# In the Air

A publication of Air Toxics LTD.

April 2006


## INSIDE THIS ISSUE



## COMING IN JULY

*New: Expanded TO-15 Capabilities: Detection of Trace VOCs in High-Level Matrices*

*SVOCs in Soil Gas*

# On the Cutting Edge...TO-17 Analysis using Diffusive Samplers

By Heidi Hayes

## Introduction to Diffusive Samplers

*Recent feasibility studies have been published in the literature[1,2] evaluating diffusive samplers for the measurement of trace levels of volatile organic compounds (VOCs) in indoor and ambient air. Traditional techniques for trace VOC collection and analysis include whole air sampling using Summa canisters (TO-15) and active sorbent sampling (TO-17).*

Diffusive samplers provide an appealing option to traditional techniques due to their ease of use and deployment in the field as well as potential cost savings. Both tube-type and a new badge style, the SKC-Ultra II, may be used for sample collection. The tube and badge can be packed with various sorbents to effectively collect the VOCs of concern. Each sampler has its advantages with regard to ease of use and sensitivity. While the tube-type style requires no preparation in the field and can be easily deployed, the SKC-Ultra badge requires the sampler to transfer a vial of sorbent to the badge housing prior to sampling. After the sampling is completed, the sampler then transfers the sorbent from the badge into the vial for shipment back to the laboratory.

However, the badge sampler has an advantage over the tube sampler with regards to VOC collection sensitivity. Because the badge style has a shorter diffusion path and greater cross-sectional area than a tube, the badge has higher adsorption rates, or uptake rates.[2] Higher uptake rates translate to shorter sampling exposure times. Despite the higher uptake rates of the badge, until recently the overall sensitivity of the sampler has been limited to ppm applications due to the reliance of solvent extraction for sample analysis. The SKC-Ultra II badge removes this limitation because of its compatibility with thermal desorption methods such as TO-17. As a result, the SKC-Ultra II badge may be used to measure ppbv and pptv levels of VOCs.

## Current Research

Initial studies by NYSDOH and NYSDEC evaluating the SKC Ultra II diffusive badge performance against Summa canisters were performed in April 2005 in conjunction with a vapor intrusion evaluation of 10 homes. Studies by OSHA evaluating the SKC Ultra II are also ongoing. The contaminants of concern were PCE and gasoline-derived compounds. Indoor and ambient air samples were taken using diffusive samplers and Summa canisters. To date, the results suggest that the badge style passive samplers analyzed using thermal desorption GC/MS can be used as an effective screening device for detecting low-level VOCs.

In addition to the badge studies, the EPA has published data evaluating the tube style samplers[1]. Utilizing Carbotrap X as the sorbent in a stainless steel tube, 27 VOCs met their established performance

*On the Cutting Edge, Cont. page 2* ►

*On the Cutting Edge, Cont. from page 1* ►

requirements. The effective concentration range was approximately 0.1 to 4.0 ppbv over a 24 hour sampling period.

## Applications—Vapor Intrusion Evaluations

Diffusive samplers may be an effective tool in vapor intrusion evaluations to supplement traditional TO-15 canisters. Currently, the NYSDOH Guidance describes the use of badges for the assessment of PCE in indoor air[3]. Diffusive samplers can supplement the indoor or ambient VOC data collected via canisters. For example, a recent client incorporated TO-17 diffusive badges into their vapor intrusion sampling plans to provide additional data points regarding TCE and PCE concentrations in indoor air. A set of canisters were used to collect TO-15 samples and additional badges were positioned at the site to gather additional data at a lower cost than a comparable number of TO-15 canisters.

Additionally, the TO-17 diffusive samplers may be used to more effectively characterize the site and more efficiently identify canister sampling locations or assist in distinguishing between background and vapor intrusion sources. A grid of samplers may be deployed to provide a more complete picture of the spatial variations in the sampling location. Alternatively, samplers may be deployed at several time intervals to assess the temporal variations of the concentrations at the location.

