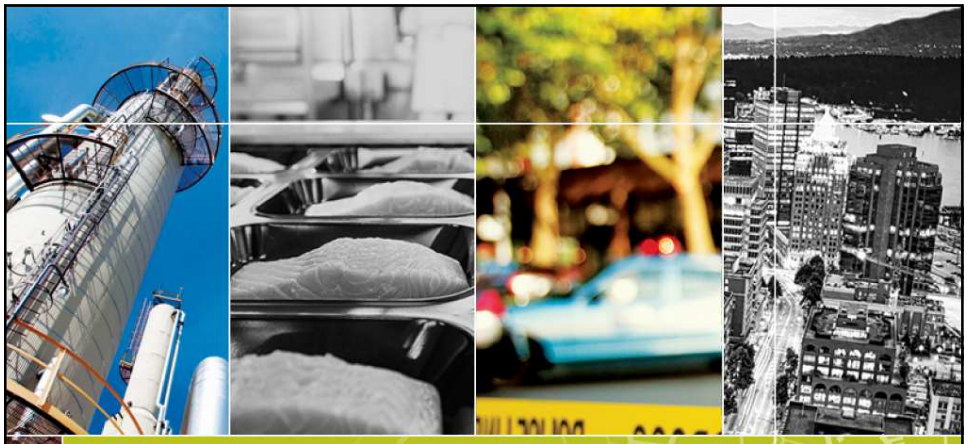

Ambient Air Collection - Updates

October 28, 2016

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Chasing air-borne contaminants for over 30 years!

Contact:

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Air Toxics

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Ambient Air - What's changed, what's new

Discussion Topics

- Implementation of O. Reg. 419 Air Standards
- Changes from the original 2009 proposal
- Discussion on specific methods – I will meander through collection procedures
- VOCs, Dioxins/Furans/PCBs, Particulates/Metals and Cr6+
- What are we sampling? (if we have time)

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Changes to O. Reg. 419/05 Implementation July 1, 2016

From the MOECC…..

- Air standards for 1,3-butadiene, benzene, hexavalent chromium, nickel, benzo-a-pyrene (as a surrogate for PAHs) and uranium, have been set directly as annual averages, rather than converting to 24-hour standards as proposed in July 2009.
- This decision is based on the consensus of the multi-stakeholder group that standards for contaminants causing effects after long-term exposure (e.g., cancer) should be set directly as annual averages rather than converting to a 24-hour standard.

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Changes to O. Reg. 419/05 Implementation July 1, 2016

- Air standards for chromium, manganese and nickel have been set as total suspended particulate (TSP) instead of inhalable (PM_{10}) particulate and TSP, as proposed in July 2009.
- The MOEEC has agreed with stakeholders that challenges in measuring different metal particulate size fractions in the emissions or the lack of availability of size-specific emission factors warrant a single regulatory limit based on TSP alone.
- The MOEEC AAQCs based on PM_{10} particulate and TSP and these remain unchanged.

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Changes to O. Reg. 419/05 Implementation July 1, 2016

- Air standards for uranium have been set as inhalable particulate (less than 10 micrometres in diameter) instead of inhalable particulate and TSP, as proposed in July 2009.
- The MOE AAQCs are based on both inhalable particulate and TSP.

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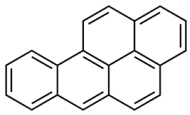
Changes to O. Reg. 419 from 2009 Implementation July 1, 2016

- **Benzene** (010-7186): **0.45 µg/m^3**, annual average [Schedule 3]
- **Benzo-a-pyrene (as a surrogate of total PAHs)** (010-6213): **0.00001 µg/m^3**, annual average [Schedule 3]
- **1,3-Butadiene** (010-6214): **2 µg/m^3**, annual average [Schedule 3]
- **Chromium and Chromium Compounds (Metallic, Divalent and Trivalent)** (010-6353): **0.5 µg/m^3**, 24-hour average [Schedule 3]
- **Chromium Compounds (Hexavalent)** (010-6353): **0.00014 µg/m^3,** annual average [Schedule 3]



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Changes to O. Reg. 419 – Implementation July 1, 2016

