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An Evaluation of DTSC/LARWQCB Holding Time Requirements for Soil Gas Samples Collected in Canisters and a Look at Liquid Leak Detection Compounds

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Overview

- **In January 2003, California Department of Toxic Substances Control (DTSC) and Regional Water Quality Control Board-Los Angeles Region (LARWQCB) released jointly developed "Advisory - Active Soil Gas Investigations"**
  - DTSC's Vapor Intrusion guidance (2005) recommends following this advisory
- **Inconsistencies were found between California guidance and USEPA analytical methods referenced:**
  - Soil Gas Advisory: Holding times for canister samples are 72 hours
  - USEPA Method TO-15: VOCs in canisters are stable for up to 30 days
- **Characteristics of a Summa canister**
- **Uncertainty of "true" Holding Time due to matrix: ambient air vs. soil gas**
- **Holding Time data for "real-world" soil gas samples will be presented**
- **Iso-propyl Alcohol as a Leak Check option will be examined**

The Summa Canister

- **Stainless steel container with a Pack-less valve and cap**
- **Internal surface is electrochemically passivated using SUMMA Process - no welds after passivation**
- **Canister is steam-cleaned to remove surface oils**
- **Moisture in air sample creates inert surface**

Courtesy of Steven D. Hoyt, Environmental Analytical Services, Inc.

Historical Overview

- **1965 – SUMMA Canister developed by Hutton and Rasmussen**
- **1970 – SUMMA Canister and Cryogenic Concentration by Rasmussen at WSU for collecting air samples**
- **1988 – EPA TO-14 Compendium Method**
- **1999 – EPA Second Edition of Compendium Methods, TO-14A and TO-15**

Courtesy of Steven D. Hoyt, Environmental Analytical Services, Inc.

How the Canister Works

- **Electropolishing creates a Nickel and Chromium Oxide Surface**
- **The water in the air or gas sample forms a film on the surface, making it inert**
- **When canister is cleaned, old water film and VOCs are removed from canister**
- **Next sample forms new inert surface**

Courtesy of Steven D. Hoyt, Environmental Analytical Services, Inc.

Questions

- **Why does DTSC's guidance vary so significantly from all other past and current Holding Times?**
- **More importantly, can we produce data that demonstrates the historical Holding Times associated with ambient air should be used for soil gas?**

Study Overview

- Performed at TestAmerica Los Angeles (Santa Ana, CA)
- More than 50 soil gas samples from different sites in California
- Analyzed within DTSC's recommended Holding Time of 72 hours, then again at 14 days and again at 30+ days
- Total of 48 analytes detected in all samples
- Presentation will focus on the following compounds:
  - Tetrachloroethene (PCE)
  - Trichloroethene (TCE)
  - cis-1,2-Dichloroethene
  - Vinyl Chloride
  - Benzene
  - Toluene
  - MTBE
  - 1,2,4-Trichlorobenzene

