

Materials and Methods

An airflow, temperature, and humidity controller (Miller-Nelson HCS-501, Assay Technologies, Livermore, CA) was used to condition the carrier air for the AGS. The carrier air was routed through a series of tubes inside the environmental chamber (model KB030-AA-DA, Darwin Chambers Co., Saint Louis, MO). The environmental chamber was used to control the temperature of the experiment. The carrier air temperature and humidity were measured with a sensor (S-THB-M002, Onset Computer Corporation, Bourne, MA) inside the environmental chamber. Additionally, temperature, pressure, and flow rate were measured with a flow meter (model 4043, TSI Incorporated, Shoreview, MN) to confirm the readings of the Miller-Nelson controller and environmental chamber. Atmosphere conditions were 50% relative humidity (RH), 20 °C, with a linear air velocity of 0.3 m/s across the samplers as it flowed through the sampling column.

All VOCs were analytical laboratory grade. Chemicals were placed in gas-tight syringes (Hamilton Company, Reno, NV). A syringe pump (Cole-Parmer, Vernon Hills, IL) was used to control the flow from the syringe. The syringe was connected to polyether ether ketone (PEEK) capillary tubing that was routed to a glass column where the volatile organic compounds (VOC)s evaporated in a stream of carrier air. The glass column was connected to a 2-liter glass mixing chamber (DWK Life Sciences LLC, Millville, NJ), then through a three-way valve that directed the atmosphere to a sampling column (Ace Glass, Vineland, NJ) or exhaust. The sampling column was a 2.54 cm (1-inch) diameter by 61 cm (24-inch) length glass tube with 12 sampling ports spaced at 5 cm intervals along the length of the column. The option to direct the air VOC mixture to the exhaust allowed the sampling ports to be opened to load samplers without exposing the samplers or laboratorians to VOCs. The carrier air containing the VOC vapors exited the sampling column and was directed to a fume hood. The evaporation and sampling components of the systems were contained inside of a temperature-controlled environmental chamber. During the generation, a Fourier-transform infrared (FTIR) gas analyzer (DX4105, Gasmeter OY, Finland) was used to monitor for stability of VOC concentrations in the generated atmospheres.

Samples of VOC atmospheres were collected on coconut shell charcoal (CSC) sorbent media in glass tubes (Anasorb CSC, Lot #2000, SKC Inc., Eighty Four, PA). Samples were collected simultaneously in sets of 4 four sorbent tube samplers per run (except where noted). The CSC sampling tube locations were selected from the twelve ports on the sampling column to cover a range of sampling proximities and locations along the sampling column. Sorbent tube samplers were placed in the ports of the sampling column so that the sampler opening was positioned in the center of the sampling column. A threaded insert was used to compress an O-ring, which created a seal between the sorbent tube and the sampling column. The glass CSC sampler tubes were connected via flexible tubing to critical orifices, and then to a vacuum manifold. The sampling flow rate was controlled by the critical orifices (Triple adjustable flow, SKI Inc., Eighty Four, PA) connected with a vacuum pump

(MZ 2 NT, Vacuubrand Inc., Essex, CT). Flow rates of air through the critical orifices with representative CSC sample tubes inline were measured using a flowmeter (Defender 510 DryCal, Mesa Labs, Lakewood, CO).

The atmospheres of n-heptane at 40, 400 and 800 ppmv were approximately 0.5 times the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) of 85 ppmv, the Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) of 500 ppmv, and the Immediately Dangerous to Life or Health (IDLH) of 750 ppmv, respectively. In a study of n-heptane concentrations of 40, 400 and 800 ppmv, the 40 ppmv and 400 ppmv samples were generated then collected at a rate of 40 mL/min for a duration of 120 minutes, while the 800 ppmv samples were collected at 40 mL/min for a duration of 60 minutes. Six CSC samplers were used to simultaneously sample the atmospheres at each of the generated concentrations.

