AGAT Laboratories

The Effect of Sampling Strategy on VOC Determination in the Laboratory

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Today’s Presentation

- The Current situation in Canada
- The EPA 5035 Methodology
- The *Encore* Sampler
- US Legislation
- The Current Evidence
- AGAT’s Ongoing Research
- Future Questions

The Current Situation in Canada

- Regions (Atlantic / Quebec / Ontario / Prairie / BC) all approach sampling similarly
- Generally, 50ml - 100ml Glass Jars, no voids and no headspace
- Samples brought to temperature and delivered to the laboratory
- Hold times usually 14 days prior to stabilization (BC calls for 7 Days from time of sampling)
- With the Exception of Ontario, most jurisdictions use “High Level” VOC approach

EPA 5035 and 5035A Methodology

- High Level Approach involves extrusion of soil Core into Methanol.
- An Aliquot of MeOH is then introduced into a VOA Vial filled with DI Water
- Sample is analyzed as a “water”
- Appropriate for 0.2 mg/Kg +
- Low Level Approach (Ontario only) involves extrusion of Soil Core into Deionized Water (with or without Sodium Bisulfate preservative).
- Sample is then “Directly Purged” into GC/MS with Purge and Trap Auto-sampler
- Appropriate for 0.005 - 0.2 mg/Kg range

EPA 5035 and 5035A Methodology

- Most Canadian Laboratories reference 5035 directly or indirectly
- 5035 (1996) and 5035A (2002) have NEVER allowed for Traditional Approach using Low Level Analysis.
- 5035 (1996) and 5035A (2002), Allow for "Traditional Approach" for High Level Analysis, however 5035A is Qualified
- "*During the 1990s, research efforts demonstrated that the VOC Bulk Sampling procedure is inaccurate and produces VOC results that are biased low. The studies showed that bulk samples can lose 90% or more of their VOC content prior to analytical measurement*"
- Preferred Sampling Techniques are Described in EPA 5035A Appendix A, and ASTM D4547-09

Reasons for Poor Analyte Recovery using Traditional Approach

- Freshly Exposed Surfaces allow for Immediate Volatilization of VOCs due to the molecular diffusion coefficients in gas phase

Surfaces Exposed by:

- Exposure of solid surface near the time of collection
- Intermediate storage containers (core barrel lines, plastic bags etc.)
- Disaggregation of the solid during collection
- “Bottle Ring” contamination during collection
- Laboratory Subsampling

Reasons for Poor Analyte Recovery using Traditional Approach

- Biodegradation (principally of aromatic compounds)
- Reaction of Chemically Reactive Compounds during transport
- Pressure Changes during sample collection and transport

Field Stabilization and use of Hermetic Sampling Devices (i.e. Encore) Attempt to Mitigate these issues

