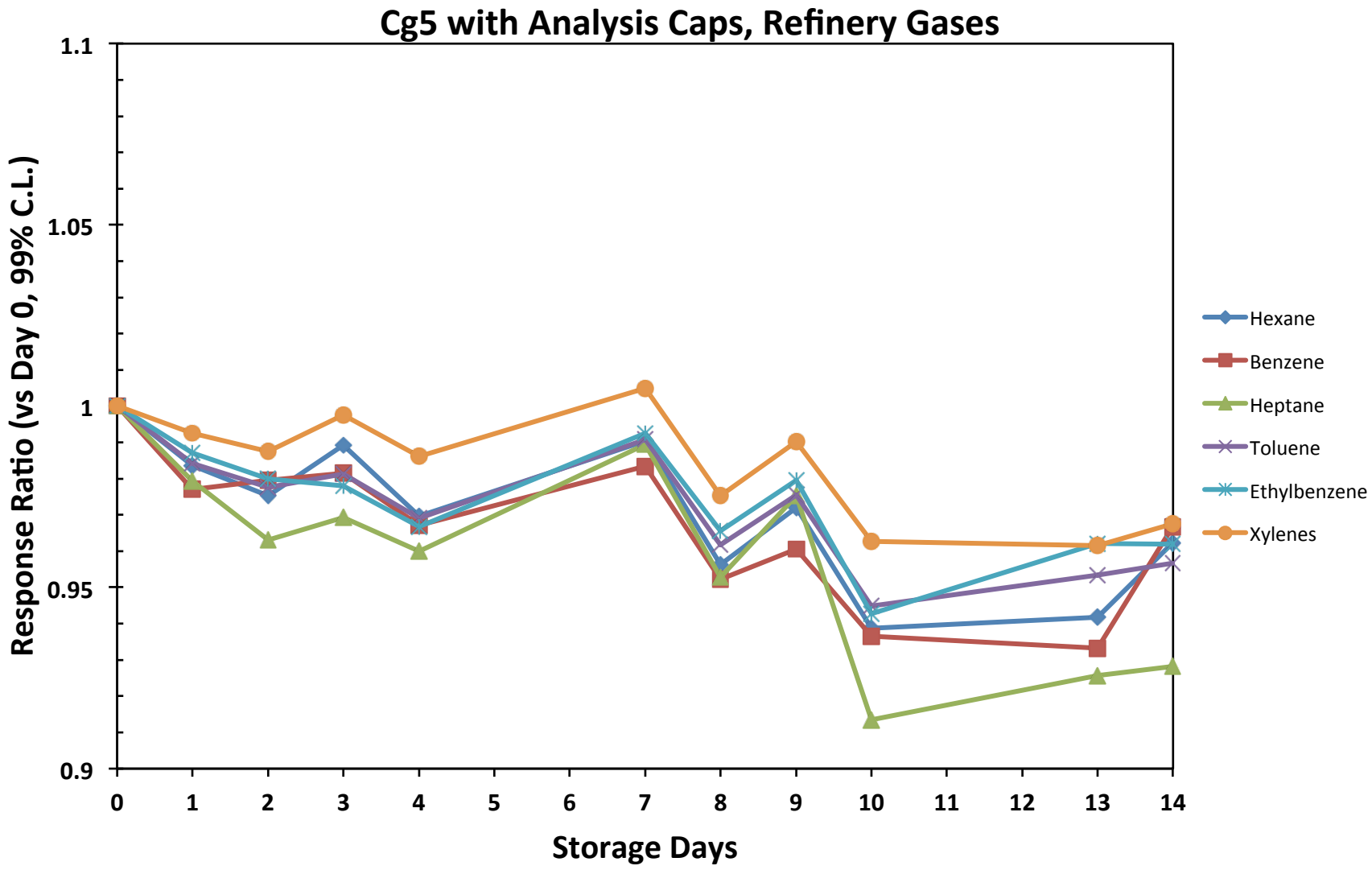

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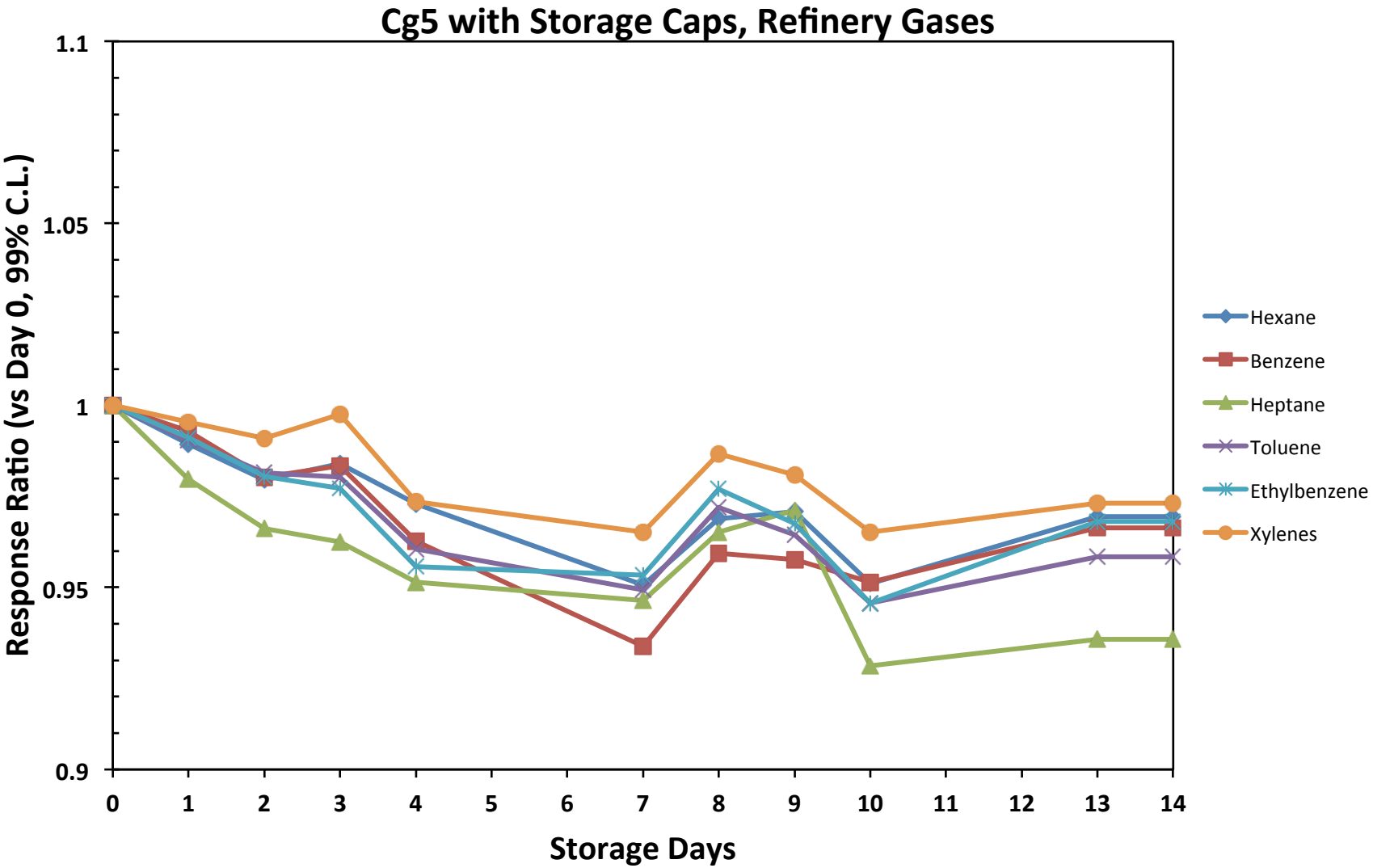

