# Initial Qualification of Stainless Steel Canisters for the Measurement of Trace (ppb) Levels of VOCs in Air

# Douglas J. Turner and Ian C. MacGregor, Battelle, Columbus, Ohio

# INTRODUCTION

#### Background

- Newly purchased stainless steel canisters cannot be assumed to be fit for use for trace-level air toxics monitoring due to the potential for:
- Manufacturing defects
- Incomplete interior surface preparation and/or coating (fused-silica lining)
- Residues from manufacturing process (e.g. cutting oils)

# RESULTS

### **Qualification – Leak Check and Zero**

- All 14 canisters leak tight (< 0.1 psi change per day)</li>
- 13 Canisters showed all 15 compounds as non-detect (ND)
- 1 canister (SN 17733) showed hits for 3 analytes:
  - acrolein (0.05 ppbv)
- 1,3-butadiene (0.10 ppbv)

Residual artifacts from quality control checks
 Canister qualification is required!

#### **Compounds for canister qualification**

| Compound               | Purpose/comment  |
|------------------------|--|
| benzene                | surrogate/recovery standard  |
| chloromethane          | surrogate/recovery standard  |
| bromoform              | assesses stability in FSL canisters                                      |
| carbon tetrachloride   | assesses stability in SUMMA canisters                                    |
| benzyl chloride        | difficult compound to recover from canisters                             |
| naphthalene            | low volatility compound difficult to recover from canisters              |
| 1,4-diethyl benzene    | C <sub>10</sub> can more easily "slide"/"nestle" into nooks and crannies |
| 1,2,4-trichlorobenzene | difficult compound to recover from canisters                             |



