CASE STUDY

Environmental Monitoring

Customer Story

Breakthroughs in Technology Help CARO Analytical Services Capture Major Share of the Western Canadian Soil Vapor Analysis Marketplace

The scientific and regulatory communities have long been aware of the potential for migration of vapors from contaminated subsurface areas into buildings. But until recently, soil vapor intrusion has not been a major concern, with the exception of radon and major fuel leaks. Then in the late 1990s, two sites in Colorado contaminated with chlorinated hydrocarbons resulted in the toxic vapors seeping into a number of residential buildings. In 2002, the United States Environmental Protection Agency (EPA) issued draft guidance that provided technical and policy recommendations for determining if the vapor intrusion pathway posed a risk to human health at cleanup sites. Since then, 23 states have issued regulations for soil vapor sampling.

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Challenge

There are two EPA methods available for the determination of toxic volatile organic compounds (VOCs) in air, TO-15[1] and TO-17[2]. TO-15 employs summa canisters, which are large stainless steel vessels. Collection volumes are typically 6 liters. Approximately 500 mL of the vapor collected is withdrawn from the canister and concentrated on an adsorbent trap. The sample is then desorbed from the trap and focused onto a gas chromatographic (GC) analytical column to facilitate separation and analysis by mass spectrometry (MS).

There are several limitations of the TO-15 approach. This method only recovers up to naphthalene (roughly nC10), while several regulatory directives in North America require measurements up to at least nC13. In addition, many soil gas samples contain diesel, and canisters cannot recover the higher boiling components of diesel. The problem is that heavier substances adsorb onto the sides of the canister and condense. Other challenges of soil vapor analysis include high moisture content and the requirement for a greater number of analytes (in many cases C3 to C24) over a wide range of concentrations. US EPA TO-17 overcomes many of these challenges. TO-17 uses a sorbent tube instead of a summa canister to collect the sample. A sorbent tube contains adsorbent material specifically selected to retain (trap) the analytes (or range of analytes) of interest. A known volume of vapor is sampled through the tube, whereby the contents are then desorbed onto a secondary trap into the analytical column to be analyzed by GC/MS.

CARO Analytical Services

One of the most prestigious laboratories in North America specializing in soil vapor intrusion analysis is CARO Analytical Services, an environmental analytical laboratory headquartered in Western Canada. In operation for over 20 years, CARO has grown into a full-service laboratory with locations in Edmonton, Alberta, and Richmond and Kelowna, British Columbia. Besides being experts in contaminated site testing of soil vapor, they also specialize in providing microbiological analysis, together with general chemical analysis of drinking water, wastewater, potable water, vegetation, soils and sediments. In the field of environmental testing, CARO is recognized for its unmatched level of customer satisfaction, going to extraordinary lengths to make sure their clients are completely satisfied with the quality of data generated and level of service support.

The company has been on the cutting-edge of soil gas analysis for over 5 years, having co-authored a number of British Columbia soil vapor standard reference methods. CARO has also received ISO/IEC 17025 accreditation for soil vapor analysis, granted by the Canadian Association for Laboratory Accreditation (CALA). CALA is an organization known for its quality assurance programs in which members participate in rigorous inter-lab comparisons and on-site assessments based on international standards[3].

Over the years, CARO has been involved in a number of different studies aimed at optimizing methodologies for the successful analysis of different VOCs in soil gas samples. One of the most influential of those studies was an "Assessment of Volatile Organic Compounds from Tubing Used for Soil Vapor Sample Collection," which was a 23-page report compiled with the Science Advisory Board for Contaminated Sites (SABCS) of British Columbia in response to the Ministry of Environment's Contaminated Site Regulations[4]. One of the many conclusions from this detailed report was that the synthetic tubing used to sample, carry and transfer the vapor, yielded quite significant VOC concentrations, which in some cases was greater than 20% of the referenced regulatory standards. There is no question that the data generated from this 2009 study standardized the selection of sampling material and enhanced the credibility and accuracy of VOC measurements.

