Appendix B. Sampling and Analysis Methods

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1.1 Time-Integrated Air Sample Collection and Analysis

Time-integrated monitoring methods are used for quantification of the responses of continuous surrogate instruments. The methods include canister sampling for VOC (BTEX, 1,3-butadiene, MTBE), solid adsorbent sampling (for ethanol) and DNPH-coated Sep Pak cartridges sampling for carbonyl compounds. The DRI Organic Analytical Laboratory (OAL) routinely uses these methods and DRI standard operating procedures (SOPs) for sampling and analysis are available upon request. Five to forty minute samples are collected depending on the ME sampled.

Sampling. The DRI custom built sampler used for this study can sample simultaneously a canister, solid adsorbent cartridges (two in parallel), and a DNPH-impregnated Sep-Pac cartridge. The sampler is compact and can be set-up in a vehicle cabin and run from a battery. Prior to use, the sampler is checked for cleanliness by sampling zero air. If the concentration of any targeted compound exceeds 0.1 ppb, the sampler is thoroughly cleaned and re-tested. As noted earlier, a remote switch is installed to allow cabin on/off control of the sampler, no longer requiring access through the van tailgate. The protocol requires that the van engine be off during changes of sampler media.

The canister sampler uses a differential pressure flow controller to supply air to the sampler canister and a calibrated mass flow controller to check the flow rate. Since the actual flow rate is less important than that the flow rate remain constant, additional quality assurance checks on the flow controllers is not necessary. For the 5-minute canister samples an additional battery-operated sampler is used that allows flows up to 3 L/minute to pressurize the 3 L canister.

Both the solid adsorbent and DNPH samplers use a common vacuum pump controlled by mass flow controllers. These controllers are calibrated at the start of the field program by using a primary flow device (e.g. Gillibrator) and then periodically checked in the field to confirm that the flow rates are accurate.

Canister samples. Prior to sampling, the canisters are cleaned by repeated evacuation and pressurization with humidified zero air, as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six sequential cycles of evacuation to ~ 0.5 torr absolute pressure, followed by pressurization with ultra-high-purity (UHP) humid zero air to ~ 20 psig are used. The differences between the DRI procedure and the EPA recommended method are that the canisters are heated in the DRI method to 140°C during the vacuum cycle and that more cycles of pressure and vacuum are used. According to our experience and that of others (Rasmussen, 1992), heating is essential to achieve the desired canister cleanliness. Also, the canisters are kept longer under vacuum cycles, about one hour in the DRI method, as opposed to half an hour in the EPA method. At the end of the cleaning procedure, one canister out of 12 in a batch is filled with humidified UHP zero air and analyzed by the gas chromatograph/flame ionization detection (GC/FID) method. The canisters are considered clean if the total non-methane organic compound (NMOC) concentration is less than 20 ppbC. The actual concentrations of blank-check canisters are typically below 10 ppbC.

Canister samples are analyzed promptly upon receipt of samples from the field, using GC/FID according to guidance provided by the EPA Method TO-15. The GC/FID response is calibrated in ppbC, using NIST Standard Reference Materials (SRM) 1805 (254 ppb of benzene in nitrogen). Based on the carbon response of the FID to hydrocarbons, the response factors determined from these calibration standards are used to convert area counts into concentration units (ppbC) for every peak in the chromatogram. Identification of individual compounds in an air sample is based on the comparison of linear retention indices (RI) with those RI values of authentic standard compounds. A DB-1 column (60 m long 0.32 mm i.d., 1 μm film thickness) is used for these analyses. Breath canisters are quantified for CO2, MTBE, and BTEX by the method of Pleil & Lindstrom using GC/MS.

Blank checks are performed once daily, while performance standards are executed three times per week. Our analysis plan and data processing standards call for the replicate analysis of approximately 10% of the samples. For canisters the replicate analysis is conducted at least 24 hours after the initial analysis to allow for re-equilibration of the compounds within the canister. The replicate analyses are flagged in our database and the programs we have for data processing extract these replicates and determine a replicate precision. Replicate analysis is important because it provides us with a continuous check on all aspects of each analysis, and indicates problems with the analysis before they become significant. A portion (5%) of the canisters is also analyzed by a second independent laboratory (Battelle-Columbus).