*Ultra II Badge and Sorbent Vial*
*Photos Courtesy of SKC®*

## Calculating Sample Concentration

When the laboratory analyzes a diffusive tube by thermal desorption GC/MS (TO-17), the total mass of each analyte on the tube is measured. To report a concentration in terms of mass of analyte per volume of air, the sample exposure duration and the uptake rate for the compound and sorbent is used. The uptake rates are determined experimentally and are typically provided by the manufacturer. The following is an example calculation for TCE using a SKC Ultra II badge:

$$\left(\frac{\text{Reporting Limit } 10\text{ ng}}{12.9\text{ mL / min Uptake Rate}}\right) \times \left(\frac{1}{24\text{ hr Sample Duration}}\right) \times \left(\frac{10^{-3}\text{ Mg}}{\text{ng}}\right) \times \left(\frac{10^{3}\text{ mL}}{\text{L}}\right) \times \left(\frac{1\text{ hr}}{60\text{ min}}\right) \times \left(\frac{1000\text{ L}}{\text{m}^{3}}\right) = 0.54\text{ ug/m}^{3}$$

This means that a 24-hour sampling period results in a TCE reporting limit of 0.54 ug/m$^3$ or 0.10 ppbv. Even lower reporting limits can be achieved using TO-17 in the Selective Ion Monitoring (SIM) mode.

*Ultra II Badge*

## Air Toxics Support

Air Toxics Ltd. offers comprehensive solutions to your diffusive sampling needs. We provide the necessary samplers, sampling instructions and sampling information. In addition, your samples will be analyzed by Method TO-17 by our team of experienced scientists. Reporting limits of less than 1 ug/m$^3$ can be achieved for a 24 hour sampling period. In addition, results can be expedited to provide near real-time information regarding your site, helping you to make informed decisions quickly. Call your Air Toxics account manager for pricing and more information on how Air Toxics' TO-17 diffusive product may be applied on your next project.

[1]W. A. McClenny, K. D. Oliver, H. H. Jacumin Jr, E. H. Daughtrey Jr, and D. A. Whitaker, J. Environ. Monit., 2005. 7, 248-256.

[2]B. Strandberg, A. Sunesson, K. Olsson, J. Levin, G. Ljudngqvist, M. Sundgren, G. Sallsten, and L. Barregard, Atmos. Environ., 2005, 39, 4101-4110.

[3]NYSDOH CEH BEEI, Guidance for Evaluating Soil Vapor Intrusion in the State of New York, Public Comment Draft, February 2005.

*In the Air*

is published by

Air Toxics LTD.

180-B Blue Ravine Rd.
Folsom, CA 95630
Phone: 800-985-5955
www.airtoxics.com

**Executive Officers**

Linda Freeman, CEO

Brad Mosakowski, President
b.mosakowski@airtoxics.com
800-985-5955 ext. 1030

Heidi Hayes, Vice President/ Technical Director
h.hayes@airtoxics.com
800-985-5955 ext. 1022

**Sales Team**

Jennifer Miller, National Sales Representative
j.miller@airtoxics.com
800-985-5955 ext. 1008

Kate Branning, Eastern & Central Account Manager
k.branning@airtoxics.com
800-985-5955 ext. 1038

Lee Ann Heathcote, Western Account Manager
l.heathcote@airtoxics.com
800-985-5955 ext. 1004

*Air Toxics Ltd. invites our clientele to participate in our technical newsletters. For more information or to suggest a topic for an upcoming issue of "In the Air", please contact Jennifer Miller at 800-985-5955 or via email at j.miller@airtoxics.com*

# Online Data Access for Clients Provides Fast, Economical Information

By Brad Mosakowski

Another connection with our clients has been established: online access to your data. We are pleased to provide a service that offers our clients many advantages. You can be assured of a user-friendly and secure method of accessing your projects from anywhere, thereby saving you time and money.

