

National Institute for Occupational Safety and Health



Generation and Evaluation of Reference Samples as part of an Evacuated Canister Interlaboratory Study

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CDC/NIOSH



Study Description

- **NIOSH Manual of Analytical Methods 3900**
- **Evacuated Canister Interlaboratory Study**
 - ASTM Internationals
- **17 volatile organic compounds (VOCs)**
 - Two concentration ranges
 - Three levels per range
 - 5, 10, & 15 PPB
 - 0.8, 1.3, & 1.7 PPM

 Volatile Organic Compounds, C1 to C10, Canister Method 3900	
Formula: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1	
METHOD: 3900, Issue 1 EVALUATION: FULL Issue 1: 30 August 2018	
OSHA: Table 3 PROPERTIES: Table 1 NIOSH REL: Table 3 Other OELs: [1-3]	
ANALYTES: ethanol, 2-propanol, acetone, 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione, dichloromethane, trichloromethane, hexane, benzene, toluene, ethylbenzene, <i>o</i> -xylene, <i>m,p</i> -xylene, methyl methacrylate, α -pinene, <i>d</i> -limonene	
SAMPLING	MEASUREMENT
SAMPLER: FUSED-SILICA LINED STAINLESS STEEL CANISTER, 6 L, 450, or 400 mL FLOW RATE: 0.06 to 50 mL/min. See SAMPLING section VOL-MIN: Depends on canister volume. See SAMPLING section SHIPMENT: Routine SAMPLE STABILITY: 58 days @ 25 °C (30 days for ethanol, 2-propanol, and acetone @ 10 ppb; 21 days for α -pinene and <i>d</i> -limonene @ 0.8 ppm) BLANKS: 1 field blank per set	TECHNIQUE: GAS CHROMATOGRAPHY, MASS SPECTROMETRY ANALYTE: Compounds listed in Table 1 PRECONCENTRATION VOLUME: 25 to 500 mL injection (ppb-levels) for a 6L canister, 25 to 250 mL injection (ppb-levels) for a 400/450 mL canister, 1 mL loop (ppm-levels) PRECONCENTRATION CONDITIONS: Module 1 (empty): Focused @ -20° C, desorbed @ 10° C, baked @ 150° C (7 min); Module 2 (glass beads): Focused @ -80° C, desorbed @ 180° C, baked @ 190° C; Module 3 (focuser): Focused @ -150° C.
ACCURACY	GC/MS CONDITIONS: Injection: preconcentrator transfer line 100°C Detector: 280° C Column: 35° C (2 min hold) to 170° C (ramp 8°C/min), ramp 20° C/min to 220° C (3 min hold) MS Source: 230° C Quadrupole: 150° C Solvent delay: 4.5 min MS Scan: 35-350 amu CARRIER GAS: Helium, 1 mL/min COLUMN: Capillary, fused silica, 60 m x 0.32-mm ID; 1- μ m film 100% dimethylpolysiloxane CALIBRATION: Gas phase analytes in canisters RANGE: Tables 4a and 4b ESTIMATED LOD: Tables 4a and 4b PRECISION (\bar{S}_y): Tables 4a and 4b
RANGE STUDIED: Tables 4a and 4b BIAS: Tables 4a and 4b OVERALL PRECISION (\bar{S}_{PT}): Tables 4a and 4b ACCURACY: Tables 4a and 4b	
APPLICABILITY: The method was developed for measuring a range of volatile organic compounds in healthcare settings (4), but may be used in other occupational settings. The method was developed to measure the following analytes: ethanol, acetone, 2-propanol, dichloromethane, hexane, trichloromethane, 2,3-butanedione, 2,3-pentanedione, and 2,3-hexanedione, benzene, methyl methacrylate, toluene, ethylbenzene, <i>m,p</i> -xylene, <i>o</i> -xylene, α -pinene, and <i>d</i> -limonene. The working range is 0.24 to 22 ppb	