Solid adsorbent samples. Ethanol is quantified from solid adsorbent cartridges as well as canister methods. Although MTBE is stable in SUMMA canisters and can be quantified with high precision and accuracy, ethanol is relatively unstable and the replicate analyses of canister samples show a high degree of scatter (Goliff and Zielinska, 2001). Thus, the solid adsorbent samples are necessary for quantification of ethanol. For sample collection we use multibed adsorbent cartridges consisting of Tenax-TA, Carbotrap (or Carboxen) and Carbosieve (Shire et al., 1996; Tsai and Weisel. 2000; Vayghani et al., 1999). Prior to use the Tenax-TA solid adsorbent is cleaned by Soxhlet extraction with hexane/acetone (4/1 v/v) overnight and dried in a vacuum oven at ~ 80 °C. The dry Tenax is packed into Pyrex glass tubes together with Carbotrap and Carbosieve and thermally conditioned for four hours in an oven at 300 °C under nitrogen purge. Approximately 10% of the precleaned tubes are tested by GC/FID prior to sampling. After cleaning, the tubes are sealed with clean Swagelok caps (brass) with graphite/Vespel ferrules, placed in metal containers with activated charcoal on the bottom, and kept in a clean environment at room temperature until use.

After sampling at monitored flows of 200-300 ml/minute, tube samples are analyzed by a thermal desorption-cryogenic preconcentration method, followed by high-resolution GC/MS. A Chrompack Thermal Desorption-Cold Trap Injection (TCT) unit is used for sample desorption and cryogenic preconcentration. The compounds of interest are quantified by MS, using the response factors of authentic standards, prepared at five different concentrations with a static dilution bulb.

Carbonyl compounds. Formaldehyde and acetaldehyde are collected with Sep-Pak cartridges that have been impregnated with an acidified 2,4-dinitrophenylhydrazine (DNPH)

reagent (Waters, Inc), according to the EPA Method TO-11A. When ambient air is drawn through the cartridge at nominal flow rates of 1 L/min, carbonyls are captured by reaction with DNPH to form hydrazones, which are separated and quantified in the laboratory using HPLC (Fung and Grosjean, 1981). The ambient measurement results are subject to various artifacts due to sorbent interactions with ozone so ozone is removed with a honeycomb denuder coated with sodium carbonate/sodium nitrite/glycerol mixture (Koutrakis, et al., 1993). After sampling, the cartridges are eluted with acetonitrile. An aliquot of the eluent is transferred into a 1-ml septum vial and injected by autosampler into a high performance liquid chromatograph (Waters Alliance System) for separation and quantization of the hydrazones (Fung and Grosjean 1981).

1.2 BTEX by Solid Phase Microextraction (SPME)

1.2.1 Sampling

Carboxen/(poly)dimethylsiloxane (CAR/PDMS) coated (75 μm) quartz fibers are used for 10-minute BTEX sampling. SPME is a passive method, thus the rate of the fiber uptake is controlled by the diffusion rate of the analytes to the fiber. In a stationary environment without air movement, a concentration gradient is formed in the boundary layer between the fiber and the surrounding environment. This situation occurs during fiber calibration in a static system, such as a Tedlar bag. However, in an outdoor environment there is always some air movement and the sorption rate will be higher in this situation, since the thickness of the boundary layer will be smaller. This phenomenon explains some of the differences observed between canister and SPME samples collected in summer 2002. To improve the agreement between these methods the Summer 2003 SPME samples were obtained using the experimental set up in Figure 1. The outlet of the SPME sampling bulb was connected to the Tenax media sampling pump. Active sampling at low constant air flows was a suitable solution of outdoor field sampling variability on windy days. With these modifications, wind speed influence is avoided and a common air stream is being sampled by all instruments. The SPME was exposed to the air stream at a fixed flow rate of about 300 ml/min. The sampling bulb temperature is not controlled.