A few of the available features:

- Download chain-of-custody (COC) documents
- Download final result reports
- Electronic data deliverables (EDD's) may be downloaded in the format specified for your particular project
- eCVP may be downloaded
- Final invoices may be downloaded
- Shipping Information including current and upcoming shipments
- Easily compare historical results by sample

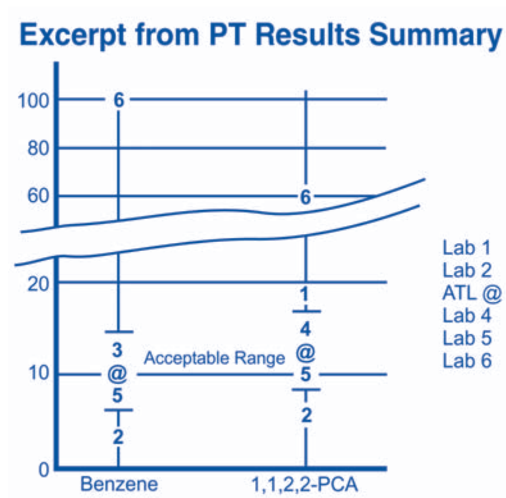
We are committed to the expansion of our online capabilities and ensuring that the resources provided are useful to your job. Check in often as we add access to technical articles, training videos, media requests, and data trending.

Getting connected is simple: Contact your ATL customer service representative. Access is provided as part of our commitment to customer service. Call 1-800-985-5955

# Performance Testing Shows the "Air Toxics Difference"

By Heidi Hayes

So, do you think you are getting the same TO-15 result from every lab? Think again. Scott Specialty Gases has reported the first round of the TO-15 Cross Reference Service. Six laboratories voluntarily participated in this introductory program. The Air Toxics difference is clear: Air Toxics was one of only two laboratories to achieve a 100% score.




While soil and water analyses have established performance testing (PT) programs to validate lab performance, gas standards are just now being developed for NELAC laboratory accreditation. Scott Specialty Gases' Cross Reference Testing Program provides an independent test of TO-15 analytical capabilities and represents the leading edge of this effort. Scott Specialty Gases sent out their second round of PT samples in March 2006 and plans to continue the program on a quarterly or semi-annual basis. Air Toxics' continued participation in this Cross Reference Testing Program reflects our commitment to quality. For the complete Cross Reference report, please call your account manager or client service representative.

# Air Toxics Presents Paper at A&WMA Vapor Intrusion Conference

Air Toxics' vice president and technical director Heidi Hayes presented "*Impact of Sampling Media on Soil Gas Measurements*" during the January 2006 A&WMA Vapor Intrusion Conference in Philadelphia, PA. The paper, written by Hayes, Diane J. Benton and Noor Khan, all of Air Toxics Ltd. in Folsom, CA, evaluates sampling media and methodologies in relationship to risk assessment. The paper asserts the importance of materials used for sample collection and storage as they relate directly to the laboratory results, with procedures playing a larger role in generating defensible results as reporting limits are lowered by regulatory agencies. An **evaluation of tubing** and an **evaluation of Tedlar® bags** used in soil gas sampling highlights potential VOC background contribution and recovery issues. **Leak test considerations** are also outlined.

An excerpt from the paper follows. To view the full text of the paper, including all tables and references, go to www.airtoxics.com and select "*Impact of Sampling Media on Soil Gas Measurements*" under the "Papers" heading on the Home page.

**Introduction**

*From "Impact of Sampling Media on Soil Gas Measurements"*
*Heidi C. Hayes, Diane J. Benton, Noor Khan*

Soil gas measurements have become one of the primary tools in assessing vapor intrusion pathways. The analytical results from soil gas samples at a site often determine whether a potential indoor inhalation risk is present. Site-specific models such as the Johnson-Ettinger Model can be used to predict indoor air concentrations. Alternatively, generic attenuation factors may be applied to estimate indoor air concentrations from soil vapor concentrations. Risk-based screening levels for soil gas contaminants have been published by the EPA and by various state agencies to assess the potential inhalation risk from subsurface contamination. For several of the carcinogenic compounds of concern, screening levels may be less than 1 ppbv. For example, in the EPA's *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway*, trichloroethene has a generic screening level of 0.041 ppbv for shallow soil gas at the $10^{-6}$ risk level[1]. The low reporting limits often dictated by the overseeing agency, and the level of defensibility needed to support health risk assessments require a careful evaluation of the collection and analytical procedures used for soil gas measurements.