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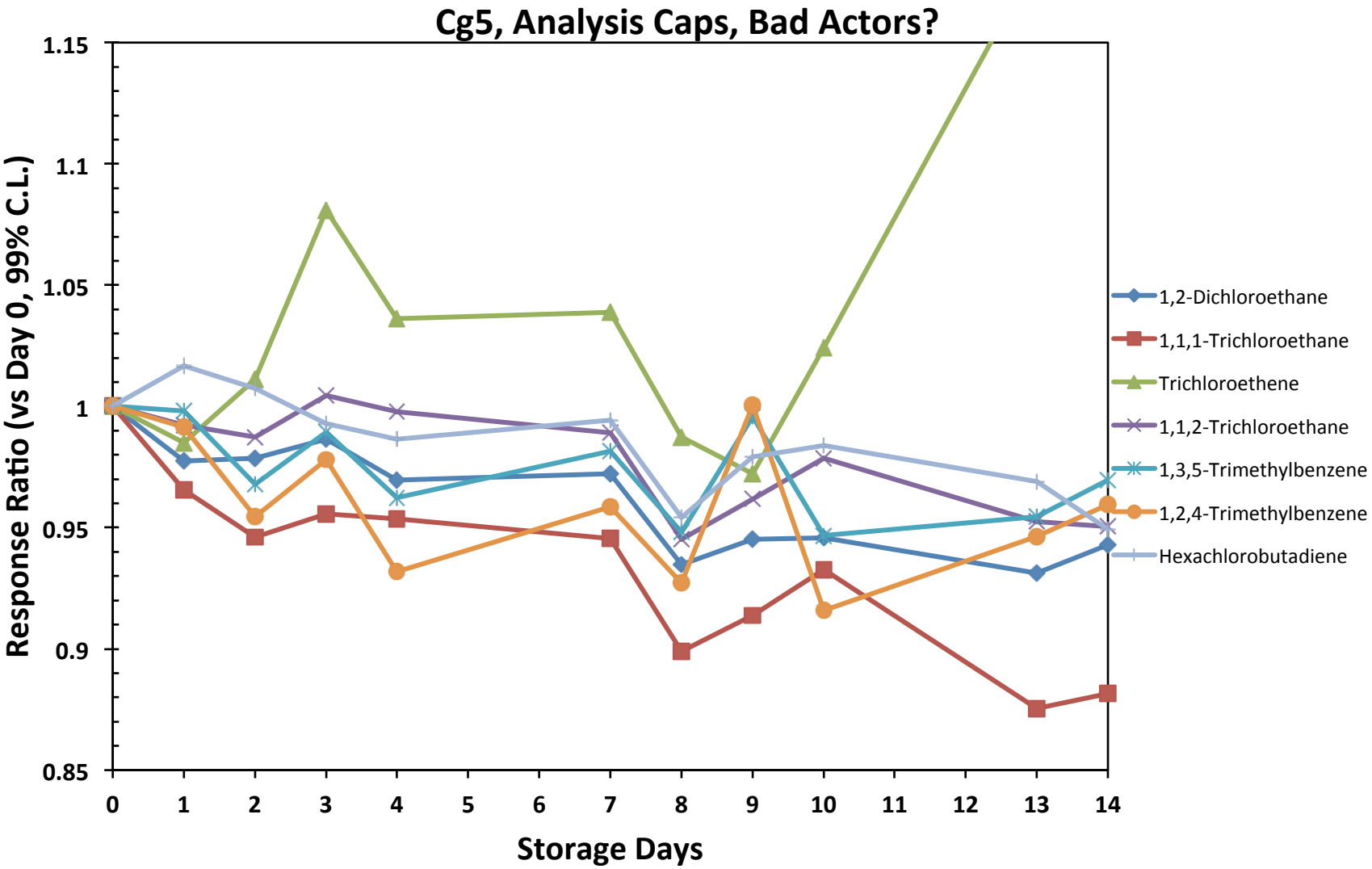