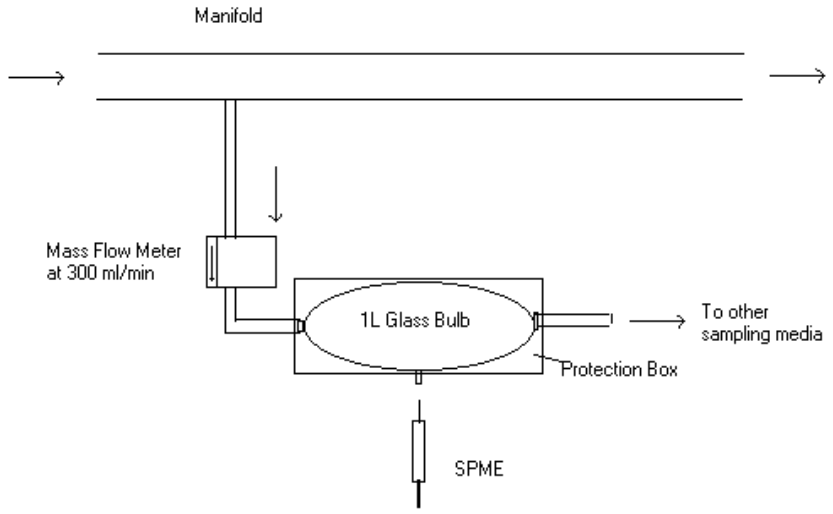

Figure 1. SPME Sampling System Set Up

1.2.2 Analysis

All SPME BTEX samples are analyzed in a mobile laboratory with a Model 8610C SRI Instruments GC equipped with a heated injection port suitable for SPME desorption, a CP-Sil 5 (Varian, Inc.) capillary column (60m, 0.32mm i.d.), and a PID detector. The heated flash vaporization injector is maintained at 250°C and the PID at 150°C. The column temperature was programmed at 60°C for 2 min, 8°C/min to 165°C (held for one minute), and then 45°C/min to 240°C. The helium carrier gas flow rate was 3 ml/min.

Blanks and calibration checks are performed daily on the SRI GC in order to determine the performance of the instrument. Fibers are kept in the injector port throughout the sample run to guarantee that the entire sample was desorbed and to begin the conditioning of the fiber. Fibers are further cleaned in a fiber conditioner at 300°C for at least one hour. One fiber per batch of 5 is checked for cleanliness after conditioning. The fiber conditioner consisted of a 70 cm x 16 cm stainless steel container with 5 ports and a Watlow heater/temperature controller capable of maintaining temperatures in the 200-300° C range. A helium flow of approximately 10 ml/min is maintained during fiber conditioning. Testing showed that the same fiber can be reused up to 40 times absent breakage of the fiber or failure of the fiber mounting mechanism.

The SRI GC is calibrated with 1 µl injections of liquid standards prepared in pentane with BTEX at different concentrations (1, 5, 10, 20, 40, 50, and 100 ng/µl). Carboxen/PDMS fibers are calibrated by introducing the SPME fiber for a defined time into a flowing standard gas containing the calibration component under the same flow-through conditions used for field sampling). The fiber is then analyzed by GC/PID. SPME gas calibrations are done throughout the study as necessary. BTEX calibration is performed with certified gas standards at different concentrations (20, 80, 100 and/or 200 ppbv for each compound).

The dependence of the SPME uptake rate on the sample flow rate is shown in Figure 2. The response changes logarithmically and reaches a plateau region after approximately 0.038 cm/s when changing flow has a lesser effect on the amount of extracted mass. Optimal flow was determined to be 0.038 cm/s. The linear velocities studied were low (0.0044-0.1126 cm/s) enough to characterize a "quasi static" environment. The flow profile showed two distinctive zones in Figure 2. In the first zone (0-0.0665 cm/s) mass transfer is controlled by diffusion through the well-developed fiber boundary layer; in the second zone (0.0665 cm/s and higher) transfer is controlled by diffusion through the fiber pores.