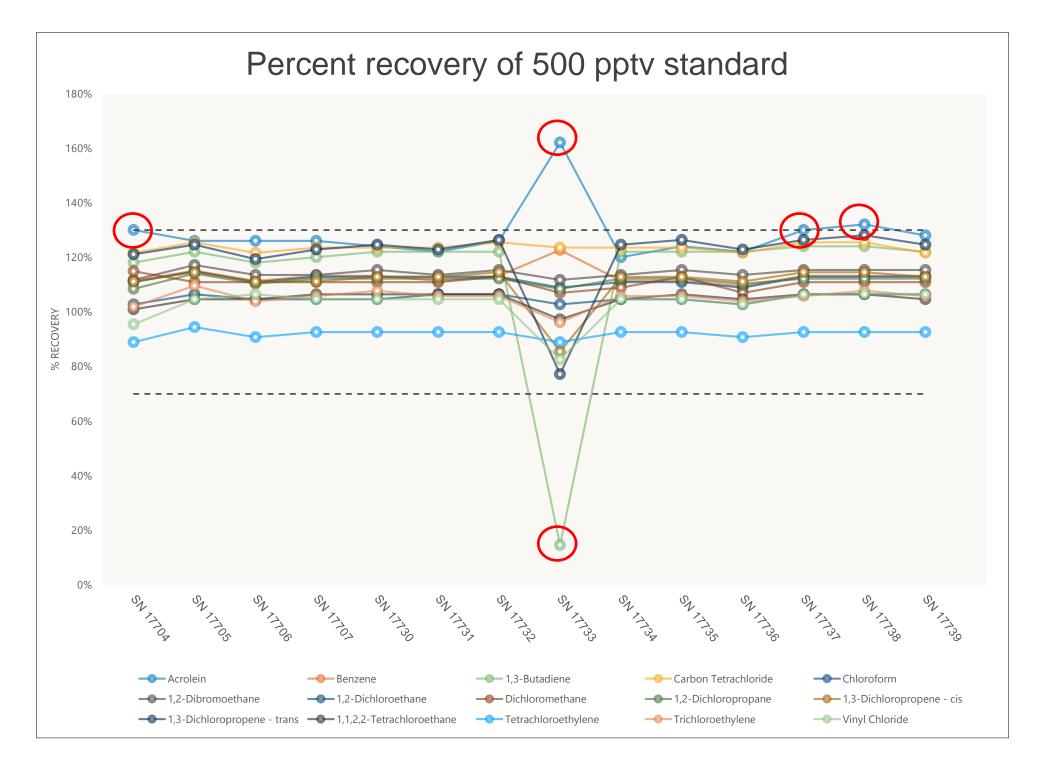


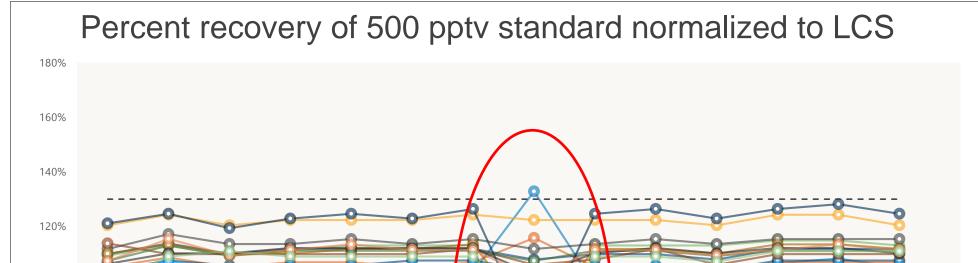
# **TECHNICAL APPROACH**

- vinyl chloride (0.03 ppbv)

#### Qualification – Known Standard Challenge

- Recovery for all analytes 70-130% in all canisters except:
  - 4 canisters for acrolein (> 130%)
  - 1 canister for 1,3-butadiene (< 70%)
- Acrolein average recovery 129%





 Laboratory control sample (LCS) indicated high bias for acrolein
 recovery +/- 12% except acrolein (+22%)

### **Canister Cleaning**

- Heat in isothermal oven to 71°C (160°F)
- 10 cycles:
  - evacuation to > 23" Hg
  - pressurization with humidified hydrocarbon free zero air (HCF) to 20 psia
- Final evacuation to < 50 mTorr

# **Experimental Design**

Canisters must be leak-tight and be shown not contribute to measurement bias

# **Qualification – Leak Check and Zero Challenge**

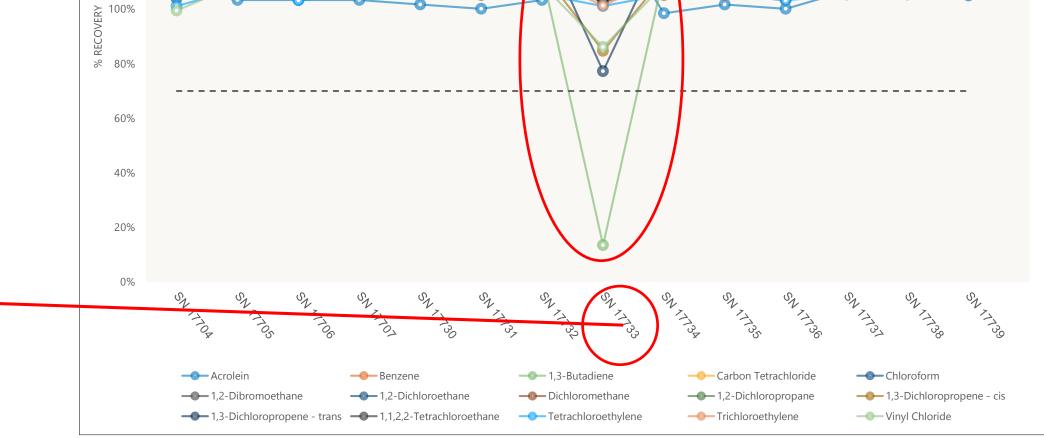
- Pressurize 14 canisters to ~ 16 psia with humidified HCF immediately following cleaning
- Measure baseline canister pressure
- Screen 2 canisters for target analytes
- Store cans at ambient laboratory conditions
- Analyze after 7 days for 15 NATTS PT VOCs
- Goal is for all target analytes < MDL (range 0.0037 [EDB] – 0.049 ppbv [acrolein])