Traditional VOC Sampling Methods

▪ Sorbent Tubes

- Rely on adsorption
- Active sampling methods
- Have analyte specificity
- Collect small sample sizes
- Can require cold storage
- Require solvent desorption



▪ Thermal Desorption Tubes

- Lack back-up section to test for breakthrough



Evacuated Canisters Advantages

- **Passive sampling method**
- **Collect whole air sample**
- **Capable of multiple sample analyses**
- **Do not require cold storage**
- **No solvent desorption**
- **Have 21-58 day storage stability**
 - Analyte dependence



Canister Limitations

- **Wall Losses**
 - VOCs can adsorb to active sites
 - Can reduce with fused-silica lining
- **High humidity conditions**
 - Dissolution of VOCs in water
- **Cost**
 - Expensive instruments and consumables such as liquid nitrogen
- **Certain classes of compounds are not amenable**



Tested Canisters with Volatile Organic Compounds (VOCs)

- Vapor Pressure > 0.1 mmHg at 25°C
- Health Effects, Pollution, Compliance
- 14 VOCs – Healthcare Setting
 - Cleaning Products, Bioaerosols, Asthmagenic
- 3 VOCs – Alpha-Diketones
 - *Obliterative Bronchiolitis*
 - Fibrosis and obstruction of airways



Suite of 17 VOCs

Ethanol	Acetone	2-Propanol
Methylene Chloride	<i>n</i> -Hexane	2,3-Butanedione
Chloroform	Benzene	2,3-Pentanedione
Methyl Methacrylate	Toluene	2,3-Hexanedione
Ethylbenzene	<i>m,p</i> -Xylene	<i>o</i> -Xylene
α -Pinene	α -Limonene	

Sample Preparation Methods

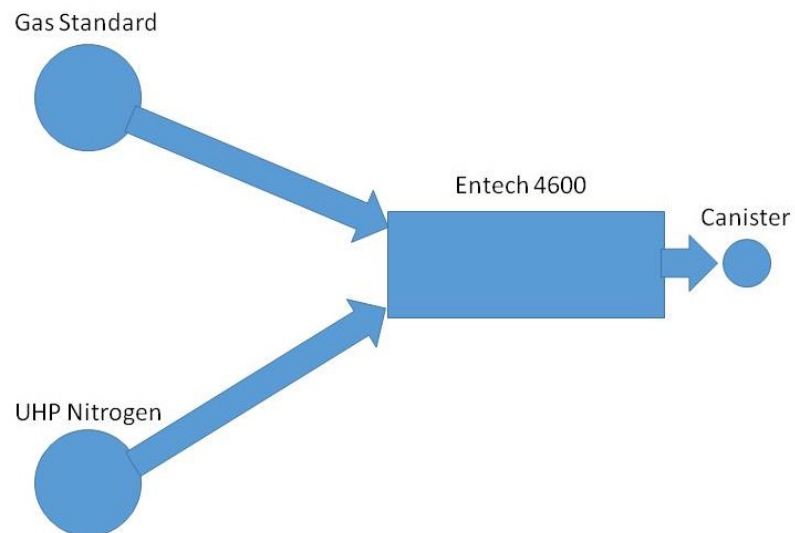
▪ 3 Total Preparation Methods

- PPB range
 - Flow method
 - Pressure transfer method
- PPM range
 - Pressure transfer method
 - Manifold method



Flow Method

- **PPB range samples only**
- **Mixture of 2 streams of gas**
 - Certified gas standard of 17 VOCs at 2 PPM
 - Ultra-high purity (UHP) nitrogen



