Laboratory Validation Report

Use of Compound Specific Stable Isotope Analysis to Distinguish Between Vapor Intrusion and Indoor Sources of VOCs

ESTCP Project ER-201025

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14. ABSTRACT

The objective of the present study is an empirical validation of selected adsorbents for preconcentration of TCE, PCE and benzene in air samples containing low concentrations of these VOCs. For validation of adsorbent tube performance, we sought to: 1) using reference data, select adsorbent-analyte pairings that would be likely to offer good quantitative recovery of the target VOCs; and 2) for those adsorbent-analyte pairings, evaluate sampling conditions that are representative of sampling indoor air and soil gas with respect to sample volume, humidity, mass of target VOC, mass of non-target VOCs, and holding time between sample collection and analysis; 3) investigate the recovery of target analytes mass and any associated isotope effects. The study results demonstrated fracrtionation-free performance for Carboxen 1016. These results allow precise isotope ratio analysis into vapor intrusion site assessment protocols and other applications where VOCs of interest are present at low ug/m3 concentrations.

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LIST OF ACRONYMS

1,1,-DCE	1,1-Dichloreoethene
2-D	Two Dimensional
AFCEE	Air Force Center for Engineering and the Environment
ANOVA	Analysis of Variance
CO_2	Carbon Dioxide
CSIA	Compound-Specific Isotope Analysis
DoD	U.S. Department of Defense
δ	Delta, an Isotope Ratio Measure (see Equation 1)
GC	Gas Chromatograph
H_2	Hydrogen
HPLC	High Performance Liquid Chromatography
IRMS	Isotope Ratio Mass Spectrometer
MEK	Methyl Ethyl Ketone
MTBE	Methyl Tertiary Butyl Ether
NYSDOH	New York State Department of Health
O_2	Oxygen
P&T	Purge and Trap
PCE	Tetrachloroethene
PI	Principal Investigator
QA/QC	Quality Assurance/Quality Control
SIM	Subscriber Identity Module
STD. DEV.	Standard Deviation
TCE	Trichloroethene
USEPA	U.S. Environmental Protection Agency
VI	Vapor Intrusion
VOCs	Volatile Organic Compounds
VPDB	Vienna Pee Dee Belemnite

1.0 INTRODUCTION

The purpose of this project is to validate the application of compound-specific stable isotope analysis (CSIA) as a tool to distinguish between vapor intrusion (VI) and indoor sources of volatile organic compounds (VOCs). The specific goals of the project are as follows:

- Task 1: Validate the use of active adsorbent samplers for the collection of vapor-phase samples for carbon, chlorine, and hydrogen CSIA of VOCs (i.e., tetrachloroethene (PCE), trichloroethene (TCE), and benzene) that commonly drive vapor intrusion investigations .
- Task 2: Develop a protocol for application of CSIA for vapor intrusion investigations:
    - Characterize the stable isotope signatures for common indoor VOCs.
    - Characterize the stable isotope signatures of subsurface sources of VOCs and the variability in these signatures in close proximity to potentially affected buildings.
    - Develop a protocol for application of CSIA to distinguish between vapor intrusion and indoor sources of VOCs.
- Task 3: Demonstrate CSIA for vapor intrusion investigations:
    - Demonstrate the performance of CSIA protocol through application at four buildings (from two different U.S. Department of Defense (DoD) facilities) potentially affected by vapor intrusion.

This report summarizes the performance for Task 1. The objective of the laboratory study was to validate the accuracy and precision in the determination of carbon and chlorine or hydrogen isotope ratios of three priority indoor air pollutants (PCE, TCE and benzene), commonly associated with vapor intrusions. Successful validation of the analytical technique for determining the isotope ratios in the VOCs is a prerequisite to future field applications in the later stages of this ESTCP project.

1.1 BACKGROUND

Indoor sources of VOCs are ubiquitous, resulting in detectable concentrations in indoor air, often at concentrations above regulatory screening levels. In residences, background concentrations of PCE, TCE, benzene, and several other VOCs commonly exceed regulatory screening levels. The background concentration of VOCs in indoor air can increase or decrease over time based on changes in the use of these VOCs in consumer products. At corrective action sites with potential vapor intrusion concerns, the presence of indoor VOC sources significantly complicates the exposure pathway investigation. Because of these indoor sources, the detection of a site-related VOC in a potentially affected building at a concentration above the regulatory screening level does not necessarily indicate a vapor intrusion impact. Instead, additional investigation is required to determine the sources of the detected VOCs. Unfortunately, the current methods for identification of indoor sources are expensive and have limited effectiveness.

Currently, the most common approaches for identification of indoor sources of VOCs during vapor intrusion investigations are: i) visual building surveys for known indoor sources; and ii) room-by-room measurements of VOC concentrations. Both of these approaches have limitations, described in detail in the original project proposal. Those traditional assessment techniques are

also relatively costly and time consuming. The novel approach to be tested in ER-1025 has the potential to greatly simplify the process of discrimination between subsurface and indoor sources of VOCs detected in indoor air samples and thus reduce the cost and duration of the building investigation program required at locations potentially impacted by vapor intrusion hazard.

The proposed approach involves determination of stable isotope ratios of the target VOCs present in the air ($^{13}C/^{12}C$, $^{37}Cl/^{35}Cl$ for PCE and TCE; $^{13}C/^{12}C$ and $^{2}H/^{1}H$ in the case of benzene) and use those ratios to differentiate between VOCs sourced from subsurface (the true vapor intrusion) and those sourced from miscellaneous household products (Figure 1). The basic hypothesis is that VOCs originating from subsurface sources commonly undergo biodegradation in groundwater and later in the unsaturated soil prior to entering indoor air. Individual molecules that contain the lighter isotopes are often preferentially biodegraded resulting in enrichment of the heavier isotope species in the undegraded residue (this enrichment process is known as isotope fractionation). The consequence of isotope fractionation is that isotope composition of VOCs originating from subsurface is often clearly different than that of pristine manufactured products in consumer products acting as indoor sources of the same VOCs. This difference allows the successful differentiation between VOCs from indoor sources and those from true vapor intrusion sources. In addition, the isotope composition of a given chemical compound manufactured at different facility and/or at different time tends to vary, reflecting the isotope ratios inherited from the manufacturing precursors and processes. Even in the absence of subsurface biodegradation, such differences in the original isotope compositions can permit discrimination between subsurface and indoor releases at certain sites.

The proposed methodology for determination of isotope ratios in VOCs present in air or in soil gas involves: 1) recovery/preconcentration of the target volatiles from soil gas or from indoor air, by sample collection according to standard methods such as TO-15 or TO-17; and 2) analysis of the collected samples for their isotope ratios, using compound-specific isotope analysis (CSIA) adopted from the protocols used for analysis of the same VOCs present in groundwater samples (USEPA, 2008).

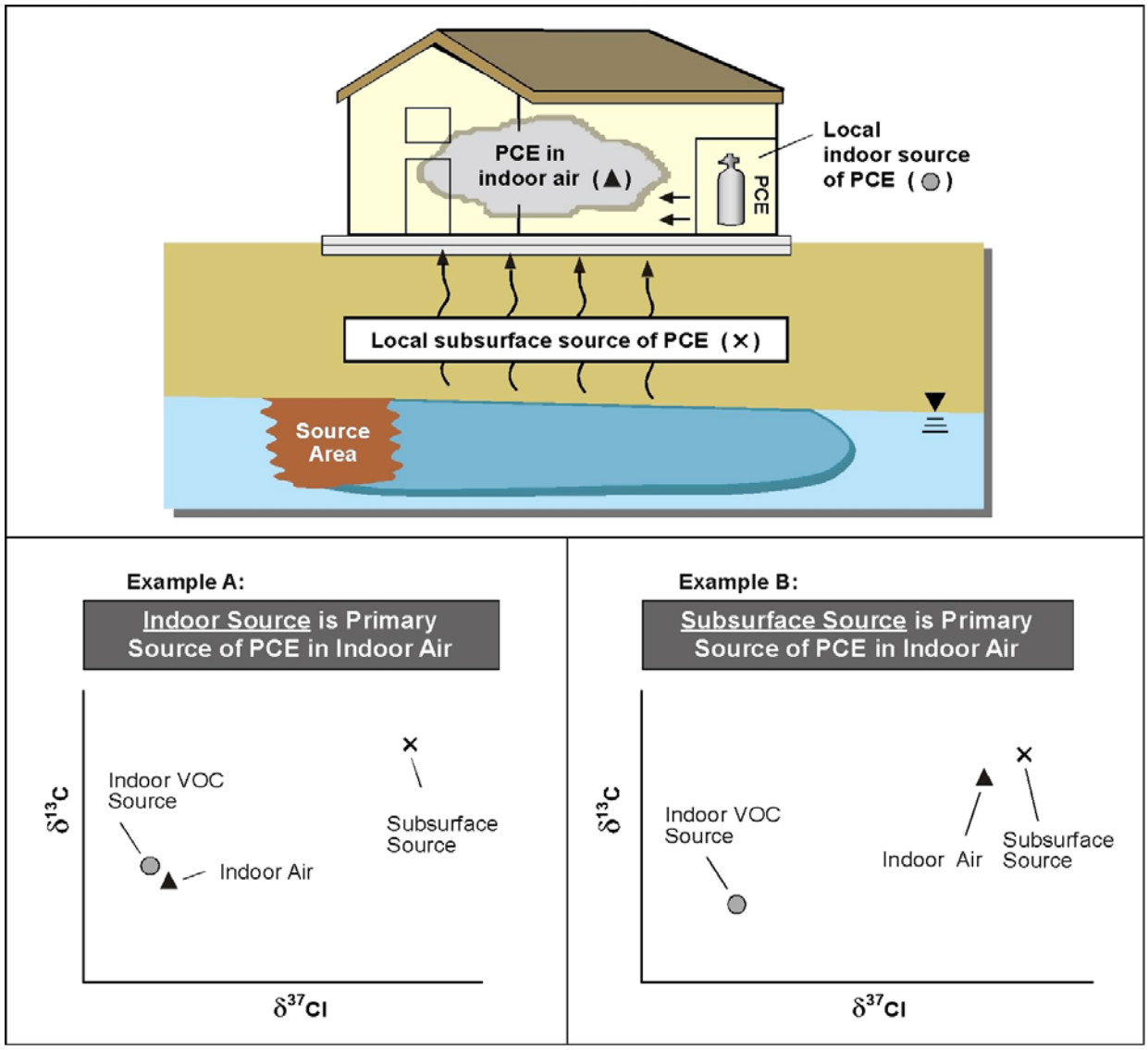


Figure 1. Conceptual diagram of stable isotope ratio-based discrimination between indoor and subsurface VOCs sources.

Interpretation of the origin of VOCs in indoor air based on CSIA results will be relatively straightforward in comparison to traditional methods. The isotope ratios will be directly compared between VOCs in indoor air, and those in soil gas and those measured for a variety of available consumer products. The isotope ratios, for example, of PCE in indoor air, can be similar to the subsurface sources and different from indoor sources and confirm the impact of vapor intrusion. On the other hand, isotope ratios dissimilar from subsurface source but similar to the values characteristic of PCE present in household products is a strong indication that the latter are responsible for the indoor air contamination (see Figure 1).

1.2 OBJECTIVE OF THE LABORATORY STUDY

The requirement for the laboratory study preceding the field application is necessitated by the novelty of the CSIA application to VOCs recovered from vapor phase. Specifically, one crucial element of the analytical procedure that was not adequately investigated in the past is the performance of thermal desorption adsorbent tubes in the preconcentration of VOCs from large volumes of air (>3L) for stable isotope analysis. This report describes the results of adsorbent performance validation under a realistic set of experimental conditions that reflect the challenge anticipated for real environmental samples.

The main challenge in the application of CSIA to VOCs vapor samples is the low concentration of the analytes. CSIA requires a specific minimum mass of analyte, defined by the mass spectrometer detector sensitivity and by the technique of sample introduction into the mass spectrometer source. Based on preliminary results (Section 4.2) the minimum mass of the target analytes is between several tens (carbon and chlorine CSIA) to several hundred (hydrogen CSIA) nanograms. To meet these requirements, for indoor air in particular, collection of as much as 100L of air may be required. The TO-15 method, involving collection of air samples in stainless cylinders (Summa) is not feasible if the required volume exceeds three to six liters. Larger air volumes can be processed on site by preconcentration of VOCs on adsorbent samplers, using the TO-17 sample collection method. However, the use of adsorbent tubes instead of Summa requires considerations of additional factors including: 1) risk of analyte breakthrough; 2) risk of incomplete desorption; 3) incomplete adsorption due to competitive adsorption fro nontarget VOCs or water vapor As illustrated in Figure 2, any of those effects reducing the analyte recovery could affect the resulting isotope ratio measurements. This study aimed at defining the magnitude of isotope fractionation caused by those interfering factors in high-volume sampling, in particular, we sought adsorbents where such fractionation is low (or preferably absent).

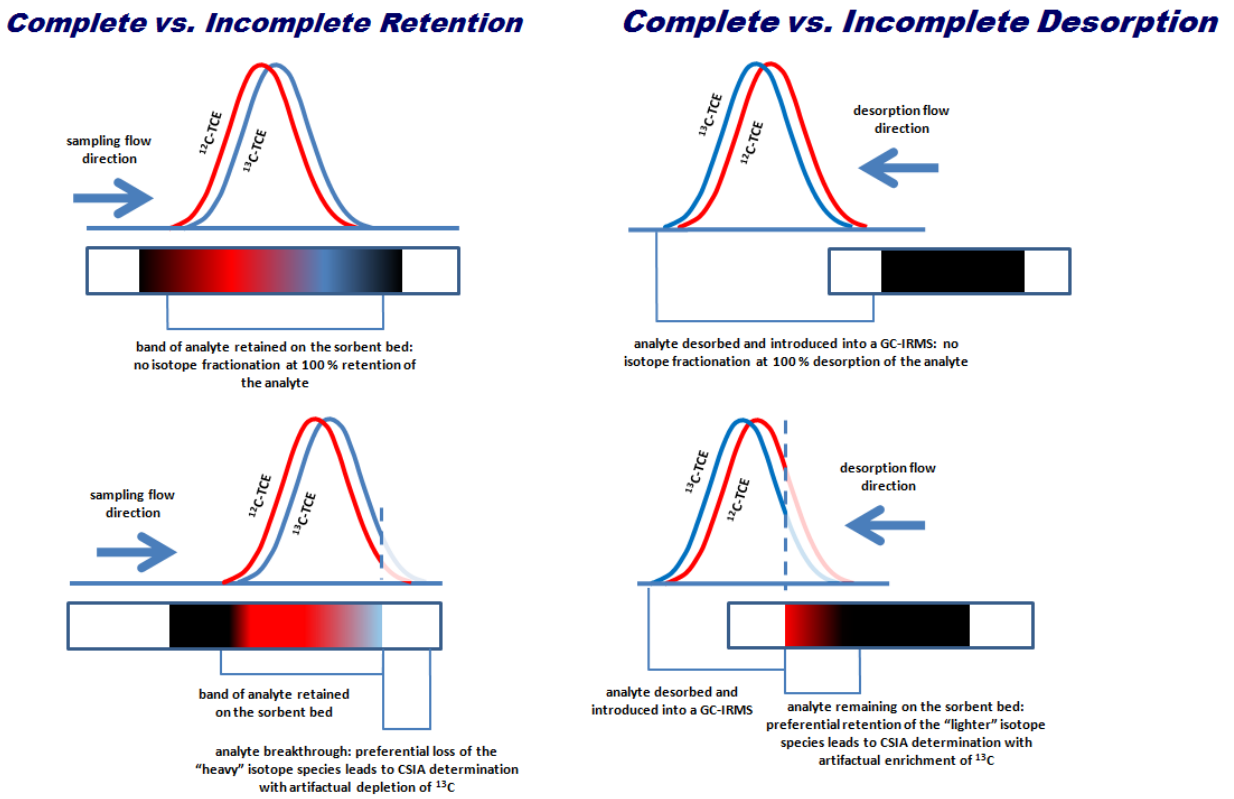


Figure 2. Conceptual model of isotope fractionation in active adsorbent sampling of VOCs from air.

1.3 REGULATORY DRIVERS

At a limited number of sites in the U.S., migration of volatile organic compounds (VOCs) from contaminated groundwater via vapor phase diffusion has impacted indoor air quality in overlying structures, posing a potentially significant, yet previously unrecognized human health concern for such properties. To address this concern, the USEPA has issued the "Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils," (USEPA 2002), providing conservative screening criteria for various VOCs in groundwater and soil gas. These conservative screening values eliminate few sites and, as a result, a majority of sites with VOCs in groundwater require field investigation of the vapor intrusion pathway. At recent conference presentations, Dr. Henry Schuver, the USEPA lead on vapor intrusion guidance, has emphasized the need for testing of indoor air at sites where VOC concentrations exceed conservative screening criteria. Based on these presentations, we expect that updated USEPA vapor intrusion guidance, due in 2012 will include increased requirements for testing of indoor air during vapor intrusion investigations. When implementing these new requirements, accurate methods to distinguish vapor intrusion from indoor sources of VOCs will be important to facilitate efficient investigation approaches and reduced investigation costs.

2.0 TECHNOLOGY

The technology discussed in this section is a variant of compound-specific isotope analysis (CSIA) that permits analysis of stable isotope ratios in individual chemical compounds such as benzene, TCE or PCE recovered from air or soil gas. The aim for the method development and optimization is to facilitate analysis of standard samples (Summa canisters and/or thermal desorption tubes) that can be collected by field technicians following the standardized protocols of TO-15 and TO-17. The method will be capable of providing isotope data to be used as the main line of evidence in future field applications to investigate origins and fate of the target VOCs present at contaminated sites.

2.1 TECHNOLOGY DESCRIPTION

2.1.1 Overview of isotope analysis

Many elements, such as carbon, occur as different isotope species, differing in their number of neutrons present in the nucleus. For example, ^{12}C, with 6 neutrons, is the most abundant form of carbon, but ^{13}C, with 7 neutrons, makes up a small fraction of the carbon in the environment (~1%). Isotopic ratios (e.g., the ratio of $^{13}C/^{12}C$) of a specific compound (e.g., TCE) can vary as a result of differences in their source material or compound synthesis or due to transformation in the environment (USEPA, 2008). Various processes can change the isotope ratios of a compound (so-called isotope fractionation). Molecular bonds containing the lighter isotopes are broken at slightly faster rates than those containing the heavier isotopes. As a result, the isotopic ratio for a compound can change over time as the compound is degraded. The parent compound becomes relatively more enriched in heavy isotopes, while transformation products are relatively depleted. Such type of fractionation occurs during biodegradation. While physical processes such as evaporation and sorption can also cause fractionation at contaminated sites, these processes are often too subtle to have a measurable effect on isotope ratios. Differences in the isotopic ratio measured in organic contaminants present in environmental samples can be used to i) distinguish between different sources of the contaminants and ii) understand biodegradation and other transformation processes occurring in the environment.