Oftentimes, achieving a risk-based screening level for a contaminant in soil gas is considered to be a laboratory concern with the challenge primarily residing in the analytical sensitivity of the instrumentation. However, the results generated by the laboratory are also a function of sample collection and storage. As the required reporting limits are pushed lower and lower by the regulatory agencies, the sampling procedures play a larger role in generating defensible results. The materials used for the sampling train, the media used for intermediate or final sample storage, and the leak check compound selected all need to be evaluated against the data quality goals of the project.

[1]OSWER *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance)*, U.S. Environmental Protection Agency: Washington D.C., November 2002; EPA530-D-02-004.

# *PITFALLS OF TO-12 CANISTER CERTIFICATION*

By Heidi Hayes

One of the most important but often overlooked steps in generating a defensible TO-15 result is the canister certification step. EPA Compendium Method TO-15 describes several analytical approaches to certify a canister as clean. The most comprehensive approach uses GC/MS analysis to certify canisters to 0.2 ppbv or less for each target VOC. Alternatively, EPA Compendium Method TO-12 may be used to certify canisters to 10 ppbC (part per billion of carbon units) for total VOCs. Air Toxics utilizes the GC/MS certification approach for all individually certified and process certified canisters. However, due to the lower analytical cost and higher throughput, TO-12 certification is widely used in the industry. How reliable is this TO-12 "Certification of Cleanliness" for a TO-15 canister?

Method TO-12 provides a measurement of Total Non-Methane Organic Carbon (TNMOC) as detected by a Flame Ionization

*Pitfalls, Cont. page 6* ►

# *Water Management and Allowable Instrumentation Among Key Differences in TO-14A and TO-15*

By Heidi Hayes

Methods TO-14A and TO-15 are both included in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* published by the EPA in January 1999. In this, the second edition of the *Compendium*, method TO-14A replaced TO-14, and method TO-15 was an addition to the *Compendium*. The most significant update to TO-14 was the inclusion of specific quality control requirements for the initial and daily calibrations in the TO-14A method. While both TO-14A and TO-15 methods determine volatile organic compounds in ambient air collected in a Summa canister, several major differences exist between the two methods, including water management and allowable instrumentation.

Water management is an important component in the analysis of air. To achieve approximate reporting limits 0.50 ppbv or less for VOCs, a large volume of air sample (up to 1.0L) is typically concentrated prior to desorption onto the gas chromatograph (GC). Since moisture present in an air sample can adversely affect the detector performance and "freeze" in the inlet of the analytical system, water vapor needs to be removed from the sample. TO-14A and TO-15 have two distinct water management approaches. TO-14A uses a Nafion® dryer to selectively remove water vapor from the sample stream. As the sample stream passes through the Nafion® tubing, water and other light, polar compounds are removed. TO-15 utilizes a multisorbent trap to control moisture prior to introduction to the GC as well as a dry purge step to reduce water content while retaining the target VOCs.

**The TO-15 multisorbent/dry purge water management technique allows for the determination of a more comprehensive list of VOCs than described in TO-14A, extending the applicability to include polar compounds.** Whereas TO-14A specifies a target list of 40 VOCs (mainly chlorinated hydrocarbons and aromatic compounds)

TO-15 is applicable to a much more comprehensive list including compounds such as MTBE, MEK, acetone, and ethanol. It is worthwhile to note that TO-15 does not have a specific target list of compounds, but states that the method should be considered when a *subset* of the 97 VOCs in the Title III Clean Air Amendment (CAA) is needed. Several of the 97 VOCs are highly reactive making standard preparation and analysis problematic. These include compounds such as formaldehyde, diazomethane, triethylamine, and methyl isocyanate. Air Toxics Ltd. routinely reports over 60 VOCs and has the ability to add to this target list for project-specific requests. Because of the superior performance, we use the more advanced multisorbent/dry purge water management system for all TO-14A and TO-15 requests and take a variance to the TO-14A requirement.