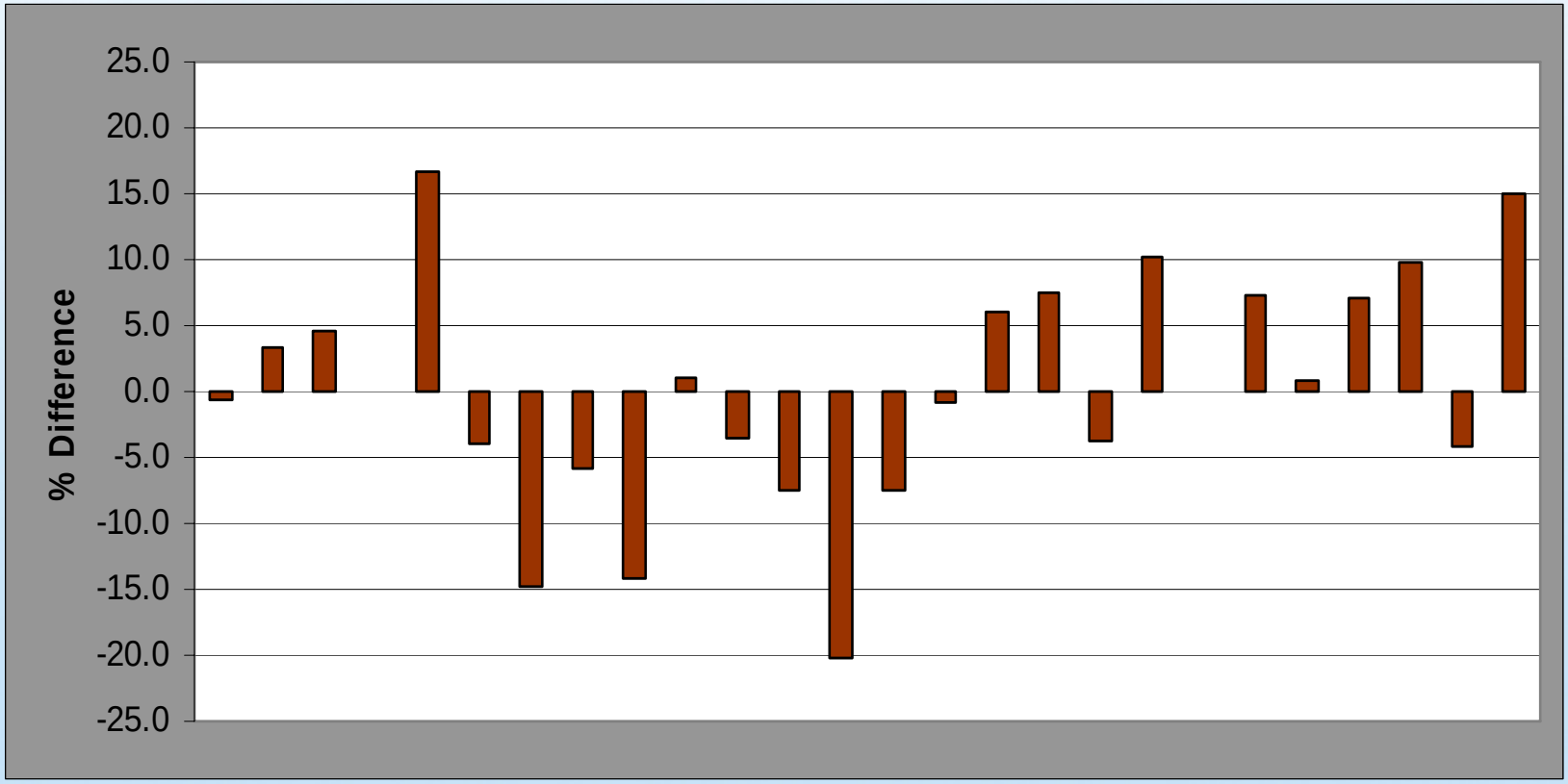
14 Day Results

Analyte	Ave. % Difference*	#Data Points
PCE	-1.4	37
TCE	1.8	26
cis-1,2-Dichloroethene	-4.6	16
Vinyl Chloride	-4.2	8
Benzene	-3.1	23
Toluene	-6.7	31
MTBE	-0.5	3
1,2,4-Trichlorobenzene	0.1	25