Sampling was performed within the plateau region where the SPME response is not greatly affected by changes in the flow.

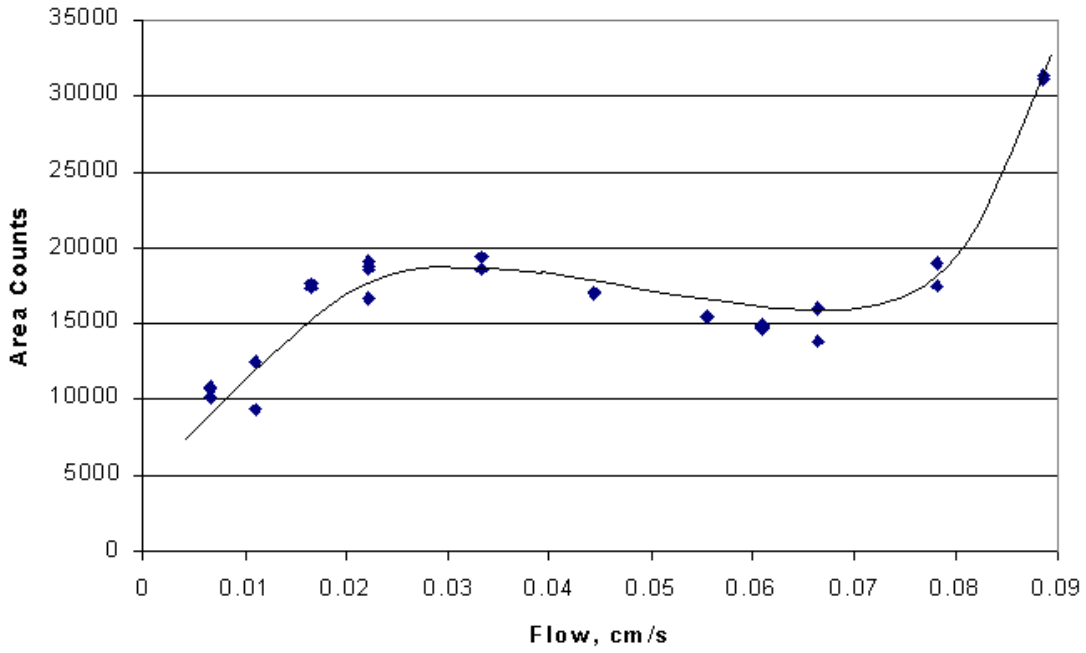

Figure 2. SPME Flow Profile

Sampling temperature and humidity are also important parameters affecting the SPME data. Temperature correction factors are obtained in the laboratory. The sampling bulb is temperature controlled with a cooling/heating system. Temperature inside the glass bulb is measured with a thermocouple. For introducing humidity, a heated injection port is added before the glass bulb entrance in order to inject water with a syringe pump to produce the desired relative humidity (Tuduri, et al., 2001; Nelson, 1992; Martos, P. and J. Pawliszyn, 1997, and Lodge 1989).

Chai and Pawliszyn, 1995, performed several experiments to determine the influence of relative humidity (RH) on the 100 μm PDMS partition coefficient (Boy-Boland, 1998). RH usually decreases the response factor (Kfg) of each individual compound. The decrease of the response is dependent on temperature. At lower temperatures humidity has a larger effect on the response factor. The highest effect of humidity was observed for a 0°C-10°C temperature range for 0% to 25% RH. Changes in the area counts at 0°C-25°C for 25%-75% RH were almost negligible. It is understood that humidity affects the fiber response because water at high concentrations competitively adsorbs into the coating of the fiber. Some compounds are less affected by humidity than others.

The 75 μm Carboxen/PDMS fiber showed no effect with RH at 100 ppbv of BTEX concentration. Experiments at 25°C and 12.5°C determined that RH does not affect the fiber uptake of BTEX compounds significantly. Figure 3 shows toluene response at 100 ppbv for different RH. All the other BTEX species behaved similarly. Data for BTEX showed a standard deviation between 5 to 13% for the range of humidity analyzed, 10% to 80% RH. Sensors are accurate as long as there is no condensation of water, which may happen above 85% RH). These differences in the response of the fiber are within the precision of the method. Low RH effects on the fiber sensitivity may be due to the low concentration ranges used for calibration. At low BTEX concentrations, water is probably not an important competitive molecule. More research in this area is suggested.

