Thermal Desorption (TD) Tube Development for Soil Vapour Analysis

RemTech 2010

Overview

1. Soil Vapour Regulatory Environment
   - BC Perspective
2. Our approach
   - R&D
     - Tubing Study
     - TD Tube Development
       - Existing Challenges
       - Perkin Elmer SVI TD Tube
     - Other Things We Learned

Introduction

Personal:

- 1990 - BSc Biochemistry
- 1991-2000 - Chemist
- 2000-2006 – Lab Manager
- **2001-2006 CALA - Lead Auditor**
- 2004 CALA - Board Member
- **2002-Current - BCELTAC Co-Chair**
- 2006 – Current – Lab Owner/President
- 2008 Professional Chemist (ACPBC, PChem) 2008

Soil Vapour Regulatory Environment

- **Why is soil vapour important?**
  - Protection of human health from subsurface VOCs
  - Primary exposure pathway for certain sites

- **Jurisdictions with Soil Vapour Regulations:**
  - 29 US States
  - British Columbia – CSR Schedule 11
    - Effective January 1, 2009
    - 118 regulated parameters
    - Stringent Regulatory Limits:
      - Trichloroethene (TCE) – 1.0 ug/m^3 (dry cleaning site)
      - Benzene – 1.5 ug/m^3 (gasoline site)
  - Health Canada - pending

- **Soil Vapour Technology is new regulatory/testing segment.**
  - Adapted from existing testing segments
  - Areas for improvement exist
  - Technology is developing

Soil Vapour Regulatory Environment

Evolution of a new regulatory segment in BC:

- 2007 – regulation concept
- 2008 Technical development
  1. Definition of Soil Vapour VOC: Henry's Law $<10^{-5}$, VP>0.05 Torr @25C
  2. Reference methods: based on EPA TO15 (Canister) and TO17 (Sorbent Tube)
  3. Method fitness: detection ability vs. regulatory needs
  4. Real life samples: moisture, broad analyte ranges, high concentrations, ambient concentrations
  5. Laboratory Processes: commissioning, development, accreditation, client processes
- Late 2008 - feedback to BCMOE
  - Reg. limit adjustments
  - BCMOE Analytical Methods Completed and Approved
- Jan 2009 – Schedule 11 Regulation
- Jan-Dec 2009 – growing pains → successful new regulatory/market segment

Soil Vapour - Our Approach

Technical Focus:

1. **BCMOE Methods 2008/2009**
   - Authored TD & VHv Methods
2. **R&D and Partnerships**
   1. VOC in Tubing Assessment – with Science Advisory Board of BC
   2. SVI TD Tube – with Perkin Elmer
   3. Detection Ability Enhancements

VOC in Tubing Study

Why does my “clean” site have soil vapour?

Approach: Comprehensive assessment of common tubing materials used to collect soil vapour.

1. Sample tubing materials:

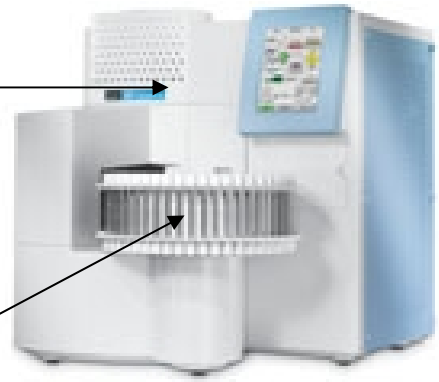
- **a) VOC/VH Detected:** PVC, Silicone, LDPE, Tygon, Nylon
- **b) VOC/VH Not Detected:** Nylaflow (Nylon) & Teflon
- **c) Softer materials yielded more VOCs**.

2. Schedule 40 PVC Pipe:

- a) PVC – acetaldehyde
- b) PVC (abraded) – several VOC’s detected including vinyl chloride

Report Available at: **www.caro.ca/soilvapour.html**

Soil Vapour Testing

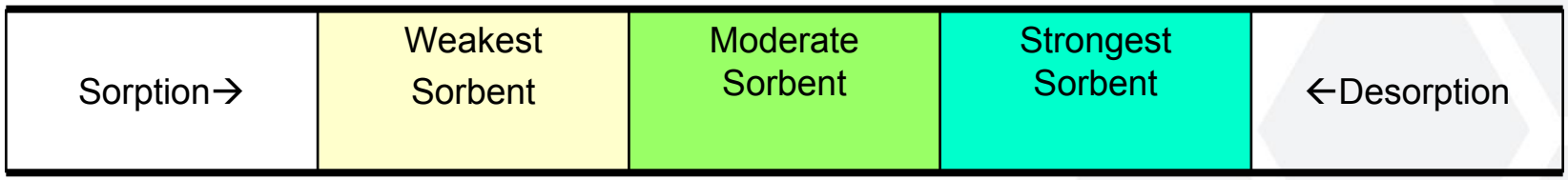


TD technology from the lab to the field.