Solution

Even though CARO is considered one of the leading authorities on soil vapor analysis, they initially approached PerkinElmer for their expertise in thermal desorption and air monitoring. CARO quickly realized they made the correct choice of partner because PerkinElmer's support and expertise helped expedite a better understanding of thermal desorption and Method TO-17. During this partnership, CARO realized that the current tube technology was insufficient to recover the higher boiling components found in soil gas such as diesel. In addition, the British Columbia Ministry of Environment wanted to add the polynuclear aromatic hydrocarbons above naphthalene to the target analyte list for soil gas. Schedule 11 of the British Columbia Contaminated Site Regulations (which regulates up to 118 different contaminants), led CARO to look for innovative ways to analyze higher boiling point compounds. The challenge they faced was that there were no thermal desorption tubes available that could fully support the new regulations and recover diesel. It was clear they had to rethink the problem in order to come up with a solution that could handle the full range of components from the most volatile gases to through C24, in order to fully meet the demands of their clients. They again took advantage of their collaboration with PerkinElmer to help arrive at a solution. As Stephen Varisco, Technical Manager of CARO Analytical Services in Richmond put it,

"We felt that PerkinElmer was a natural fit for our company to collaborate with, as they had been the undisputed leaders in this field for almost 30 years. After our initial discussions, we felt very reassured that they wanted this partnership to work as much as us."

The main objective of this new collaboration was to design a new tube to meet the new regulations and the challenges of soil gas using adsorbent materials with the following capabilities:

- Extend the current analyte range beyond naphthalene
- Achieve high recovery of the high boiling components
- Ensure retention of the most volatile components during sampling
- Contain adsorbents that do not produce target artifacts
- Enable quick clean-up of the tubes with no carry-over for re-sampling purposes
- Optimize water management
- Increase sampling volumes to achieve regulatory detection limits while enabling the re-collection of the sample if re-injection is required

Outcome

The result of this collaboration was the new PerkinElmer Soil Vapor Intrusion (SVI) desorption tube, designed to meet the demands of the greater boiling point component range found in soil gases. The tubes contain multiple layers of different charcoal-based sorbents, arranged so that the sample is exposed to increasingly stronger sorbents as it penetrates the tube[5]. This design prevents the absorption of the heavier components onto the stronger sorbents that would otherwise not release them. Instead, the heavier components are adsorbed onto the weaker sorbents in the front of the tube, while the lighter components are adsorbed onto the stronger sorbents in the back end of the tube. The weaker sorbents protect the strong adsorbents from irreversible adsorption and leave the tube clean after one desorption cycle. The new tube, which is shown in Figure 1, handles the broadest possible analyte range from dichlorodifluoromethane (nC3) to phenanthrene (nC24).

The tubes were designed to fit onto the PerkinElmer TurboMatrix 650 ATD automatic thermal desorber with 50 tube autosampler for analysis. This instrument features a two-stage thermal desorption process that concentrates analytes before they are introduced into the PerkinElmer Clarus™ SQ8 GC-MS system[6]. TurboMatrix thermal desorbers provide high temperature desorption capability that allows the determination of analytes up to nC44 hydrocarbons. Automatic addition of gaseous internal standard mixtures onto the tube before sampling and analysis helps to ensure sample integrity, thus improving analytical quantification and accuracy. To minimize water vapor entering the system, which can quench target response in MS detection, the system offers optimized dry purging of both the tube and the trap, ensuring efficient water elimination even for high moisture samples like soil gas. Study data indicates that up to 30 liters of 90% relative humidity air can be sampled.

Real-World Capability

The breakthrough volume is a critical factor in the performance of an adsorbent. It is defined according to EPA TO-17 as the volume sampled when the amount of analyte collected in a backup sorbent tube reaches 5% of the total amount collected by both sorbent tubes. The results from a rigorous, real-world experiment of spiking a sample in triplicate with 0.3 µg of 83 VOC mixture, 0.25 ug of a suite of polynuclear aromatic hydrocarbons (PAHs) and 10 ug of diesel (total of 34.6 µg) using a flow rate of 100 mL/min of humidified nitrogen (85% relative humidity) for 100 minutes, detected only two components that showed a slight breakthrough - dichlorofluoromethane (1%) and choromethane (5.4%). Figure 2 illustrates this experiment in greater detail. In fact none of the other 81 VOCs, including some of the gaseous hydrocarbons, such as vinyl chloride, bromomethane, chloroethane, 1, 3-butadiene or trichlorofluoromethane, were detected on the second "unspiked" tube.