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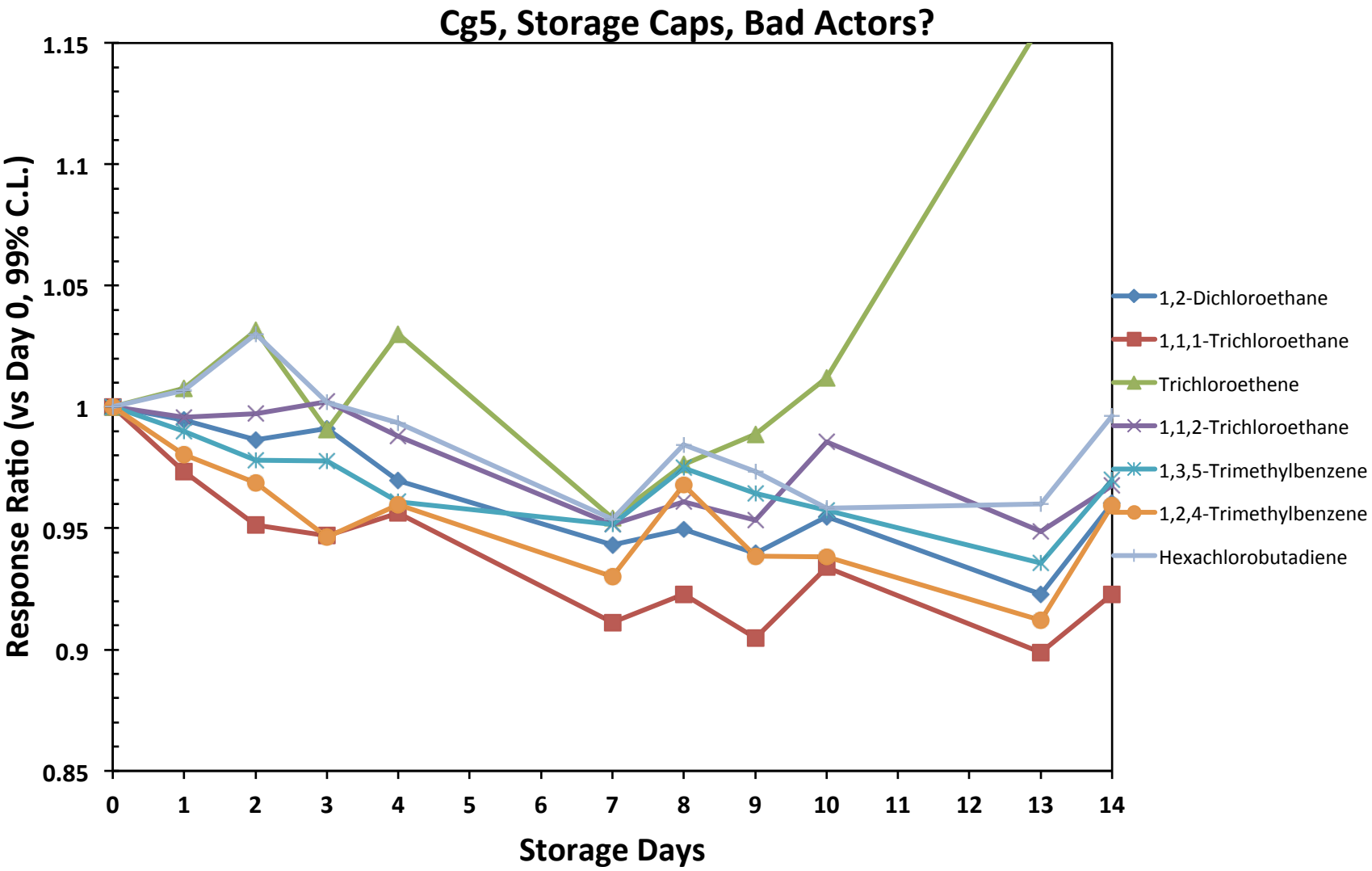
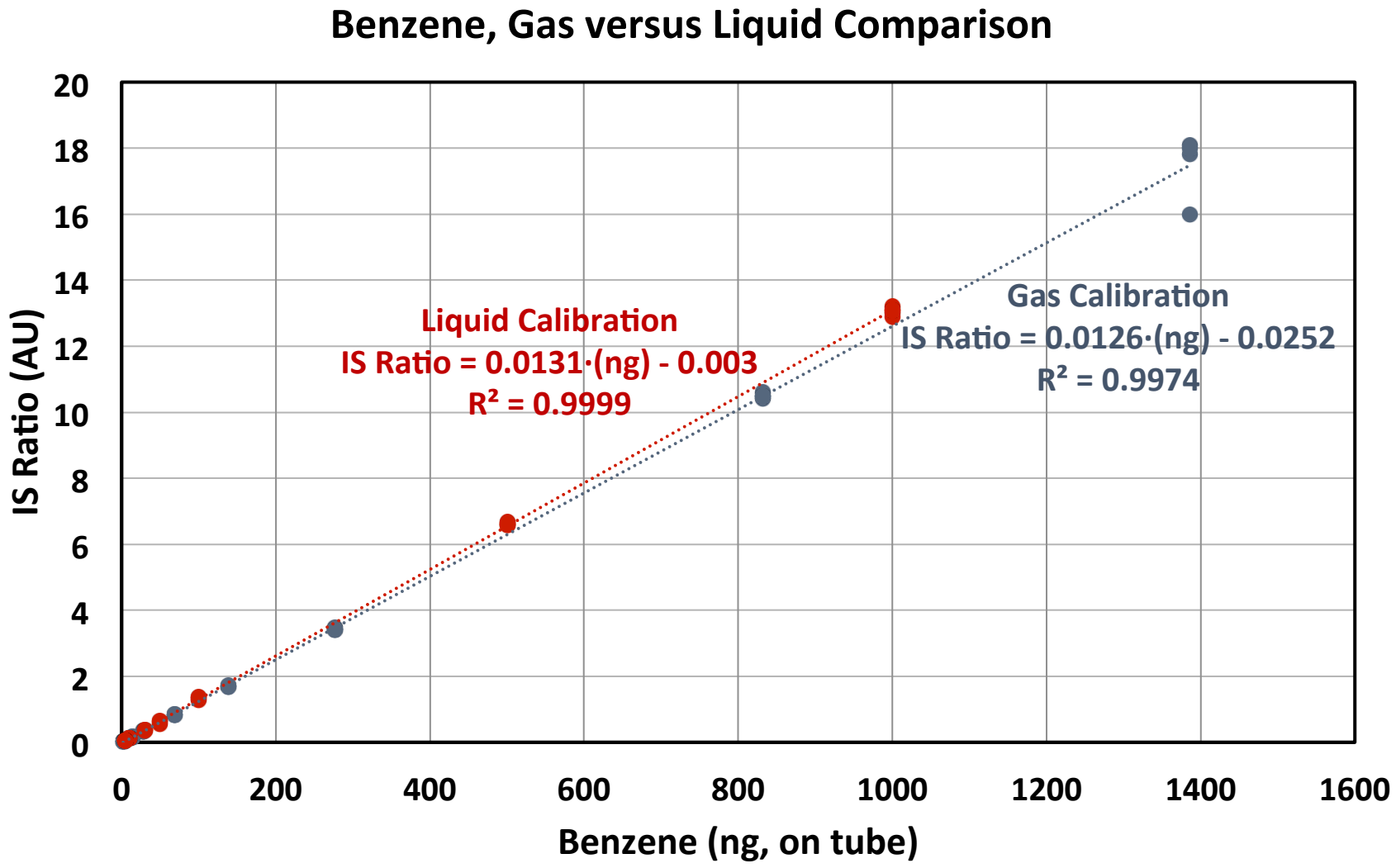