TD Tube Development

Challenges with Existing Commercial TD Tubes:

1. **Safe Sampling Volumes (SSV):**
   - Low regulatory detection limits require high volumes
   - Breakthrough for LMW compounds
2. **Broad contaminant profiles:**
   - Contaminant Diversity/Ranges – nC3-nC18, gasoline, solvents, diesel, etc.
   - Contaminant Concentrations - ≥ 7 orders of magnitude
   - Irreversible binding of HMW compounds on moderate-strongest sorbents
     - Affects tube integrity, causes carryover/bleed
3. **Moisture:**
   - Soil vapour is wet, negatively affects:
     - Sorption performance, particularly on the strongest sorbent
     - Instrumental analysis



TD Tube Development

Objective: A TD tube designed specifically for soil vapour sampling and analysis from a broad range of contaminated sites.

Development Approach:

1. More strong sorbent – to improve sorption for LMW compounds
2. More weak sorbent - to improve adsorption ***"and"*** desorption of HMW compounds
3. More hydrophobic sorbent materials – to mitigate water issues

Validation Approach:

1. Breakthrough assessment
2. Recovery/Robustness (Carry Over) Assessment
3. Water Management Assessment

Result:

- Partnership with Perkin Elmer
- Perkin Elmer SVI™ TD Tube

Breakthrough Assessment

Objective: TD tube with no detectable breakthrough for regulated compounds using sample volumes needed to conservatively achieve regulatory limits.

- **EPA TO-17 Definitions:**
  - **Break Through (BT):** when the amount of analyte in a back-up [in series] sorbent tube reaches [typically 5%] of the total amount collected by both sorbent tubes.
  - **Safe Sampling Volume (SSV):** 2/3 of Breakthrough Volume

- **Approach:**
  - Two tubes in series; 79 VOC gasses; various concentrations; multiple replicates; various volumes (10L; 5L;1L); ~70% RH air
  - Comparison with commercial available TD tubes: Air Toxics, Carbotrap 300, etc.

- **Results:**
  - Chloromethane BT @ 10L; SSV = 6.6L
  - No breakthrough at 5L
  - Regulatory sample volume = 1-2L with confidence (sub-ng)

- **Conclusion:**
  - Improvement over commercially available TD tubes;
  - e.g. Benzene BT occurred at 1L (A&WMA Sept 2007)

Analyte	%BT	
	10L	5L
Dichlorodifluoromethane	1.0	nd
Chloromethane	5.4	nd
Vinyl Chloride	nd	nd
Bromomethane	nd	nd
Chloroethane	nd	nd
Trichlorofluoromethane	nd	nd

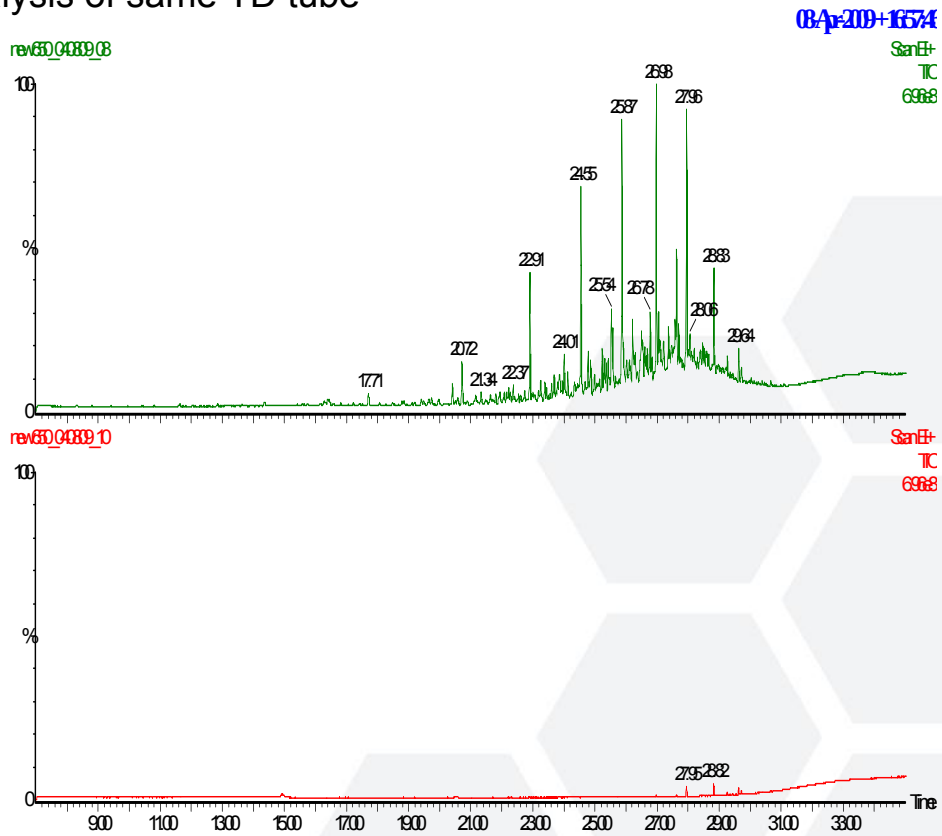
Recovery/Carry Over Assessment

Objective: to ensure that high analyte concentrations, (including HMW compounds) are desorbed after one test cycle (TD tube reusability).