Compound-specific isotope analysis (CSIA) determines carbon, chlorine, and/or hydrogen isotope ratios for individual chemicals. Such differences in environmental samples are used to identify different pollutant sources or to understand pollutant transformation processes (USEPA 2008). CSIA involves the separation of chemical compounds using gas chromatography (GC), followed by conversion of the separated target compound to an easily measurable surrogate compound (e.g., CO_2 for $^{13}C/^{12}C$ measurements) in an inline reactor. Finally, the abundance of stable isotopes of the surrogate compound is measured by isotope ratio mass spectrometry. For $^{37}Cl/^{35}Cl$, owing to the relatively high abundance of ^{37}Cl, CSIA methods have been devised that use conventional GC-MS analysis (similar to that of USEPA Method 8260) thereby eliminating the need for conversion of the target chemical to a surrogate compound (Sakaguchi et al., 2007).

While the ability to analyze isotope ratios in single-compound samples dates back to the first half of the last century, compound-specific isotope analysis is still a relatively new approach.

Commercially available CSIA instrumentation was introduced two decades ago, initially only for carbon and nitrogen isotopes (Sessions, 2006). The hydrogen CSIA option became available a decade ago (Sessions, 2006). Chlorine CSIA is relatively novel and miscellaneous examples of applications were published in the past five years, while the technique based on GC-MS was first presented only 3 years ago (Sakaguchi et al., 2007). Applications of CSIA in environmental contaminant studies appeared shortly after the instrumentation became available (for example, Sherwood-Lollar et al., 1999), and were almost exclusively centered on aqueous and sediment samples. In the past decade, CSIA evolved from purely academic research to a technique with widespread application in environmental cleanup projects. The increased practical interest in CSIA is illustrated by the recent EPA publication of a CSIA guidance document (USEPA, 2008). This document provides recommended procedures and data quality measures for proper application of CSIA for contaminants in groundwater samples.

2.1.2 CSIA for analysis of airborne VOCs

While active adsorbent samplers offer logistic benefits in handling large volumes of air, their performance in preserving VOCs isotope ratios was not previously tested under sampling conditions required for the present project: in particular, the envisioned sample volume (≤100 L) is relatively large, and handling such high volumes may present a technical challenge. Ideally, an adsorbent sampling process with 100% mass recovery would ensure that no isotope fractionation occurs (isotope fractionation implies some sort of analyte mass speciation). At incomplete mass recovery, the different physical properties of molecules with different isotope substitution come to play. Based on literature on the isotope effects in phase partitioning, it can be predicted that for organic polymer adsorbents, molecules exclusively containing the light isotope species (^{12}C or ^{1}H) will be adsorbed stronger relative to the molecules containing a ^{13}C or ^{2}H atom. This difference is irrelevant if the mass recovery is complete; however, if part of the analyte is lost the preferential retention of the light isotope species on the adsorbent will lead to isotope fractionation apparent in the CSIA results. Analyte breakthrough, or losses during storage of the samplers, will result with an artifact of abnormally low isotope ratios (e.g., $^{13}C/^{12}C$); however, incomplete desorption can be expected to have the opposite effect of producing increased isotope ratios (e.g., $^{13}C/^{12}C$) in the desorbed analyte (Figure 2). Similar phenomena of isotope species disproportionation have been previously observed, in a dynamic flow system involving carbonaceous solids (adsorbent) and aqueous medium (Figure 3; Kopinke et al., 2005).

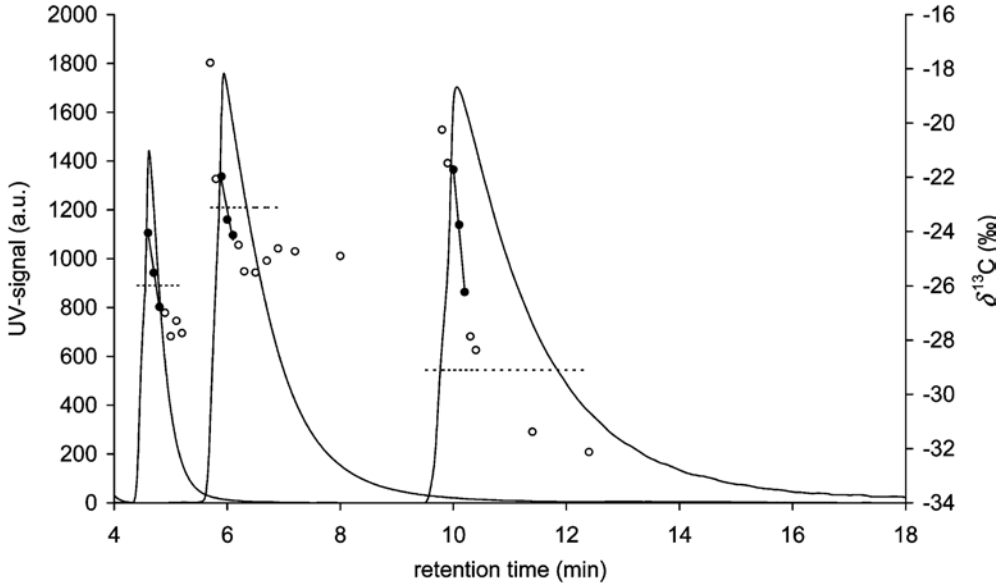


Figure 3. Superimposed HPLC chromatograms of benzene, 2,4-dimethylphenol, and o-xylene together with their isotope composition (circles) along the peak shapes. The dashed lines correspond to the d13C of the analytes. The HPLC column was packed with carbonaceous material (humic acids) and the analytes were eluted in aqueous solution. Note that the 13C-substituted molecules traverse the length of the column faster, resulting in a significant 13C enrichment followed by a 12C depletion. Figure taken from Kopinke et al., 2005.

To date, only a limited number of studies specifically focusing on VOCs collected from the gas phase have been published, in all cases involving some form of preconcentration of VOCs from larger volumes of air on adsorbents or cryogenic traps. Researchers in atmospheric chemistry developed methods permitting analysis of isotope ratios in VOCs at extremely low concentrations (Goldstein and Shaw, 2003). Large volumes of air in that case are collected in multiple stainless cylinders and the VOCs are recovered by cryogenic focusing. This approach is logistically difficult for routine VI assessment application. Two published studies utilized adsorbent tubes and thermal desorption, similar to TO-17, however in those cases the air samples <3L (Turner et al., 2006; Mead et al., 2008). None of the published studies deal with the complex chromatography required to separate VOCs in indoor air samples.

Having the limitations imposed by untested parameters in mind, adaptation of CSIA to VOCs occurring in air is conceptually similar to the past applications in aqueous VOCs analysis, with an additional step of recovery/preconcentration of VOCs prior to introduction of the sample onto the gas chromatograph (GC). Two alternative approaches to be used for this project are adapted from conventional VOCs analysis, following the lines of TO-15 (Summa canister sampling) and TO-17 (Adsorbent tube sampling); see Figures 4 and 5. Samples of vapor from Summa cylinders are directed into a second-stage concentrator (for example, a standard commercial purge and trap (P&T)) and then transferred into a chromatographic column. Alternatively, samples collected on adsorbent tubes are thermally desorbed (at the University of Oklahoma, we use a purge and trap instrument with a thermal desorption module), reconcentrated and directed into a

chromatographic column. VOCs introduced into the GC can be focused on a liquid nitrogen trap to facilitate splitless injection from the P&T (Figure 5) and an advanced 2-D chromatography can be utilized to resolve the target analytes from other VOCs present in the samples (Figure 5B). The need for 2-D chromatography was highlighted by the result from the preliminary study (Section 4.2), where indoor air samples showed high loads of VOCs and standard single-column GC was not adequate.

Accurate measurement of carbon or chlorine isotope ratios requires approximately 100 ng of TCE or PCE. Accurate measurement of carbon isotope ratio requires approximately 50 ng of benzene, while measurement of hydrogen isotope ratio requires approximately 1000 ng of benzene (these values apply for 2D-GC CSIA, better detection limits are possible if 2D-GC is not required). As a result, Summa canister sampling is practical only for soil gas samples with VOC concentrations greater than 10-20 ug/m^3. For indoor air samples, where the concentration of VOCs of concern are commonly less than 5 ug/m^3, and for soil gas samples with similarly low VOC concentrations, the use of adsorbent samplers are required to obtain sufficient sample mass.

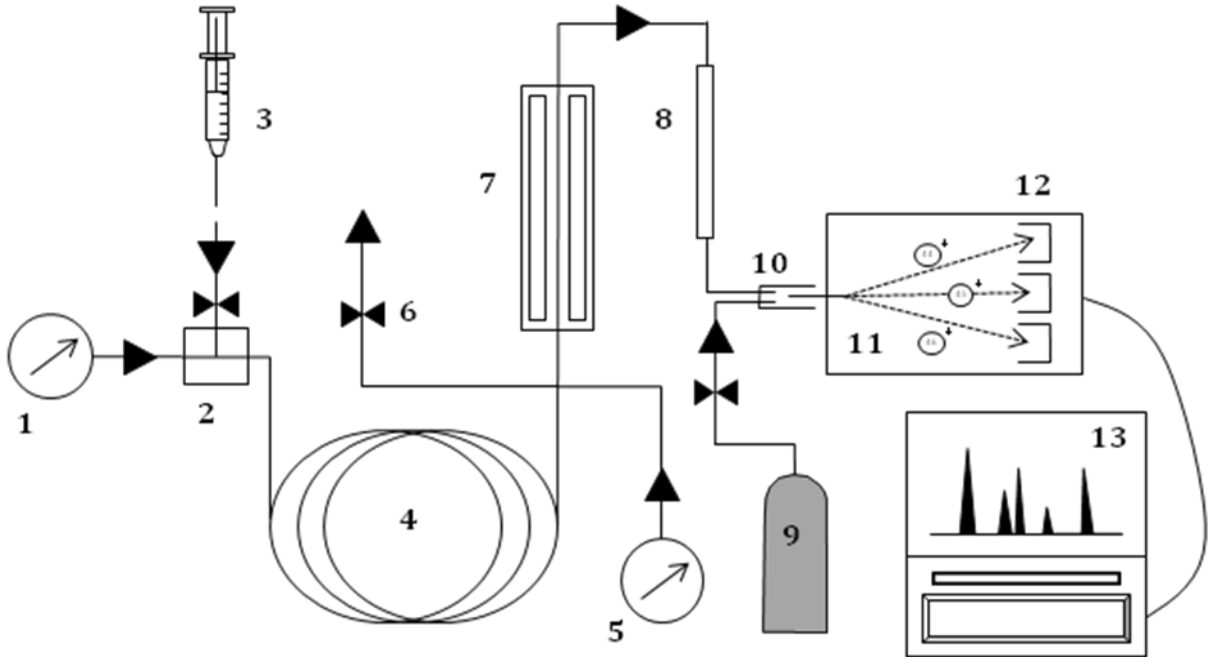


Figure 4. Schematic diagram of the GC-IRMS instrumentation. This is the basic instrumental configuration. See Figure 5 for information of the configurations used for environmental VOCs. 1) GC carrier gas pressure regulator; 2) GC injector: 3) Sample (configuration for manual injection); 4) GC column; 5) Oxygen pressure regulator ($^{13}C/^{12}C$ mode only); 6) Backflush valve; 7) Thermal conversion reactor (combustion to CO_2 in $^{13}C/^{12}C$ mode, pyrolysis to H_2 in $^{2}H/^{1}H$ mode); 8) Nafion membrane for water removal; 9) Reference standard gas (CO_2 or H_2); 10) Open split interface; 11) IRMS: ion source and ion optics; 12) IRMS: Faraday cups set for different isotope species (shown for $^{13}C/^{12}C$ mode, where 44, 45 and 46 represent $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{16}O^{18}O$); 13) Data acquisition and processing.

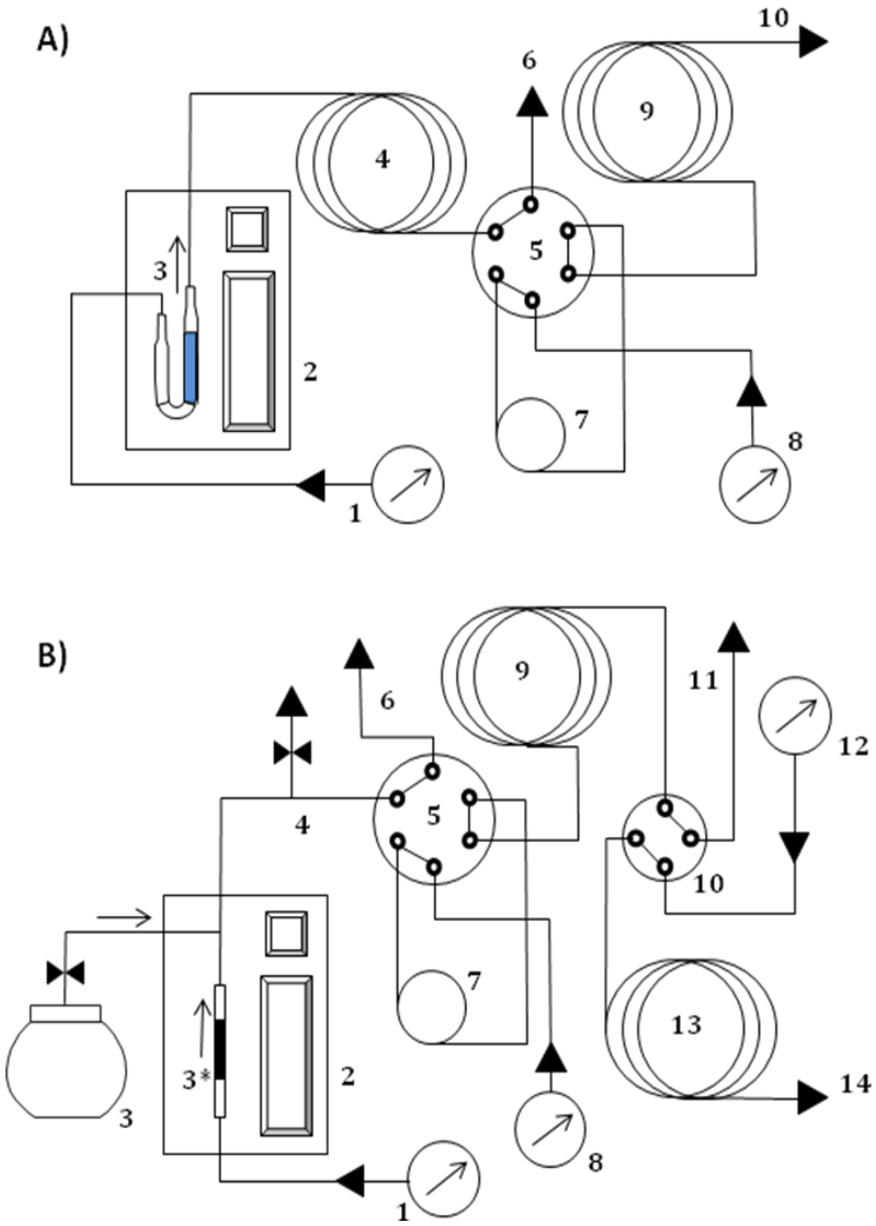


Figure 5. Diagram of the CSIA instrumentation as applied to analysis of environmental VOCs. A) Basic configuration for analysis of VOCs in environmental samples, aqueous sample configuration shown: 1) Desorption & Column #1 gas pressure regulator; 2) Purge and Trap unit; 3) Aqueous VOCs sample in sparge vessel; 4) GC column #1 (optional, precolumn used for water separation); 5) Switching valve; 6) Vent with capillary flow restrictor; 7) Cryotrap (LN_2); 8) GC column #2 carrier gas pressure regulator; 9) GC column #2; 10) Extension to the thermal conversion reactor. B) Configuration for analysis of complex matrix VOCs with 2-D GC, airborne VOCs sample configuration shown: 1) Desorption & Column #1 gas pressure regulator; 2) Purge and Trap unit; 3-3*) VOCs sample in Summa canister as in TO-15 or in thermal desorption tube* as in TO-17; 4) Splitter; 5) Switching valve; 6) Vent with capillary flow restrictor; 7) Cryotrap (LN_2); 8) GC column #1 carrier gas pressure regulator; 9) GC column #1; 10) Switching valve; 11) Vent with capillary flow restrictor; 12) GC column #21 carrier gas pressure regulator; 13) GC column #2; 14) Extension to the thermal conversion reactor.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

CSIA is the only available technique permitting direct individualization of single chemical species, such as TCE or benzene. In that sense the CSIA approach is unique and cannot be replaced by another technology. Regarding comparisons of the proposed protocol of CSIA of vapor-phase samples vs. other alternative vapor-phase sampling approaches, the only other published examples of isotope analysis of VOCs present in air were conceptually similar and involved preconcentration of VOCs on cryogenic and/or adsorbent traps prior to analysis. On the other hand, none of the published protocols successfully addressed all issues necessary for successful application to indoor air samples: 1) ability to measure isotope ratios at low concentrations of VOCs; 2) ability to chromatographically resolve complex VOC mixtures encountered in indoor air; and last but not least 3) to allow transition to a commercial analytical technique.

The main limitations of the CSIA approach are those related to the analytical protocol and those related to the follow up data interpretation. In the former category, the analyte mass requirement of CSIA is relatively large, and the air volumes pumped through an adsorbent tube increase as the VOC concentrations decrease. This extends sampling time and increases the cost of the field program. A potential limitation of increased analytical uncertainty for the large volume samples is investigated in this experimental program. Finally, chromatographic resolution, even with 2-D GC approach has its limitations. While the samples analyzed to date were successfully resolved on the 2-D configuration, it is possible that in certain cases the interfering compounds will be a problem. The latter issue is also addressed in this report.

In the second category of problems related to data interpretation, the main issue is that if the isotope composition of subsurface VOCs and those from household products is identical, CSIA yields inconclusive answers (i.e., if no degradation affects the subsurface VOCs, their isotope ratios range will overlap with the range for the same species in household products, so that in certain situations the ratios of a given household product and a given subsurface VOC may be identical). The full strength of source discrimination will be realized if samples of indoor air and sub-slab gas are available. If sub-slab samples are not available, the interpretation has to rely on a more conservative approach of comparison of indoor VOCs isotope ratios with those from more remote subsurface samples. Similarly, if products containing the target VOCs can be identified at a given location, the isotope ratios from the specific product and from indoor air may be compared directly, otherwise the data have to be evaluated against a wide range of products containing a given pollutant, for example, TCE, with a wider margin of uncertainty. Based on the current understanding of isotope fractionation in degradation and transport of various VOCs, isotope ratio differences in those species that readily fractionate in degradation (e.g., TCE and benzene) will be magnified by biodegradation and CSIA will be more likely to show diagnostic differences in the isotope ratios between subsurface and indoor samples. PCE that often does not undergo significant isotope fractionation in degradation (esp. in aerobic degradation) may be more difficult to evaluate and the differences in isotope ratios in various samples will have a narrower range, representing the ratios of manufactured PCE released into environment.

