

THERMAL EXTRACTION AND ANALYSIS OF ATMOSPHERIC SEMIVOLATILE ORGANIC COMPOUNDS FROM MULTICAPILLARY COLLECTION DEVICES

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Introduction

Several technologies exist for sorptive sampling of semivolatile organic chemicals (SOCs) from ambient air including hi-vol samplers, passive samplers, and low-volume sorbent tubes. We have designed, built, and tested low-flow rate ¹ (13 L min⁻¹) and high-flow rate ² (300 L min⁻¹) diffusion denuders for collection of trace SOC from ambient air and extraction using thermal desorption methods. The diffusion denuders developed in our research group offer advantages over existing methods in applications in which it is desirable to minimize detection limits with a relatively small sample volume and to separate gaseous from particle-associated SOC. In conventional solvent-extraction methods, a small fraction of the concentrated extract is introduced into the gas chromatograph (GC). Extraction by thermal desorption allows introduction of the entire sample into the GC at one time, meaning that sample volume can be reduced by as much as a factor of 100 relative to conventional solvent extraction methods. The samplers may be used for short or long duration sampling depending on analyte, temperature, and temporal resolution desired. For example, short sampling times are necessary for micrometeorological SOC flux measurements because atmospheric stationarity must be maintained during sampling ³. For indoor air sampling it is advantageous to use quiet, low-flow-rate diaphragm pumps and sample volumes much less than the room volume to avoid depletion of analytes and low-biased concentrations ^{4,5}. Our diffusion denuders are designed to be used within a multicapillary collection device (MCCD) sampling system. The MCCD consists of a diffusion denuder followed by a filter, followed by an additional diffusion denuder or sorbent bed. This arrangement is designed to avoid artifacts caused by adsorption of gas-phase analytes onto the filter and to capture analytes volatilized from particles captured on the filter. The use of polydimethylsiloxane (PDMS) stationary phase as a sorbent in our diffusion denuders enables extraction of captured gas-phase analytes by thermal desorption. A further advantage of PDMS samplers is that breakthrough can be predicted as a function of analyte properties and ambient temperature using GC retention time measurements and chromatographic theory ⁶.

This paper focuses on recent efforts to improve signal-to-noise ratio in electron capture detection through development of a gas-phase cleanup method. Organic compounds in air are subject to photochemical reactions in the presence of oxidizers including hydroxyl radical, ozone, and nitrate radical, which lead to the addition of oxygen-containing functional groups to organic compounds. This background matrix of oxidized organic compounds can interfere with chromatographic separations and with electron capture detection. A method was developed to separate nonpolar analytes from the oxidized organic background matrix in a thermal desorption method by packed-column gas chromatography on silica gel.

Materials and Methods

A high-flow rate diffusion denuder was designed using a modeling approach ⁶ with the goal of achieving 2- to 3-hour breakthrough-limited sampling times at 300 L min⁻¹ for relatively volatile SOC such as hexachlorobenzene (HCB). The high-flow denuders were constructed of deactivated stainless steel honeycombs with dimensions of 4-in outside diameter, 0.041-in cell diameter, 4-in depth. The honeycombs were deactivated with Sulfinert coating (Restek, Bellefonte, PA), then coated in our lab with cross-linked and bonded PDMS stationary phase (RTX-1, Restek). Anodized aluminum sampler housings hold the diffusion denuders and filter holder in the MCCD and seal the flow path with PTFE gaskets. A mass-flow controlled blower motor (Tisch Environmental, Village of Cleves, OH) provides flow through the sampling train. Inlets were designed to protect the samplers from rain during sampling as well as to maximize coarse particle transmission.

Methods described by Tobias et al. ¹ to thermally extract SOC from low-flow denuders were modified to develop a thermal extraction method for high-flow denuders. Thermal extraction of high-flow denuders is performed in a custom-fabricated, Sulfinert-deactivated (Restek, Bellefonte, PA), stainless steel vessel. Diffusion denuders were thermally extracted at 230 °C and a N₂ carrier gas flowrate of 3 L min⁻¹ into cooled, Sulfinert-deactivated stainless steel minitubes (4 mm ID, 130 mm bed length) containing PDMS-coated GC