- **Dioxins, Furans and Dioxin-like PCBs** (010-7193): **0.0000001 µg/m^3**, 24-hour average [Schedule 3]
- **Manganese and Manganese Compounds** (010-6253): **0.4 µg/m^3**, 24-hour average [Schedule 3]
- **Nickel and Nickel Compounds** (010-7188): **0.04 µg/m^3,** annual average [Schedule 3]
- **Uranium and Uranium Compound (in the PM$_{10}$ fraction)** (010-7192): **0.03 µg/m^3**, annual average [Schedule 3]

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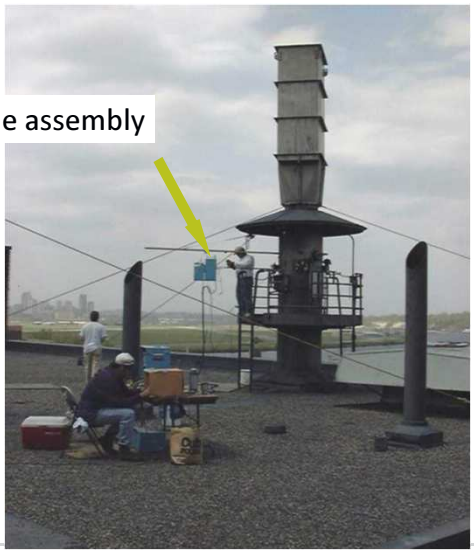
Stack Gas Sampling affected by Ambient Standards



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EPA Methods TO4/TO13/TO9 for PCBs/PAHs/Dioxins&Furans due to change

High Volume Sampler

- Houses PUF cartridge with pre-filter
- Collects 300 m^3 over 24 hours
- B(a)P RDL in lab needs to be

0.00001 **µg/m³** x 300 **m³** = 0.003 ug

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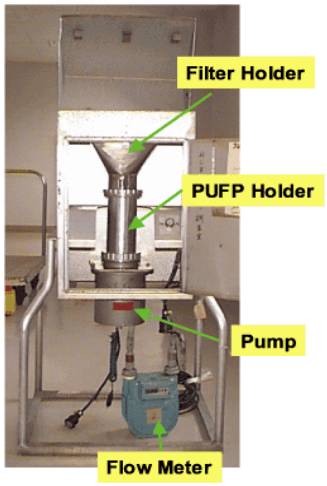
EPA Methods TO4/TO13/TO9 for PCBs/PAHs/Dioxins

- PCBs, PAHs and Dioxins/Furans
- using PUF cartridge with XAD-2 resin
- (XAD-2 helps with naphthalene retention)



High Volume Air Sampler(inside view)

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EPA Method TO9 for Dioxins/Furans/PCBs – each has a TEF

Polychlorinated dioxins	Non-ortho-substituted PCBs
2,3,7,8-TCDD	3,3',4,4'-TCB (PCB77)
1,2,3,7,8-PeCDD	3,4,4',5-TCB (PCB81)
1,2,3,4,7,8-HxCDD	3,3',4,4',5-PeCB (PCB126)
1,2,3,6,7,8-HxCDD	3,3',4,4',5,5'-HxCB (PCB169)
1,2,3,7,8,9-HxCDD	Mono-ortho-substituted PCBs
1,2,3,4,6,7,8-HpCDD	2,3,3',4,4'-PeCB (PCB105)
OCDD	2,3,4,4',5-PeCB (PCB114)
Polychlorinated dibenzofurans	2,3',4,4',5-PeCB (PCB118)
2,3,7,8-TCDF	2',3,4,4',5-PeCB (PCB123)
1,2,3,7,8-PeCDF	2,3,3',4,4',5-HxCB (PCB156)
2,3,4,7,8-PeCDF	2,3,3',4,4',5'-HxCB (PCB157)
1,2,3,4,7,8-HxCDF	2,3',4,4',5,5'-HxCB (PCB167)
1,2,3,6,7,8-HxCDF	2,3,3',4,4',5,5'-HpCB (PCB189)
1,2,3,7,8,9-HxCDF	
2,3,4,6,7,8-HxCDF	
1,2,3,4,6,7,8-HpCDF	
1,2,3,4,7,8,9-HpCDF	
OCDF	

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Sampling for VOCs such as Benzene and 1,3-Butadiene

Evacuated, highly polished, stainless steel sampling container

Canisters prevent permeation of VOCs through the vessel wall, and degradation due to exposure to sunlight during shipment to the analytical laboratory.