Entech 4600



Pressure Transfer Method

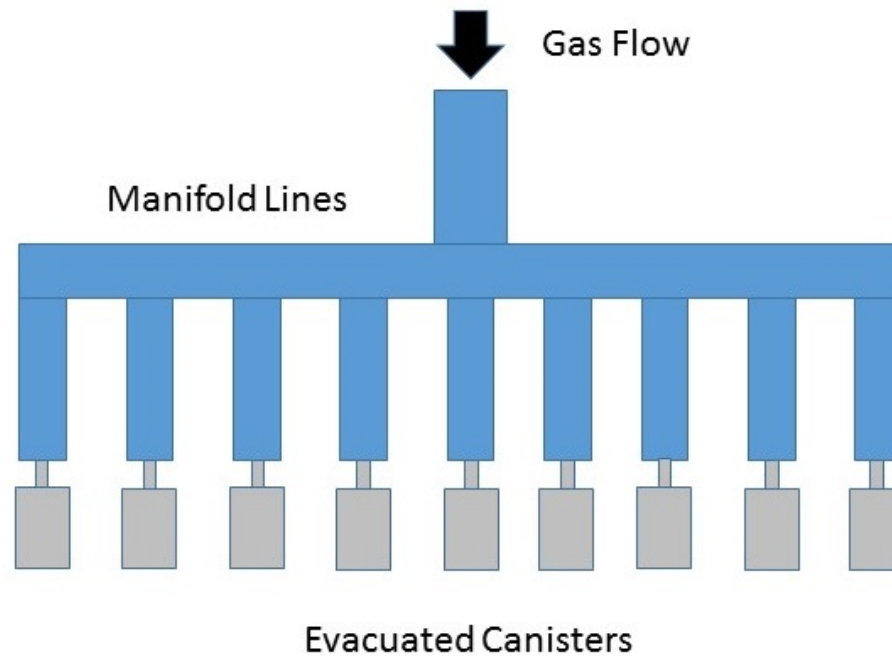
- **PPB and PPM range samples**
- **Certified gas standard pressure diluted by UHP nitrogen into 6L canister at nominal concentration level**
- **Pressure transferred from 6L canister to multiple 450 cc canisters**

Entech 4700



Manifold Method

- PPM range only
- Multiple 450 cc canisters generated in parallel via pressure dilution using Entech 4700.



Sample Counts by Preparation Method

Preparation Method	Manifold	Pressure	Pressure	Flow
Concentration Range	PPM	PPM	PPB	PPB
Canister <i>N</i>	63	18	18	54