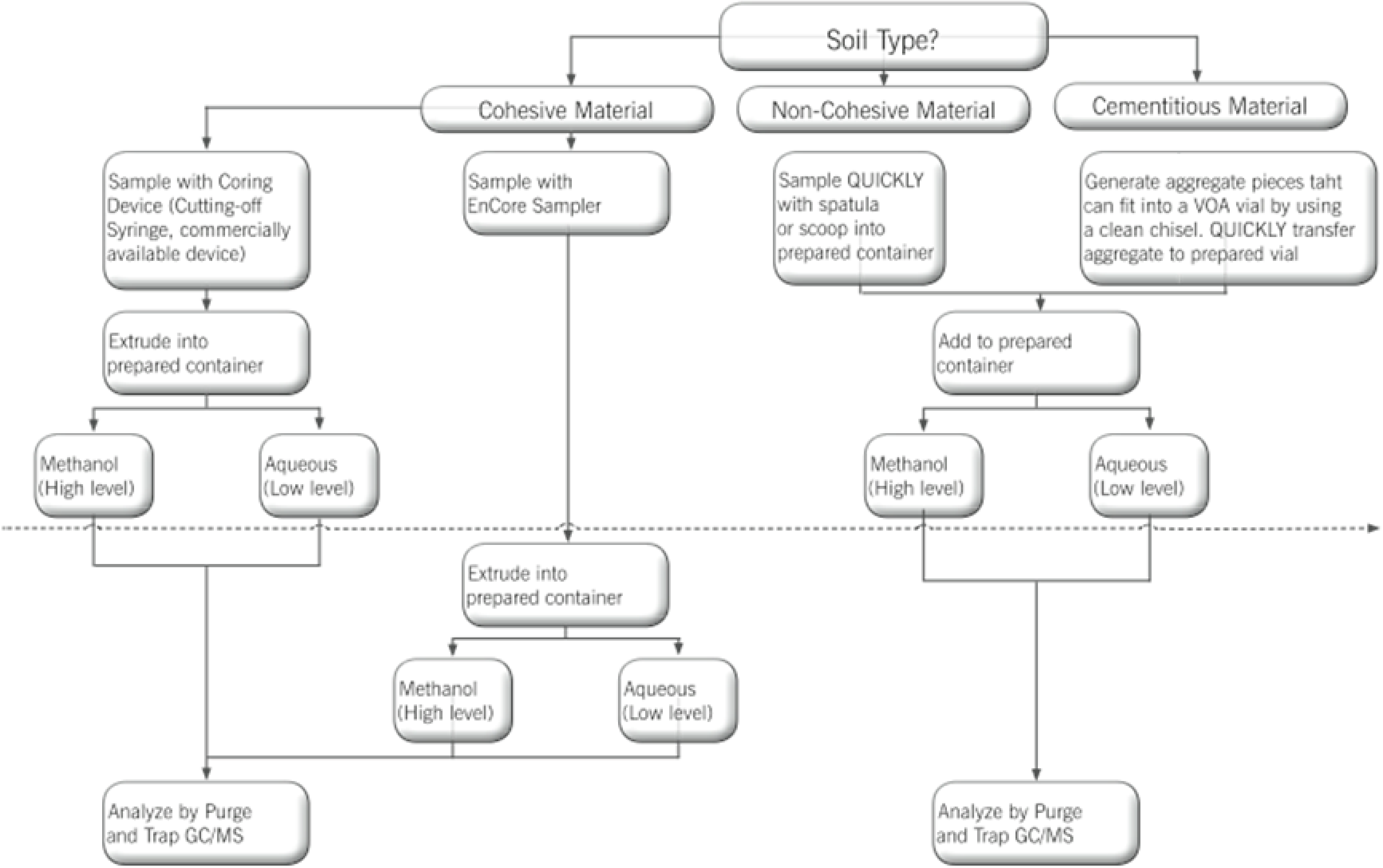
Field Stabilization / Preservation - Methanol and DI with Sodium Bisulfate

- Move the laboratory to the field
- Samples extruded directly into a pre-weighed, pre-charged VOA vial, charged either with MeOH (High Level) or DI and Sodium Bisulfate (Low Level)
- “High Level” would apply to most jurisdictions in Canada, therefore MeOH Field Stabilization.
- In addition, the use of the EnCORE Sampler (or Equivalent) is allowed.

Field Stabilization / Preservation - EnCore Sampler

- Hermetically Seals the sample until laboratory extrusion into MeOH
- Limits exposure of surface to air and eliminates any intermediate storage containers
- Easier to use in field than MeOH, but short hold time is the tradeoff
- Device has been proven equivalent to MeOH Field Stabilization

EPA 5035
Sampling Flow Chart



Soil Type?