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TO15 (and TO14) – SUMMA Canister

Effective sample collection procedure for stack, ambient, indoor air and soil vapour at most sites contaminated with:

- Hydrocarbons
- Chlorinated Solvents

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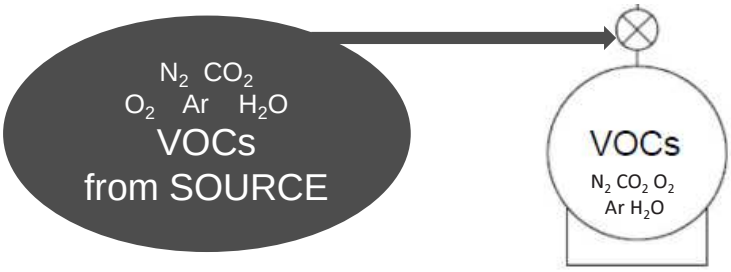
Using the SUMMA Canister

- In air/gas sampling, SUMMA canisters fill with air/gas that contain the VOC analytes of interest.
- The other parameters are also collected and can be tested
- No breakthrough, and can dilute high samples



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SUMMA Canister – Flow Controller

Flow controller is connected to the valve of the Summa canister to regulate air flow over a specific time period
(e.g. 10 min, 20 min, 1 hr, 8 hr, 24hr)

No controller = Grab sample, SUMMA will fill within several seconds

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SUMMA Canister – Flow Controller

The sampling program can be set up to include any of these intervals:
(e.g. 10 min, 20 min, 1 hr, 8 hr, 24hr)

The flow rate cannot exceed 200 mL per minute, but can be slower.

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Fixed Gases from SUMMA Canister

Atmospheric Gases:

- Oxygen
- Carbon Dioxide
- Methane

(DL <0.1%)

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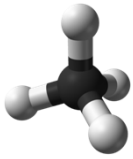
LIGHT HYDROCARBONS by SUMMA

- Methane
- Ethene
- Acetylene
- Butane
- Ethane
- Propane
- Propene
- Propyne
- Pentane



SUMMA, TEDLAR BAG (DL <0.1 ppm)

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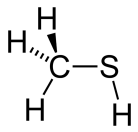
SULPHUR COMPOUNDS by Silanized SUMMA Canister

- Hydrogen sulphide
- Carbonyl sulphide
- Methyl mercaptan
- Ethyl mercaptan
- 1- Propyl mercaptan
- Dimethyl sulphide
- Methyl ethyl sulphide
- Dimethyl disulphide
- Sulphur dioxide
- Carbon Disulfide

SILANIZED SUMMA, TEDLAR BAG (DL <0.1 to 5 ppm)



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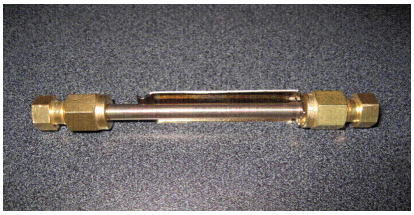
Sampling by Thermal Desorption Tube

- Made of inert metal
- Contains three sampling media
- Based on US EPA Method TO-17
- Active sampling with pump
- Concentrates sample



Perkin-ElmerR AirToxicsTM
Thermal Desorption Tube

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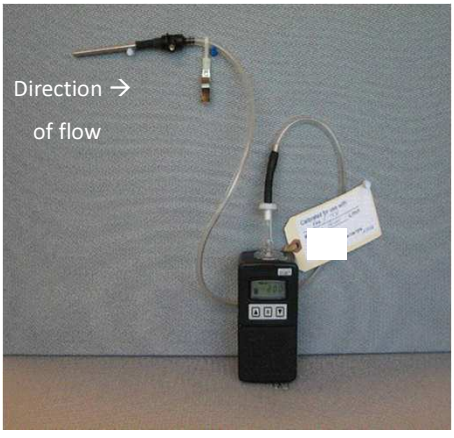
Using the TD Tube – Collects VOCs and some SVOCs



Sampling rate must be less than 1000 mL/min

Example calculation:

