# **Canisters v. Sorbent Tubes: Vapor Intrusion Test Method Comparison**

Joseph E. Odencrantz (joe.odencrantz@beacon-usa.com: Beacon Environmental Services, Newport Beach, California, USA) Harry O`Neill (Beacon Environmental Services, Bel Air, Maryland, USA) James T. Kirkland (Professional Consulting Corporation, Gaithersburg, Maryland)

**ABSTRACT:** A carefully designed field vapor intrusion investigation consisted of three one-foot deep borings spaced one-foot apart at three locations within the perimeter of a former dry cleaner. One six-liter Summa canister (EPA Method TO-15) and two pump/packed tube assemblies (EPA Method TO-17) were used in each three-boring arrangement for a total of nine sampling locations. A <sup>1</sup>/<sub>4</sub>"-diameter length of Teflon<sup>®</sup> tubing was lowered into the hole until it was approximately one-inch from the bottom. The tubing had a screen frit (implanted prior to field work) in the end lowered down the hole to prevent the uptake of particle matter. The end of the tubing extending above ground had a stainless steel valve that had been swaged to it prior to sampling. Eight-hour tests were conducted at a gas flow rate of approximately 10 mL/min.

The results of the field comparisons compared exceptionally well (R-squared = 0.98 for PCE) on a relative concentration basis from location to location for PCE, TCE and 1,2-DCE (reported concentration range:  $3.7-22,200 \text{ ug/m}^3$ ). A comparison of the concentrations measured by each method revealed a linear relationship between molecular weight and the difference in concentration between the two methods. The TO-17 results were between 0.27 and 0.67 times lower than the TO-15 results on a consistent basis for PCE. The authors believe the major factors contributing to the differences are flow rates of sample collection, moisture effects and dilution procedures with the TO-15 method. Subsequent indoor air testing inside the structure allowed attenuation factor calculations for PCE that varied from 0.05 to 0.002 across the site.

## **INTRODUCTION**

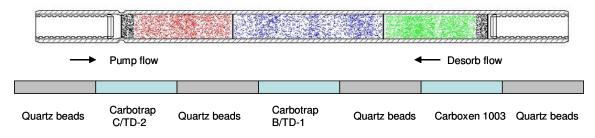
The importance of evaluating the vapor intrusion pathway recently has been emphasized by many states incorporating air phase regulations as the means to evaluate human health risk and to mange caseloads. The recent emphasis on the testing for vapor intrusion has invigorated the means to perform such testing. The results of a field comparison of the two most promising methods for testing the vapor phase for organic constituents are presented herein. The authors demonstrate that both methods compare well at multiple locations at a former dry cleaning facility. The results are promising with respect to options at sites.

A former dry cleaning operation existed at the site from 1964 to 2003. During this period of time the PCE usage varied from 900 gallons per year in 1975 to approximately 300 gallons per year in 1994. In 2006, five soil borings revealed extensive PCE in the shallow soils. The regulatory agency required an assessment of both vapor intrusion risk at the back entrance to the office building (the same area where the former dry cleaning machine was located) and measurements of the indoor air quality. The results of the soil gas investigation and initial indoor air measurements are the subject of this paper.

#### LABORATORY METHODS AND PROCEDURES

Samples collected on multisorbent tubes were analyzed by Beacon Environmental following EPA Method TO-17 procedures and samples collected in six-liter Summa canisters were analyzed by Analytical Laboratory Service, Inc. following EPA Method TO-15. Both methods are internal calibration methods using gas chromatography/ mass spectrometry instrumentation.

**Sorbent Tube Composition** The multisorbent tubes used by Beacon Environmental were prepared and are nearly identical to the Tube Style 3 referred to in EPA Method TO-17 (1999) and in accordance with ASTM D6196-03. The tubes were Silcosteel<sup>®</sup> coated stainless steel and the sorbent beds were packed from weakest to strongest adsorbents in the sample (*i.e.*, pump) flow direction. Figure 1 is a schematic diagram of the tubes used in this research.