Cohesive Material

Non-Cohesive Material

Cementitious Material

Sample with Coring Device (Cutting-off Syringe, commercially available device)

Sample with EnCore Sampler

Sample QUICKLY with spatula or scoop into prepared container

Generate aggregate pieces taht can fit into a VOA vial by using a clean chisel. QUICKLY transfer aggregate to prepared vial

Extrude into prepared container

Add to prepared container

Methanol (High level)

Aqueous (Low level)

Methanol (High level)

Aqueous (Low level)

Extrude into prepared container

Methanol (High level)

Aqueous (Low level)

Analyze by Purge and Trap GC/MS

Analyze by Purge and Trap GC/MS

US and Canadian Legislation

- When the new approach was mandated in different States, a significant jump in VOC determinations resulted. In some cases 10-100X or more.
- In addition, it was determined 14 day hold times are not appropriate for VOCs without Freezing or other stabilization techniques.
- 22 States are compelled to follow MeOH or EnCore techniques, with another 10 states where it is “encouraged”
- Current Discussions with the Ontario Ministry of the Environment surrounding amendments to Brownfield legislations
- No other current movement in other Canadian jurisdictions

US Usage of MeOH or EnCore Field Stabilization Techniques

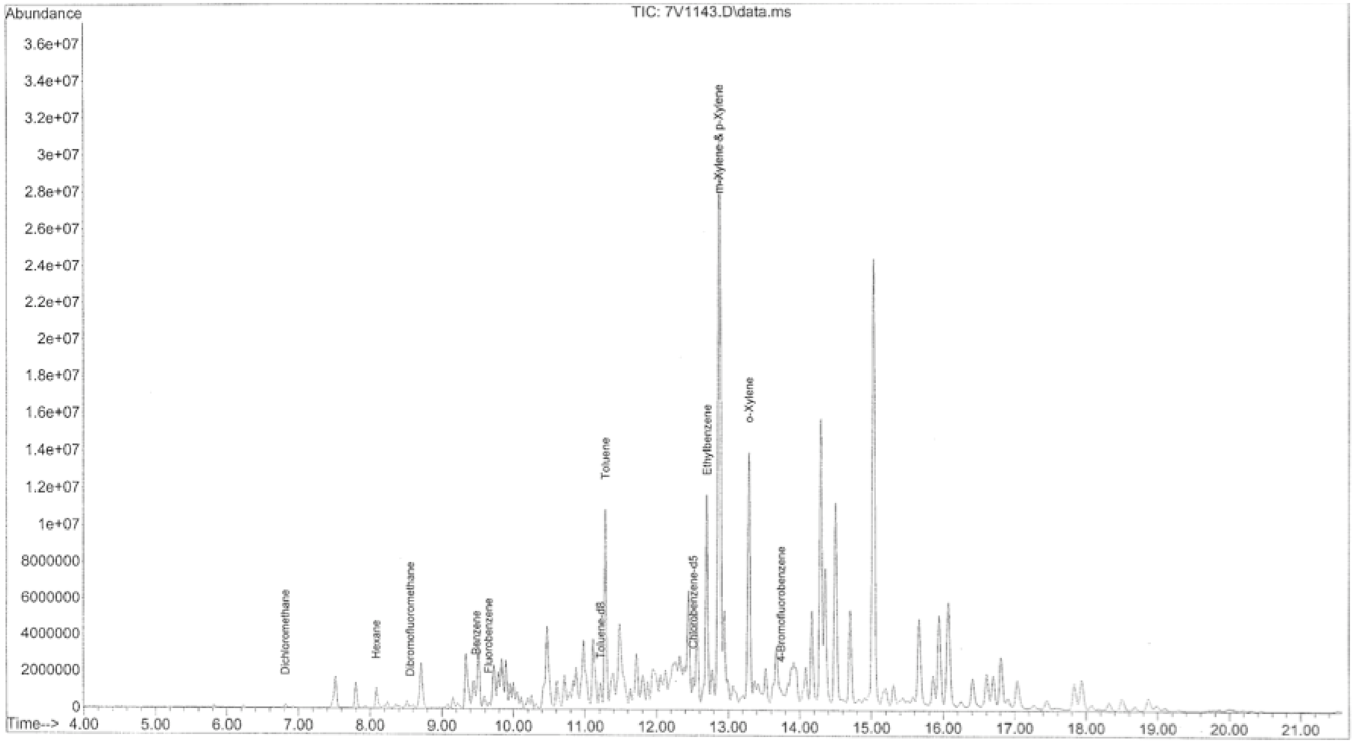
The AGAT Study

- Study was based in Ontario (for now) where potential legislative change has peaked interest
- 15 participating client firms
- Over 100 distinct samples with Appropriate duplicates
- Study is confined to MeOH field duplicates taken vs. traditional approaches (for now)
- Generally, “Clean” samples remained clean (with some exceptions)
- Samples with “Hits” were seen to have distinct bias, particularly with light ends, between sampling approaches