3.0 PERFORMANCE OBJECTIVES

Precise and accurate determination of isotope ratios of VOCs after preconcentration on adsorbent tubes and thermal desorption onto a GC-IRMS instrument requires that one of the following criteria is met: 1) the sorption/desorption process does not introduce isotope fractionation (this is the most desirable situation); 2) if isotope fractionation does occur, the magnitude of the fractionation has to be predictably linked to sampling parameters. One approach to deal with fractionation in sampling process was applied for publication of results from our preliminary study (AFCEE BAA Contract 09-C-8016 "Validation of New Tools to Better Manage Vapor Intrusion Liability", PI Tom McHugh/GSI Environmental Inc.; published as McHugh et al., 2011). In that study, maximum fractionation (isotope ratio bias) was defined for two parameters apparently linked to fractionation, namely for the sample volume and the holding time prior to CSIA (holding at room temperature). Such maximum bias defines the added analytical uncertainty for the method attributable to the sampling process.

Ideally, an adsorbent sampling process with 100% mass recovery would assure that no isotope fractionation occurs (isotope fractionation implies some sort of analyte mass speciation). At incomplete mass recovery, the different physical properties of molecules with different isotope substitution come to play. Therefore, selection of adsorbents permitting recovery of as close to 100% of analyte with minimum isotope fractionation is of key importance. Another potential problem with analysis of indoor air VOCs samples, not related to the adsorbent performance, is the difficulty to chromatographically resolve the complex VOCs mixtures encountered in indoor air. Based on preliminary data (the AFCEE study), the performance of the 2D-GC had to be improved to permit robust analysis of certain indoor air samples with excessive loads of non-target VOCs.

Therefore, the objectives of the laboratory validation study were:

1) Initial screening of adsorbents to identify candidate adsorbents for full validation
2) Full validation of adsorbent performance to verify fractionation-free VOCs preconcentration.
3) In the absence of fractionation-free performance, developing a QA/QC approach to correct for the observed fractionation associate with sample collection
4) Optimization of the 2D chromatography for the analysis of samples containing complex mixtures of non-target VOCs.

The performance objectives are also summarized in greater detail in Table 1. Based on the laboratory results in support of Objectives 1 and 2, an adsorbent was identified that provides fractionation-free performance. As a result, no work was required in support of Objective 3.

3.1 PERFORMANCE OBJECTIVE: INITIAL EVALUATION OF ADSORBENTS

For given set of sampling conditions (including air volume, air humidity, the presence of non-target VOCs etc.), the maximum range of isotope fractionation during air VOCs sampling and CSIA defines the level of uncertainty when using isotope ratios to correlate/discriminate VOCs sources. High isotope fractionation exceeding normal analytical precision of CSIA reduces the

resolving power of CSIA. It was anticipated that selection of adsorbents will be significant in minimizing isotope fractionation, by preventing relative losses of isotopomers in analyte breakthrough and irreversible sorption. As a result, the first performance objective was to identify adsorbents that yield minimal fractionation for a range of sampling conditions.

3.1.1 Data requirements

To identify adsorbents that are ideally fractionation-free, we have determined C, Cl or H isotope ratios of benzene TCE, PCE and benzene concentrated on adsorbent tubes from 100 L air samples. The fractionation effects associated for the adsorbents-analyte pairings were evaluated by comparison of the determined isotope ratios with those independently known for the TCE, PCE and benzene used to load the adsorbent tubes.

3.1.2 Success criteria

To validate that there is no fractionation occurring during sampling, the values determined for the target analytes, should be not significantly different than the isotope ratios determined independently (e.g., by direct injection of the same analytes into the GC-IRMS instrument). The isotope ratios difference between the analytes introduced via thermal desorption tube samples and the same analytes analyzed directly should not exceed the normal analytical precision of CSIA to conclude that the process is indeed fractionation-free. Ideally, the difference should be no greater than ±0.5‰ for $\delta^{13}C$, ±1 ‰ for $\delta^{37}Cl$, and ±5 ‰ for $\delta^{2}H$. The isotope ratio differences (if any) are also confirmed by ANOVA and pair-wise t-test, comparing the data subsets for different experimental configurations. Fractionation-free adsorbent-analyte pairings identified in the first stage of the project are then subjected to a second tier validation of performance (Task 2A).

3.2 PERFORMANCE OBJECTIVE: VALIDATE ADSORBENT PERFORMANCE FOR A RANGE OF SAMPLING CONDITIONS

It is proposed that the absence of fractionation under increased sampling challenge would validate the adsorbent for the TO-17 process without the need of additional calibration of the (missing) fractionation. On the other hand, if no fractionation-free adsorbent-analyte pairings were identified, additional work would be required to better define such fractionation (Section 3.3). Testing of the adsorbent-analyte pairings selected after fulfillment of Objective 1, was performed for a number of experimental treatments representing various combinations of environmental conditions potentially occurring during sampling.

3.2.1 Data requirements

The primary objective is identification of the presence or the absence of fractionation under sampling challenge representing the proposed application range (here, while we will restrict the overall recommendation for the method to air volumes ≤100 L, the validation involved testing of the performance for 200 L sample volume for more robust conclusions). The data collected are similar as for Objective 1, but for more diverse sampling conditions, with varying expression of

the environmental parameters (sampling volume, humidity, target VOC mass, non-target VOC mass, adsorbent tube holding time).

3.2.2 Success criteria

For each of the tested adsorbent-analyte pairings and each of the sampling treatment, the objective is to determine the presence or absence of a measurable fractionation effect (e.g., for carbon isotope ratios, the measured $\delta^{13}C$ values should not deviate by more than 0.5‰ from the expected values). If no fractionation is encountered in any of the tested treatments, the adsorbent-analyte pairing is considered a safe choice for fractionation-free sampling.

3.3 PERFORMANCE OBJECTIVE: IDENTIFY AND CALIBRATE THE VARIABLES AFFECTING THE ISOTOPE FRACTIONATION IN ADSORBENT TUBES

If no fractionation-free adsorbent-analyte pairings were identified, work performed for this Objective would provide data to test whether the fractionation can be corrected in the QA/QC protocol. Laboratory work in support of this objective was not required based on the identification of fractionation-free adsorbents while completing Objectives 1-2.

3.4 PERFORMANCE OBJECTIVE: 2D-GC OPTIMIZATION

This objective is independent from the adsorbent performance testing (Sections 3.1-3.3) and concerns chromatographic separation of the target VOCs from complex VOCs mixtures encountered in indoor air. Accurate measurement of carbon or hydrogen isotope ratios requires the elution of the target VOC from the GC free of any co-eluting non-target VOC peaks (chlorine CSIA utilizes single ion mass spectrometry and is more tolerant of coelutions). For complex mixtures typical of indoor air, this requires 2D-GC separation. Efficient 2D-GC separation requires stable retention times for the 1st GC column even in the presence of high non-target VOC loads. The sensitive element of the method appears to be the performance of the 1st GC column (DB-Wax column, Item 9, Figure 5B). The objective is to improve the performance of the 2D-GC method to eliminate the first column retention time problems encountered in the preliminary AFCEE study (Section 4.2).

3.4.1 Data requirements

To confirm that 2D-GC performance is replicable, readings of the analyte retention times for variable loading of interfering non-target VOCs were collected. To confirm that the 2D-GC is capable of separating the target analytes from the complex VOCs matrix, samples of real indoor air were examined. For these samples, the visual quality of GC resolution (well-resolved analyte peaks) was evaluated to evaluate the performance of the 2D-GC analysis.

3.4.2 Success criteria

The qualitative criterion for GC resolution is a visual lack of coelutions in the obtained chromatograms for air VOCs samples. A quantitative criterion was reduction of the retention time fluctuations to <30 sec. for variable loading of interfering non-target VOCs (changed from <20 sec. proposed in the Laboratory Plan), as further discussed in section (4.6.2).

Table 1. Performance Objectives

Performance Objective	Data Requirements	Success Criteria	Results
(1) Evaluate relative performance of adsorbents for use in vapor-phase CSIA (for 100 L of humidified air, with non-target VOCs present)	Isotope ratios of benzene (C, H), TCE (C, Cl) and PCE (C, Cl) collected under simulated indoor air sampling.	Quantitative criteria: For each adsorbent-analyte pairing, determination of whether fractionations effect is greater than analytical precision ($\delta^{13}C$: ±0.5 ‰; $\delta^{37}Cl$: ±1 ‰;$\delta^{2}H$: ±5 ‰;). Sorbents with least fractionation are retained for further evaluation[1].	For benzene, TCE and PCE, Carboxen 1016 and Carbopack B were fractionation-free for carbon, chlorine and/or hydrogen CSIA. Carbopack X was evaluated only for C isotope effects. While sampling of benzene and PCE was fractionation-free, there was a significant fractionation observed for TCE. Carbopack X evaluation was stopped at that point. Carbopack B and Carboxen 1016 were retained for further evaluation.
(2) Validate adsorbent performance for wire range of sampling conditions	Sorbent/analyte combinations tested for experimental treatments differing in their: - sampling volume - humidity - target VOC mass - nontarget VOC mass - holding time prior to analysis Analytical data collected as in Objective 1.	Quantitative criteria: As in Objective 1. If no significant fractionation is observed under increased analytical challenge, stop evaluation. Adsorbent-analyte pairings that are fractionation-free under the tested conditions can be considered safe for CSIA sampling. If no fractionation-free adsorbents are identified for each of the tested analytes, proceed with Objective 3.	Fractionation-free performance was observed for all treatments for Carboxen 1016. For Carbopack B, certain experimental conditions were associated with isotope fractionation. Carboxen 1016 is recommended for fractionation-free sampling of benzene (C, H), TCE (C, Cl) and/or PCE (C, Cl).

Performance Objective	Data Requirements	Success Criteria	Results
(3) Identify and calibrate the variables affecting the isotope fractionation in adsorbent tubes.	As in Objective (2), data collected if necessary to add to the data available from Objectives 1 and 2, to improve the statistical significance of calibration lines.	Quantitative Criteria: For each sampling factor with significant fractionation effect, define relationship between sampling factor and fractionation effect (e.g., zero order, first order, etc). Use regression analysis to define a single-variable model to correct for observed fractionation effect. The objective is for the correction factor to reduce the observed fractionation effect associated with the sampling variable to less than the analytical precision ($\delta^{13}C$: ±0.5 ‰; $\delta^{37}Cl$: ±1 ‰;$\delta^{2}H$: ±5 ‰;).	Objective 3 was nullified by the successful validation of fractionation-free performance of Carboxen 1016 (and to limited extent, Carbopack B).
(4) 2D-GC optimization	Retention times and GC resolution for the target VOCs run in the presence of high mass of non-target VOCs.	Qualitative Criteria: Target analytes are well-resolved from non-target VOCs. Quantitative Criteria: Change of retention times of the target analytes co-occurring with high mass of non-target VOCs does not result with excessive shift of analyte retention time.	With optimized 2D-GC conditions, benzene, TCE and PCE were responding to increased loadings of non-target VOCs by retention time offset of under 30 sec. Analysis of authentic indoor air samples permitted clean separation of the analyte (TCE was used in the test) from the non-target VOCs.

4.0 EXPERIMENTAL DESIGN

The laboratory validation of the sample collection and analysis method included two independent tasks of adsorbent performance validation (Sections 4.1-4.5, cf. Sections 3.1-3.3) and of 2D-GC performance optimization (Section 4.6, cf. Section 3.4). Section 4.7 gives additional details on experimental procedures, including preparation of test samples (4.7.1) and CSIA (4.7.2)

4.1 CONCEPTUAL EXPERIMENTAL DESIGN

4.1.1 Adsorbent validation

As previously illustrated in Figure 2 above, either incomplete retention of the target analyte on the adsorbent or incomplete desorption of the analyte from the adsorbent can result in isotope fractionation if the adsorption or desorption efficiency is different for the two isotopes. Adsorbent efficiency, in turn, can be affected by sampling conditions. Therefore, full validation of adsorbents requires evaluation of adsorbent efficiency for a range of sampling conditions representative of those expected to be encountered in the field. The tests were performed for maximized sample volume (100 L or 200 L). Increased potential of isotope fractionation is to be expected for increased sample volume for the two scenarios summarized in Figure 2. Therefore, if no fractionation is observed at these samples, the results can be extrapolated to demonstrate no fractionation at lower volumes. Most of the testing was done with humidified air and with non-target VOCs present. Both can partially saturate the adsorbent's active sites and enhance the potential of analyte breakthrough or permit the analyte to reach deeper into the bed of the adsorbent. In the preliminary AFCEE study, it was observed that sampling of TCE from air that did not contain other VOCs or water vapor on a relatively strong adsorbent resulted with an increased potential of isotope fractionation. This phenomenon was proposed to result from the lack of competition for adsorbents active sites between TCE and water/other VOCs present in the samples. It was proposed that in the strong adsorbents, the absence of water and non-target VOCs increases the potential of irreversible retention of the analytes and attendant isotope fractionation.

The potential of water and non-target analytes to cause isotope fractionation was evaluated by testing the process at variable air humidity and with/without non-target VOCs. In the AFCEE study it was found that extending holding time can magnify isotope fractionation determined for VOC analytes. The following rationalization can be proposed: 1) for an adsorbent with strong affinity to the analyte, extended holding time would permit diffusive redistribution of the analyte within the adsorbent bed, with more molecules irreversibly trapped by stronger active sites, resulting with a more pronounced effect of reduced recovery of the lighter isotope species during desorption; and 2) for an adsorbent with weak affinity to the analyte, extended holding time would permit diffusive redistribution of the analyte within the adsorbent bed and eventually an escape of analyte molecules out of the adsorbent bed, resulting with preferential loss of the weaker adsorbed heavy isotope molecules. Both processes would magnify the fractionation illustrated in Figure 2, for the adsorbent-analyte pairings prone to analyte breakthrough and for the pairings prone to irreversible sorption, respectively. Some of the experimental treatments involved extended holding time, to magnify any fractionation problems that might be otherwise

not apparent. Moreover, in normal analytical practice, thermal desorption tubes would not be analyzed immediately, and conducting a test with holding time is more realistic.

The experimental work for evaluation of adsorbent performance was divided into stages, corresponding to the Performance Objectives described in Section 3 and shown in Table 1. The present arrangement of the activities has been modified from that given in the Laboratory Study Plan. The present version is streamlined to reflect the findings from the actual study. Mainly, 8 out of 9 adsorbent-analyte pairings tested initially were fractionation-free. Considering this, the focus of the project was on validation of fractionation-free performance under extended set of experimental treatments rather than identification of the variables responsible for (the absent) fractionation.

Task 1 of the validation study aimed at quickly identifying those adsorbents where fractionation is a problem and those where fractionation-free performance is apparent under a baseline testing condition. Task 2 was a further evaluation of the retained adsorbent-analyte pairings under an extended range of experimental conditions corresponding to the range of conditions to be encountered in air VOC sampling. The preferred outcome of the second stage would be validation of fractionation-free adsorbent performance for all treatments tested. The necessity for further activities (Objective 3) would depend on whether such fractionation-free adsorbent-analyte pairings were identified for the analytes of interest. If no fractionation-free adsorbent-analyte pairings were available, additional work would be required to identify the experimental parameters responsible for isotope fractionation and devise a method for bias correction. Scheme 1 shows the proposed options in focusing the work based on preliminary results generated in early stages of the project. As discussed in Section 5, fractionation-free adsorbent performance was obtained eliminating the need for the analyses presented as Task 3 in the laboratory validation plan.

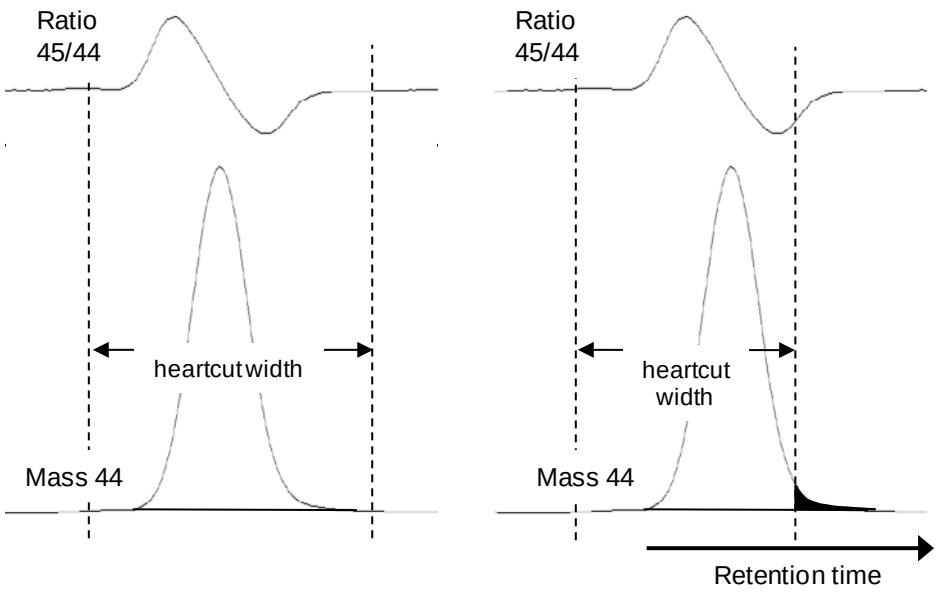
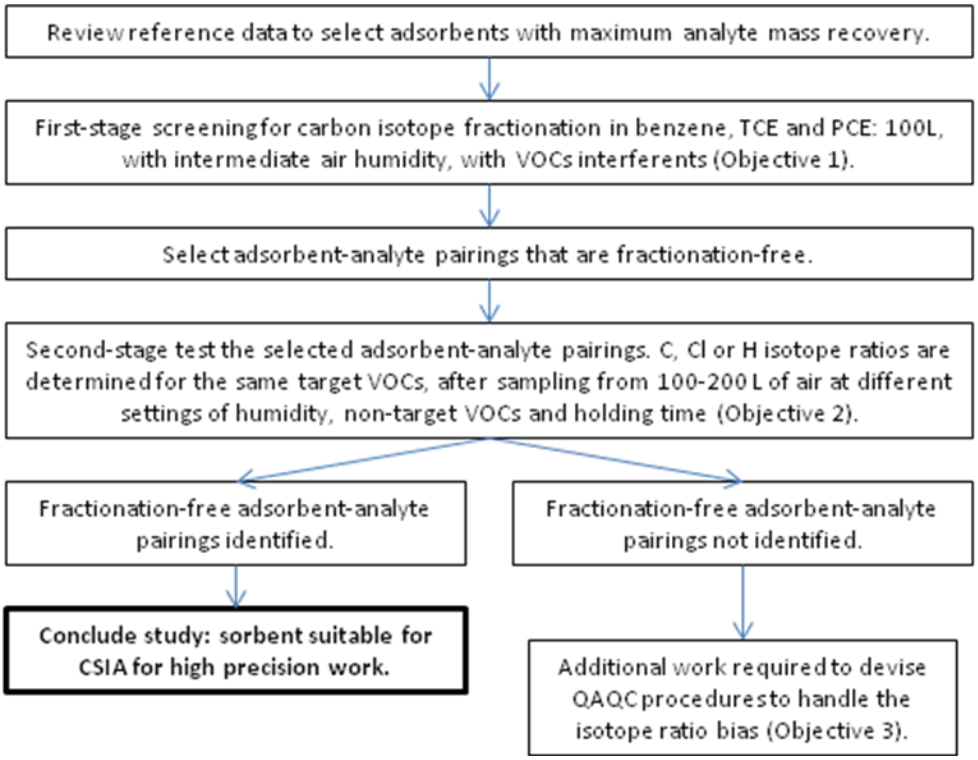


Figure 6. The effect of incorrect timing of the heartcut valve (Figure 5b, Item 10) in 2D-GC CSIA. In the scenario depicted to the left, the heartcut is positioned correctly, and whole mass of analyte is transferred from the 1st to the 2nd GC dimensions. In the scenario depicted to the right, the heartcut is terminated too soon, resulting with loss of the GC peak tail. Due to isotopic depletion of the lost part of the peak (note the appearance of the 45/44 ratio) the mass within the heartcut would be abnormally enriched in the heavy isotope.