Sample Analyses

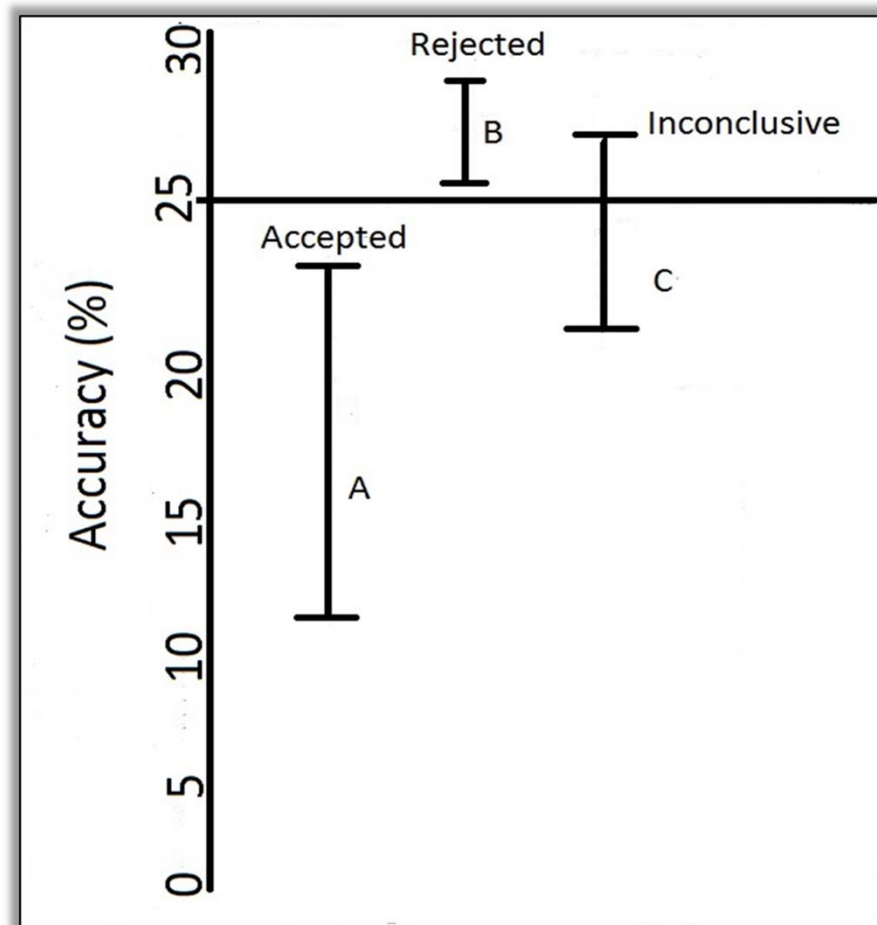
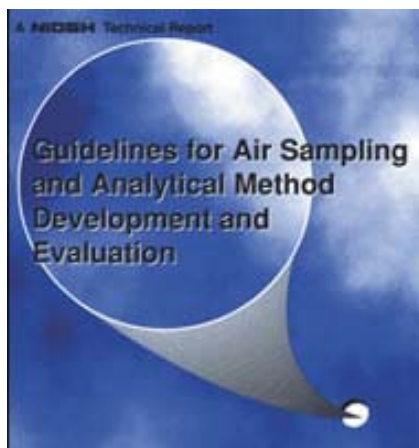
■ Three Methods

- Part Per Billion
 - No dilution
 - 250 cc injection volume cryogenically pre-concentrated
 - 72 samples
- Diluted Part Per Million
 - Can to can dilution using Entech 4700
 - 250 cc injection volume cryogenically pre-concentrated
 - 63 samples
- Loop Part Per Million
 - 1 cc volume sample loop
 - no pre-concentration