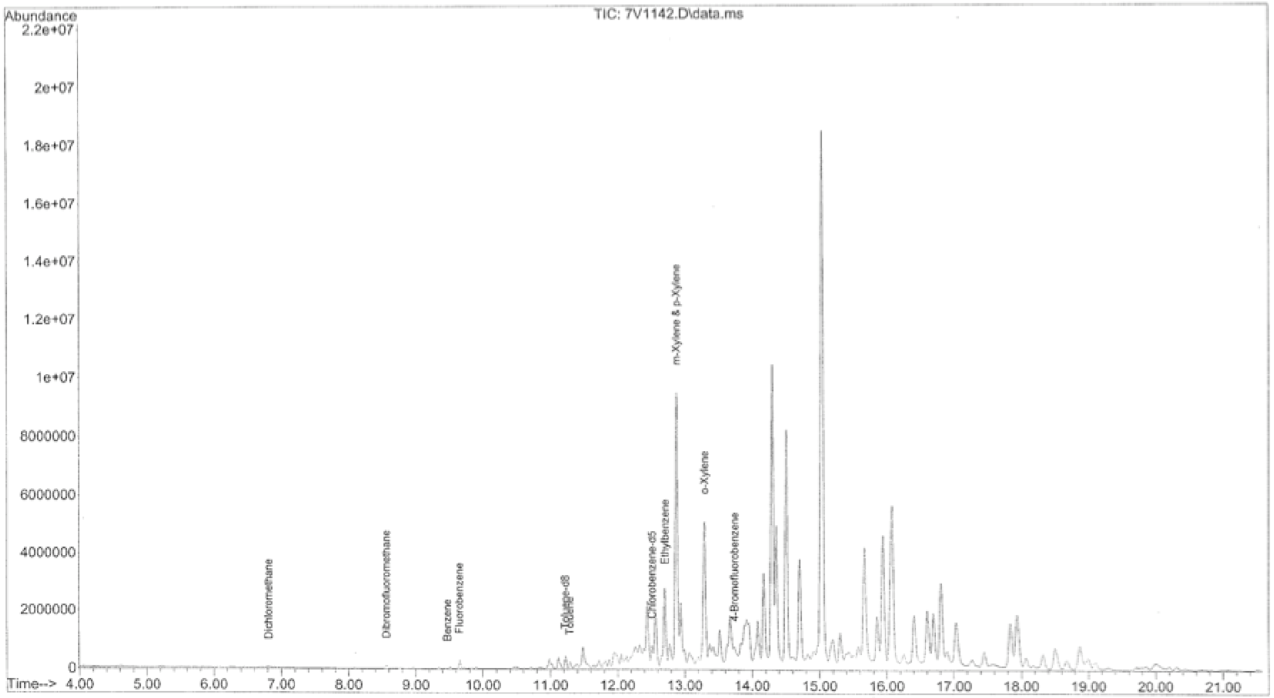
AGAT Typical Data

Compound	**Traditional Approach**		**Field**	
	Sample 1	**Sample 2**	**Sample 1**	**Sample 2**
Benzene	0.04 mg/Kg	<0.02 mg/Kg	2.78 mg/Kg	0.13 mg/Kg
Toluene	0.48 mg/Kg	0.84 mg/Kg	31.2 mg/Kg	9.6 mg/Kg
Ethylbenzene	6.83 mg/Kg	1.09 mg/Kg	31.1 mg/Kg	10.5 mg/Kg
m & p Xylenes	30.1 mg/Kg	7.67 mg/Kg	97.5 mg/Kg	51.3 mg/Kg
o-Xylene	15.6 mg/Kg	3.32 mg/Kg	44.2 mg/Kg	18.3 mg/Kg