Figure 1. The new PerkinElmer Soil Vapor Extraction desorption tube using multiple adsorbents to accommodate VOCs with a wide boiling point range

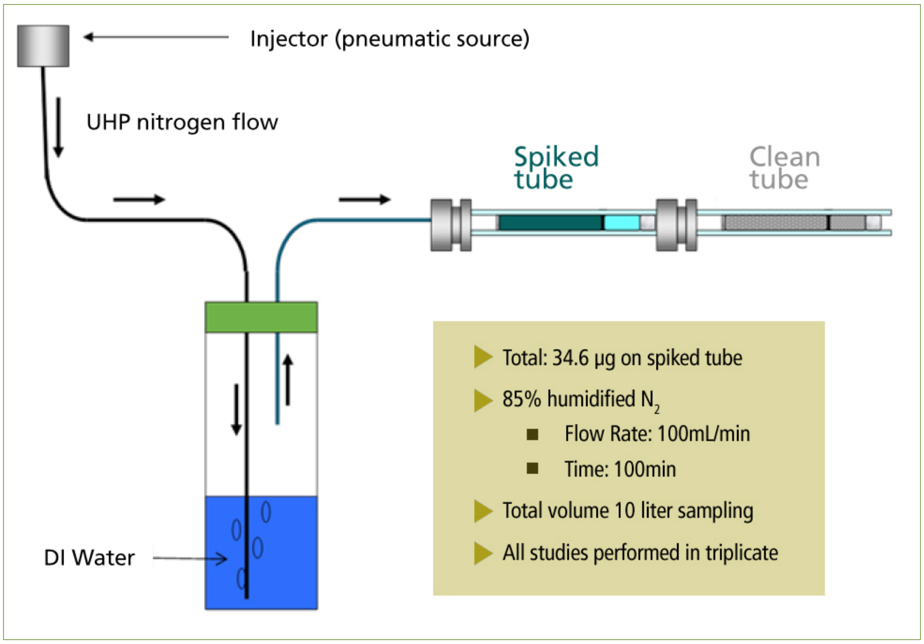

Figure 2. Schematic of a real-world breakthrough experiment using EPA TO-17 methodology

PAH Compound	% Recovery
1-Methyl Napthalene	99.7
Anthracene	99.8
Fluorene	99.4
Phenanthrene	98.8
Diesel	99.8

Table 1. % Recovery of the higher boiling point analytes

Another very important performance criterion is spike recovery, which involved analysis of the spiked tube described earlier, by analyzing a blank tube and then re-analyzing the spiked tube to see if all analytes were desorbed off the tube from the first desorption. Table 1 demonstrates the excellent recovery of the higher boiling point analytes, while Figure 3 displays the chromatograms for diesel comparing the first (top) and second (bottom) injections of the spiked tubes.

Lower Detection Capability

One of the major objectives of the collaboration was to develop procedures that significantly reduced soil gas detection limits in order to report much lower levels than were previously achievable. The major benefits of lowering thermal desorption detection capability include:

- Lower Sampling Time and Volume: As little as 10 minutes sample collection time is required (1 L@ 0.1 L/min) compared to 60 minutes with traditional tubes, saving considerable time and expense
- Minimized Tube Overload: By reducing sample volumes, VOC loading is reduced and the impact of high concentration samples is minimized
- Reduced Water Effects: Lower sample size also reduces moisture loading, which improves GC/MS chromatographic performance