Supporting Information

Liquid verses Gas Calibration Comparison

Supporting Information



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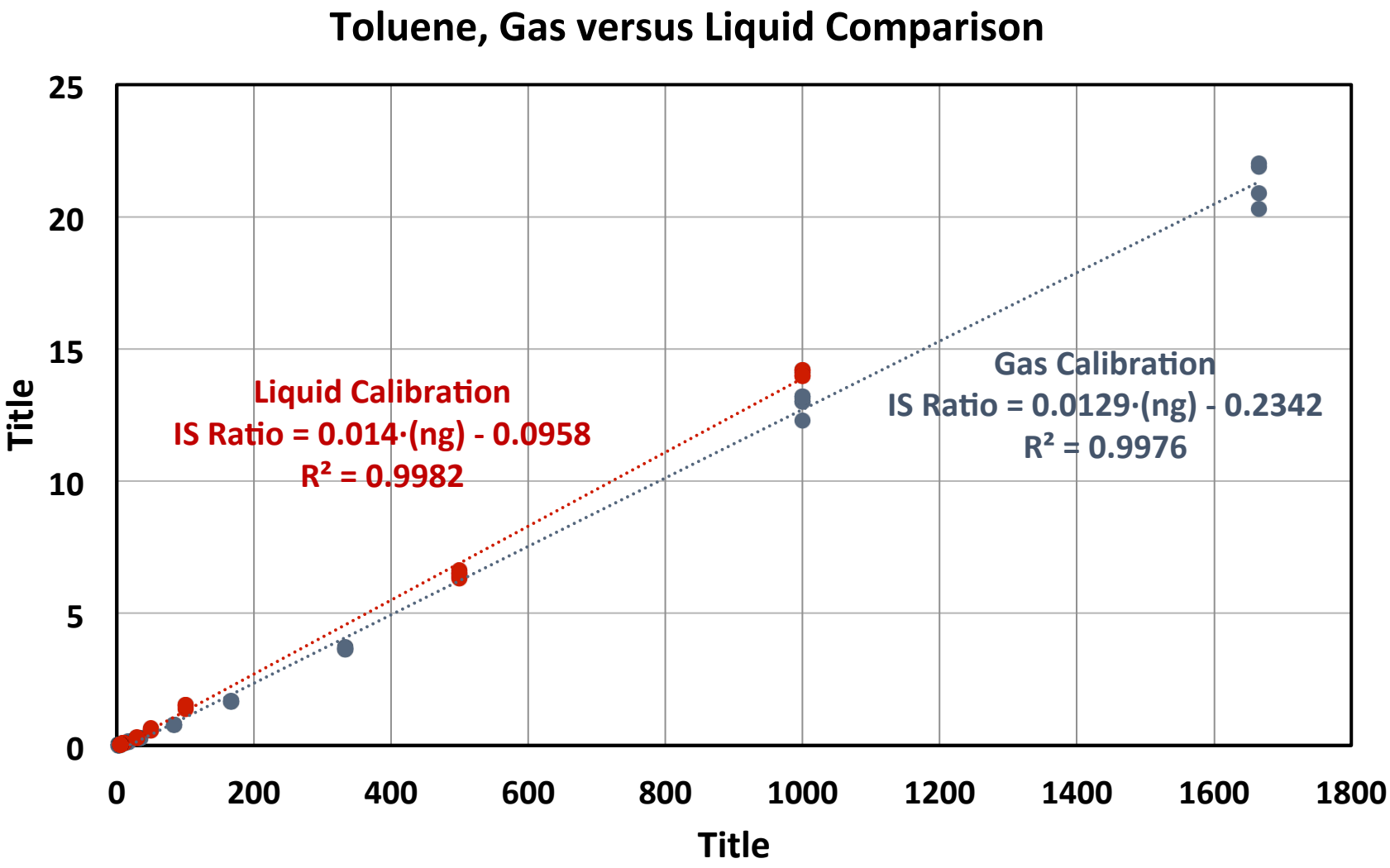

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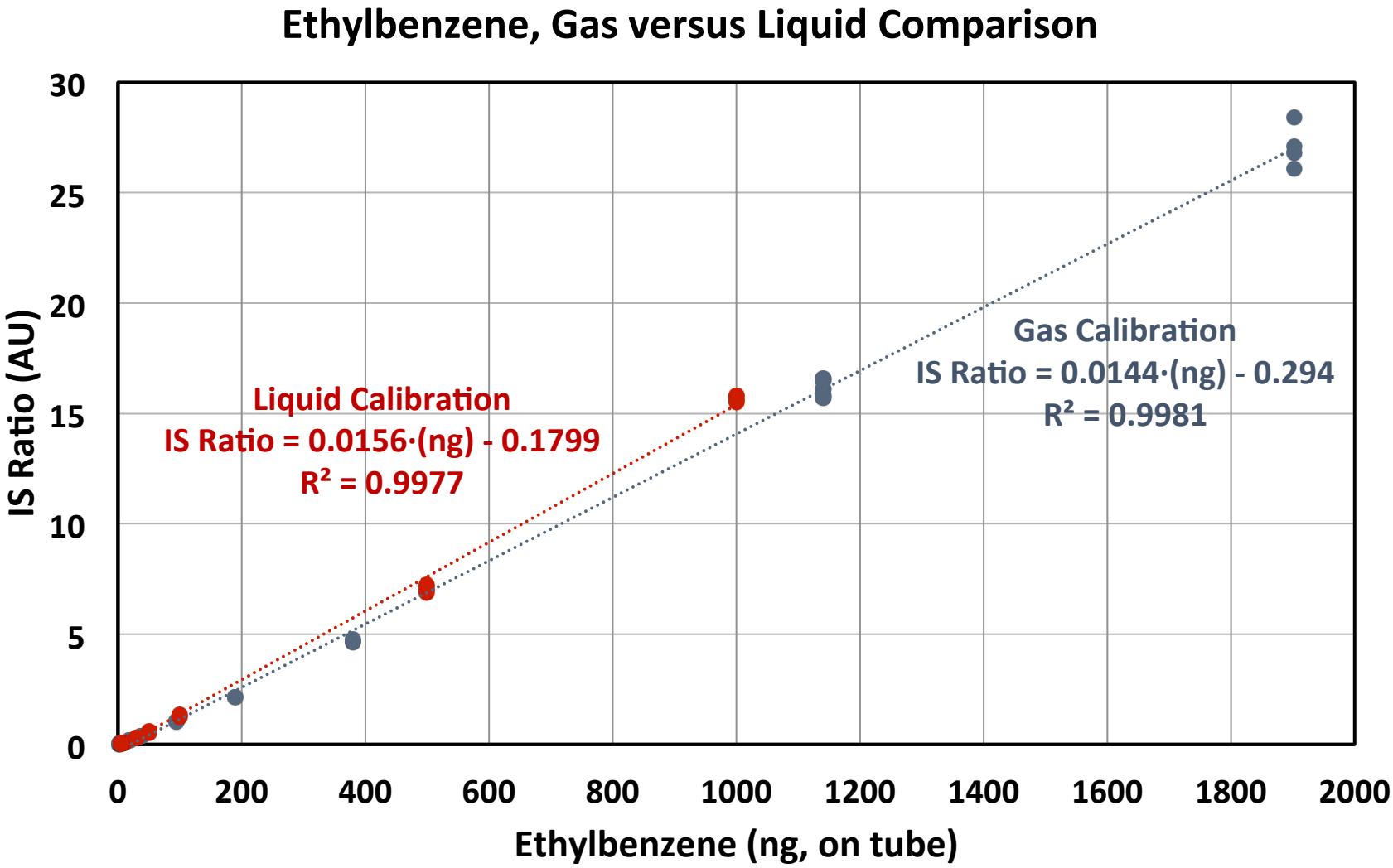