- ***% Difference from original analysis**

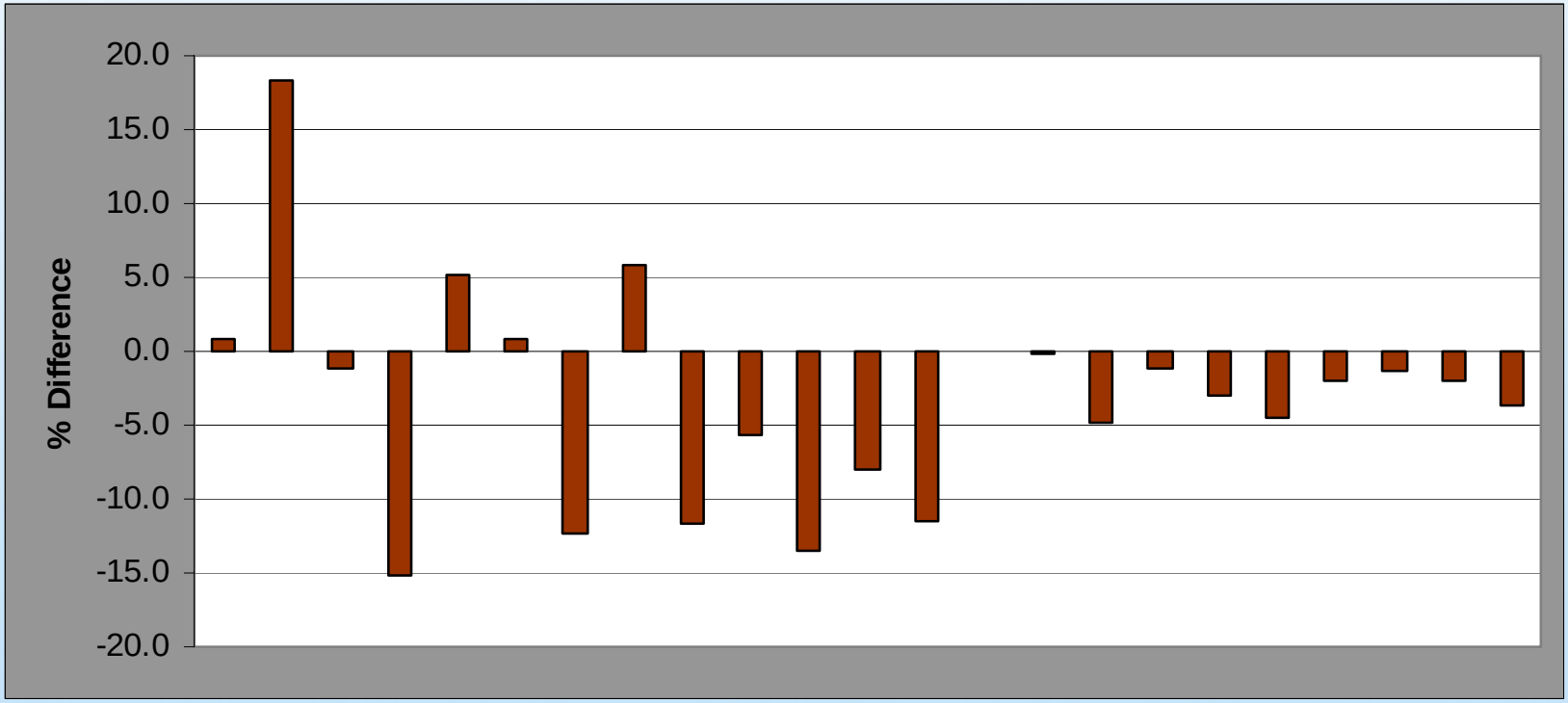
TCE at 14 Days

- High concentration: 6020 ppbV
- Low concentration: 2.1 ppbV
- Average %D = 5.7%



Benzene at 14 Days

- High concentration: 980 ppbV
- Low concentration: 2.1 ppbV
- Average %D = -3.1%