For the remainder of the experiments, VOC atmospheres were generated and sampled in sets of 16 runs, where 4 CSC samplers were used in each run. Atmospheres containing 40 ppmv n-heptane were generated, then sampled at a rate of 50 mL/min for 30 minutes on CSC samplers for a 1.5-liter sample volume with replicates of 16 runs of 4 samplers each.

A mixture of benzene, toluene, ethylbenzene, and o-xylene (BTEX) in an equimolar solution was used to generate atmospheres at a target concentration of 0.1 ppmv for each compound, which was sampled at a rate of 100 mL/min for a duration of 60 minutes. BTEX samples generated at 0.1 ppmv were chosen because of the 0.1 ppmv REL for benzene.

Ten VOCs (mesitylene, benzene, chloroform, ethylbenzene, n-heptane, o-xylene, tetrachloroethylene, p-xylene, toluene, and trichloroethylene) in an equimolar solution were used to generate atmospheres at a target concentration of 0.1 ppmv each. Atmospheres containing the 10 VOC mixture were generated and then sampled at a rate of 50 mL/min for 1 hour, equating to a total of 3-liter sample volumes collected on the CSC sorbent tube.

Identical dynamic AGS systems were constructed at two laboratories, designated Laboratory A and Laboratory B. The n-heptane concentration study and the BTEX set were generated and sampled at Laboratory B. The n-heptane 16 run set and the 10 VOC set were generated and sampled at Laboratory A, with each 16 run set done by separate laboratorians. Analysis of all samples was done at Laboratory B.

The CSC sampling tube media were desorbed and analyzed by gas chromatography-flame ionization detection (GC-FID) with a Phenomenex ZB-1 column (60 m X 0.32 mm ID 1- μ m film thickness) following procedures listed in NIOSH Method 1500. As part of the quality control done during the analysis of samples, two laboratory control spikes (LCS) were made on CSC tubes. The desorption efficiency as mean bias from the recovery of the two spikes was used to correct the results of the analysis.

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Dataset 1.

n-Heptane was obtained from Sigma Aldrich (Burlington, MA). The single component *n*-heptane atmospheres at 40, 400 and 800 ppmv concentrations were convenient to generate concentrations, with the significance that they were approximations adjacent to 0.5 times the NIOSH recommended exposure limit (REL) of 85 ppmv and an immediate danger to life or health (IDLH) of 750 ppmv and the OSHA permissible exposure limit (PEL) of 500 ppmv.

Benzene, toluene, ethyl benzene, and xylene (BTEX) samples were generated at 0.1 ppmv each of the components (which is relevant to the 0.1 ppmv REL for benzene) and collected at a rate of 100 mL/min for the duration of 60 minutes. The CSC sampling tube media were then desorbed and analyzed by GC-FID with a Phenomenex ZB-1 column (60 m X 0.32 mm ID 1- μ m film thickness) following procedures listed in method NIOSH 1500.

The percentage recovery was the mass observed from the analysis of the CSC samples divided by the mass expected given the generation system settings, and sampling conditions.

Dataset 2.

For the 10 VOC mixture (at 0.1 ppm each compound), atmospheres were sampled at a rate of 50 mL per minute for 1 hour, equaling a total of 3-liter sample volumes collected on the CSC sorbent tube. . The CSC sampling tube media were then desorbed and analyzed by GC-FID with a Phenomenex ZB-1 column (60 m X 0.32 mm ID 1- μ m film thickness) following procedures listed in method NIOSH 1500.

The percentage recovery was the mass observed from the analysis of the CSC samples divided by the mass expected given the generation system settings, and sampling conditions. The mass observed from analysis was corrected versus the results of the laboratory control spikes.

Dataset 3.

As part of the QC procedures during the analysis of the CSC samples (via GC-FID) laboratory control spike, blind spikes, and customer sample replicate samples were analyzed in replicate. The laboratory control spikes, and the blind spikes were prepared in the carbon disulfide desorption solution.