- **Approach:**
  - Spike samples: Diesel: 100,000 ng; PAHs: 250ng mix; VOCs: 400ng mix
  - Conduct test cycle, then multiple re-analysis of same TD tube

- **Results:**
  - Analyte recovery 84-106%
  - VOCs & Diesel carryover = ND
  - Slight carryover of 4 heaviest PAHs (<0.05%)

- **Conclusion:**
  - Improvement over commercially available TD tubes;
  - Little-to-no irreversible binding of HMW compounds;
  - Observation: better duplicates, <15% RPD

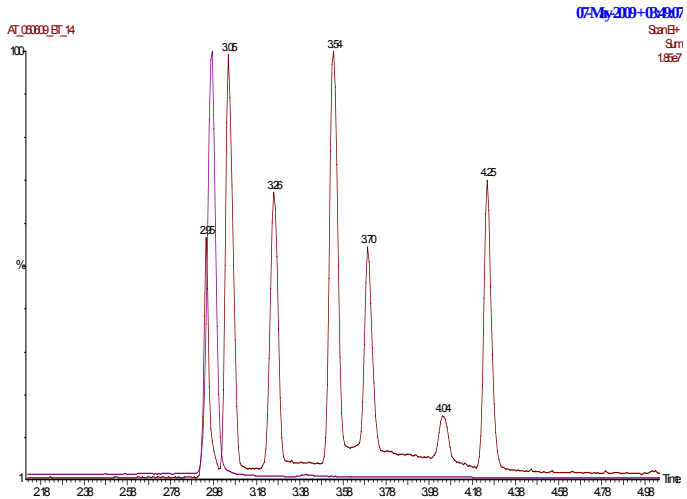


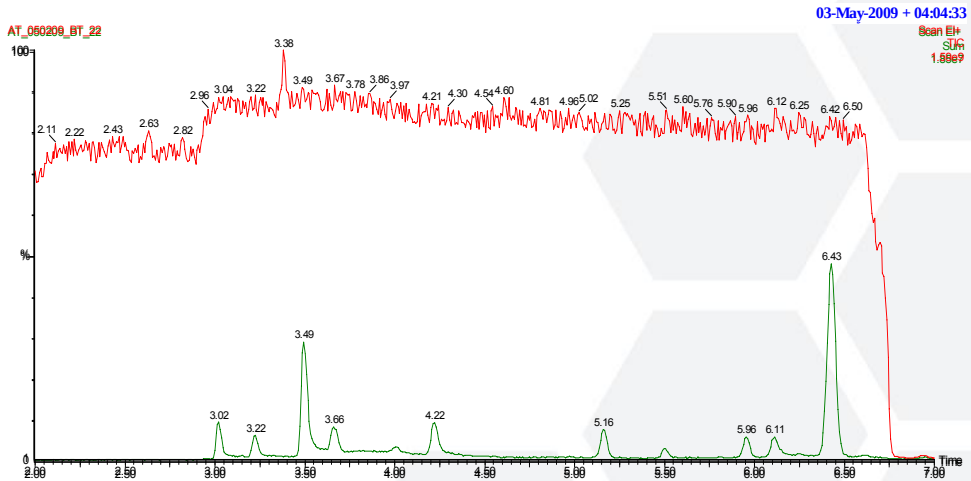
Water Management

Objective: to mitigate negative impacts of moisture on 1) TD tube sorption performance and 2) GC/MS instrumental analysis

- Drier Tubes – remove polar compounds – Do Not Use!

- Hybrid Approach: TD Tube Design / Water Management Practices
  1. Hydrophobic adsorbents
  2. Minimize sampling volumes while maintaining regulated detection limits
  3. Dry purging





Perkin Elmer SVI™ Summary

Perkin Elmer SVI™ TD Tube Benefits:

1. **High Safe Sampling Volumes (SSVs)**
   - SSVs greater than 5 L and up to 10L
   - Less risk of breakthrough
2. **Broad Performance Range**
   - Sorption/desorption from nC3 to nC18; high capacity
   - Protects TD tube integrity, better sorption performance, better duplicates
3. **Water Management Improvements**
   - Mitigates water's impact on sorption and instrumental analysis
   - Better data, better DLs

Publication mid-2011

Why does this matter to clients?

1. **Quality** - more defensible data
2. **Ease of Use** - broad applications in single device
3. **Cost** - relatively inexpensive capital and operational cost

Other Benefits

Numerous associated benefits of the development process.

- Challenge: extreme concentration samples; lost data due to overloads, and dilutions >> regulatory limits
- Solution: Lower DLs allow lower sample volumes. Benefits:
  1. Less “lost” data
  2. Less water loading improves sorption performance and GC/MS performance.
  3. Reduced Sampling Time: from 60 to 5 minutes (6→0.5L)

Conclusion

The new soil vapour regulation forced comprehensive understanding of science, regulatory requirements, client needs.

We were able make meaningful and practical improvements to the state of the art.

…. an opportunity to bring science back to the analytical lab industry

Thanks

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