50 mL/min x 20 min = 1000 mL
=> 1 L

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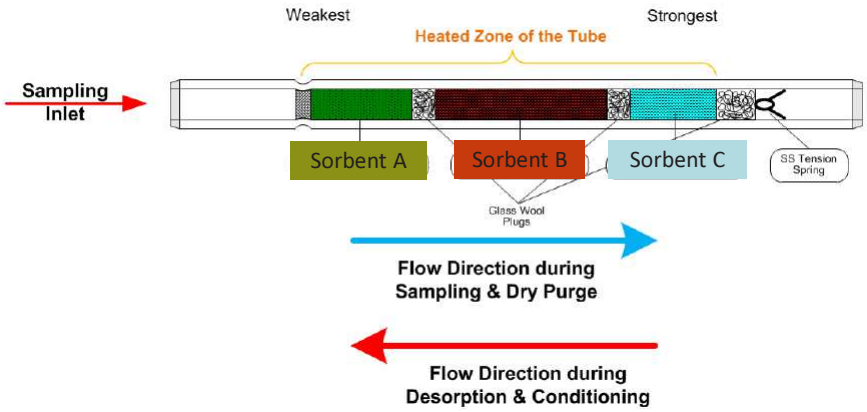
Using the multi-bed TD Tube (schematic from Supleco)



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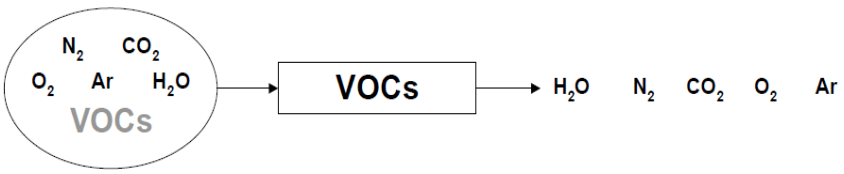
Using the TD Tube

- In air/gas sampling, TD tubes concentrate the analytes of interest (in this case the VOCs)
- The other parameters cannot be tested using TD tubes



SOURCE

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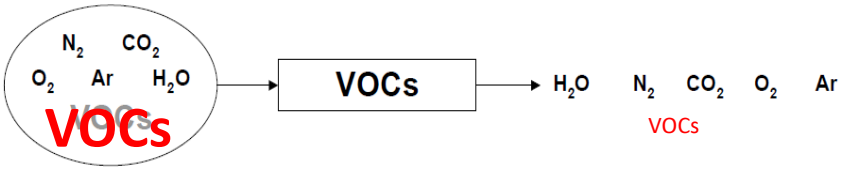
Using the TD Tube

- Capacity of TD tube is about 0.5 mg (500,000 ng) for gasoline and
- 0.1 mg (100,000 ng) for diesel range organics
- Breakthrough possible with high sources and is a concern



SOURCE

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Using the TD Tube

Breakthrough

- High sources may need backup tubes
- Breakthrough is indicated where analytes in the back tube are >10% by mass than the first tube. In this case, results should be considered as semi- quantitative.
- Safe sampling volumes cannot be exceeded

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FUN FACT Stability Study - TD Tube

Stability - Maxxam Internal Study over One Month

- A set of TD tubes was identically spiked with 100 ng of calibration standard
- TD tubes were stored at lab temperature
- Separate tubes were tested at one week intervals over one month
- Results did not indicate significant degradation over one month

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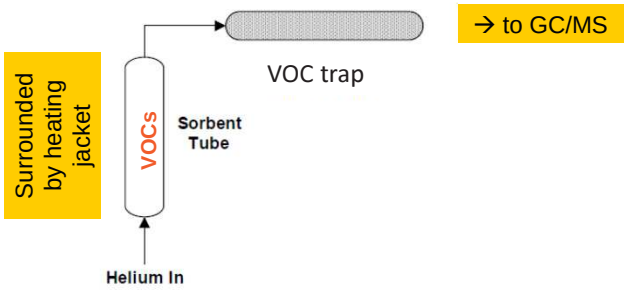
EPA Method TO17 – GC/MS

Schematic of desorption system



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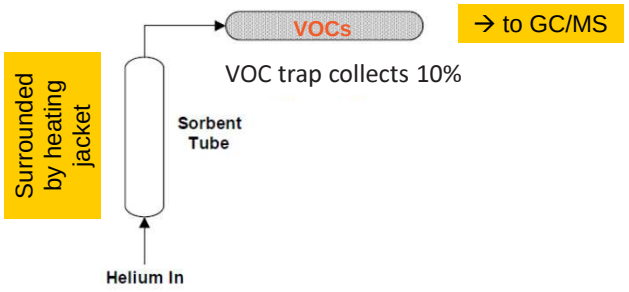
EPA Method TO17 – GC/MS