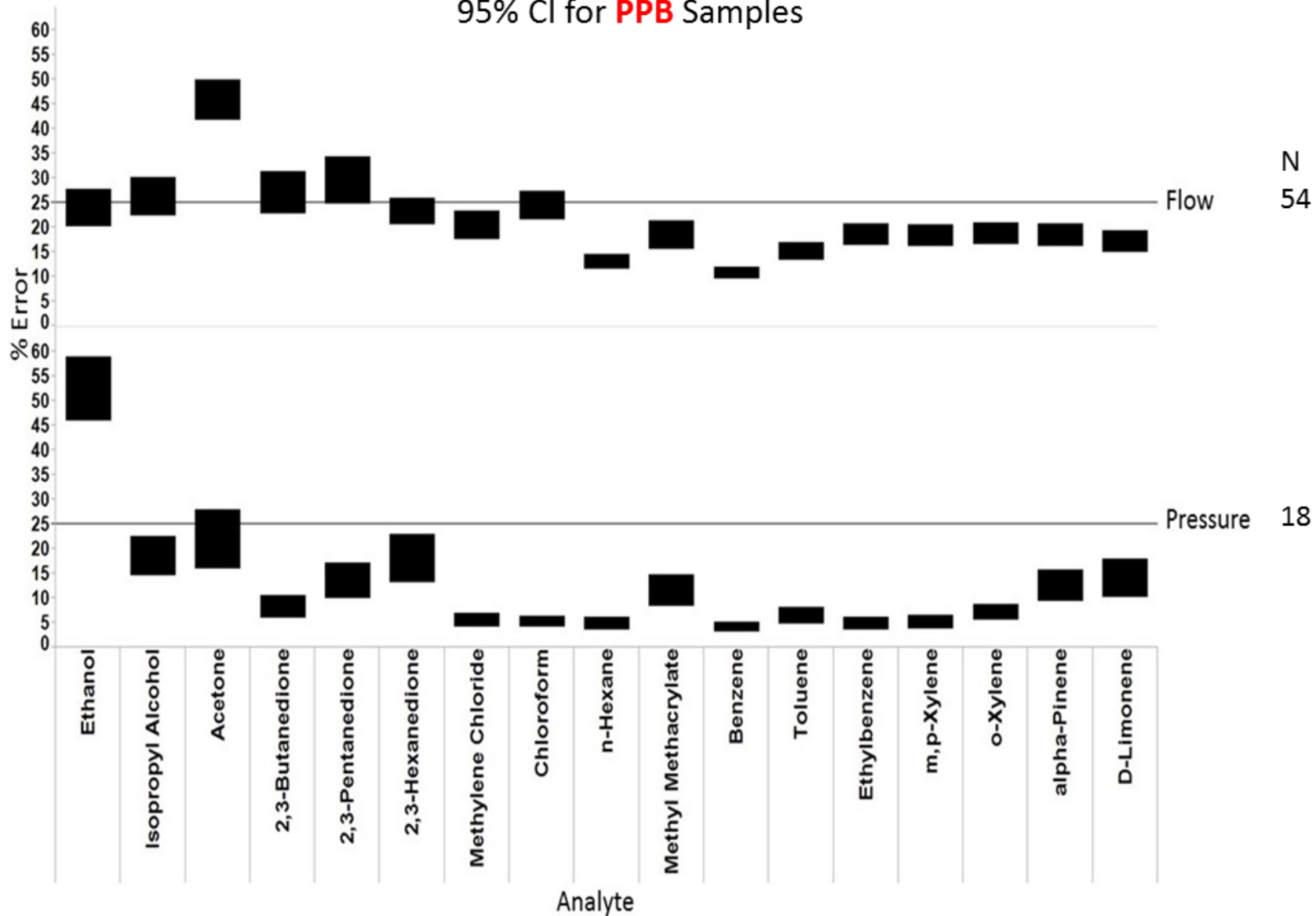


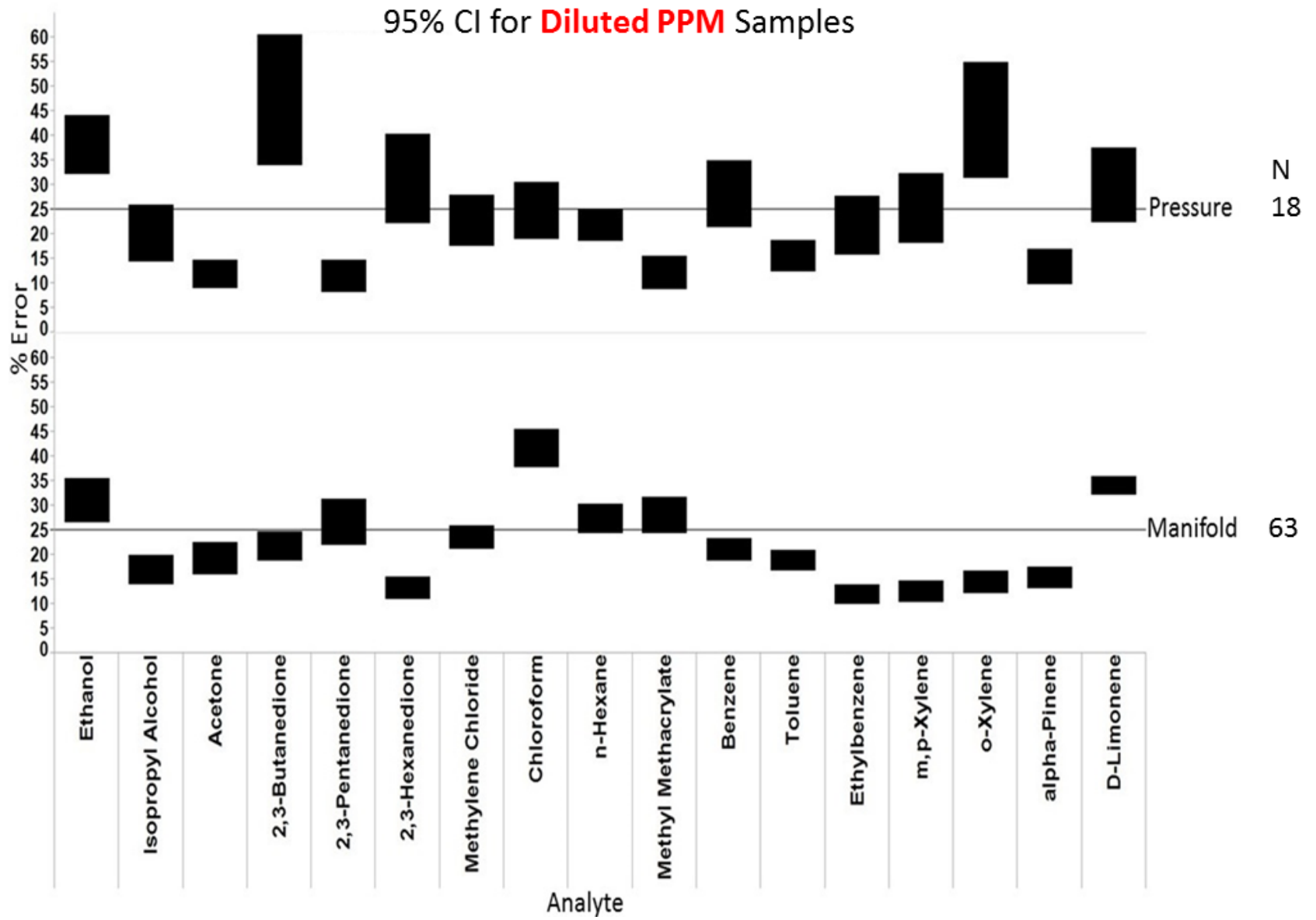
NIOSH Accuracy Criterion

- **Accuracy**
 - +/- 25% error
 - Bias and precision
- **95% Confidence interval (CI) on accuracy**
 - UCL must be below 25% error to pass
 - CI encompassing 25% error is inconclusive
 - LCL above 25% error is failure