Total Ion Chromatograph for MeOH Stabilized Sample

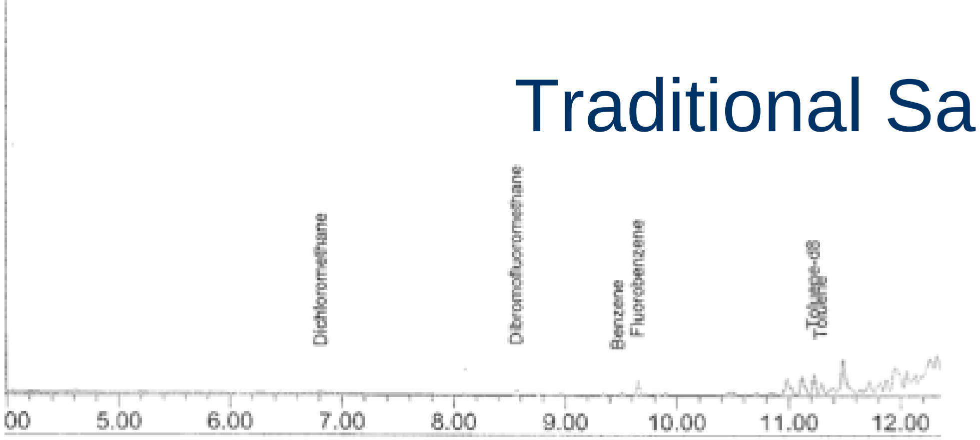


Total Ion Chromatograph for Traditional Sample

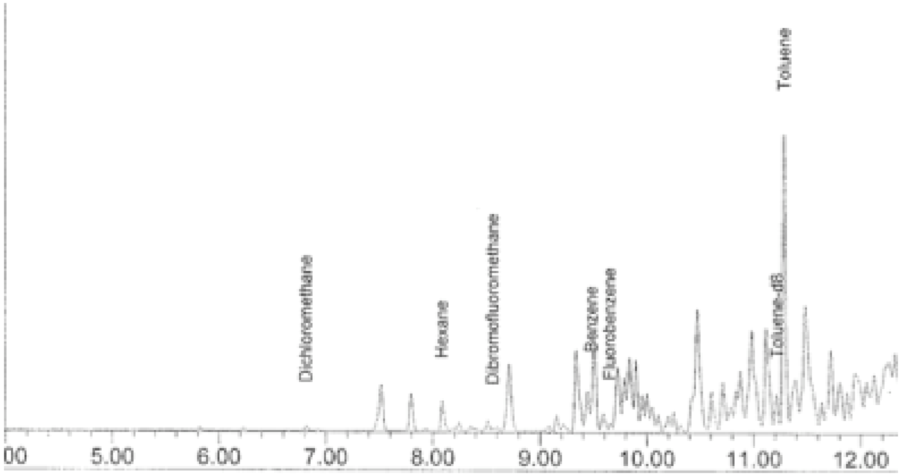


Light End Close up

Traditional Sample



MeOH Stabilized Sample



AGAT Findings

- A very Significant Jump in detected light End VOCs, often times making the difference between a “Clean” site and a contaminated Site (i.e. Benzene and Toluene)
- Light ends jumped in Concentration often by 100X or more
- Less impact seen in heavier VOCs, to be expected
- Typically a 2X to 10X increase in concentrations realized (i.e. Ethylbenzene and Xylenes)
- Results can impact decisions on contaminated sites based on government criteria

Further Study

- Impact of Hold Times vs. MeOH or EnCore Field Stabilization
- Impact of Freezing traditional samples vs. MeOH or EnCore Field Stabilization
- Differentiation of VOC losses based on molecular mass and categorization (i.e. aliphatic vs. aromatic)

Questions and Discussion