Schematic of desorption system – 1 in 10 split



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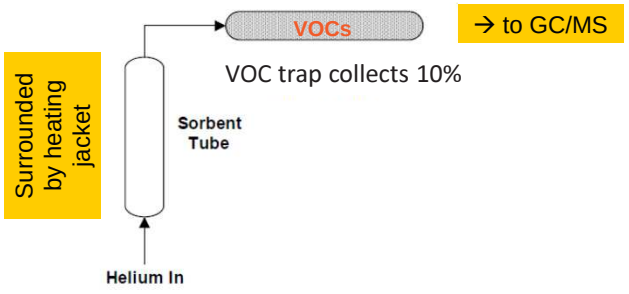
EPA Method TO17 – GC/MS

Schematic of desorption system – further 1 in 10 split means 100x dilution overall



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EPA Methods IO-2 and IO-3 for TSP/PM10 and Metals

High volume (hi-vol) Sampling

for Metals and Particulates

- Based on EPA Methods
- IO-2 specific to Particulates
- IO-3 specific to Metals
- Typical sampling volume 2000 to 3000 m^3

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Hi-vol Sampler - Particulates and Metals

Hi-vol filter assembly

3000 m^3 sampled

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Hi-vol Sampling – Particulates/Metals

Parameter	MDL (ug)	DL based on 3000 m3 (ug/m3)
Particulates (TSP, PM10)	500	0.17
Aluminum (Al)	20	0.007
Antimony (Sb)	10	0.003
Arsenic (As)	6	0.002
Barium (Ba)	1	0.0003
Beryllium (Be)	1	0.0003
Bismuth (Bi)	6	0.002
Boron (B)	6	0.002
Cadmium (Cd)	2	0.001
Calcium (Ca)	10	0.003
Chromium (Cr)	2	0.001
Cobalt (Co)	2	0.001
Copper (Cu)	2	0.001
Iron (Fe)	5	0.002
Lead (Pb)	3	0.001
Magnesium (Mg)	10	0.003
Manganese (Mn)	1	0.0003

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Hi-vol Sampling - Metals

Parameter	MDL (ug)	DL based on 3000 m3 (ug/m3)
Molybdenum (Mo)	3	0.001
Nickel (Ni)	3	0.001
Phosphorus (P)	25	0.008
Potassium (K)	20	0.007
Selenium (Se)	10	0.003
Silver (Ag)	1	0.0003
Sodium (Na)	5	0.002
Strontium (Sr)	1	0.0003
Sulphur (S)	25	0.008
Thallium (Tl)	10	0.003
Tin (Sn)	10	0.003
Titanium (Ti)	1	0.0003
Uranium (U)	30	0.010
Vanadium (V)	2	0.001
Zinc (Zn)	5	0.002
Zirconium (Zr)	1	0.0003

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Hexavalent Chromium (Cr^{6+}) by CARB Method 039 and ASTM D7614

- Apparatus can be used for low volume sampling for other Metals and Particulates
- Typical sampling volume 20 m^3

For Cr6+, use a bicarbonate coated cellulose filter

Lab RDL about 0.008 ug

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Hexavalent Chromium (Cr^{6+})

Hexavalent Chromium in Emissions

- In accordance with the United States Department of Labour (Occupational Safety and Health Administration**), hexavalent chromium [Cr(VI),** which is one of the valence states (+6) of the element chromium, is known to cause cancer. In addition, it targets the respiratory system, kidneys, liver, skin and eyes.
- It is estimated that >500,000 workers are potentially exposed to Cr(VI) in the United States. Workplace exposures occur mainly in the following areas:

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Hexavalent Chromium (Cr^{6+})

- Hexavalent chromium is separated from other metallic anions such as chromate by a high capacity anion separator column and a coloured product having a wide absorption band centered at 530 nm is formed with the colorimetric reagent.
- The coloured product is detected photometrically and quantitation of Cr(VI) is accomplished by linear regression of peak area on the concentration of a series of Cr(VI) calibration standards.