#### NATTS PT VOCs

| acrolein             | 1,2-dibromoethane         | 1,3-dichloropropene - trans |
|----------------------|---------------------------|-----------------------------|
| benzene              | 1,2-dichloroethane        | 1,1,2,2-tetrachloroethane   |
| 1,3-butadiene        | dichloromethane           | tetrachloroethylene         |
| carbon tetrachloride | 1,2-dichloropropane       | trichloroethylene           |
| chloroform           | 1,3-dichloropropene - cis | vinyl chloride              |



 All results normalized to laboratory LCS One canister shows poor recovery for two compounds and clearly stands out from the others
 SN 17733



# **Investigating SN 17733**

- 3 contaminants in HCF zero check: 0.03 0.10 ppbv
- High acrolein recovery (162%)
- Suppressed response (compared to 13 other canisters) for:
- 1,3-butadiene (15% recovery)
- cis-1,3-dichloropropene (86% recovery)
- trans-1,3-dichloropropene (77% recovery)
- 1,1,2,2-tetrachloroethane (97% recovery)
- vinyl chloride (83% recovery)
- Investigate SN 17733:

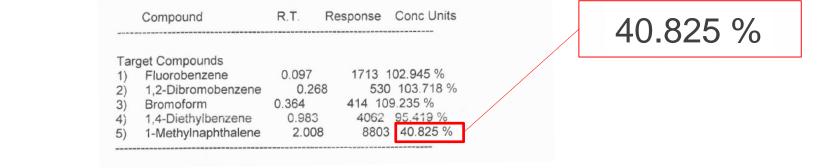
|                                      | Sample : 620 SN 17731<br>Misc<br>ALS Vial : 30 Sample Multiplier: 1  |
|--------------------------------------|--|
|                                      | Integration File: rteint.p<br>Quant Time: Jan 06 10:14:08 2015<br>Quant Method : C:\MSDCHEM\1\METHODS\CAN03.M<br>Quant Title : Canister Recovery Check<br>QLast Update : Tue Jan 06 07:04:52 2015<br>Response via : Continuing Cal File: C:\msdchem\1\data\150106\15010603.d<br>Integrator: RTE 6890 Scale Mode: Small noise peaks clipped |
|                                      | Volume Inj. :<br>Signal Phase :<br>Signal Info :   |
|                                      | Compound R.T. Response Conc Units  |
|                                      | Target Compounds      1)    Fluorobenzene    0.081    1739    104.507 %      2)    1,2-Dibromobenzene    0.255    554    108.415 %      3)    Bromoform    0.352    404    106.596 %      4)    1,4-Diethylbenzene    0.979    4466    104.910 %      5)    1-Methylnaphthalene    2.004    22943    106.400 %                             |
|                                      |  |
| 103.M                                | 106.400 %  |
| 1\data\150106\15010<br>beaks clipped | 603.d  |

# **Qualification – Known Standard Challenge**

- Pressurize 14 canisters to ~16 psia with 0.5 ppbv standard (69-component VOC mix) diluted with humidified HCF
- Store cans at ambient laboratory conditions
- Analyze after 7 days
- Goal is for recovery of all NATTS PT VOCs to be 70-130%



- Manufacturer supplies QC check analysis data:
- Poor methylnaphthalene recovery (40.8%)



Sample : 620 SN 17733

Signal Phase Signal Info :

Misc : ALS Vial : 32 Sample Multiplier

tegration File: rteint.p uant Time: Jan 06 10:29:58 2015

ant Method : C:\MSDCHEM\1\METHODS\0

onse via : Continuing Cal File: C:\msdch

ant Title :Canister Recovery Check ast Update:Tue Jan 06 07:04:52 201



- New canisters must be qualified before initial use for in trace-level air toxics work
  Qualify your constant the conjector manufacturer if the constant fit for use
- Qualify your cans and contact the canister manufacturer if the cans are not fit for use!



#### National Ambient Air Monitoring Conference

August 2016