All beds target mass is 125 mg with the exception of Carboxen 1003 which is 65 mg.

FIGURE 1. Schematic diagrams of EPA Method TO-17 tubes.

Quartz beads are the weakest and also act to separate the adsorbent beds, much like quartz or glass wool, but much more manageable and easier to measure on an analytical balance. Quartz does not react with any of the targeted compounds and it effectively seals the adsorbent beds from direct exposure to the atmosphere, or each other. Also, very heavy, low volatility compounds will get adsorbed to the surface of this glass bead protecting the stronger adsorbents packed behind it. Each quartz bead bed weighed 125 mg.

Carbotrap C/TD-2--Type J known to perform as specified in this practice is Carbotrap C manufactured by Supelco Inc., USA. An example of sorbent Type K known to perform as specified in this practice is Carbopack C manufactured by Supelco Inc., USA. weak graphitized carbon. This bed weighed 125 mg.

Carbotrap B/TD-1--An example of sorbent Type F known to perform as specified in this practice is Carbopack B, a medium strength graphitized carbon, manufactured by Supelco Inc., USA. This bed weighed 65 mg.

Carboxen 1003-- An example of sorbent Type M known to perform as specified in this practice is Carboxen 1000, a strong carbon molecular sieve, manufactured by Supelco Inc., USA. This bed weighed 65 mg.

#### SITE INFORMATION AND SAMPLING LOCATIONS

A former dry cleaning operation existed at the site from 1964 to 2003. During this period of time the PCE usage varied from 900 gallons per year in 1975 to approximately 300 gallons per year in 1994. In 2006, five soil borings were installed and found extensive PCE in the shallow soils. All of these borings were converted to groundwater monitoring wells and the

PCE concentration in the groundwater in the vicinity of the dry cleaning operation varied from 160 ug/L to 179 ug/L in October and November 2006, respectively. The depth to the groundwater table was approximately 20 feet below ground surface (bgs). The boring logs indicate the soils are clayey sand with interbedded clay layers approximately one-inch thick. The PCE concentration at one-foot bgs was 62 ug/kg at the rear entrance to the former dry-cleaning facility.



Sample Location SG-02



Sample Location SG-03

## FIGURE 2. Photographs of sampling locations SG-02 and SG-03.

Figure 2 provides photographs of the experimental layout at SG-02 and -03. Twelve inches separate each sampling hole, with the multisorbent tubes samples collected on the ends and the summa canister samples collected in the middle. Both SG-02 and SG-03 are located in the back area of the office space, in proximity to where the dry cleaning machine reportedly was located, and are separated by a distance of approximately 20 feet. SG-02 is west of SG-03 and SG-04 is located approximately 45 feet due north of SG-03. The office space is approximately 35 feet wide by 80 feet in length.

## SAMPLE COLLECTION AND METHODS

At each sampling location the field technician drilled three holes through the slab. Each hole was drilled using a hammer drill with a  $1-\frac{1}{2}$ "-diameter drill bit to a depth of 12 inches. A  $\frac{1}{4}$ "-diameter length of Teflon<sup>®</sup> tubing was lowered down the hole until it was approximately one-inch from the bottom of the hole. The tubing had a screen frit (implanted prior to field work) in the end that was lowered down the hole to prevent the uptake of particle matter. The end of the tubing extending above slab had a stainless steel valve that had been swaged to it prior to sampling.

After the tubing was lowered into the hole, dry, clean silica was slowly poured into the hole until reaching the lower level of the concrete slab. A layer of bentonite, approximately 1-inch thick, was then poured on top of the silica and moistened by adding distilled water. This process was repeated until the hydrated bentonite filled the annular space of the hole to grade. The hydrated bentonite slurry was then compacted around the tubing and finished once again to grade. Using a 60 mL syringe, the sampling hole and train was purged of three volumes of gas and the valve was left in the closed position.