4.1.2 2D-GC optimization

The premise for this task is based on the preliminary data (Section 4.2), where the GC retention times were observed to increase for samples with large mass of non-target compounds. 2D-GC involves a transfer of a narrow heartcut of GC effluent from the 1st dimension GC column to the 2nd dimension GC column. The heartcut position and width are defined by the retention time of the analyte on the 1st dimension GC column. If the analyte migrates too far and is not completely recovered within the heartcut width, the measured isotope ratio can be heavily biased. The mechanism of fractionation is very similar to that shown in Figure 2 – molecules with heavy isotope substitutions move through a GC column at slightly faster velocity, resulting with strong enrichment of the heavy isotope in the front and depletion in the tail of a chromatographic peak. Collection of a heartcut of the 1st GC dimension effluent must avoid missing the peak extremities to avoid isotope ratio bias. Figure 6 shows the appearance of two GC peaks, one from a well-performing method, and another, with a too narrow heartcut interval. The latter shows a characteristically heavy isotope ratio due to losing the most depleted part of the chromatographic peak. Task 4 aimed at GC performance optimization to avoid incomplete peak transfer from the 1st dimension GC column to the 2nd dimension GC column, while maintaining narrow transfer retention time interval.

Scheme 1.



4.2 RESULTS FROM AFCEE STUDY

As part of the AFCEE study (Air Force Center for Engineering and the Environment, BAA Contract 09-C-8016 "Validation of New Tools to Better Manage Vapor Intrusion Liability", PI Tom McHugh/GSI Environmental Inc.), several experimental parameters were evaluated for an adsorbent tube that was a combination of Tenax GR and Carboxen 569. Figure 7 summarizes the effect of challenge volume on carbon isotope ratio for TCE. The carbon isotope ratios of TCE were clearly affected by the sampling volume and the hold time, in both cases the measured isotope ratios were enriched in ^{13}C. There was no difference between sampling capacities of 40 vs. 100 mL/min. Humidity may have an effect of reducing the fractionation caused by extending the sampling volume, however this parameter was not tested in great detail. In the case of chlorine isotopes in TCE, there was no readily discernible fractionation connected to sampling volume. In the case of PCE, there was no discernible fractionation related to volume; however the range of volumes tested was lower than for TCE. The observed effects can be rationalized by the published properties of Tenax GR and Carboxen 569. Tenax GR has a good affinity for PCE and is expected to yield ~100% recovery even at high sampling volumes (published data were for a 100 L challenge volume following PCE standard injection into a tube). On the other hand, TCE breaks through Tenax GR at sampling volumes exceeding several L. TCE recovery in such case relies on the second bed of adsorbent (Carboxen 569). The published data show that TCE desorption from Carboxen 569 may be incomplete, with the problem increasing at the increasing sampling volume. Incomplete desorption would favor recovery of ^{13}C-TCE (cf. Figure 2) and

this agrees with the enrichment of ^{13}C-TCE observed in the AFCEE study. These results confirm the potential of isotope fractionation occurring in TO-17 process but also suggest that proper adsorbent selection may eliminate the problem of fractionation (as apparent in the preliminary data on PCE).

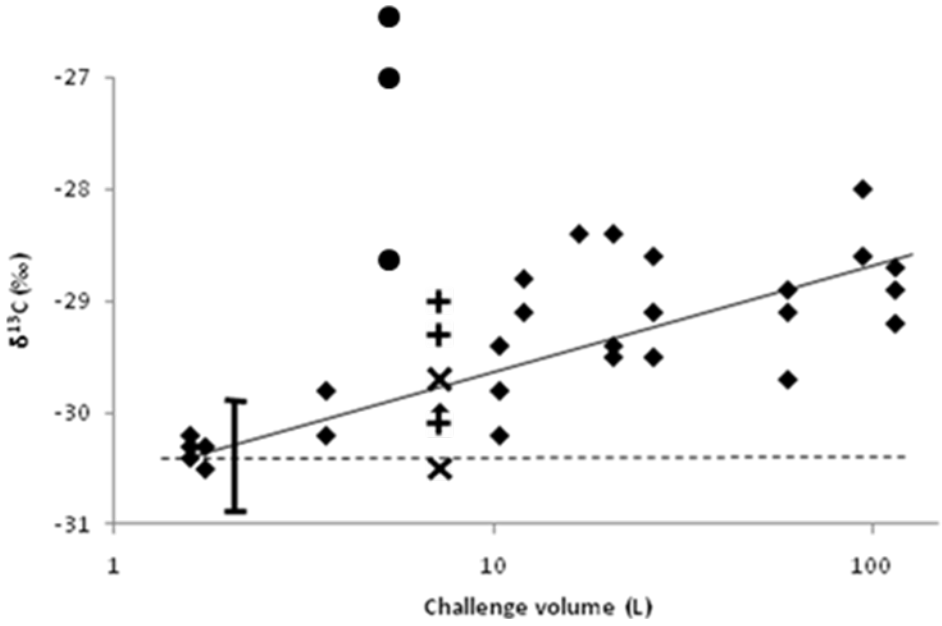


Figure 7. Isotope ratios of TCE standards injected on Tenax GR/Carboxen 569, flushed by variable air volume (challenge volume). Relative humidity (H) of air at 23-24^{o}C: H=30% (+); H=60% (♦); H=90% (×). Three standards loaded at H=60% were analyzed after 18 days hold time at room temperature (●). The horizontal dashed line represents isotope ratio of TCE without adsorbent effect (δ_0). The solid line is an empirical regression line for the H=60% data, with the equation 0.4 × ln (L) – δ_0. The Y-axis error bar represents normal analytical uncertainty of carbon CSIA.

Another important result from the AFCEE study was to highlight the potential problems resulting from excessive loadings of non-target VOCs. Several of the indoor air samples exhibited a shift in their GC retention times, caused by GC column overload with VOCs. As the 2D-GC method involves collection of narrow retention time window from the 1st dimension column and discarding the rest of the effluent, precise prediction of the targets retention times is extremely important. A retention time shift greater that the expected value leads to partial loss of the analyte and a major isotope ratio bias. While this problem is apparent in data evaluation, and can be corrected by modifying the range of the retention time window, this approach requires analysis of additional tubes, increasing the expense of sampling (additional replicates have to be collected) and analysis. Additional 2D-GC optimization was proposed to reduce the impact of non-target VOCs (Sections 3.4 and 4.6).

4.3 TASK 1: INITIAL EVALUATION OF ADSORBENTS

Adsorbents for testing were selected based on manufacturer data (Supelco document "A Tool for Selecting an Adsorbent for Thermal Desorption Applications" available online at www.sigma-aldrich.com/supelco-literature). The selected adsorbents showed high recovery of the target analytes for high volume sampling, and by inference, good potential of fractionation-free sampling. This set of samples was analyzed for carbon isotope effects for a default set of conditions to identify the adsorbent-analyte pairings that show fractionation-free performance and eliminate those that result in isotope fractionation (if no fractionation-free pairings were identified, those with least fractionation would be retained for further study).

4.3.1 Lab program

Samples were prepared by injecting target analytes into the adsorbent tubes and flushing them with 100 L of air. The tubes were preloaded with 400 ug of non-target VOCs and air was humidified (Table 2 lists experimental settings of the test). The samples were analyzed for C isotope ratios within 48 hrs after preparation. Replicates ($n \geq 3$) were analyzed for each adsorbent-analyte pairing.

4.3.2 Data analysis

For Task 1, the performance of the adsorbent-analyte pairings in different treatments has been evaluated based on subsets of 3 or more replicate data points (replicate measurements of isotope ratios) per a treatment. The absence of significant fractionation was identified based on the following criteria: 1) the difference between the measured isotope ratios after adsorption/desorption and that measured by direct injection of the same analyte onto the focusing trap of the thermal desorption unit did not exceed the normal analytical uncertainty of given CSIA method; and 2) there was no statistically significant difference between the data subsets from the thermal desorption tubes and those from direct injection (confirmed by t-test). The former criterion is required to claim fractionation absence. The second criterion is sensitive to random clustering of data points that cannot be excluded for data sets with a low number of samples, and is also subject to artifactual biases of isotope ratios caused by minor coelutions (background noise that affects the accuracy of isotope ratio measurements). The t-test result of significant difference in data subsets (at 95 % confidence) is therefore of secondary importance and is overridden by the criterion of net difference of isotope ratios lower that the nominal CSIA uncertainty (e.g., for carbon CSIA, the accepted uncertainty is ±0.5 ‰ of $\delta^{13}C$ unit).

Table 2. Experimental Conditions for Each Study Task

Task	Experimental variables	Remarks
(1) Initial evaluation of adsorbents	Target analytes: benzene, TCE, and PCE, only C CSIA. Adsorbents: 4.5" tubes, packed with Carbopack B, Carbopack X and Carboxen 1016, respectively. Desorption conditions: 330^{o}C Replicates: all CSIA analyses run in at least in triplicate Default sampling conditions: Sampling volume 100 L, sampled at 100 mL/min Mass of target analytes: 150 ng (TCE, PCE), 60 ng (benzene) Preloaded with 400 ug of non-target VOCs[1] Humidity set to 60% at 23-24^{o}C Hold time < 48 hr at 4^{o}C	Set of conditions referred to as Treatment 1 (Table 3 and elsewhere in the report).
(2) Validate fractionation-free performance of adsorbents	Target analytes: benzene (C, H), TCE (C, Cl), PCE (C, Cl) Adsorbents: 4.5" tubes, packed with Carbopack B and Carboxen 1016, respectively. Desorption conditions: 330^{o}C Replicates: all CSIA analyses run in at least in triplicate Sampling conditions: Sampling volume 100 L or 200 L, sampled at 100 mL/min Mass of analytes (Treatments 1-6): 150 ng (TCE, PCE), 60 ng (benzene, C CSIA); 1 ug (benzene, H CSIA). Mass of analytes (Treatment 7): 2 ug (TCE, PCE), 1 ug (benzene, C CSIA), 2.5 ug (benzene, H CSIA) Preloaded with 400 ug of non-target VOCs[1] (except of Treatment 4) Air humidity settings (at 23-24^{o}C): 10%, 30%, 60%, 90% (varies among Treatments 1-7) Hold time settings: < 48 hr, 2 weeks (varies among Treatments 1-7) at 4^{o}C	The experimental variables were tested for 7 different combinations of the variables (Treatments 1-7, Table 3).

Task	Experimental variables	Remarks
(3) Identify and calibrate the variables affecting the isotope fractionation	Target analytes and adsorbents: as above, optionally those where calibration of isotope effects is required Sampling conditions: varied relatively to those listed in (2) to obtain responses in isotope fractionation that would be indicative of the significance of given parameter in causing the fractionation.	Not required based on the results obtained from Task 2. See Scheme 1.
(4) 2D-GC optimization	Target analytes: as above Sorbents: Carboxen 1016. Replicates: (see Section 4.6) Sampling conditions: samples prepared by spiking adsorbent tubes with the target analytes followed by drawing 100 L of residential air with the locally present VOCs. GC conditions: 1st dimension GC diameter was 0.5 mm (maximum available) to make it least prone of phase overload. The column length was 60 m (maximum available) to maximize the GC resolution strength. GC temperature during the 1st dimension separation was 40°C (benzene, TCE) or 50°C (PCE) and the GC carrier flow was 2.5 mL/min, to allow ~40-50 minutes of analyte retention time and powerful separation from non-target analytes.	

[1] See section 4.7.1. for details on the non-target VOCs.

Table 3. Experimental Treatments Tested.

#	Experimental Conditions	Adsorbents	Comments
T1[1]	100 L; w/ non-target VOCs; water 12 mg/L, <48 hrs holding time.	Carbopack B Carbopack X Carboxen 1016	Intermediate humidity (equivalent of 60 % relative humidity at 23°C). Considered "typical" for indoor air sampling.
T2	100 L w/ non-target VOCs; water 18 mg/L, 2 wks holding time.	Carbopack B Carboxen 1016	Increased humidity (equivalent of 90 % relative humidity at 23°C) represents sampling at higher indoor air temperature.
T3[2]	100 L w/ non-target VOCs; water 2 mg/L, 2 wks holding time.	Carbopack B Carboxen 1016	Reduced humidity (equivalent of 10 % relative humidity at 23°C) represents sampling at low indoor air temperature.
T4	100 L w/out non-target VOCs; water 6 mg/L, <48 hrs holding time.	Carbopack B Carboxen 1016	Test for adsorbent performance at conditions increasing the potential of strong/irreversible adsorption[3]
T5	100 L w/ non-target VOCs; water 12 mg/L, 2 wks holding time.	Carbopack B Carboxen 1016	Validation of the absence of fractionation during sample holding.
T6	200 L w/ non-target VOCs; water 12 mg/L, <48 hrs holding time.	Carbopack B Carboxen 1016	Validation of the absence of fractionation at extended air volume challenge.
T7	Identical to #1, mass of target analytes increased 15 × for C and Cl CSIA, or 5 × for H CSIA[4].	Carbopack B Carboxen 1016	Validation of the absence of fractionation for increased mass of analyte.

[1] Carbon data for T1 represent preliminary screening of the adsorbents (Task 1), Cl and H data have been produced for the same treatment in Task 2; [2] For Carbopack B, C CSIA was performed within 48 hrs, no Cl CSIA was performed (this treatment was considered unnecessary due to low probability of sampling at extremely low humidity, moreover, T4 replicates some of the premises of T3); [3] In the preliminary AFCEE adsorbent study (McHugh et al., 2011) it was observed that Carboxen 569 performed better if air was humidified and non-target VOCs were present, possibly due to partial deactivation of the adsorbent's active sites and reduced problems with irreversible sorption; the treatment with humidity reduced to 30% and no additional VOCs was included to magnify any problems caused by irreversible adsorption; [4] The minimum mass required for H CSIA of benzene is relatively large, and an increase of 5 × is sufficient to simulate the upper range of concentrations to be encountered on-site.

4.4 TASK 2: VALIDATION OF FRACTIONATION-FREE PERFORMANCE OF THE ADSORBENTS

This task comprises the bulk of the experimental work performed in this project. The individual tests were performed for samples prepared under combined impact of several variables: e.g., volume, humidity, the presence of non-target VOCs and/or holding time prior to CSIA. These combinations of experimental parameters are referred to as "treatments" (Table 3 lists the treatments used in this study).

The work performed was similar in scope to the original Task 1 with elements of Task 2 outlined in the Laboratory Study Plan. An additional test not proposed originally was performed: samples prepared at reduced humidity and without non-target VOCs, to enhance the potential of irreversible sorption similar to that observed in the AFCEE study that would lead to artifactual enrichment of the heavy isotope species. No attempt was made to incorporate desorption temperature and time into the treatments. Such parameters are independent of adsorption-related phenomena. While a too low desorption time/temperature can result with isotope fractionation similar to that occurring for true irreversible adsorption, we considered it impractical to attempt optimization of desorption in the cases where there was apparent potential of isotope fractionation due to incomplete desorption. Instead, the effort was directed to validation of those adsorbents where no apparent fractionation was observed.

4.4.1 Lab program

Table 3 shows a list of treatments that were evaluated to determine whether the adsorbents performed without isotope fractionation. Treatment 1 is identical to that tested in the preceding task (Cl and H data are collected to complete the C isotope ratios collected previously for the same sampling conditions). Additional six treatments test various combinations of experimental parameters. In general, carbon and chlorine (TCE, PCE) and carbon and hydrogen (benzene) isotope ratios were determined. Some treatments were omitted for the adsorbent-analyte pairings that were not performing wells based on the interim results. Complete set of data for all treatments were collected for adsorbent-analyte pairings proposed as fractionation-free.

4.4.2 Data analysis

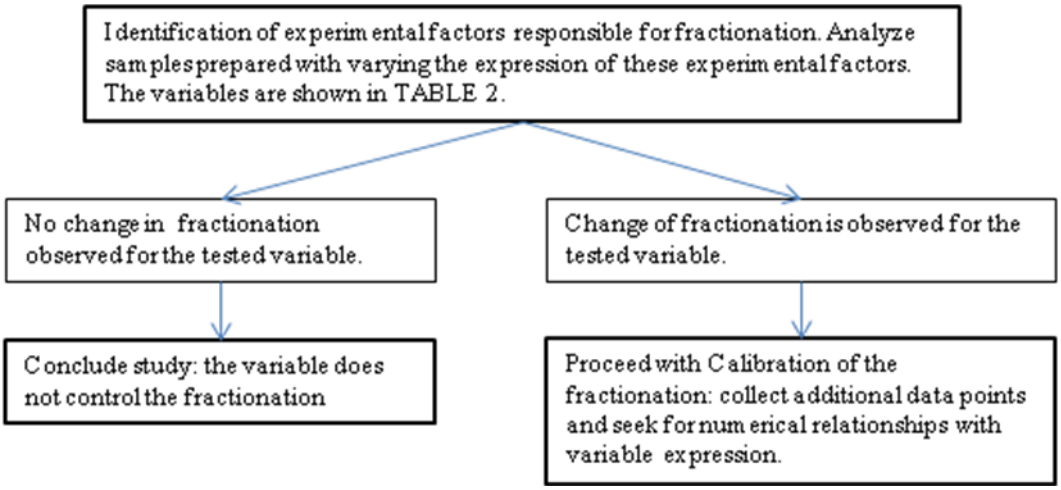
The approach for data evaluation will be similar as in Section 4.3.2. Ideal scenario of fractionation-free performance would have all individual analyses for all treatments falling within the ±range of CSIA uncertainty (Criterion 1) and the t-test results should show that none of the data subsets (individual treatments) are significantly different from the data collected for direct injection of the standard.