SPME Carboxen/PDMS coated (75 μm) fibers are used with portable or manual samplers. When manual samplers are used, the tip of the needle is closed with a septum or Teflon tape (Martos and Pawliszyn, 1997 and Chai and Pawliszyn, 1995). Prior to sampling, the pre-cleaned fibers are kept at ambient temperature within an activated charcoal protector. This storage method has been tested in the laboratory and BTEX backgrounds are stable up to 48 hours in storage following cleaning (the longest tested period). After sampling, fibers are kept in sealed Mylar bags inside a cooler with dry ice. Samples are analyzed 4-10 hours after sampling, on average, with a minimum of 1 hour and a maximum of 20 hours between sampling and analysis.

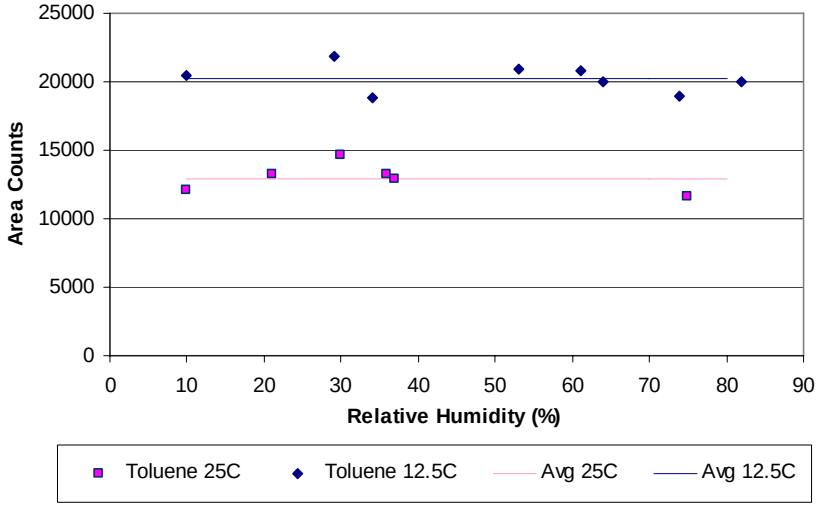

Figure 3. Humidity Effect in GC/PID response for a 100 ppbv BTEX standard at 25ºC and 12.5ºC (with a standard deviation of 5% for the 12.5 °C and 8% for 25 °C from the respective mean)

1.3 Continuous Methods

The continuous Kore MS200 is used to monitor BTEX on a one-minute basis, sampling during the initial 10 second portion of each 60 second period. This instrument uses a time-of-flight mass spectrometer to separate compounds of interest. Rather than using a gas chromatograph, this instrument uses a software solution and a library of 70 eV electron ionization fragmentation patterns to apportion the contribution of each parent species to the time-of-flight (TOF) mass spectrum recorded by the instrument. The software program does not distinguish between specific isomers so xylenes and ethylbenzene are reported together. The inlet uses a polydimethylsiloxane membrane preferentially to allow non-polar organic compounds into the analyzer while impeding polar species and air components to maintain the vacuum inside the analyzer chamber. The instrument performed well during the pilot studies and early field work, comparing favorably with the canister measurements for most samples, although it became increasingly unreliable in subsequent field studies. Given the corroborative role proposed for this device, we do not believe the information provided by this instrument, while desirable, is necessary to fulfill the goals of the screening study.