packing media (Restek, Bellefonte, PA). The contents of the minitubes were then cleaned by gas-phase thermal elution through minitubes packed with silica gel (Davisil, 35-60 mesh, 150 Å pore) into minitubes containing the PDMS-coated packing media at 80 mL min⁻¹ flowrate of N₂ and 270 °C for 30 min. The minitubes containing the cleaned extract were thermally extracted into the cooled programmable temperature vaporization inlet of an Agilent 6890 GC equipped with electron capture detection (ECD) for analysis using the thermal desorption unit described by Tobias et al.¹ at a helium flowrate of 80 mL min⁻¹ and 300 °C. A hot gas spike apparatus is used to introduce surrogate standards, internal standards, and calibration standards into minitubes and diffusion denuders¹. The GC is calibrated by spiking authentic standards into minitubes, followed by transfer into the GC. Analytes are identified by relative retention time, and quantified by relative response using multi-level calibration curves.

After preliminary experiments indicated that gas-phase elution through silica gel showed promise as a cleanup method, the adsorption model described by Goss⁷ was employed in an effort to quantitatively predict retention of analytes in the gas-phase cleanup process:

$$\log(K) = aA + bB + lL - 8.47 \quad (1)$$

where K = adsorption constant for a given adsorbate (m³/m²), a, A = adsorbent hydrogen bond base, adsorbate hydrogen bond acid interaction parameter, b, B = adsorbent hydrogen bond acid, adsorbate hydrogen bond base interaction parameter, and l, L = adsorbent, adsorbate van der Waals interaction parameter. The constant -8.47 is derived from the standard state of adsorption. The constants A, B , and L are the solute molecular interaction parameters used in the solvation model of Abraham and co-workers⁸. These temperature-independent molecular interaction parameters have been determined for many organic molecules, and are available in the literature⁸⁻¹⁰. Goss separated the adsorbent parameters (a, b , and l) into an adsorbent property and an empirical coefficient; here they are simply used as temperature-dependent empirical coefficients. The values of the adsorbent parameters are determined in experiments in which the adsorbent is used as stationary phase in a GC system, and the observed retention of a compound is a function of its adsorption behavior⁷. Adsorption constants for adsorbates with known A, B , and L are determined from the retention volume, which is computed as the product of the net retention time and the corrected flow rate of the carrier gas. Methods described by Poole¹¹ were used to determine the corrected flow rate, including corrections for temperature, pressure drop across the column, and vapor pressure of water in the soap-film flow meter.

A minitube packed with silica gel was set up in an aluminum block heater using an Agilent 6890 GC to provide a constant flow rate and to sample the column effluent for analysis by ECD. The hot gas spike apparatus was attached to the head of the minitube column for analyte injection. The smallest detectable analyte mass was used to determine retention times. The minitube was conditioned at 300 °C in flowing, dry helium prior to performing experiments at 200, 250, and 300 °C. Two flow rates (80 and 15.4 mL min⁻¹) were tested at each temperature to ensure flow-rate independence (adsorption equilibrium). A set of 15 compounds was used to determine a, b , and l parameters with known values of A, B , and L ranging from 0-0.69, 0-0.68, and 1.76-10.14, respectively. Adsorbent parameters were determined at 200, 250, and 300 °C by using multiple linear regression to minimize the sum of squared error between modeled (Eq. 1) and measured K by varying a, b , and l .

Results and Discussion

The experiments to determine the adsorption parameters of silica gel resulted in a goodness of fit between modeled (Eq. 1) and measured K characterized by R² (n) values of 0.99 (55), 0.98 (32), and 0.86 (62) at 200, 250 and 300 °C, respectively. Hydrogen-bond base (a) and acid (b) interactions contributed significantly to retention on silica gel at 200 °C (Figure 1). The strength of the hydrogen bonding interactions decreased with temperature more rapidly than the van der Waals interaction (l), such that at 300 °C hydrogen bonding contributed little to retention.