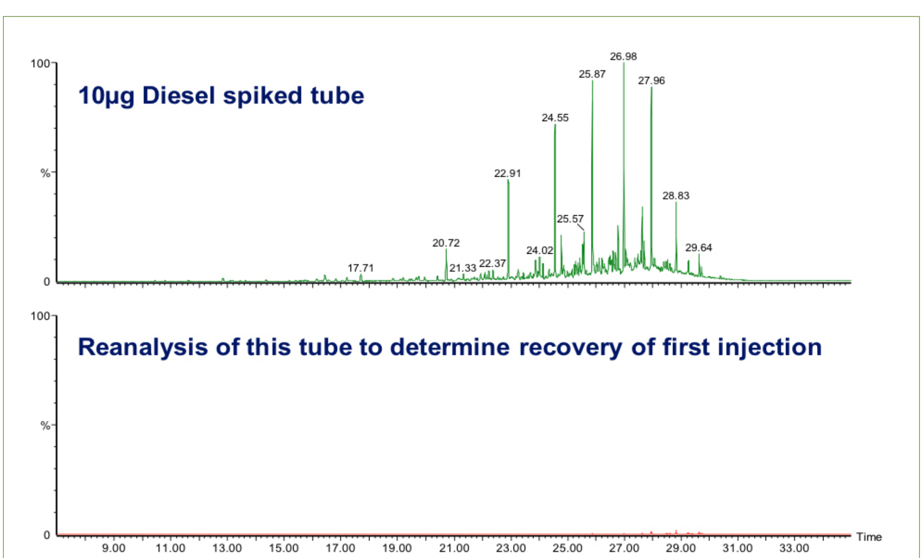

Figure 3. 10 ug of diesel from the spiked tube comparing the first injection (top) to the second injection (bottom).

There is no question this collaboration has been very successful in developing a new solution to resolving a limitation in detection capability. The result is a thermal desorption tube that is clearly better suited to real-world applications than any other design, which has enabled CARO to meet the demands of its customers. By bringing together the expertise of CARO and PerkinElmer, this challenge was met very quickly, as emphasized by Patrick Novak, Vice President of CARO Analytical Services, who was a key member of the partnership team.

"Our ability to test for the new soil vapor standards at much lower levels and with far better real-world performance has put us ahead of other laboratories in this very competitive arena. There is no question that PerkinElmer's expertise in thermal desorption technology has allowed us to respond to the needs of our clients, and as a result achieve a significant market share of the British Columbian soil vapor intrusion testing marketplace in very short space of time."

Further Reading

1. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-15- The Determination of Volatile Organic Compounds (VOCs) in Air Collected In Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS), Office of Research and Development U.S. EPA, 1999, http://www.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf

2. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes, Center for Environmental Research Information, Office of Research and Development U.S. EPA, 1999, http://www.epa.gov/ttnamti1/files/ambient/airtox/to-17r.pdf

3. Principles Behind the Requirements of ISO/IEC 17025: The Canadian Association for Laboratory Accreditation Inc, http://www.cala.ca/A121-17025_Principles.pdf

4. Assessment of Volatile Organic Compounds from Tubing Used for Soil Vapor Sample Collection: B. Mussato, S. Varisco, L. Tsurikova, Report prepared by CARO Analytical Services, http://www.caro.ca/Documents/CARO%20-%20VOCs%20in%20Tubing%20Assessment,%20Final,%20April%2014,%202009.pdf

5. Optimizing Sampling and Analytical Parameters for Soil Vapor Samples using Automated Thermal Desorption/Gas Chromatography (ATD/GC/MS): S. Varisco, L. Marotta, M. Snow, CARO Application Presentation, http://www.caro.ca/Documents/Thermal%20Desorption%20Optimization%20for%20Soil%20Vapour,%20AIHce2009,%20CARO-SV.pdf

6. The Analysis of Volatile Organic Compounds (VOCs) in Air with Thermal Desorption/Gas Chromatography/Mass Spectrometry (TD/GC/MS) using US EPA Method TO-17: L. Marotta, M. Snow, S. Varisco, PerkinElmer Inc. Application Note, Currently in draft form, (please contact PerkinElmer Inc. for a copy)

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