4.5 TASK 3: CALIBRATION OF THE ISOTOPE FRACTIONATION IN ADSORBENT TUBES

Task 3 would be necessary if no fractionation-free adsorbent-analyte pairings can be identified (Scheme 2 shows that optional work). However, as discussed in Section 5, Task 3 was not

required based on the absence of fractionation for Carboxen 1016 over a broad range of sampling conditions.

Scheme 2.



4.6 TASK 4: OPTIMIZATION OF THE 2D-GC CONDITIONS

Analyte retention times tend to increase as the GC column is loaded with a larger mass of total sample (including target analytes and non-target compounds). For indoor air in general, the mass of non-target VOCs can be significant, as those compounds are concentrated from large volumes of air. The predicted direction of drift of GC retention times was observed in several of the AFCEE samples, in one case exceeding 30 sec for a column retention time of 15 minutes. This phenomenon is undesirable in 2D applications, because of the precise time setting of the valve link between the two GC columns. If the drift of retention time of the 1st GC dimension (Item 9, Figure 5B) exceeds the time limit set for the valve, part of analyte peak is lost, with major isotope discrimination. While this problem may be to certain extent compensated by increasing the width of heartcut directed from the 1st GC dimension into the 2nd GC dimension, this increases the risk of GC coelution for complex VOCs mixtures. An alternative solution for the problem – reanalysis of the problematic samples with modified timing of the valve events – requires additional replicate tubes and increases the cost of analysis. The purpose of this task was to modify the GC conditions to reduce the drift of the retention time in high non-target VOCs samples without losing the GC resolution, to eliminate the need of reanalysis of the problem samples.

4.6.1 Lab program

The 2D-GC performance is only important for complex samples (e.g., VOCs in indoor air) and the task of optimization can be initiated independently from the adsorbent testing. A column of

identical type as that used in the AFCEE study was acquired (DB-WAX), but with larger diameter (0.5 mm instead of 0.25 mm), as the problems caused by column overload are reduced as the column internal diameter is increased. GC resolution potential of given type of column is inversely proportional to the column's diameter and proportional to its length. To maintain the resolution of the 1st GC dimension, the increase of the column ID has to be compensated by increasing the column length to 60 m (DB-WAX with dimensions of 0.5 mm × 60 m is the maximum available from the manufacturer).
The GC performance was tested for the maximum column ID and length, for normal (recommended by manufacturer) carrier gas flow (2.5 mL/min) at low oven temperature (40°C for TCE and benzene, 50°C for PCE) that is conducive of high degree of GC resolution.

To assess the performance of an improved GC configuration, the functional width of the GC effluent heartcut was defined after analysis of control samples with variable loads of non-target compounds (the non-target mixture is described in Section 4.7.1) (Figure 8). The timing of the heartcut event of the 2D-GC depends on the retention time of the analyte at the exit from the 1st GC column. Direct reading of analyte retention time delay from the chromatograms was not informative, due to on-column focusing of the analytes entering the 2nd GC column. Due to the focusing, the net retention times would be less skewed than those at the exit from the 1st GC column. An indirect approach was used instead:

1. The compound of interest was analyzed without coinjected interferents. The effluent heartcut was positioned close enough to the peak center to result with slight termination of the peak tail. Peak width was recorded as shown in Figure 8A.
2. The heartcut window was reprogrammed to terminate 30 sec. sooner and the compound of interest was reanalyzed without coinjected interferents. Reduction of peak width was recorded due to faster peak termination (Figure 8B). The observed peak width reduction was always lower than the reduction of the heartcut width, due to additional focusing of the peak at the entry of the 2nd GC column.
3. The heartcut window was then reprogrammed to the original settings. The compound of interest was reanalyzed with coinjected interferents. The presence of the interferents resulted with a delay of the peak retention time. The analyte peak width was recorded (Figure 8C).
4. The analyte peak widths were compared among the three tests. Peak width in the third test should be equal or larger than that in the second test if the retention time delay caused by column overloading with non-target VOCs does not exceed 30 sec.
5. The performance of the method was further verified by analysis of real indoor air samples, where the target analytes were present together with complex VOCs matrix.

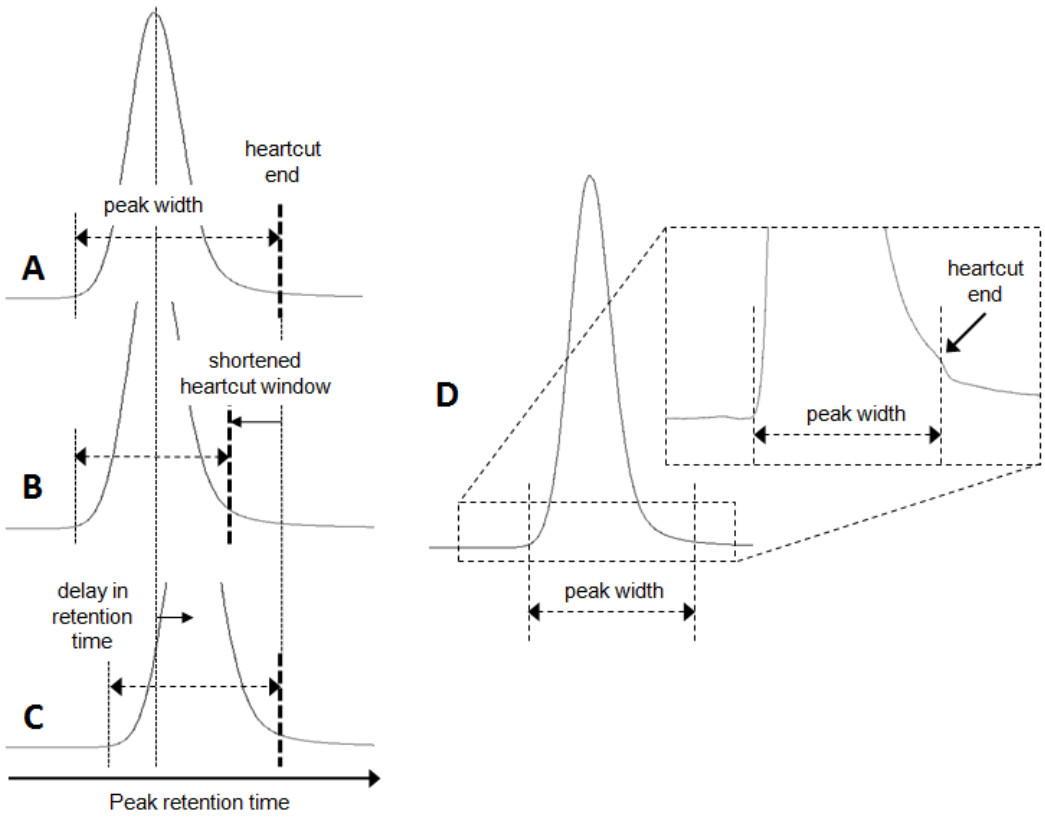


Figure 8. Determination of peak retention time delay caused by co-injected interferents, as applied in 2D-GC optimization. Panels A-C show the principle of the retention time delay assessment by comparison of GC peak widths obtained without interferents, with default heartcut window (A), without interferents, with shortened heartcut window (B) and with interferents, with default heartcut window. Panel D is an illustration of peak width definition. Termination of the GC peak by the heartcut valve results with a characteristic peak geometry anomaly. Note that the anomaly is only visible for highly magnified Y axis. Normal peak integration for the purpose of determination of δ discards the low intensity peak tail and the normal reported peak widths are much shorter than that shown herein. Also see Figure 6 for visualization of the significance of the heartcut definition.

4.6.2 Data analysis

The performance objective of adequate GC separation of the target VOCs from non-target VOCs is validated by visual inspection of the chromatograms and confirmation that the separation was achieved. The proposed quantitative test of comparing the retention time difference for the samples with and without interferents was modified, to account for a dramatic increase of analyte retention time in the modified GC configuration. In the original laboratory plan, a threshold value of 20 sec. was proposed. The program on the 1st dimension GC column employed in this study resulted with retention times of the target analytes of 40, 50 and 55 min (benzene, PCE and TCE, respectively). The GC separation in the present case was more powerful than in the

AFCEE study (retention times <12 min, the width of the effluent heartcut 1.5 min) and it was reasonable to extend the tolerance threshold from 20 to 30 sec.

4.7 EXPERIMENTAL PROCEDURES

4.7.1 Preparation of Samples

Table 4 shows a list of adsorbents with good compatibility with the three target VOC analytes (Based on "A Tool for Selecting an Adsorbent for Thermal Desorption Applications" available online at www.sigma-aldrich.com/supelco-literature). Thermal desorption tubes with Carbopack B were ordered from Supelco catalogue (Carbotrap 100™), Carbopack X and Carboxen 1016 were custom ordered from Supelco (custom-packed tubes are available within 2-3 weeks). Carbopack X and Carboxen 1016 were combined with a 1.5 cm of Carbopack C (at the sample inlet). The function of Carbopack C is to protect the stronger adsorbents from irreversible adsorption of the less volatile non-target VOCs. Carbopack C retains those less volatile VOCs, but it does not retain the three analytes of interest to any significant degree (for 100 L samples, manufacturer's data show retention in the range of 0-20 % of the injected mass), and its inclusion should not compromise the conclusions on the performance of the stronger adsorbent.

Table 4. List of adsorbents identified as compatible with the target VOCs. Three adsorbents selected for detailed study are shown in bold.

Benzene	TCE	PCE
Carbopack B Carbopack X[1] Carboxen 563[1] Carboxen 1000[1] Carboxen 1001[1] Carboxen 1016[1]	Carbopack B Carbopack X Carboxen 569[1,2] Carboxen 1000[1] Carboxen 1001[1] Carboxen 1002[1] Carboxen 1003[1] Carboxen 1016[1] Carboxen 1018[1]	Carbopack B Carbopack X[1] Carboxen 1016[1] Hayesep D Tenax GR[2]

[1]Several adsorbents, in particular in the Carboxen class, are damaged by irreversible sorption of higher molecular mass VOCs. Those tubes were protected by a bed of Carbopack C to intercept those compounds prior to the Carboxen bed. [2]Carboxen 569 and Tenax GR were partially evaluated as part of a preliminary study (Section 4.2).

Target analytes were injected into the adsorbent tubes and flushed by a controlled volume of air, using a manifold depicted in Figure 9. For practical reasons, direct replication of the sampling conditions (continuous sampling of air with uniform, low concentration of the target VOCs) was not attempted. Handling of large volumes of airborne VOCs to deliver net amounts of a few tens to few hundred nanograms amounts of the target species on an adsorbent tube is likely to bias isotope ratios independently from the tested sampling process. One problem that can be

anticipated is that at low mass loadings of the analytes, the losses from sorption on the experimental apparatus would be proportionally large, potentially resulting with additional isotope fractionation, and difficult to maintain constant over the extended period. While the magnitude of such isotope effects would be relatively low and close to the CSIA analytical error, the additional noise in analytical data would complicate identification of the fractionation produced by interactions between the airborne VOCs and the adsorbents.

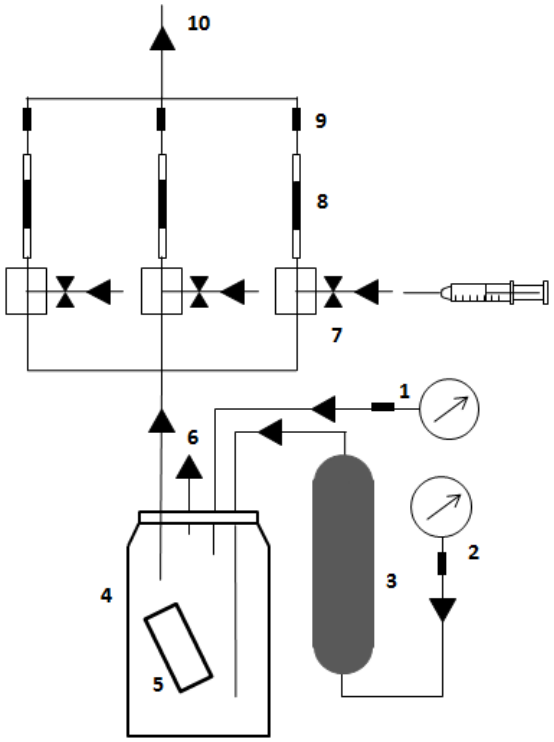


Figure 9. Laboratory apparatus for loading target VOCs into adsorbent tubes.1) & 2) Purified air supply pressure regulators with capillary flow restrictors; 3) Humidifier tank; 4) Mixing chamber; 5) Humidity and temperature sensors; 6) Vent; 7) Injection port; 8) adsorbent tube; 9) Capillary flow restrictors (in this study, the flow was set at 100 mL/min per tube); 10) Flow driven by a vacuum pump. The actual device has been extended for simultaneous loading of 5 tubes.

The samples were prepared by instantaneous loading of the full target mass of the analyte on the adsorbent tube, followed by drawing a required volume of air (a so-called challenge volume). The conceptualization of isotope fractionation occurring during VOCs preconcentration on adsorbent tubes (Figure 4) proposes that the fractionation is caused by analyte breakthrough (selectively more pronounced for one of the isotopomers) or by incomplete desorption, that is also more significant if the analyte resides deeper into the adsorbent bed. Both mechanisms can be tested in the challenge volume approach. In comparison with continuous sampling of diluted vapor, the challenge volume represents the behavior of the analyte increment introduced into the adsorbent tube at the very beginning of sampling, which is also the one most prone to fractionation. Thus, any fractionation observed in a challenge volume experiment, magnifies the fractionation that would be observed in continuous sampling. The conclusions from a challenge

volume test are conservative relative to real sampling of the same volume of air. For testing the impact of non-target VOCs, the adsorbent tubes were pre-injected with the non-target VOCs mixture. Non-target VOCs were then flushed into the adsorbent bed by 0.5 L of air. The combination of non-target VOCs contained fewer chemical species than proposed initially. A mixture on non-target VOCs was prepared with ethanol as the major species, with lower contributions of aromatic, aliphatic and chlorinated hydrocarbons. The full list of the compounds included (weight %):

ethanol – 69 %
n-decane – 4 %
p-xylene – 9 %
MEK – 10 %
n-pentane – 5 %
dichloromethane – 3 %

Based on reference data (NYSDOH, 2006), median concentrations of only a handful VOCs are significant, with the strong predominance of ethanol exceeding the second most abundant compound by an order of magnitude. It was decided that adding additional compounds with broadly similar adsorption/desorption characteristics as those already present would provide no benefit while adding additional difficulty in controlling the chromatographic separation of the analytes.

4.7.2 Isotope Analysis

Figures 4 and 5 show schematic diagrams of CSIA instrumentation. $^{13}C/^{12}C$ and $^{2}H/^{1}H$ isotope ratios of VOCs retained on adsorbent tubes were analyzed after thermal desorption into a GC-IRMS instrument (Thermo Finnigan MAT252 and Thermo Finnigan XL). $^{37}Cl/^{35}Cl$ ratios were analyzed by GC-quadrupole MS (Agilent 5790), using a purge and trap instrument (Eclipse 4660, OI Analytical) with an Air-Tube Desorber Accessory (OI Analytical). The desorber replaces PT sparge vessel and converts the PT unit into a thermal desorption concentrator, with similar functionality to the instrumentation used in TO-17. A tube mounted in the desorber is initially flushed with He to remove moisture and O_2, then the tube is heated and VOCs are purged into the sample concentrator's trap. VOCs collected on the concentrator's trap were transferred onto GC-IRMS/MS.

In standard method, GC separation on single, non-polar phase column (Figure 4) is sufficient. Most of the test samples for adsorbent validation were analyzed using conventional GC. A modified approach was necessary to analyze carbon isotope ratios in certain air VOCs samples. In the past, indoor air samples, and also some of soil vapor samples, showed interfering non-target VOCs that could not be chromatographically resolved from target VOCs. For those samples, 2-D GC separation is necessary (Figure 5b), utilizing a polar phase (DB-Wax) and a non-polar phase (DB-MTBE) in a sequence. 2-D separation is often successful in resolving extremely complex mixtures of compounds, because few compounds have identical retention times on polar and non-polar GC columns. The 2D process requires that a heartcut of the polar DB-Wax column effluent with the compound of interest is transferred on the non-polar DB-MTBE column for secondary GC separation.

For chlorine CSIA the transfer line of the PT is connected to a split-splitless injector of the GC (Agilent 7890) and typically the sample is split by a factor of 20. The GC oven temperature remains constant during data acquisition to stabilize background noise. The detector is set to SIM for acquisition of only two mass fragments: 130 and 132 for TCE or 164 and 166 for PCE. The pairs represent molecular masses of the analytes with ^{35}Cl-only substitution vs. those with one atom of ^{37}Cl. The ratio of integrated peak areas (e.g., for SIM masses 132/130) are converted into the isotope ratios of $^{37}Cl/^{35}Cl$, with mathematical correction accounting for the number of chlorines in the molecule. The $^{37}Cl/^{35}Cl$ of the target analyte is calibrated against a co-injected standard with known $^{37}Cl/^{35}Cl$.