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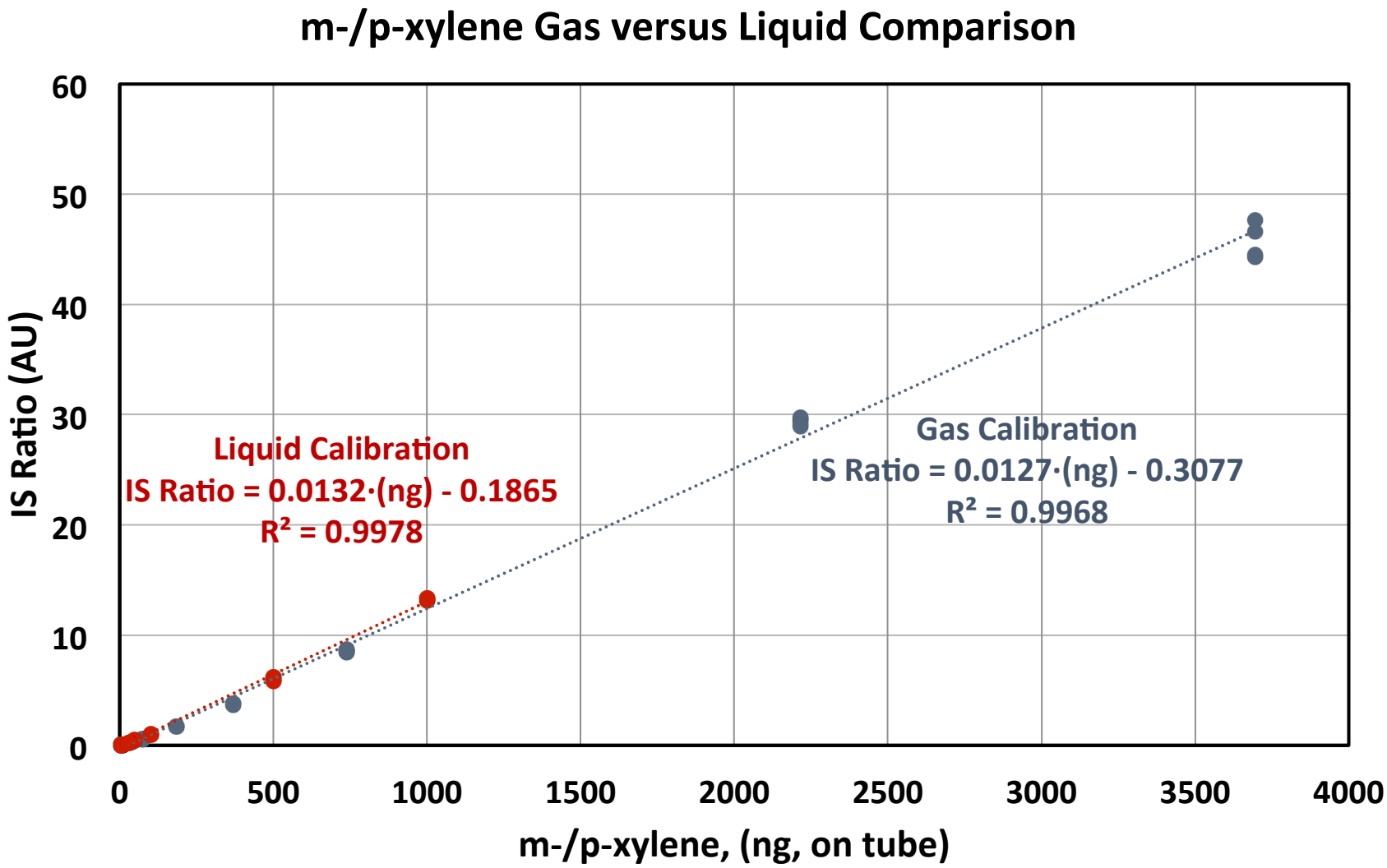