After each of the nine temporary vapor ports had been developed, the sampling equipment was connected to the valves. For summa canister samples (Method TO-15), Teflon<sup>®</sup> tubing was connected using Swage<sup>®</sup> fittings from the valve to the flow controller on the canister. The valve on the flow controller was then opened to allow gas to enter the evacuated canister throughout the 8-hour period. For the multisorbent tube samples (Method TO-17), Teflon<sup>®</sup> tubing was connected with Swage<sup>®</sup> fittings from the valve to two tubes, which were then connected to a low-flow adapter. The adaptor allowed the primary tube to sample at a 10 mL/min flow rate and the second tube to sample at a flow rate of 1 mL/min. Tubing was used to connect the low-flow adaptor to the sampling pump, which was then switched to the on position. After 480 minutes the valves were closed on the canisters' flow controllers and the pumps were turned off. The testing occurred during normal business hours on December 5, 2006.

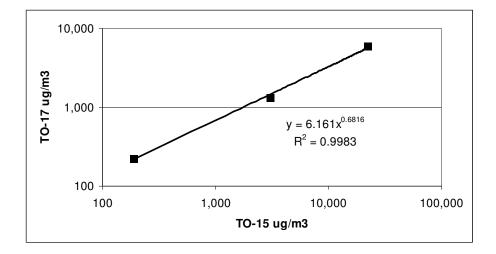
#### VAPOR INTRUSION TESTING RESULTS: COMPARISON OF EPA METHOD TO-15 AND TO-17 METHODS

The results of the side-by-side testing are presented and discussed in this section, including a log-log correlation between measured concentrations of the two methods. Table 1 is a summary of the four target compounds from the study with the average of two tubes reported for each location. The results show SG-03 is closest to a source area with SG-02 in relatively close proximity to the same source area. SG-04, which is approximately 45 feet north of SG-02, reveals significantly lower concentrations proportional to the distance from the source. The differences in measured values between the methods are examined next.

Table 1. Summary of Results from Side-Dy-Side Cans V. Tubes Study						
Sample Location	SG-02	SG-02	SG-03	SG-03	SG-04	SG-04
Sample/Tube Number		Mi52/Mi 32		Mi23/31		Mi28/47
Analytical Method	TO-15	TO-17	TO-15	TO-17	TO-15	TO-17
Compound / Units	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3	ug/m3
trans-1,2-Dichloroethene	ND (<2.0)	ND (<1.7)	ND (<39.6)	33.4	ND (<2.0)	ND (<1.7)
cis-1,2-Dichloroethene	12.8	8.5	307	207.2	ND (<2.0)	3.7
Trichloroethene	20.5	10.5	292	149	ND (<2.7)	ND (<1.7)
Tetrachloroethene	3,070	1,357	22,200	5,917	187	225.2

Table 1. Summary of Results from Side-By-Side Cans v. Tubes Study

Figure 3 is a plot of the PCE concentration at each of the three locations for both EPA Methods TO-15 and TO-17. As reflected in Table 1 above, the TO-15 (cans) is significantly larger in concentration at the two source area locations, SG-02 and -03. The correlation between the methods is extremely good with a linear correlation coefficient of 99.83%.



# FIGURE 3. Correlation of Cans v. Tubes for PCE for the three sample locations (SG-04, 02, and 03 with increasing concentration).

In an effort to examine the differences in concentration between the two methods, the ratio of TO-15 to TO-17 concentrations at SG-02 and SG-03 are plotted as a function of molecular weight of cis-1,2-DCE, TCE and PCE in Figure 4. There is a strong relationship between the reported concentrations at SG-02 and -03 with increasing molecular weight, which implies there is a partitioning effect that is potentially influencing one of the methods. The correlation coefficient for SG-03 is 0.99 and for SG-02 is 0.96 that implies that the relationship is stronger with increasing concentrations. In an attempt at understanding the transport phenomenon that might be a substantial factor contributing to these trends, the vapor pressure for each of the compounds was examined in relation to the ratio of TO-15 to TO-17 concentrations at SG-03 shown in Figure 5 (Montgomery and Welkom, 1990).