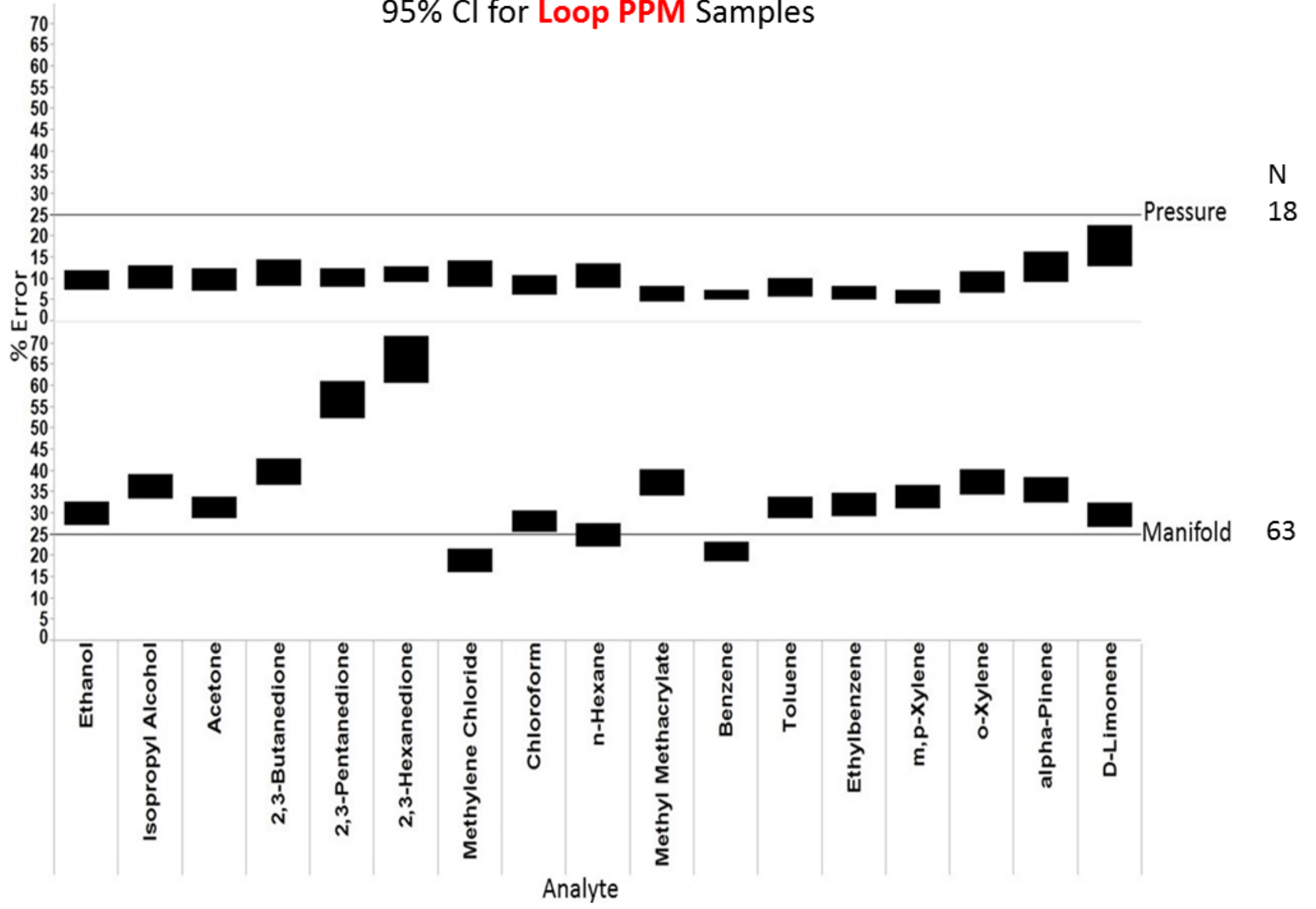


95% CI for **PPB** Samples





95% CI for Loop PPM Samples



Conclusions

- 15 of the 17 VOCs in the PPB-range passed the NIOSH Accuracy and 95% CI criterion when samples were produced by pressure transfer method.
- All 17 VOCs in the PPM-range passed the NIOSH Accuracy and 95% CI criterion when samples were produced by pressure transfer method and were analyzed via the loop injection method.

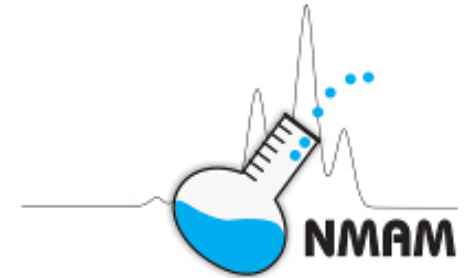
Takeaways

1. Method performance dependent on concentration (PPB or PPM)
2. Pressure transfers better for standard/spike canister generation
3. Loop injection sometimes better than pressure dilutions
4. NMAM 3900 – Volatile Organic Compounds, C1 to C10, Canister Method
 - <https://www.cdc.gov/niosh/nmam/pdf/3900.pdf>

Questions?

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The findings and conclusions in this report are those of the authors and do not necessarily represent the official position of the Centers for Disease Control and Prevention.



Selected References

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