4.7.3 Data presentation and QAQC in CSIA

Isotope ratios determined by CSIA are presented in delta (δ) notation (Equation 1). The sample isotope ratios (e.g., $R_{sample} = {}^{13}C/{}^{12}C$) are normalized to an international standard scale (e.g., VPDB for carbon isotope ratios). Thus, δ units represent the difference between the sample's ratio and the ratio of the international standard, reported in parts per thousand (‰).

$$\delta^{13}C = (R_{sample}/R_{standard} - 1) \times 1000 \qquad (1)$$

QAQC in CSIA is required to control the analytical precision and accuracy of isotope ratio determination. The precision reflects the stability and linearity of the mass spectrometer detector (adversely affected by electronic noise and by fluctuations of water and oxygen present in trace amounts in the mass spectrometer source) and by fluctuations of baseline noise that affects the quality of quantitation of individual isotope peak areas for calculation of isotope ratios. A build-in routine of using internal standard gas for calibration of mass spectrometer output (Item 9, Figure 2) eliminates the problem of uncertain accuracy of the mass spectrometer detector (see technology description). The overall accuracy can be adversely affected by less than ideal thermal conversion of the analyte to the IRMS-amenable surrogate, by the quality of GC peak separation (peak tailing resulting with a portion of analyte mass lost to integration and coelutions resulting with integration of the target peaks together with additional signal added by coeluent) and by isotope species disproportionation by incomplete recovery from sample matrix. The latter applies specifically to environmental samples run by methods involving techniques such as P&T and thermal desorption. Matrix spikes prepared with standards (e.g., TCE, PCE and benzene) of known isotope composition are analyzed under identical conditions as the environmental samples of interest, to determine the analytical bias. GC separation quality poses a separate challenge that cannot be addressed adequately by matrix spikes, because the GC interferents in real samples are usually more abundant and diverse than in a matrix spike. The quality of GC separation has to be assessed by trained operator, who can identify compromised peaks by examination of peak geometry and the geometry of isotope ratio output (Figure 10). Minor coelutions are acceptable (and unavoidable). The net analytical uncertainty should account for all those potential problems, including those caused by minor coelutions and peak integration deficiencies. Stated uncertainty for different isotopes is typically higher than the performance for clean matrix spikes, because it allows for additional factors present in actual samples. Stated uncertainty should be given for specific analytes analyzed by particular method. The performance for the same isotope for different analytes and for the same analyte and isotope for

different analytical methods is not necessarily identical. The values given in this report CSIA (C: ±0.5 ‰; Cl ±1 ‰; H: ±5 ‰) apply to the analytes of interest and the methods of interest.

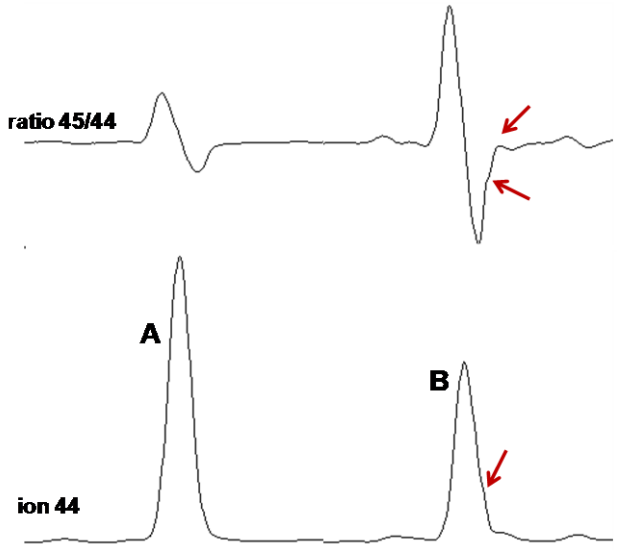


Figure 10. An example of a CSIA chromatogram. The lower trace is a chromatogram drawn for mass 44 ($^{12}C^{16}O_2$). The upper trace is drawn for the ratio of masses 45/44 ($^{13}C^{16}O_2/^{12}C^{16}O_2$). The characteristic sinusoid appearance of the ratio trace results from slightly faster travel of ^{13}C species through the GC column. Compound A is well-resolved, permitting accurate definition of isotope ratio. Compound B overlaps (coelutes) with another unidentified compound, mostly hidden underneath peak B. The coelution can be identified by careful examination of the geometry of the GC peak and the corresponding 45/44 ratio trace (arrows point asymmetries resulting from such coelution).

In the present project, the key question was the determination of the added bias (or an assessment of the reduced precision) caused by incorporation of adsorbent preconcentration and the thermal desorption. This was determined by comparison of analyte isotope ratios obtained from the adsorbent tube samples (δ_{ads}) to those obtained by injection of the same standard material directly into purge gas of the thermal desorption unit (δ_{inj}). The use of the same batches of the standard materials permitted direct comparison of the obtained isotope ratios. The reported values (δ_{norm}) are normalized as shown in Equation 2.

$$\delta_{normalized} = \delta_{ads} - \delta_{inj} \qquad (2)$$

The values of δ_{inj} are averages for days or weeks of analytical instrumentation usage. Typically, a direct injection standard was run in the morning and then after each 3-4 adsorbent tube samples. The analytical precision of the direct injection standard population, defined as the net difference of δ of individual data points from a long-term average was within the stated uncertainty of CSIA (C: ±0.5 ‰; Cl ±1 ‰; H: ±5 ‰). After normalization, a δ that was equal zero would imply no fractionation attributed to the adsorption/desorption process, a positive δ value would imply a

net enrichment of the heavy isotope in the analyte after adsorption/desorption; while a negative δ value would imply a net depletion of the heavy isotope in the analyte after adsorption/desorption.

The primary criterion of fractionation-free performance for given adsorbent-analyte combination was that its normalized δ value should fall within stated uncertainty range for given isotope ratio. A secondary criterion for such performance would be no statistically significant difference (e.g., by t-test) of the isotope ratio results from the adsorbent tube samples from zero (i.e., compared to the laboratory reference analyzed directly). The latter criterion is sensitive to random clustering of data points that cannot be excluded for low *n*, and is also subject to artifactual biases of isotope ratios caused by minor coelutions (background noise that affects the accuracy of isotope ratio measurements). The t-test result of significant difference in data subsets (at 95 % confidence) is therefore of secondary importance and is overridden by the criterion of net difference of isotope ratios lower that the nominal CSIA uncertainty (e.g., for carbon CSIA, the accepted uncertainty is ±0.5 ‰ of δ13C unit).

5.0 RESULTS AND PERFORMANCE ASSESSEMENT

The results are organized by Task. The isotope ratio results for each individual experiment are provided in Appendix A. The results of statistical tests (t-test) are provided in Appendix B.

5.1 TASK 1: INITIAL EVALUATION OF ADSORBENTS

Three adsorbents, Carbopack B, Carbopack X and Carboxen 1016, were initially selected for evaluation. These adsorbents could be expected to have good recovery for benzene, TCE and PCE based on the performance data published by the manufacturer (Table 4). The three adsorbents with three analytes each permitted the preliminary test of nine adsorbent-analyte pairings.

Figure 11 shows the performance of the nine adsorbent-analyte pairings in retaining the analytes and their isotope signatures after a 100 L challenge volume flushing. Only one of the data subsets shows isotope fractionation: for Carboxen X, TCE is measured with major enrichment of ^{13}C (fractionation of +12 ‰, clearly exceeding the C CSIA uncertainty of ±0.5 ‰). The peaks of TCE recovered from Carbopack X were approximately only ½ of the expected value. The enrichment of ^{13}C in the analyte peak would imply that the low recovery was due poor desorption rather than due to analyte breakthrough. The lack of fractionation in the eight remaining adsorbent-analyte pairings was confirmed both by the normalized isotope ratios of the analytes lower than the C CSIA uncertainty (±0.5 ‰). The results from t-test (the difference of the fractionation from zero, see Appendix B) confirmed significant fractionation for the TCE-Carbopack X pairing (p=0.00). In three additional adsorbent-analyte pairings (PCE-Carbopack B, PCE-Carboxen 1016 and benzene-Carbopack X), the *p* values were <0.05, also suggesting a statistically significant fractionation. However, in those cases, the net magnitudes of fractionation well within the C CSIA uncertainty of ±0.5 ‰, and were consistent with normal performance fluctuations of CSIA instrumentation.

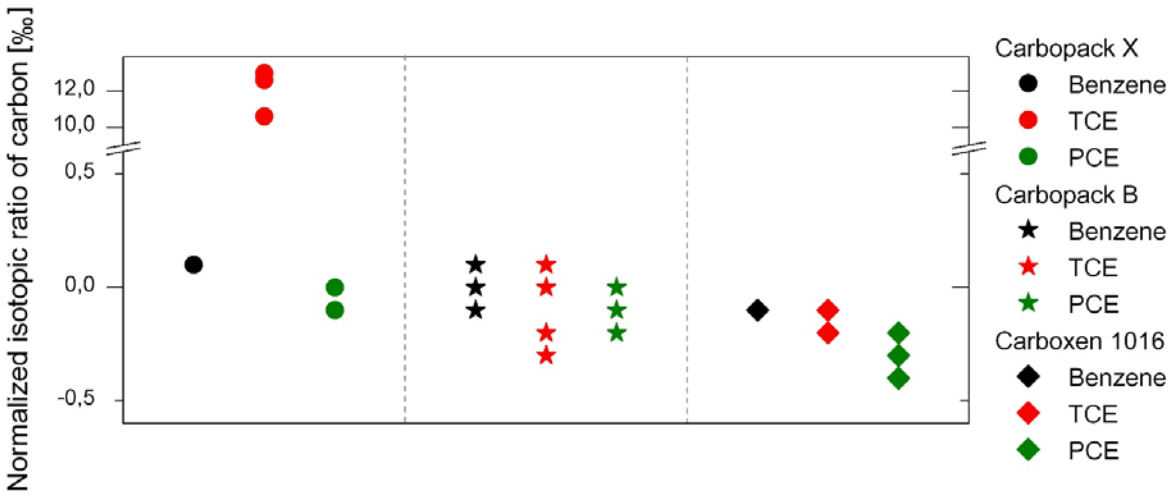


Figure 11. Carbon isotope ratios of benzene, TCE and PCE for 100 L of humidified air, with non-target VOCs present (Treatment T1, Table 3).

Given high success rate of the fractionation-free performance, no additional adsorbents were tested at this stage. Carbopack B and Carboxen 1016 that performed well for the 3 target analytes were retained for further testing.

5.2 TASK 2: VALIDATION OF FRACTIONATION-FREE PERFORMANCE OF SELECTED ADSORBENT-ANALYTE PAIRINGS

The two retained adsorbents were used to study the behavior of the target VOCs under modified adsorbent sampling conditions. The isotope ratios of the target analytes were determined in seven sampling treatments listed in Table 3.

Figure 12 illustrates the analyte recovery for the two adsorbents. The recovery of the analytes after thermal desorption was evaluated by comparison of the analyte peaks obtained after thermal desorption of the samples and by injection of the same mass of the same analytes, directly onto a focusing trap of the thermal desorption unit (Figure 3). While the analyte recovery with Carboxen 1016 was good for all treatments, the recovery of TCE was significantly reduced with Carbopack B in Treatment 2 and 6 (at high air humidity and at sample volume increased to 200 L, respectively), while recovery of benzene was reduced for Carbopack B in Treatment 7 (increased target analyte mass for H CSIA). In all of the instances where analyte recovery was significantly reduced, attendant excessive isotope fractionation were observed, but significant isotope fractionation was also observed in some of the treatments where mass recovery did not appear affected, especially for hydrogen CSIA of benzene. This is not unexpected, because while the recovery of the analyte is controlled by the air/adsorbent partitioning coefficients, the isotope effects are controlled by the difference of those coefficients for the light and heavy isotope species, respectively. The latter produces meaningful isotope effects for differences as low as parts per thousands, which would not significantly affect the net mass of analyte recovered from an adsorbent. There were discrepancies observed in analyte recovery, as compared to the manufacturer's data ("A Tool for Selecting an Adsorbent for Thermal Desorption Applications"

available online at www.sigma-aldrich.com/supelco-literature). Specifically, recoveries for two adsorbent-analyte pairings were significantly lower than in the Supelco study. TCE was poorly retained on Carbopack X (Treatment 1) and Carbopack B (Treatments 2 and 6). For Carbopack X, the recovery was shown in the top performance tier, while for Carbopack B it was in the middle tier. The observed discrepancies might be explained by differences in respective analytical protocols (e.g., the Supelco study utilized dry air without non-target VOCs present, potentially increasing the strength of adsorbent-analyte interactions).

Figures 13 through 18 show the isotope ratios of the three analytes for the seven sampling treatments. The data are plotted in comparison to the formal uncertainty limits of CSIA for given isotope (see Section 4.7.3 for additional discussion of those limits).

Carboxen 1016 showed consistent good performance for all the three analytes in all treatments (Figures 13-18). All averages for isotope ratios within given treatment were within the nominal limits of analytical uncertainty for given CSIA method. Virtually all replicate readings (n≥3 for individual treatment) for the three target analytes prepared in all treatments yielded isotope ratios within the nominal limits of analytical uncertainty. One replicate only, for PCE concentrated from high humidity air (T2), yielded an isotope ratio slightly exceeding the nominal limit of analytical uncertainty.

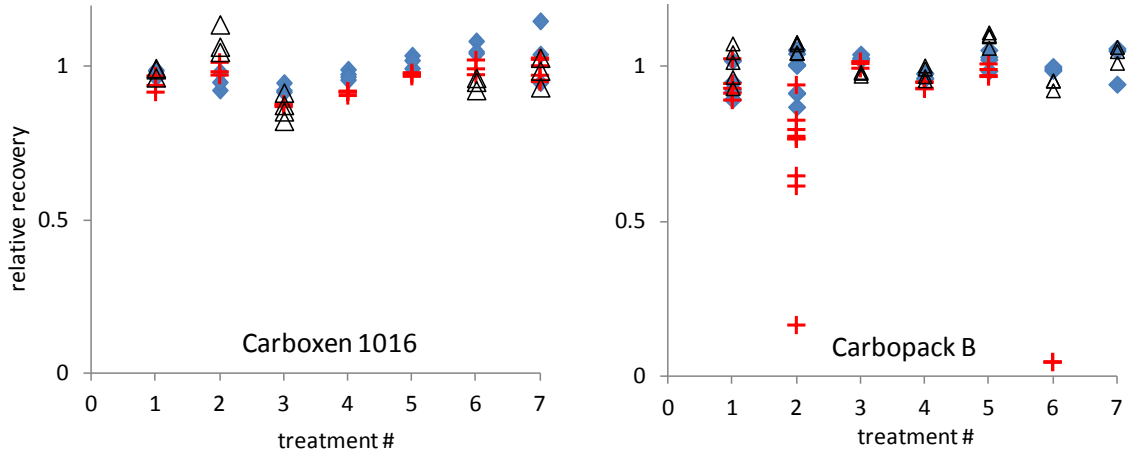


Figure 12. Recovery of target analytes in different treatments (Table 3) for Carboxen 1016 and Carbopack B. Results normalized to 100% (full recovery) by comparison with the responses from standards injected directly onto the thermal desorption unit's focusing trap. (♦) benzene; (+) TCE; (Δ) PCE.

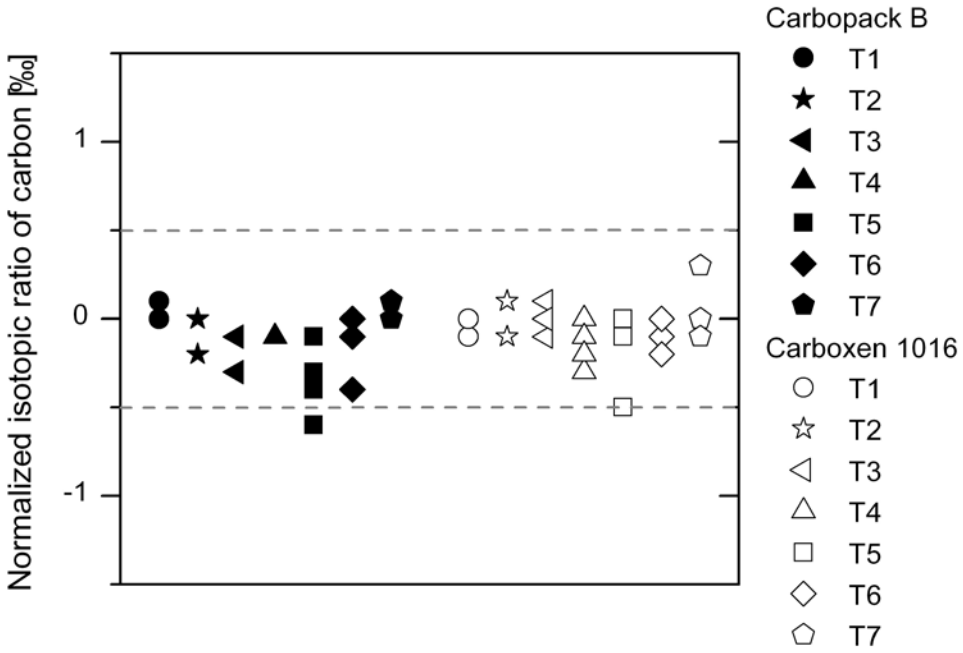


Figure 13. Results for adsorbent validation for carbon isotope ratios of benzene. Dashed horizontal lines represent $\delta^{13}C$ uncertainty of ±0.5 ‰. See Table 3 for treatment list.

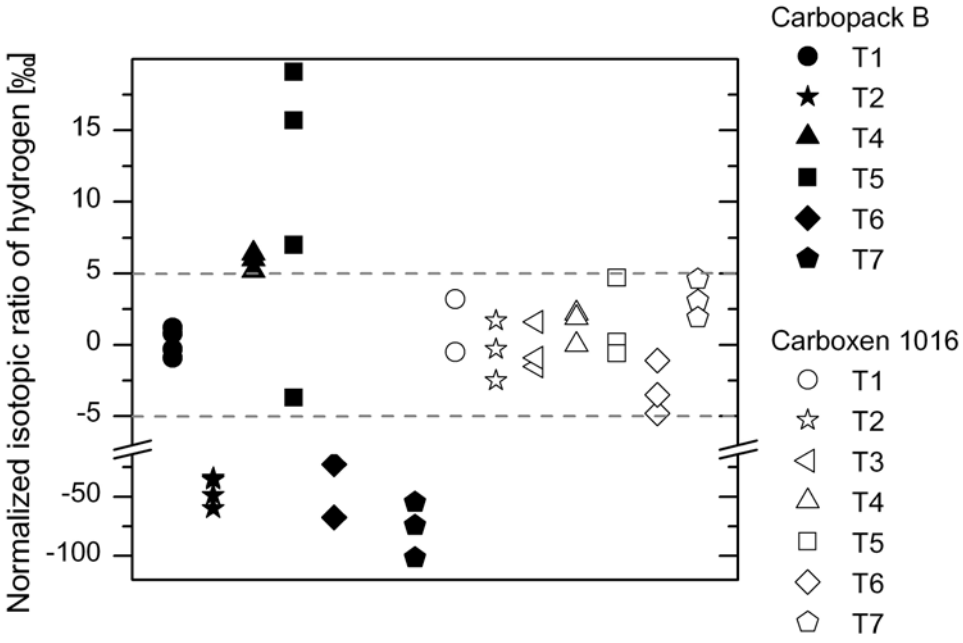


Figure 14. Results for adsorbent validation for hydrogen isotope ratios of benzene. Dashed horizontal lines represent $\delta^{2}H$ uncertainty of ±5 ‰. T3 not performed for Carbopack B (results to date indicated that this adsorbent is not suitable for H CSIA). See Table 3 for treatment list.