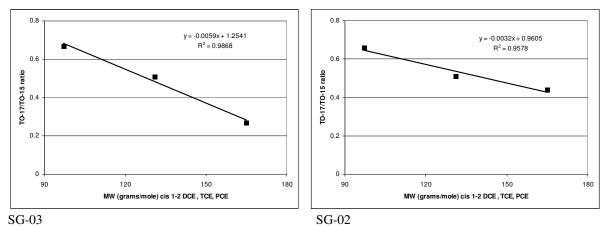


FIGURE 4. Molecular weight and ratio of tubes to cans correlation for SG-03 and SG-02.

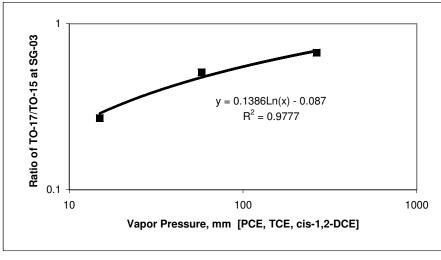


FIGURE 5. Vapor Pressure versus TO-17/TO-15 Ratio at SG-03.

There is a very clear relationship between the compound's vapor pressure and the ratio of TO-15 to TO-17 at SG-03 that implies there are partitioning effects influencing one of the methods. The correlation coefficient is 97.77%, which is strong relationship. The authors are familiar with potential moisture effects that have an impact of the partitioning within the TO-15 cans that could be a plausible explanation of the trends seen in Figures 3, 4 and 5. The laboratory analyzing the canisters noted slight problems with quality control and possible matrix interference issues on selected samples. In Europe, EPA Method TO-17 (sorbent tubes) is used exclusively due to issues related to canisters, EPA Method TO-15 (Woolfenden, 2007). A future body of study is necessary to verify all the relevant mechanisms on the methods used in high concentration settings.

Two indoor air samples were also collected using multisorbent tubes and pumps at a fourfoot height between sample location SG-02 and SG-03 during the same 8-hour collection period. The average PCE concentration in the breathing zone was 12.3 ug/m3. The indoor air testing inside the structure allowed attenuation factor calculations for PCE that varied from 0.05 to 0.002 using subslab data from SG-04 and SG-03, respectively.

#### CONCLUSIONS

The following summarize the research completed in the study and are in order of their appearance in the paper.

- The results of side-by-side comparisons of EPA Method TO-15 (cans) and EPA Method TO-17 (multisorbent tubes) at three locations revealed the same trends in vapor concentrations of chlorinated compounds from a former dry cleaning operation release.
- The ratio of reported concentrations for Method TO-17 to Method TO-15, plotted for PCE, TCE and cis-1,2-DCE at two locations, revealed a decreasing trend with increasing molecular weight.
- Upon further examination of the increasing trends in concentration with the TO-15 Method, a strong correlation was established at one of the sampling locations with the vapor pressure of three chlorinated compounds.

- EPA Method TO-17 (sorbent tubes) is used exclusively in Europe due to issues related to canisters and EPA Method TO-15.
- Indoor air samples that were collected during the same 8-hour sampling period revealed attenuation factors that ranged from 0.05 to 0.002 above SG-04 and SG-03, respectively.

# ACKNOWLEDGEMENTS

The authors wish to express their thanks to Mr. Ryan Schneider and Mr. Steven Thornley of Beacon Environmental Services, Inc. for assisting with the implementation of the field testing

## REFERENCES

U.S.E.P.A. (1999). Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition Compendium 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. Environmental Protection Agency, Cincinnati, OH 45268.

U.S.E.P.A. (1999). Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition Compendium Method TO-15, Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), Center for Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268.

ASTM Standard D6196-03. Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air. ASTM International, West Conshohocken, Pennsylvania.

Montgomery, J.H. and L.M. Welkom. 1990. Groundwater Chemicals Desk Reference. Lewis Publishers, Chelsea, Michigan, 640 pp.

Woolfenden. 2007. Personal communication with Ms. Liz Woolfenden of Markes International, Wales.