Carbon monoxide is monitored continuously by the Langan T15 electrochemical monitor for CO and by a nondispersive infrared (NDIR) analyzer. The response time of Langan T15 instrument is slower than the response of the infrared-based instruments. Prior to each period of field measurement the instrument is calibrated using a zero-air generator and

span gas to provide two reference points encompassing the expected range of concentrations anticipated during actual testing. The two-point calibration procedure is as follows:

1. Allow instrument to stabilize for a minimum of 15 minutes.
2. Record ambient concentration as determined by the instrument.
3. Connect inlet lines from the instrument to a zero-air source (for a passive sampler use the flooder cap provided by manufacturer) and check for a flow rate of >1 lpm with rotometer.
4. Let instrument stabilize, record current baseline, then adjust zero.
5. Connect inlet lines to a tank of span gas with an appropriate CO concentration for anticipated range and verify flow rate
6. Let instrument stabilize, record current reading, and adjust span to correct value.
7. Re-connect instrument to zero-air source, let stabilize and check baseline zero reading.
8. Repeat steps 4-7 if necessary.
9. Check a third concentration level with span gas if available.

During field measurements the passive sampler is checked against the reference unit, which has automatic baseline stabilization and an internal zero-air source. Baseline readings will be recorded at the beginning and end of each sampling day. If significant deviations are observed a re-calibration will be performed.

RAE Systems Model PGM-7240 (ppbRAE) portable PID monitors are used to continuously monitor ambient VOC levels in high end microenvironments. The monitor is sensitive to organic and inorganic gases that have an ionization potential of less than 10.6 eV, which includes most compounds of interest in this study. It does not respond to light hydrocarbons such as methane, ethane, propane, and acetyleneor to CO or formaldehyde.

A Continuous Formaldehyde Monitor was purchased from Alpha-Omega Power Technology, Ltd. (Albuquerque, NM). The Alpha-Omega (AO) a wet instrument that utilizes the Hantzch reaction, absorbing formaldehyde in acidified water, reacting it with 2,4-pentanedione and ammonia to form a cyclized product, 3,5-diacetyl-1, and 4-dihydrolutidene, which is continuously detected by fluorescence. The method is sensitive and highly specific for formaldehyde.

1.4 Breath Collection and Analysis

Breath is collected from technicians who participate in a scripted exposure. Since this study requires the use of human subjects, the final protocol was reviewed by an Institutional Review Board that is certified with the National Institute of Health.

Technicians were instructed to avoid exposure to materials that may compromise the exposure assessment prior to and during the scripted exposures. This includes avoiding alcohol ingestion (ethanol) and cigarette smoke for at least 3 days prior to the scripted exposures. Breath samples collected before the exposure were used to assess background levels in the technician.

The test subject takes the three breath samples. One sample is taken before initiating ME sampling for background purposes; the second sample, ten seconds (timed with a stopwatch) immediately after completing an active refueling task or experiencing a measured peak exposure in another ME, and the third sample 1 minute immediately following the second sample. The 3rd backup sample is analyzed in case there is a problem with the second sample. The technician takes a 1-liter canister, places the tube in his mouth, and breathes smoothly and regularly through the mouth around the tube until a resting breath pattern is established. At the end of a normal exhalation, the technician closes the mouth, opens the canister valve, and continues to expel the expiratory reserve. The canister vacuum will collect 1 L of the expiratory reserve. When the flow stops, the technician closes the canister valve to capture the sample (Pleil and Lindstrom, 1995; 2002). Breath samples are collected in 1 L silico-steel steel canisters (Restek, Inc). .

Gas Chromatography-Mass Spectrometry. The analysis of VOC in breath samples is conducted as described by Pleil and Lindstrom (1995, 2002). Prior to the commencement of sampling, the CO_2 level in alveolar breath of all technician subjects is measured using GC/FID. Since the FID does not respond to CO_2, this species is converted to methane by a methanator, positioned after the GC column, but ahead of the FID. Three breath samples are collected and analyzed, and the mean CO_2 value is used for further comparison. After breath sample collection, the CO_2 is measured using the same method. The target VOC (MTBE, 1,3-butadiene, ethanol, BTEX) is measured using a GC/MS technique. The GC/MS system includes an Entech 7100 preconcentrator, a Varian 3800 gas chromatograph with FID and column switching valve, and a Varian Saturn 2000 ion trap mass spectrometer.

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