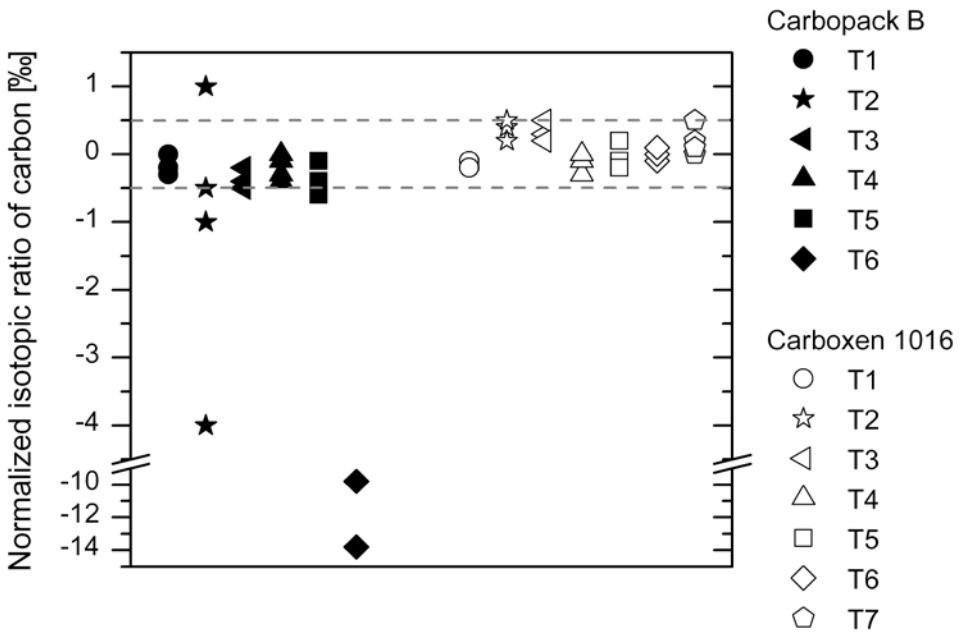


Figure 15. Results for adsorbent validation for carbon isotope ratios of TCE. Dashed horizontal lines represent $\delta^{13}C$ uncertainty of ±0.5 ‰. T7 not performed for Carbopack B (results to date indicated that this adsorbent is not suitable for TCE). See Table 3 for treatment list.

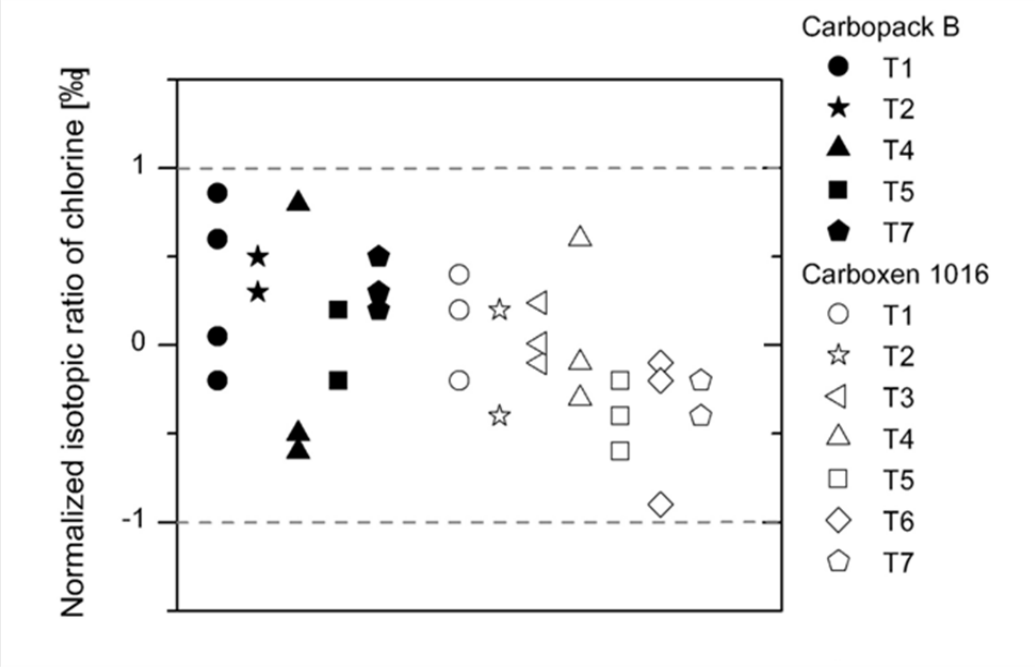


Figure 16. Results for adsorbent validation for chlorine isotope ratios of TCE. Dashed horizontal lines represent $\delta^{37}Cl$ uncertainty of ±1 ‰. T3 and T6 not performed for Carbopack B (results to date indicated that this adsorbent is not suitable for TCE). See Table 3 for treatment list.

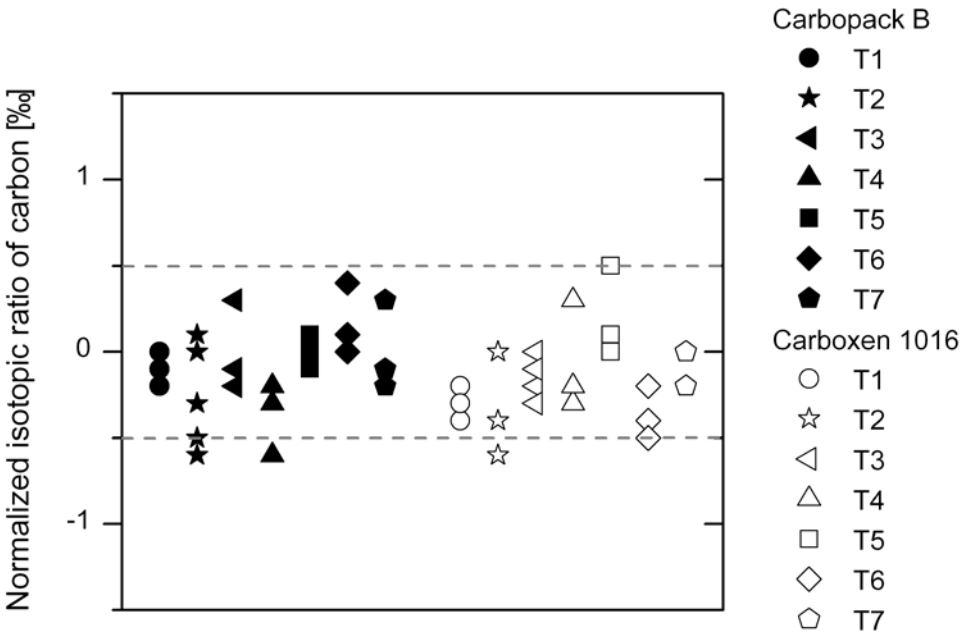


Figure 17. Results for adsorbent validation for carbon isotope ratios of PCE. Dashed horizontal lines represent normal $\delta^{13}C$ uncertainty of ±0.5 ‰. See Table 3 for treatment list.

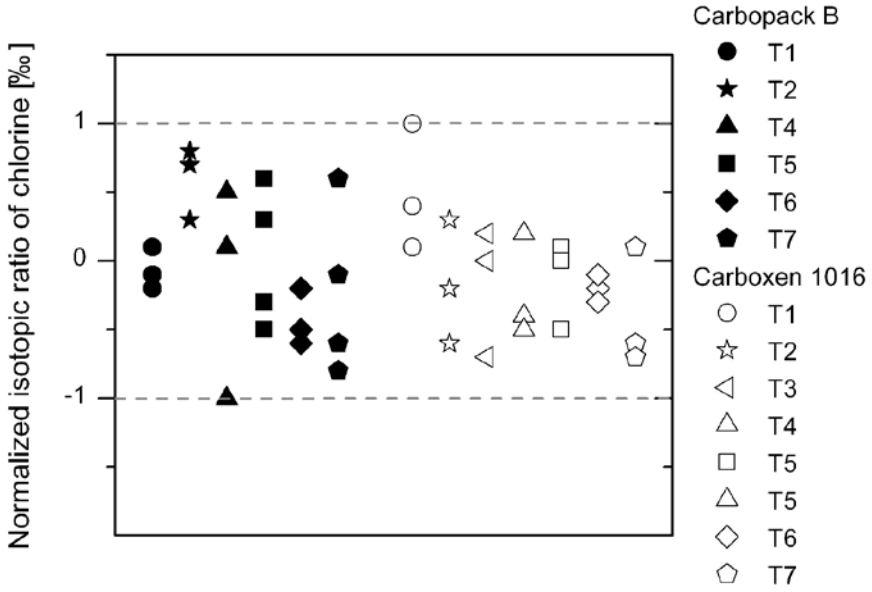


Figure 18. Results for adsorbent validation for chlorine isotope ratios of PCE. Dashed horizontal lines represent normal $\delta^{37}Cl$ uncertainty of ±1 ‰. T3 not performed for Carbopack B. See Table 3 for treatment list.

Carbopack B performed well for analysis of carbon isotope ratios in benzene (one outlier observed for Treatment 5, Figure 13), but significant hydrogen isotope fractionation occurred in all treatments except for T1 (Figure 14). The direction of that hydrogen isotope fractionation varied among the treatments. Following the logic of the conceptual model shown in Figure 4, such variability would suggest that in some treatments the fractionation was primarily caused by analyte breakthrough (preferential breakthrough of the heavier isotope species is consistent with published data on stronger adsorption of the lighter isotope molecules) while in other treatments the fractionation was primarily due to poor desorption (recovery of the heavier isotope molecules was preferred, consistent with weaker adsorption of those molecules).

Carbopack B performance for TCE and PCE was adequate for chlorine isotope analysis in all tested treatments (Figures 16 and 18). Similarly, virtually no carbon isotope fractionation was observed for PCE (Figure 17, with two individual outlier measurements slightly exceeding the ±0.5 ‰ error).

TCE exhibited significant carbon isotope fractionation at high humidity and at 200 L air volume (T2 and T6, Figure 15). Following the logic of the conceptual model shown in Figure 4, the direction of fractionation was consistent with TCE breakthrough at high sampling volume. The scattering of data points for the high humidity treatment (T2), predominantly shows isotope ratio depletion consistent with analyte breakthrough. The different behavior of carbon vs. hydrogen or carbon vs. chlorine isotope ratios is not unexpected, and can be rationalized by the isotope-specific differences in phase partitioning coefficients. For example, organic phase-vapor isotope partitioning coefficients for toluene (no equivalent data for benzene have been published) favor volatilization of ^{2}H (vapor enriched by 4 ‰) while only slight effect occurs for ^{13}C (vapor enriched by 0.2 ‰) (Kuder et al., 2009). Similar contrast in ^{13}C vs. ^{2}H behavior can be expected in the retention of isotope species by adsorption on carbonaceous adsorbents. A large isotope effect for hydrogen translates to higher susceptibility to fractionation even if relatively small portion of benzene breaks through the adsorbent bed or is retained in incomplete desorption. Unfortunately, no experimental data are available on chlorine isotope effects in phase partitioning, to make a direct statement on the C-Cl contrast.

The conclusions based on data clustering within the uncertainty margins of the specific CSIA methods were further tested by statistical analysis. Groups of data points (isotope ratios) were tested for significant difference from zero (zero=ideal lack of fractionation) by t-test. Full data sets for adsorbent-analyte pairings (pooled for all treatments) and subsets for individual treatments were tested vs. zero (Appendix B). With two exceptions (Cl data for PCE for both tested adsorbents), for all tested adsorbent-analyte pairings, including those where the CSIA uncertainty was not exceeded, certain data subsets showed $p < 0.05$, implying statistically significant fractionation. For data sets pooled for all treatments for given adsorbent-analyte pairing, most of the obtained p values were <0.05. In those larger data sets, the results from t-test were driven by the variance contribution from the treatments with largest isotopic bias. As discussed in Section 4.7.3, t-test and similar statistical tools are sensitive to relatively small biases of δ determination. Unless the isotope ratios are determined for ideal chromatograms (not practical in most applications) simple statistics is not productive in data interpretation.

5.3 ADSORBENT TESTING: SUMMARY AND RECOMMENDATIONS

5.3.1 Adsorbent recommendation for sampling TCE, PCE and benzene

The results from Tasks 1 and 2 serve to fully validate the use of Carboxen 1016 for adsorbent sampling of TCE, PCE, and benzene in indoor air and soil gas for CSIA. The study results showed an absence of isotope fractionation over a broad range of sample collection conditions. Based on the study results, isotope fractionation is not expected for the range of field sampling conditions show in Table 5. The results validate the use of Carbopack B for adsorbent sampling of PCE (C, Cl) and benzene (C only). While Carbopack B was not suitable for hydrogen CSIA of benzene, C-only application may be of interest for most indoor samples. Based on the study results, isotope fractionation is not expected for the range of field sampling conditions show in Table 6.

Additional validation work would be required to demonstrate an absence of fractionation for sampling conditions outside the ranges provided in Tables 5-6.

Table 5. Sampling Conditions for Fractionation-Free Performance with Carboxen 1016

Parameter	Validated Range
Target VOCs/isotopes	benzene (C, H), TCE (C, Cl), PCE (C, Cl)
Sample Volume	≤100 L[1]
Sample Collection Rate	≤100 mL/min
Relative Humidity (at 23°C)	10 % - 90 %
Target VOC mass: benzene	30 to 900 ng[2]
Target VOC mass: TCE, PCE	100 to 2250 ng
Non-target VOC mass	0 to 800 ug
Sample Holding Time (at 4˚C)[3]	0 to 14 days

[1] Laboratory study showed an absence of fractionation for sample volumes up to 200L. However, 100L sample volume limit is recommended as a conservative measure to ensure an absence of fractionation; [2] A higher minimum sample mass of 1000 ng is required to measure the hydrogen isotope ratio for benzene. Performance for up to 5000 ng was validated; [3] Storage of samples at room temperature is not recommended.

Table 6. Sampling Conditions for Fractionation-Free Performance with Carbopack B

Parameter	Validated Range
Target VOCs/isotopes	benzene (C only), PCE (C, Cl)
Sample Volume	≤100 L[1]
Sample Collection Rate	≤100 mL/min
Relative Humidity (at 23°C)	10 % - 90 %
Target VOC mass: benzene	50 to 900 ng
Target VOC mass: PCE	100 to 2250 ng

Non-target VOC mass	0 to 800 ug
Sample Holding Time (at 4˚C)[2]	0 to 14 days

[1] Laboratory study showed an absence of fractionation for sample volumes up to 200 L. However, 100 L sample volume limit is recommended as a conservative measure to ensure an absence of fractionation; [2] Storage of samples at room temperature is not recommended.

5.3.2 Recommended Testing Procedures for Validation of Additional Adsorbents or Target Analytes

The application of CSIA to vapor intrusion is expected to be most useful for benzene, TCE, and PCE because these three VOCs are commonly risk drivers at vapor intrusion sites and indoor sources of these VOCs are common. Indoor sources of other chlorinated VOC risk drivers such as 1,1-DCE and vinyl chloride are less common and do not typically result in indoor air concentrations that exceed screening values.

However, if practitioners identify other vapor-phase target VOCs for CSIA, additional laboratory testing would be required to identify a suitable adsorbent for sample collection. Based on the results of this laboratory study, we recommend the following streamlined testing program to evaluate potential fractionation for new analyte/adsorbent combinations:

- 200 L volume test, with humidified air and non-target VOCs present (Treatment 6). This test will test an adsorbent-analyte pairing for fractionation resulting from analyte breakthrough and/or from driving the analyte too deep into the adsorbent layer (in single bed adsorbent tubes possibly making it more difficult to achieve complete desorption; in multi-bed adsorbent tubes by pushing the analyte into a bed of stronger adsorbent prone to irreversible sorption). This test should be performed first, for the isotope species most prone to fractionation (H fractionation > C fractionation > Cl fractionation). If fractionation-free performance is confirmed, additional isotope(s) should be tested for 200 L volume, followed by the two additional tests discussed below. If fractionation-free performance is not achieved, the remaining tests can be avoided and work should focus of another, more suitable adsorbent tube.

- 100 L volume test, dry air and no non-target VOCs present (modified Treatment 4). This test will highlight any problems caused by strong/irreversible adsorption that might not be apparent if water and/or non-target VOCs blocked the strongest adsorption sites. The test should be performed independently for all isotope species of interest, as the absence of fractionation of one isotope ratio does not imply the same for another isotope ratio.

- A 100 L test with humidified air and non-target VOCs present, with increased mass of the analyte (Treatment 7) for the isotope species that is most prone to fractionation (H fractionation > C fractionation > Cl fractionation). The mass increase should be chosen to

match the upper limit of the analyte concentration recommended for adsorbent tube sampling (i.e., the conclusions of fractionation-free performance should not be extrapolated to an analyte mass that is higher than that used in the actual test).

A success in the three tests described above would offer evidence of fractionation-free performance under realistic field sampling conditions. If no fractionation-free adsorbents are identified, additional tests would be required to define the actual uncertainty ranges and/or develop a calibration procedure.

5.4 OPTIMIZATION OF 2D-GC

Retention time delay in the presence of non-target VOCs was assessed for benzene (early eluting peak) and PCE (late eluting peak). In both cases, the delays were estimated by comparison to a simulated peak delay of 30 sec. (baseline data were obtained by programming the heartcut valve to trim 30 sec. of the GC peak tail and cause peak width shortening, see Section 4.6.1 and Figure 8). Figure 19 shows the relationship of benzene peak width with coinjected non-target VOCs mass, for the default heartcut program. The retention time delay (apparent as peak width shortening) was increasing for increasing mass of non-targets. The delay was under 30 sec for the maximum of non-target VOCs mass (1.2 mg). For PCE, only the maximum load of non target VOCs was tested. In that case, the retention time delay was also under 30 sec.