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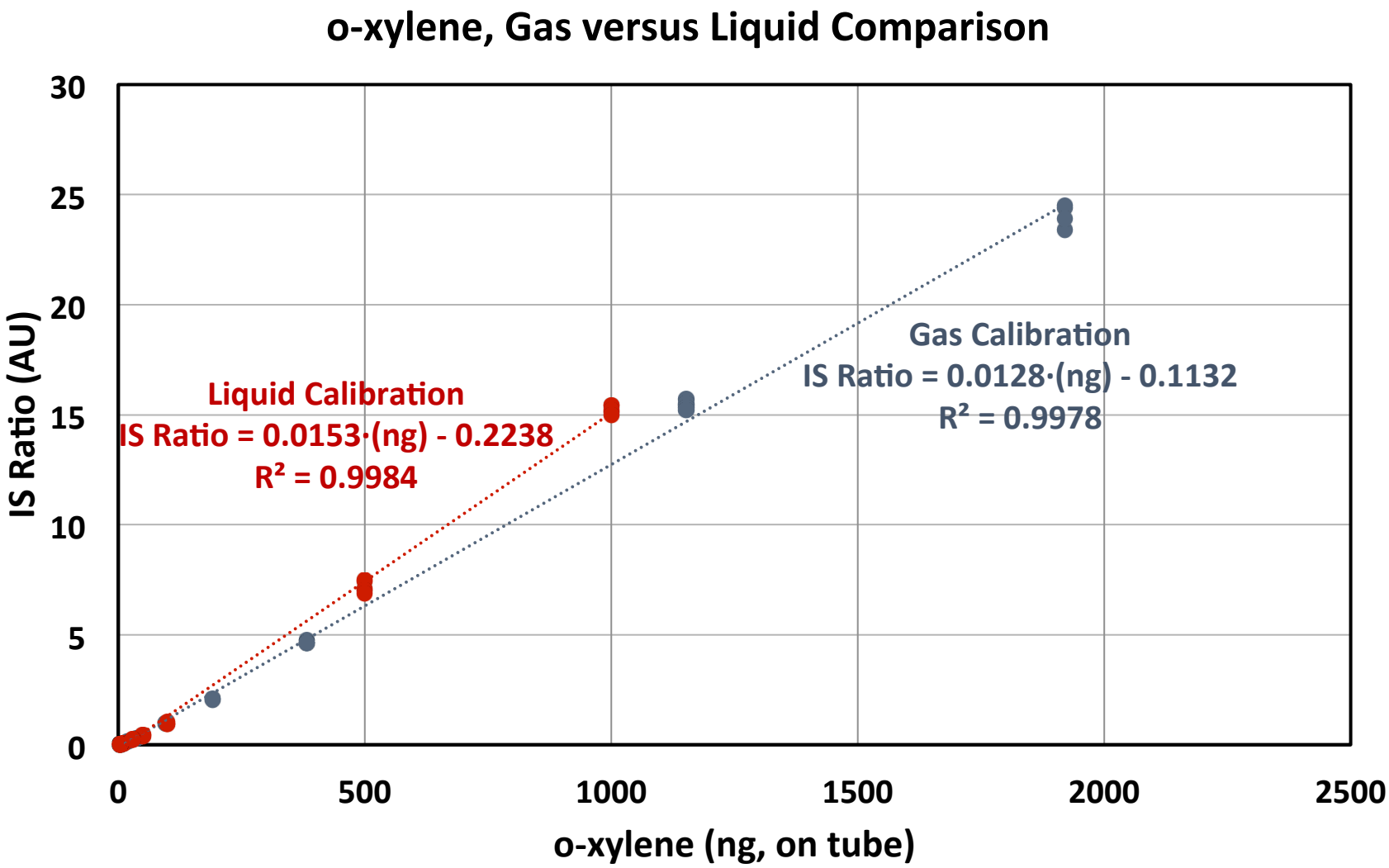
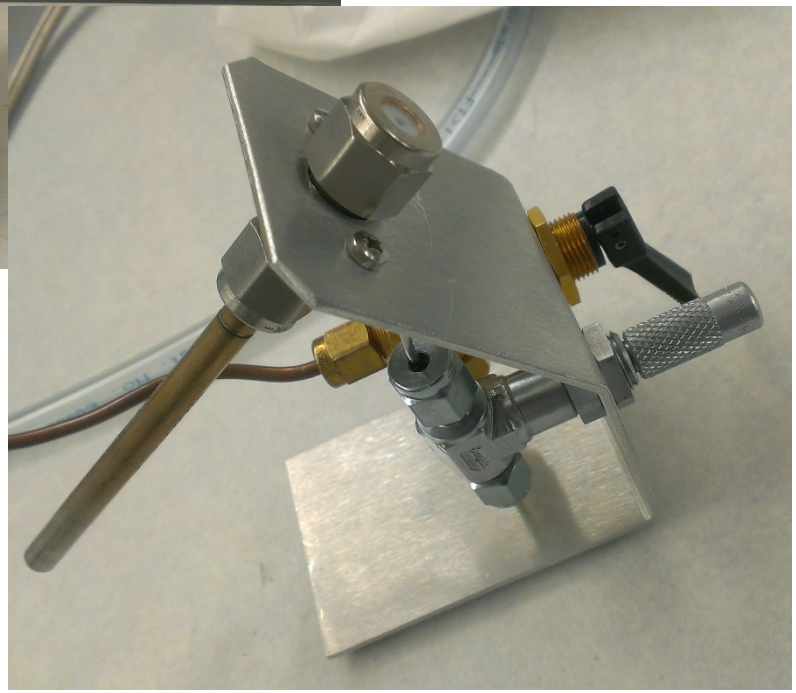