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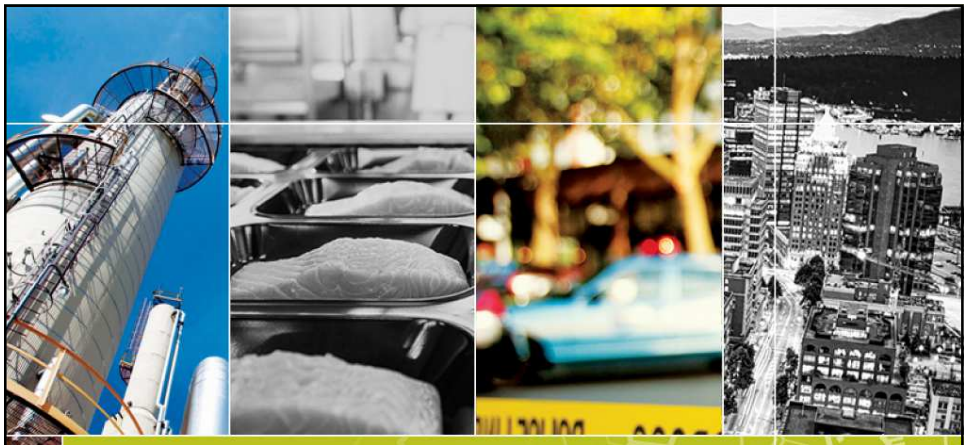

Random Thoughts about
Sampling and Analysis

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Measurement of Uncertainty M(u)

- The uncertainty value provides an estimate of all sources of variability in the analysis, including sample homogeneity, preparation and analysis.
- Nineteen out of twenty measurements of any sample should fall within the confidence interval predicted by the equation.
- Maxxam uses a coverage factor "k" (multiplier of the combined standard uncertainty) to obtain an Expanded Uncertainty. The estimated uncertainty of measurement [M(u)], can be reported as

concentration ± $M(u)_{95\%}$ (k=2)

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Measurement of Uncertainty M(u)

- Uncertainty is expressed as the standard deviation of the mean of a set of data (Blank Spikes/Laboratory Control Samples).
- The reported Expanded Uncertainty of an analyte is specific to the laboratory method used and incorporates laboratory procedures; physical measurements, (volume, temperature and mass), environmental variation, reagent and standard purity, sample preparation procedures (if applicable), personnel and instrumental parameters.

Trichloroethene in Air M(u) is ± 22%

(95% Confidence Interval or k=2) for values > 10x RDL

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REPORTS and Field Duplicates

Laboratory duplicate should be within 25% RPD for values 5x higher than the RDL

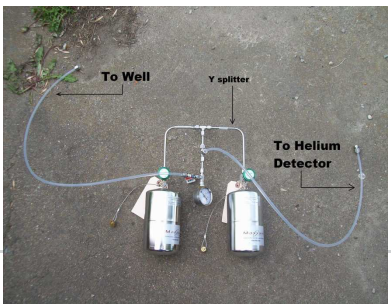
% RPD = square root $[(error1)^2 + (error2)^2]$

For example, TCE M(u) is 22% for the laboratory portion of the error in field duplicate determination:

% RPD = square root $[(22)^2 + (22)^2]$

% RPD = square root [968]

% RPD = 31



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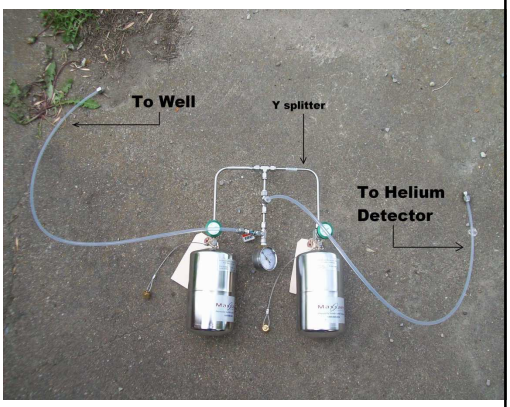
Other Consideration: Field Duplicates

The draft Ontario guidance does not specify a range of acceptance, but a 50% RPD would be reasonable in accordance with the California EPA 2015



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Petroleum Hydrocarbons – Ratio of F1 to n-Hexane

General literature states the n-hexane comprises about 1 to 3% of freshly refined gasoline – here are some recent results….

Soil Vapour Samples		
F1 (ug/m3)	**Hexane (ug/m3)**	**% Hexane**
6,830,000	566,000	8.3%
127,000	11,300	8.9%
6,720,000	573,000	8.5%
168,000	830	0.5%
96,800	171	0.2%
171,000	858	0.5%
28,200	3,430	12%
129,000	3,380	2.6%

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