The second important difference between TO-14A and TO-15 is that TO-14A allows for the use of non-specific detectors as well as specific detectors (such as Mass Spectrometers). **TO-15 only allows the use of Mass Spectrometer (MS) for the detection of VOCs.** Non-specific detectors such as the Flame Ionization Detector (FID), Electron Capture Detector (ECD), and Photoionization Detector (PID) can be used to quantify VOCs by TO-14A. Both TO-14A and TO-15 describe the use of GC/MS both in the full scan and SIM mode. For many applications, GC/MS provides the data user with more definitive results than a non-specific detector.

*Pitfalls, Cont. from page 4* ►

Detector (FID). The total peak area measured by the FID is referenced to propane and mathematically converted to units of carbon, expressed as ppbC (parts per billion carbon). The FID operates by burning compounds in a hydrogen-air flame. Ions, primarily CHO+ originating from a C-H radical, generate a detector response.

In general, the FID response is proportional to the number of carbons. This means that 1 ppbv of ethane ($C_2H_6$) is equivalent to 2 ppbv methane. Likewise, 1 ppbv of propane ($C_3H_8$) is equivalent to 3 ppbv methane, or 3 ppbC. Additionally, the FID response is greatest with hydrocarbons and generally decreases with increasing substitution of other elements. For example, methane ($CH_4$) has a greater FID response than dichloromethane ($CH_2Cl_2$), and dichloromethane has a greater response than chloroform ($CHCl_3$). ***Unfortunately, some of the most important compounds of concern at a site are chlorinated solvents containing only 1 or 2 carbon atoms, resulting in a poor response on the FID.***

Let's consider a scenario in which trichloroethene ($C_2HCl_3$) is the primary compound of concern. To minimize canister artifacts in your data set, you require the laboratory to individually certify all the canisters as clean. The laboratory performs 100% certification of the canisters by TO-12 applying a more stringent certification criterion of 3 ppbC. Samples are collected and analyzed by the laboratory for TO-15. When the results are reported, several samples have detections just above the reporting limit of 0.50 ppbv. Do you have confidence that the Trichloroethene (TCE) is real? Are your detected results defensible?

Before you answer, consider these facts. Because TCE has 2 carbons, the FID response for a "clean" canister containing 1 ppbv TCE, would be <2 ppbC. The canister could falsely pass with flying colors using a TO-12 certification even against the more rigorous 3 ppbC criterion. Alternatively, if the laboratory utilized a GC/MS certification, a peak of TCE would have been identified qualitatively and measured quantitatively as 1 ppbv. Clearly the canister fails against the 0.2 ppbv GC/MS criterion. The canister is re-cleaned and re-certified before it gets to you. Now, which certification approach do you want? When the results matter, use GC/MS certification for your TO-15 canisters and sampling trains.

## e-Seminars

Air Toxics Ltd. strives to provide on-going, valuable information to our clients with regard to the world of air sampling and analysis. One easy way is with web-based seminars reaching you...reaching your office mates...or reaching multiple offices within your organization.

Please choose from the following:

- Air Sampling and Analyses—The Basics
- Vapor Intrusion—Soil Gas, Sub-slab, Indoor Air
- Sampling Media and Vapor Intrusion
- Is Your Air Lab Qualified? Questions You Should Ask
- 8260B vs. TO-15—Getting the Defensible Data You Need
- TO-17—Cost-Effective Approach for VI Pathway Screening
- The Effects of Air Sampling Media on Your Project
- NCASI 99.02—Involved, but not Impossible
- Lumen Data Validation—Is This the Software Tool for You?

To sign up for an e-Seminar, please email Jennifer Miller at j.miller@airtoxics.com or call 800-985-5955 ext. 1008. Please also let us know of your specific topic(s) of interest.

## Available Online at www.airtoxics.com

Visit our web site for PDF versions of white papers and information on valuable solutions and services.

Currently available online:

- Leak Check
  Paper: Evaluating leaks in a soil gas sample train
- TO-15/8260B
  Paper: The precision and accuracy of 8260B and TO-15 are compared
- NCASI 99.02
  Stationary source emissions analysis for wood product facilities
- Lumen Data Services
  Software for independent data validation allows for 100% validation of your data set in mere seconds, giving your engineers the ability to make faster, more cost-effective decisions based on more accurate data validation