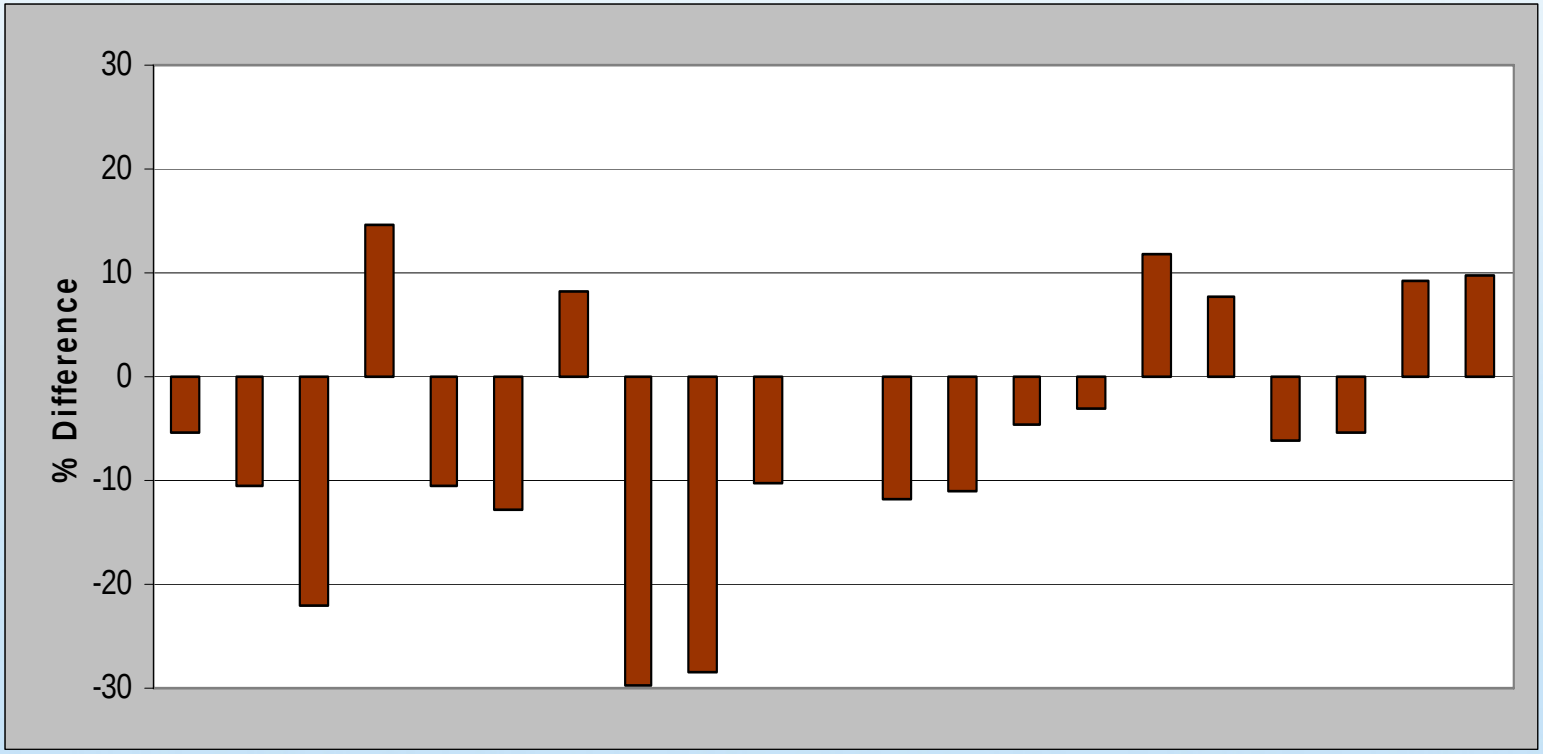
30+ Day Results

Analyte	Ave. % Difference*	#Data Points
PCE	-4.4	27
TCE	-5.3	21
cis-1,2-Dichloroethene	-10.9	11
Vinyl Chloride	-16.3	6
Benzene	-6.7	15
Toluene	-11.8	21
MTBE	-14.8	2
1,2,4-Trichlorobenzene	-11.4	15