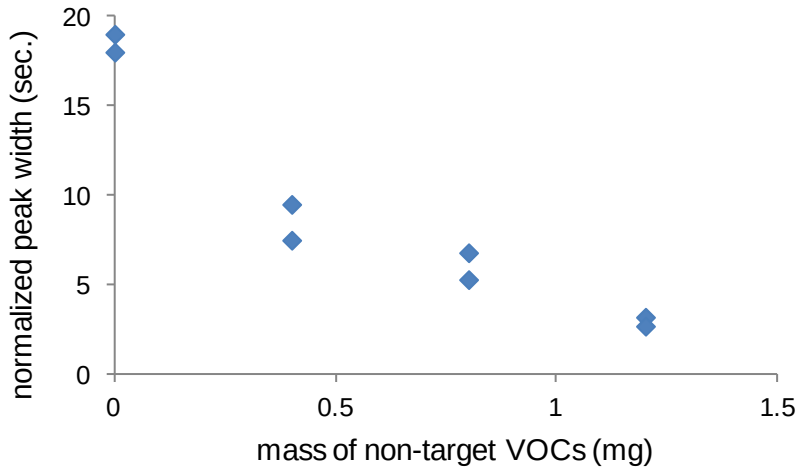


Figure 19. Relationship benzene peak width with coinjected non-target VOCs mass. Peak widths are normalized by subtracting the width for relay window shortened by 30 sec. Normalized peak width of zero corresponds to retention time delay of 30 sec.

The performance of 2D-GC was further validated for complex VOCs matrix collected from residential indoor air. Replicates of indoor air VOCs were collected in tubes with and without pre-spiked with the target VOCs. Unspiked replicates were analyzed by GCMS (full scan mode). CSIA was performed for either spiked or unspiked replicates, depending on the determined mass of the target analytes. Figure 20 shows the chromatogram of an indoor VOCs sample. In that

sample, the indoor air concentration of TCE was negligible and ~100% of TCE originated from the spike ($\delta^{13}C$ -30.8 ‰). After 2D-GC, TCE peak was fully resolved and the isotope ratios determined in 2 duplicates were within ±0.5 ‰ from the expected values. PCE originating from indoor air in the pre-spiked samples accounted for several percent of the total (minor effect on net $\delta^{13}C$ due to mixing of the spike and the indoor source could occur). After 2D-GC, PCE peaks were also fully resolved, and their isotope ratios were within ±0.5 ‰ from the expected values. Figure 21 shows another sample of indoor VOCs collected elsewhere. In that sample, relatively high concentration of benzene was present (approximately 250 ng were present in the unspiked sample). 2D-GC permitted to resolve the benzene peak from the coelutants. The value of $\delta^{13}C$ for indoor benzene was -27.5 ‰.

The 2D-GC approach is fully capable of handling complex VOCs samples. The tradeoff of the approach is the extended time of analysis, required to obtain good separation on two GC dimensions. A typical analytical cycle including thermal desorption and GC is approximately 2 hours. 2D-GC produces a single analyte peak per analytical run, requiring separate runs for each target analyte present in the sample. While it is possible to program multiple valve events to collect multiple heartcuts with more than 1 analyte, this was not tested in the present study. Increasing the number of heartcuts introduced into the 2nd GC dimension increases the possibility of coelutions interfering with the analyte of interest.

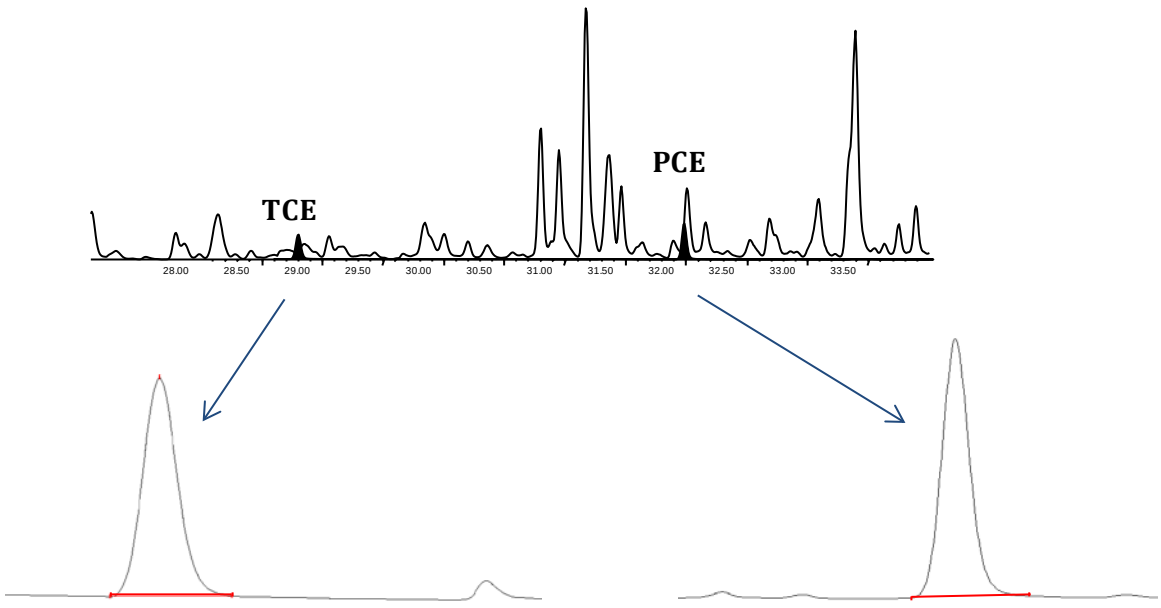


Figure 20. Separation of TCE and PCE by 2D-GC. The upper chromatogram represents a full GCMS scan of indoor air VOCs (100 L at 100 mL/min, Carboxen 1016) with TCE and PCE peaks identified. The lower chromatogram shows 2D-GC separation of TCE from replicate adsorbent tubes with the same VOCs matrix (graphic output from IRMS).

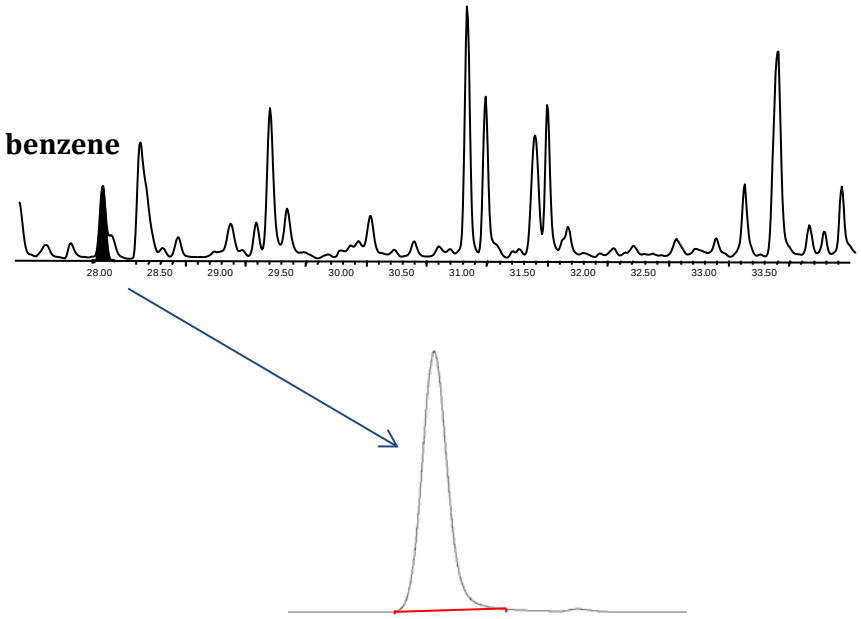


Figure 21. Separation of benzene by 2D-GC. The upper chromatogram represents a full GCMS scan of indoor air VOCs (100 L at 100 mL/min, Carboxen 1016) with benzene peak identified. The lower chromatogram shows 2D-GC separation of benzene from replicate adsorbent tubes with the same VOCs matrix (graphic output from IRMS).

5.5 SUMMARY AND CONCLUSIONS

The objective of the laboratory validation study was to fully validate the CSIA for low concentration vapor samples collected from indoor air and soil gas using adsorbent samplers. Specifically, the objectives were to i) identify an adsorbent that could be used for collection of indoor air and soil gas samples without inducing isotope fractionation effect and ii) develop an optimized 2D-GC method to allow for clean separation of target analytes from non-target VOCs. The results of the laboratory validation study are as follows:

- An optimized 2D-GC separation method has been developed that provides reliable separation of the target analyte from non-target VOCs.
- Carboxen 1016 has been validated as an adsorbent that provides fractionation-free performance for PCE, TCE, and benzene for a wide-range of field sampling conditions.
- If the analysis of additional target analytes is needed, a streamlined laboratory study is recommended to verify fractionation-free performance (See Section 5.3.2)

The results of this laboratory validation study indicate that adsorbent tubes (using Carboxen 1016) can be used to collect indoor air and soil gas samples containing low concentrations of PCE, TCE or benzene for accurate measurement of carbon, chlorine, and hydrogen isotope ratios. Based on these findings, we recommend proceeding with the field demonstration of the use of CSIA to distinguish between vapor intrusion and indoor sources of VOCs.

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Appendix A. Isotope ratio results for TCE, PCE and benzene for each individual experiment. Result shown is difference between isotope ratio for adsorbent tube sample and laboratory reference sample analyzed directly.

Analyte / Sorbent	TCE		PCE		BENZENE	
	C	CL	C	CL	C	H
	Treatment T1					
Carbopack B	0.0	0.9	-0.1	0.1	0.1	0.8
	-0.3	0.1	-0.1	-0.2	0.1	-0.9
	-0.2	-0.2	-0.2	-0.1	0.1	1.2
	0.1	0.6	-0.1	-	0.0	-0.3
	-0.3	-	0.0	-	-0.1	-
Average	**-0.1**	**0.3**	**-0.1**	**-0.1**	**0.0**	**0.2**
Std. Dev.	**0.2**	**0.5**	**0.1**	**0.2**	**0.1**	**1.0**
Carboxen 1016	-0.1	0.2	-0.2	0.4	-0.1	3.2
	-0.1	0.4	-0.4	1.0	-0.1	-0.5
	-0.2	-0.2	-0.2	0.1	-0.1	-0.5
	-	-	-0.3	-	-	-
Average	**-0.1**	**0.1**	**-0.3**	**0.5**	**-0.1**	**0.7**
Std. Dev.	**0.1**	**0.3**	**0.1**	**0.5**	**0.0**	**2.2**
Carbopack X	13.0	-	-0.1	-	0.1	-
	10.6	-	0.0	-	0.1	-
	12.6	-	-0.1	-	0.1	-
Average	**12.1**	**-**	**-0.1**	**-**	**0.1**	**-**
Std. Dev.	**1.3**	**-**	**0.1**	**-**	**0.0**	**-**
	Treatment T2					
Carbopack B	1.0	0.3	-0.6	0.7	-0.2	-34.1
	-1.0	0.5	-0.3	0.3	0.0	-59.7
	-4.0	0.5	-0.5	0.8	-0.2	-48.6
	-0.5	-	0.0	-	-0.2	-35.6
	-3.1	-	0.0	-	-0.3	-
	0.7	-	0.1	-	-0.1	-
	-3.4	-	-	-	-0.1	-
	-2.7	-	-	-	0.1	-
	-12.3	-	-	-	0.2	-
Average	**-2.8**	**0.4**	**-0.2**	**0.6**	**-0.1**	**-44.5**
Std. Dev.	**4.0**	**0.1**	**0.3**	**0.3**	**0.2**	**12.0**
Carboxen 1016	0.4	-0.4	0.0	0.3	*0.1*	1.7
	0.5	-0.4	-0.4	-0.2	*0.1*	-2.5
	0.2	0.2	-0.6	-0.6	*-0.1*	-0.3
	-	-	-	-	*-0.1*	-
Average	**0.4**	**-0.2**	**-0.3**	**-0.2**	**0.0**	**-0.4**
Std. Dev.	**0.2**	**0.3**	**0.3**	**0.4**	**0.1**	**2.1**
	Treatment T3					
Carbopack B	-0.2	-	-0.1	-	-0.3	-
	-0.4	-	-0.2	-	-0.1	-
	-0.5	-	0.3	-	-0.1	-
Average	**-0.3**	**-**	**0.0**	**-**	**-0.2**	**-**

Analyte / Sorbent	TCE		PCE		BENZENE	
	C	CL	C	CL	C	H
Std. Dev.	**0.2**	**-**	**0.3**	**-**	**0.1**	**-**
Carboxen 1016	0.3	-0.1	-0.1	0.2	0.1	-1.5
	0.3	0.0	-0.2	0.0	0.0	-0.9
	0.5	0.2	-0.3	-0.7	-0.1	1.6
	0.2	-	0.0	-	0.0	-
	-	-	-0.1	-	-	-
Average	**0.3**	**0.1**	**-0.1**	**-0.2**	**0.0**	**-0.3**
Std. Dev.	**0.1**	**0.2**	**0.1**	**0.5**	**0.1**	**1.7**
	Treatment T4					
Carbopack B	-0.3	-0.6	-0.2	0.5	-0.1	5.2
	-0.4	0.8	-0.6	-1.0	-0.1	6.4
	0.0	-0.5	-0.3	0.1	-0.1	6.0
	-0.1		-0.3		-0.1	
Average	**-0.2**	**-0.1**	**-0.4**	**-0.1**	**-0.1**	**5.9**
Std. Dev.	**0.2**	**0.8**	**0.2**	**0.8**	**0.0**	**0.6**
Carboxen 1016	-0.3	0.6	-0.3	0.2	0.0	0.0
	-0.1	-0.1	-0.2	-0.4	-0.3	2.2
	-0.1	-0.3	0.3	-0.5	-0.1	1.9
	0.0	-	-	-	-0.2	-
Average	**-0.1**	**0.1**	**0.0**	**-0.2**	**-0.2**	**1.3**
Std. Dev.	**0.1**	**0.5**	**0.3**	**0.4**	**0.1**	**1.2**
	Treatment T5					
Carbopack B	-0.1	0.2	0.1	-0.5	-0.1	19.1
	-0.4	0.2	-0.1	-0.3	-0.3	15.7
	-0.5	-0.2	0.0	0.6	-0.6	7.0
	-0.6		-0.1	0.3	-0.4	-3.7
Average	**-0.4**	**0.0**	**0.0**	**0.0**	**-0.4**	**9.5**
Std. Dev.	**0.2**	**0.2**	**0.1**	**0.5**	**0.2**	**10.2**
Carboxen 1016	0.2	-0.4	0.0	0.1	0.0	0.2
	-0.1	-0.6	0.5	0.0	-0.5	4.7
	-0.2	-0.2	0.1	0.0	-0.1	-0.6
	-	-	-	-0.5	-	-
Average	**0.0**	**-0.4**	**0.2**	**-0.1**	**-0.2**	**1.4**
Std. Dev.	**0.2**	**0.2**	**0.3**	**0.2**	**0.3**	**2.9**
	Treatment T6					
Carbopack B	-13.8	-	0.8	-0.5	-0.1	-22.7
	-9.8	-	0.7	-0.6	-0.4	-67.3
	-9.8	-	0.4	-0.2	0.0	-67.4
Average	**-11.1**	**-**	**0.6**	**-0.4**	**-0.2**	**-52.5**
Std. Dev.	**2.3**	**-**	**0.2**	**0.2**	**0.2**	**25.8**
1016	-0.1	-0.1	-0.2	-0.2	-0.1	-4.8
	0.0	-0.2	-0.4	-0.1	-0.2	-1.1
	0.1	-0.2	-0.5	-0.3	0.0	-3.5
	-	-0.9	-	-	-	-
Average	**0.0**	**-0.3**	**-0.4**	**-0.2**	**-0.1**	**-3.2**
Std. Dev.	**0.1**	**0.4**	**0.2**	**0.1**	**0.1**	**1.9**

Analyte / Sorbent	TCE		PCE		BENZENE	
	C	CL	C	CL	C	H
Carpotrap 302	-	0.2	0.2	-	-	-
	-	-0.1	-0.3	-	-	-
	-	0.6	-0.2	-	-	-
Average	**-**	**0.2**	**-0.1**	**-**	**-**	**-**
Std. Dev.	**-**	**0.4**	**0.3**	**-**	**-**	**-**
	Treatment T7					
Carbopack B	-	0.2		0.6		-101.4
	-	0.5		-0.1		-74.3
	-	0.3		-0.6		-54.6
	-			-0.8		
Average	-	**0.3**		**-0.2**		**-76.8**
Std. Dev.	-	**0.2**		**0.6**		**23.5**
Carboxen 1016	0.0	-0.2	0.0	0.1	0.0	4.6
	0.5	-0.2	-0.2	-0.6	0.3	3.1
	0.2	-0.4	0.0	-0.7	-0.1	1.9
	0.1	-	-	-	-	-
Average	**0.2**	**-0.3**	**-0.1**	**-0.4**	**0.1**	**3.2**
Std. Dev.	**0.2**	**0.1**	**0.1**	**0.5**	**0.2**	**1.4**

Appendix B. P-values for TCE, PCE and benzene for each individual treatment from T1 to T7 and for pooled results from all treatments. Students t-test used to compare sample mean to zero. P-value is probability that mean is equal to zero (i.e., probability that the average isotope ratio for the adsorbent tube samples was the same as for the directly analyzed laboratory reference). See Table 3 for treatment descriptions.

Carboxen 1016

Analyte / Treatment	TCE		PCE		BENZENE	
	C	**Cl**	**C**	**Cl**	**C**	**H**
T1	0.06	0.50	**0.01**	0.20	1.00	0.62
T2	0.04	0.37	0.22	0.53	1.00	0.80
T3	0.01	0.67	**0.05**	0.60	1.00	0.78
T4	0.14	0.75	0.87	0.39	0.10	0.19
T5	0.81	0.09	0.27	0.47	0.32	0.48
T6	1.00	0.16	**0.05**	0.12	0.23	0.10
T7	0.17	**0.04**	0.42	0.27	0.63	0.05
T1-T7	0.07	0.06	**0.01**	0.23	**0.04**	0.46

Carbopack B

Analyte / Treatment	TCE		PCE		BENZENE	
	C	**Cl**	**C**	**Cl**	**C**	**H**
T1	0.16	0.27	**0.03**	0.60	0.37	0.68
T2	*0.07*[2]	**0.03**	0.16	0.08	0.14	***0.01***[2]
T3	0.06	n/a[1]	0.89	n/a[1]	0.13	n/a[1]
T4	0.09	0.85	**0.03**	0.84	1.00	***0.00***[2]
T5	0.03	0.75	0.64	0.97	0.04	*0.16*[2]
T6	***0.01***[2]	n/a[1]	0.30	0.07	0.30	*0.07*[2]
T7	n/a[1]	n/a[1]	1.00	0.51	0.42	***0.03***[2]
T1-T7	**0.01**	0.06	**0.05**	0.72	**0.00**	**0.01**

Carbopack X

Analyte / Treatment	TCE		PCE		BENZENE	
	C	**Cl**	**C**	**Cl**	**C**	**H**
T1	***0.00***[2]	n/a[1]	0.64	n/a[1]	**0.00**	n/a[2]

[1] No data were collected for this treatment. [2] Difference between adsorbent tube samples and laboratory reference was greater than analytical precision (i.e., +/-0.5‰ for C, +/-1‰ for Cl, and +/-5‰ for H)