Supporting Information

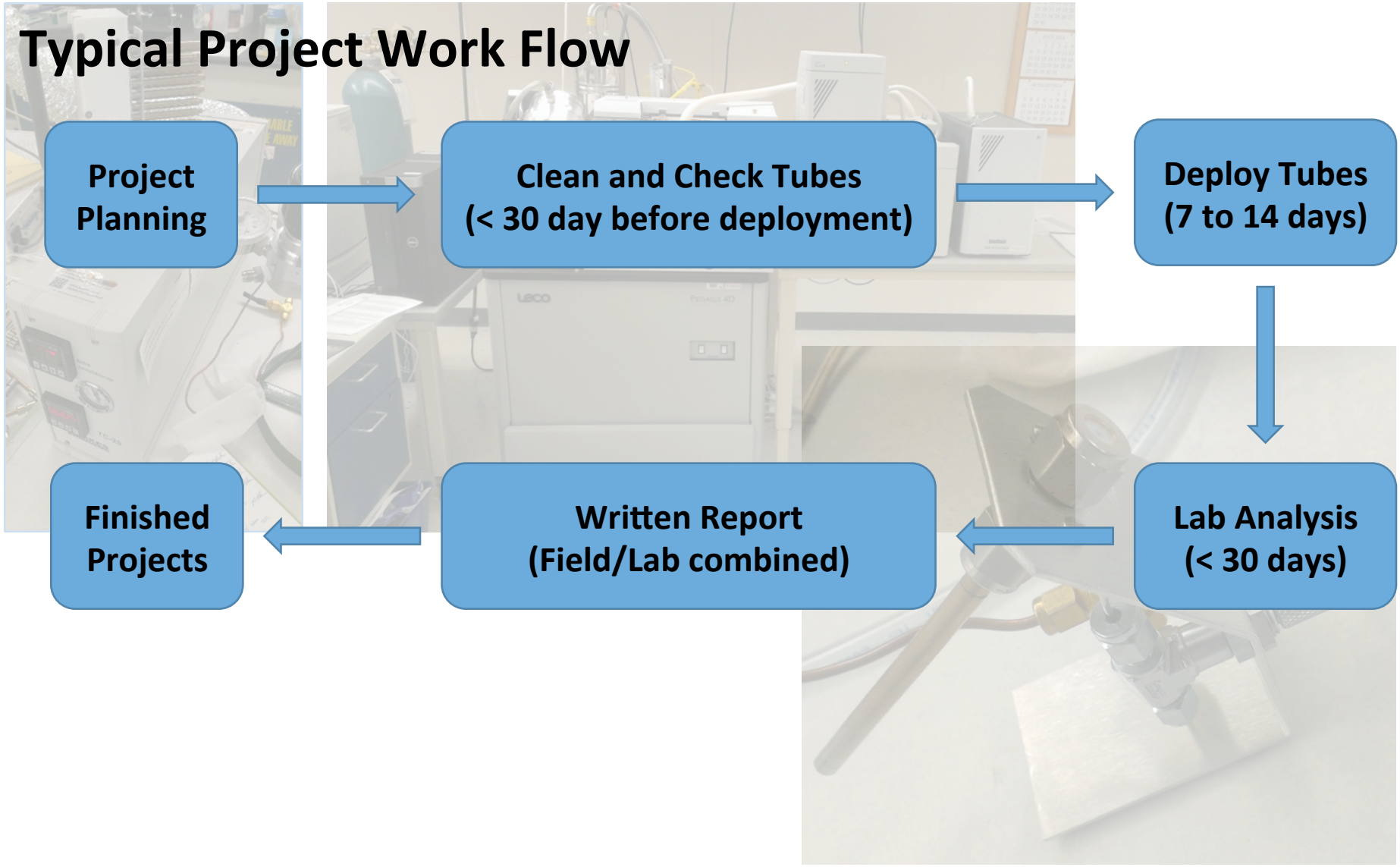
Instrumentation and Equipment

Supporting Information



Supporting Information

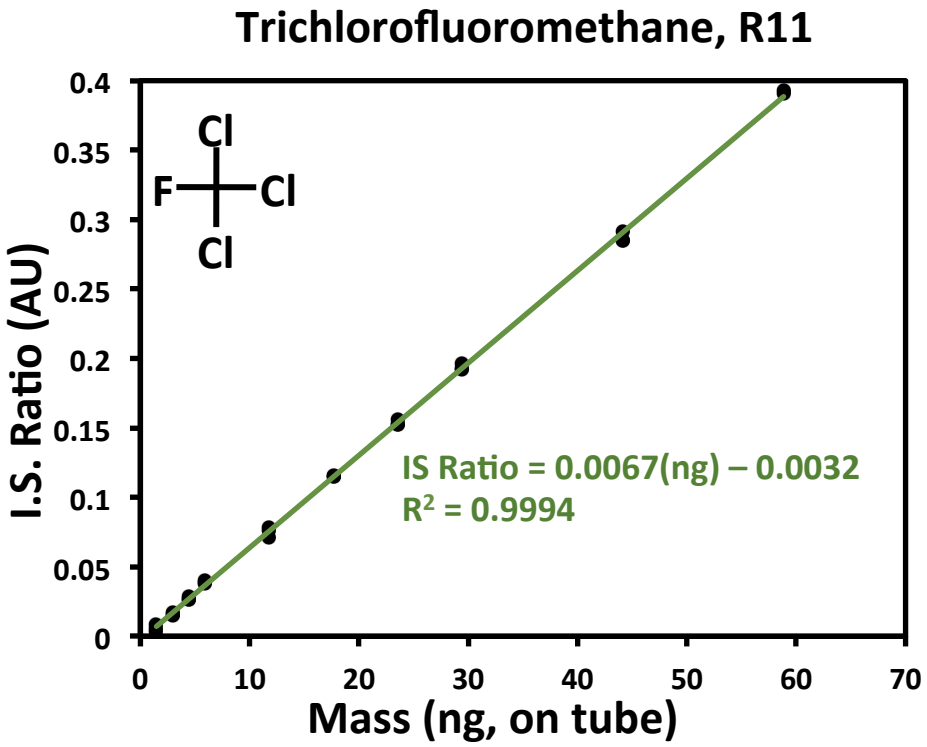
Typical Project Work Flow

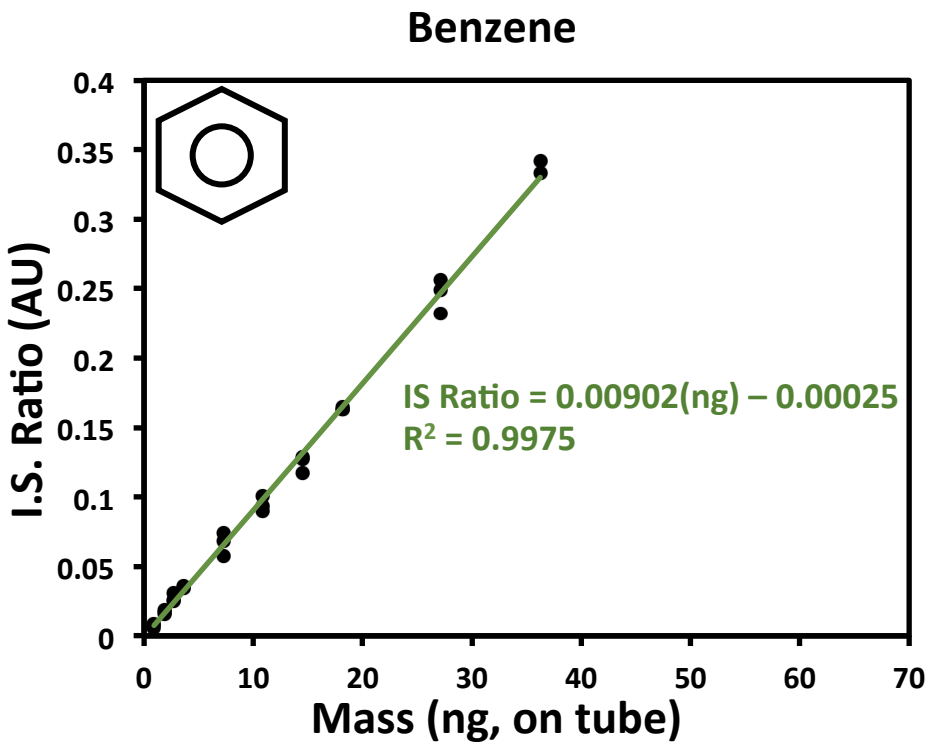


Supporting Information

Sorption Tube Limitations

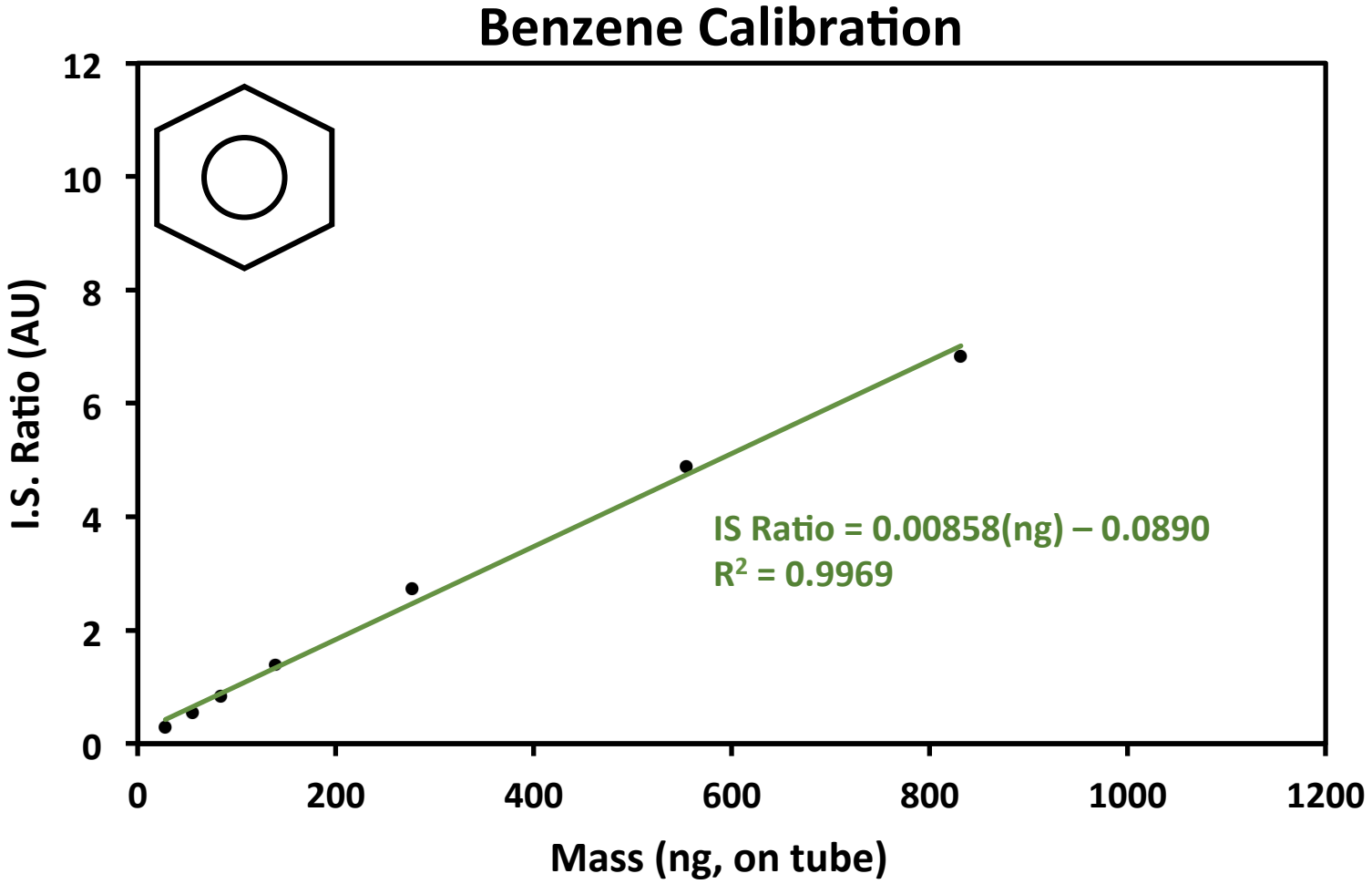
Limitations





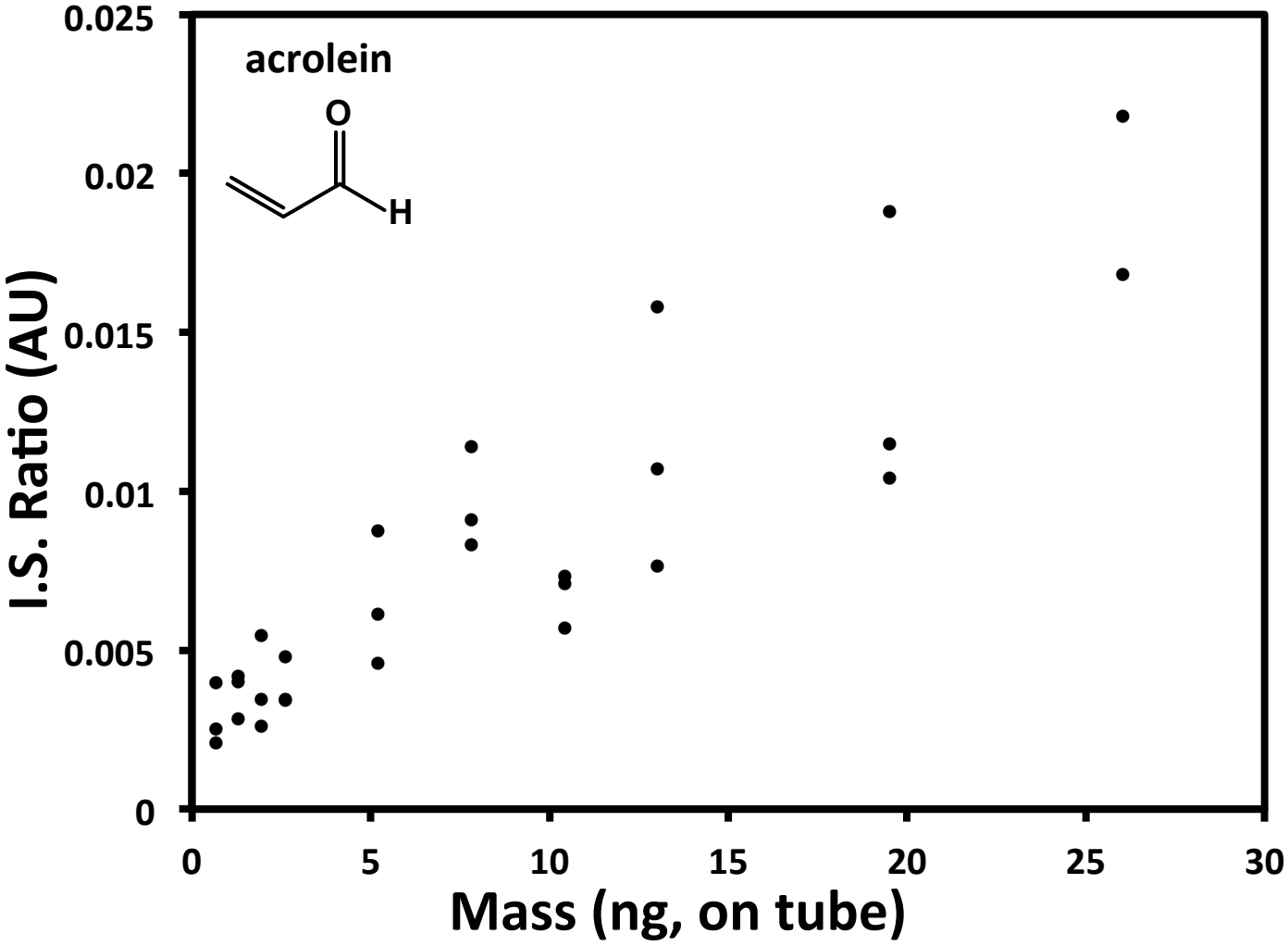
Some compounds calibrate very well.

Limitations



Large, linear dynamic range.

Limitations



Some compounds show poor linear response.

Limitations

Not all chemicals are amenable to passive monitoring.

Must know uptake/sampling rate for each compound!

- ✓ **Benzene**
- ✓ **Toluene**
- ✓ **Ethylbenzene**
- ✓ **Xylenes**

- × **Unknown for many other compounds!**