- ***% Difference from original analysis**

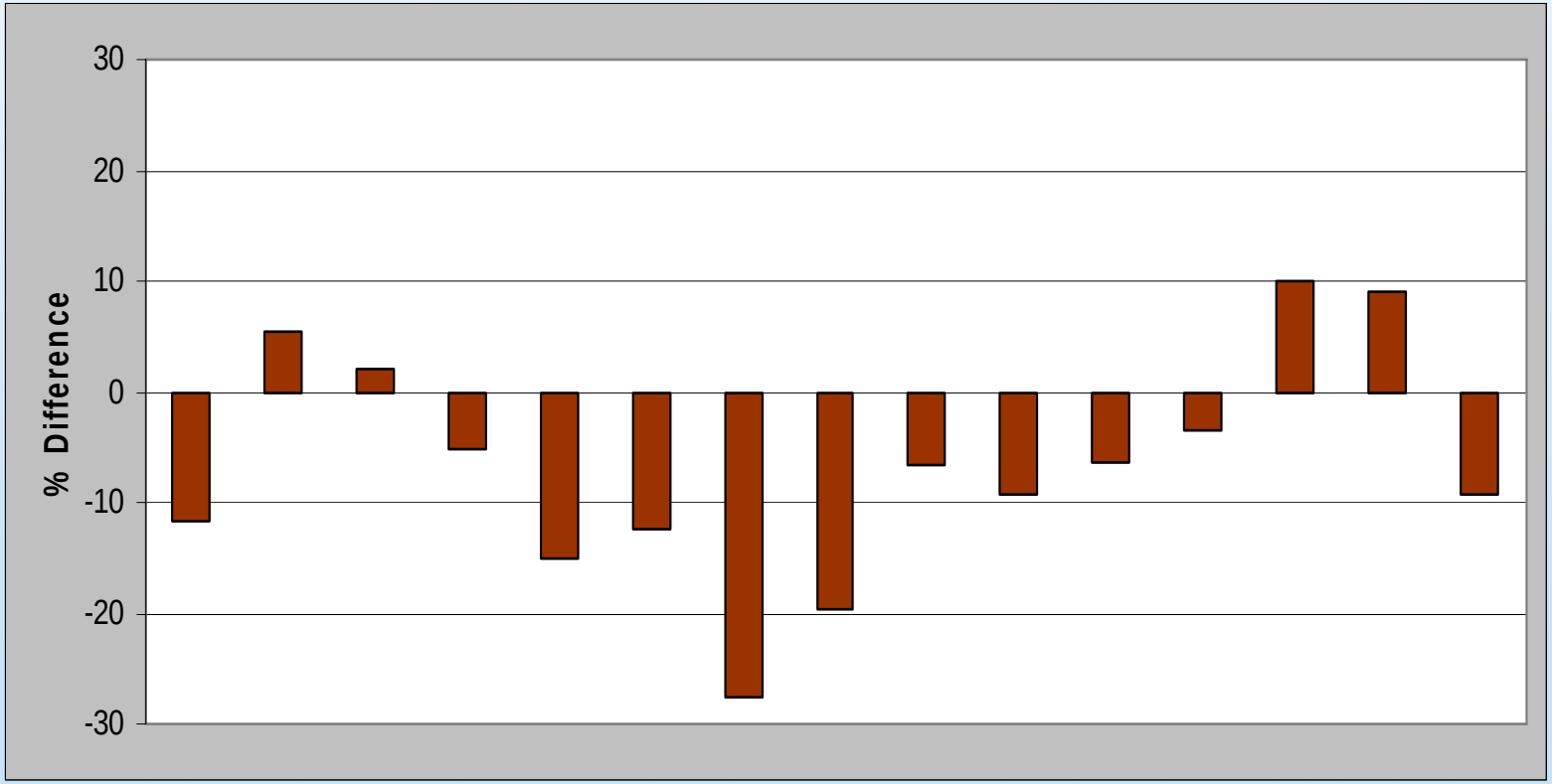
TCE at 30+ Days

- High concentration: 6020 ppbV
- Low concentration: 2.1 ppbV
- Average %D = -5.3%



Benzene at 30+ Days

- High concentration: 980 ppbV
- Low concentration: 2.1 ppbV
- Average %D = -6.7%



Ambient Intrusion

- Guidance recognizes that ambient air entering probe or other connections through seal leakage during sampling may represent significant dilution of the sample.
- Addresses potential for leakage by proposing that all points of potential ambient intrusion be evaluated by using “Leak Check” compounds.
- Leak test should include analysis of the Leak Check compound in the sample. If detected then corrective action is required.