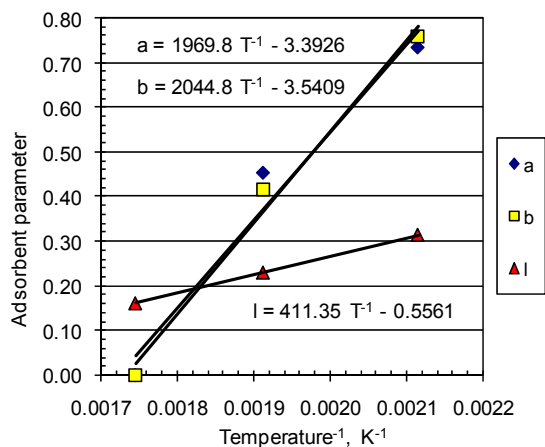


Figure 1: Adsorbent parameters for silica gel at 200, 250, and 300 °C.

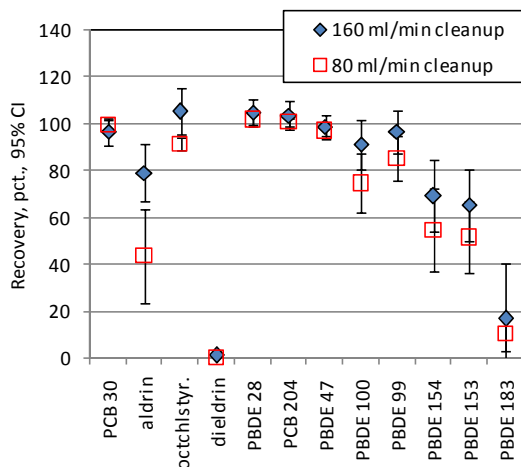


Figure 2: Recovery of analytes through the gas-phase cleanup method at two elution flow rates.

A suite of 174 SOCs of interest including organochlorine pesticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) was tested for recovery through the cleanup method. Standards were hotspiked into minitubes, processed through the cleanup method, and thermally transferred into the GC. Recovery was determined relative to instrument response resulting from direct transfer of hotspiked minitubes into the GC (without cleanup). A subset of these data are shown in Figure 2; complete results are reported elsewhere¹². Recovery through the cleanup method was correlated to the sum of hydrogen donor/acceptor parameters ($A+B$) for each analyte, with values <0.3 giving recoveries between 80 and 120 % for most analytes, and values >0.3 giving complete removal from the sample, for example, dieldrin in Figure 2. By optimizing flow rate during cleanup, it was possible to obtain acceptable recoveries for analytes as involatile as pentaBDEs ($L=12.2$), e.g., BDEs 99 and 100 in Figure 2. Recoveries between 80 and 120 % were obtained for all PCBs tested, penta and lesser-brominated BDEs, HCB, and octachlorostyrene.

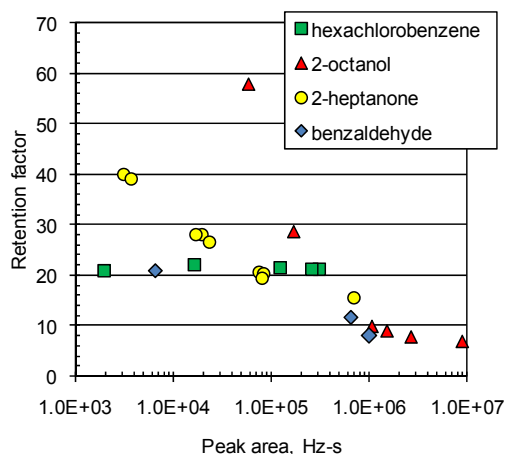


Figure 3: Retention on silica gel vs. adsorbate concentration (approximated by peak area) for adsorbates of varying polarity at 200 °C. Retention factor is the ratio of analyte net retention time to the retention time of an unretained tracer.

While the adsorption parameters shown in Figure 1 elucidate the mechanisms of retention on silica gel and the varying polarity of silica gel with temperature, these adsorption parameters failed to predict the strong retention of small quantities (~ 500 pg) of polar analytes observed in the cleanup method. For example, dieldrin ($A=0$, $B=0.65$) is predicted to elute prior to PBDE 99 based on retention times calculated from Eq. 1 (with a , b , and l from Fig. 1), but dieldrin was retained longer than PBDE 99 in the cleanup method (Fig. 2). Adsorption isotherms for polar compounds on silica gel were found to be nonlinear, that is, adsorption was much stronger at low adsorbate concentration. Retention for nonpolar compounds was independent of adsorbate concentration, while retention became increasingly concentration dependent as the sum of adsorbate hydrogen bonding parameters increased. This trend is demonstrated in Figure 3 for hexachlorobenzene ($A=B=0$), benzaldehyde ($A=0$; $B=0.39$), 2-heptanone ($A=0$; $B=0.51$), and 2-octanol ($A=0.33$; $B=0.56$). Therefore, the model of Eq. 1 could not predict relative retention in the cleanup method because the parameters a and b are concentration dependent for silica gel. Nonlinear

adsorption isotherms can be caused by a heterogeneous surface with both strongly and weakly adsorbing sites⁷.