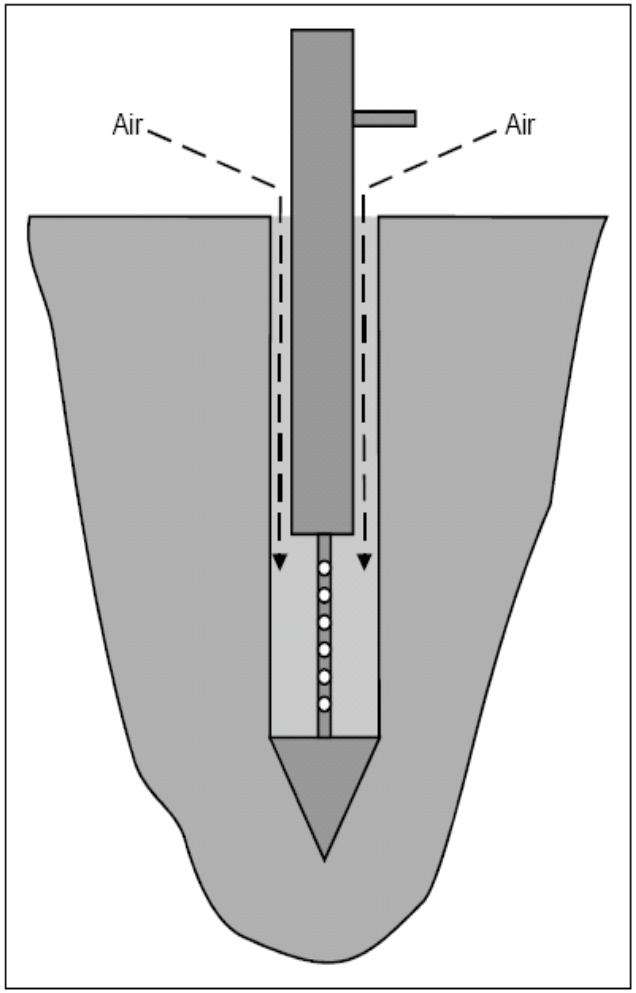


Figure 9.8 Ground Probes Ambient Air Short Circuiting

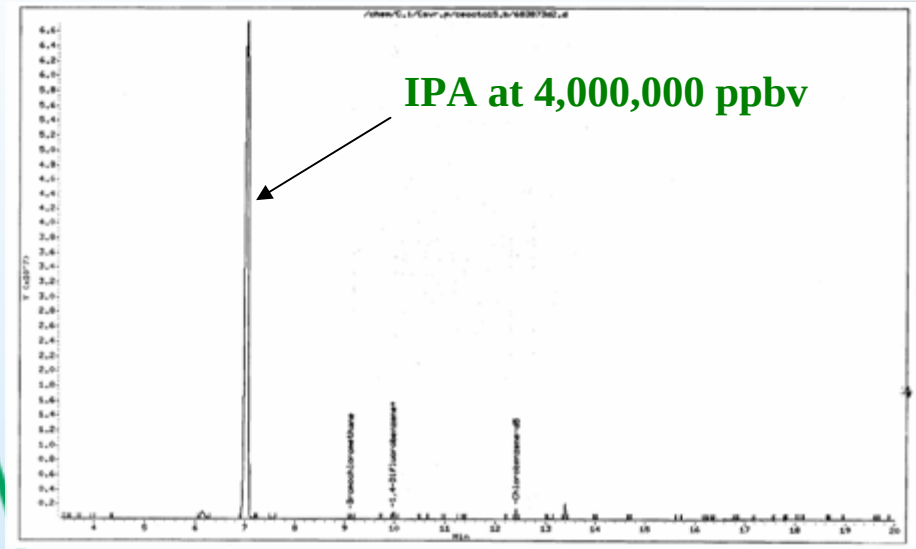
Leak Check Compounds

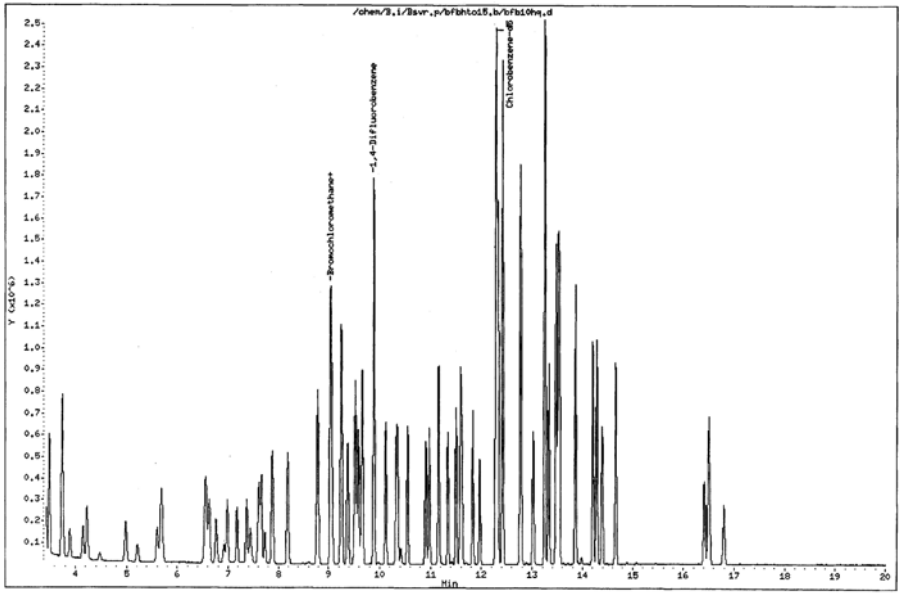
Section 2.4.2:

Tracer compounds, such as pentane, isopropanol, isobutene, propane, and butane, may be used as leak check compounds, if a detection limit (DL) of 10 ug/L or less can be achieved. These compounds may be contained in common products such as shaving cream.

- Compounds listed in guidance are detected by the MS detector, potentially impacting data reported by methods TO-15/14. If present and not analyzed until received at the laboratory, it's too late to mitigate leak.
- Compounds currently in guidance will also provide positive response in varying degrees to field meters (PIDs and FIDs). The responses cannot be separated from potential compounds of concern at the site.
- Use of liquids presents additional challenges, as liquids represent a 100% concentrated compound. Even statistically small leaks will have significant impact; for example, 0.1% leak represents 1,000 ppmV.

Leak Check with Liquids





Iso-Propyl alcohol (iso-propanol)

Sample with high level of IPA from field leak checking

- **All hits diluted out to non-detects**

LCS sample, mid-range standard

The leak is not detected until laboratory analysis!

Summary & Recommendations

- Summa canister samples showed acceptable stability for 30+ days for all analytes studied
- All average % Differences were well within the Method TO-15 recommendations of 30%, with the majority being within 15%
- Suggest DTSC Holding Time requirement for soil gas samples collected in canisters be changed to 30 days:
  - Study shows that even 14 days is a conservative Holding Time
  - Would be in line with EPA TO-15 Holding Time
- Propose that helium be recommended as Leak Check compound, because helium can be analyzed by alternate method and can be verified in the field with success

Questions or Comments?

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