A practical implication is that polar interferences may be partially transmitted through the cleanup method if they are heavily loaded into the silica gel column.

Development of the gas-phase cleanup method was critical to successful application of the high-flow MCCDs to ambient air sampling with thermal extraction. An example partial chromatogram is shown in Figure 4 from a 22.5 m³ (71 min.) ambient air sample collected on 29 April, 2008 (4.7 °C, 39 % RH). Similar samples collected and analyzed without the gas-phase cleanup method overloaded the ECD and required solvent backwashing of the column to re-establish the baseline. Several of the analytes identified in Figure 4 (HCB, PCBs 16, 18, 22, 28, 31, 33) are among the most frequently detected by conventional hi-vol sampling at the nearby Integrated Atmospheric Deposition Network site for Lake Superior in Eagle Harbor, Michigan, with geometric mean concentrations of 1.6 to 5 pg m⁻³ (PCBs) and 61 pg m⁻³ (HCB)¹³. The gas-phase cleanup method has also been applied to low-flow MCCD samples of ambient air, indoor air (11-84 % RH)¹² and air-surface exchange flux measurements (85-89 % RH)¹⁴. Water is eliminated during the first transfer step because it is not significantly retained in a ~15 °C minitube packed with hydrophobic media. No adverse effects of humidity have been observed. Addition of the cleanup to the low-flow MCCD method resulted in improved surrogate recoveries, improved precision, and reduced method detection limits^{12,14}.

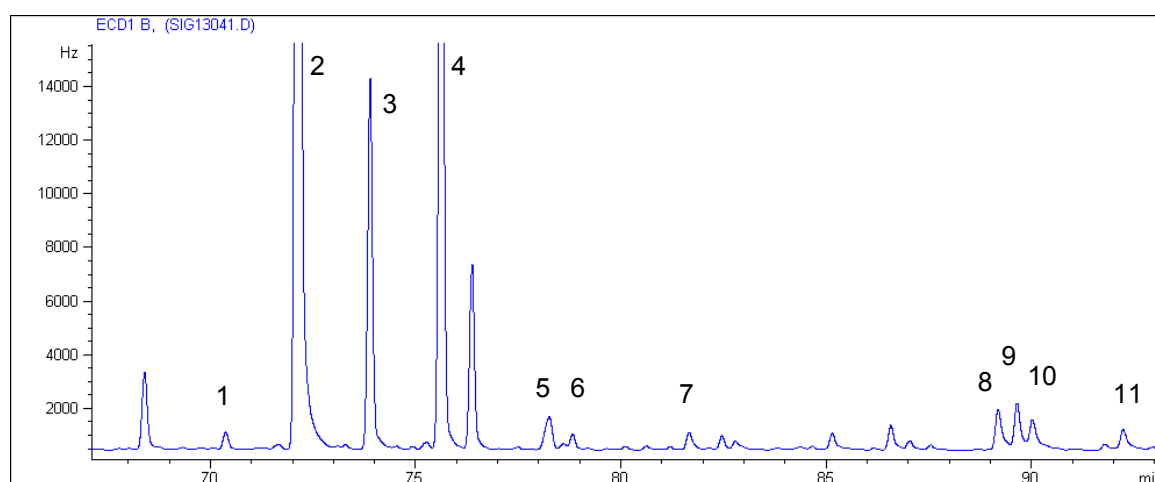


Figure 4: ECD chromatogram of a 22.5 m³ high-flow MCCD ambient air sample collected in Houghton, MI and processed through the gas-phase cleanup. Peak identification: PCB 8 (1), HCB (2), surrogate PCB 14 (3), internal standard PCB 30 (4), PCBs 18 (5), 17 (6), 16 (7), 31+53 (8), 28 (9), 33+20 (10), and 22. (11).

Acknowledgements

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