

Evaluation of a valveless thermal desorption system for organic aerosols and vapors

Transfer lines and preconcentration module

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Abstract

Semivolatile organic compounds (SVOCs) are distributed in the atmosphere between the gas- and aerosol-phases. The low vapor pressures of some SVOCs makes thermal extraction and transfer through gas chromatographic (GC) systems difficult. We evaluated a programmable temperature vaporization (PTV) GC inlet, which served as the preconcentration module, and four open-tubular capillaries (Silcosteel- and Siltek-treated stainless steel, Silcosteel-treated stainless steel coated with 100% dimethylpolysiloxane, and deactivated fused silica) as transfer lines in a valveless, whole-sample analytic system. Thermal extraction of C₉–C₃₆ *n*-alkanes at 300 and 320 °C from fused silica and quartz wool in the PTV inlet was equally efficient. Adsorptive losses of C₂₂–C₃₆ *n*-alkanes to stainless steel surfaces that protruded into the PTV inlet were suspected. Thus, treatment of the outer surfaces of transfer lines is recommended for effective thermal transfer of SVOCs. Transfer efficiencies began to decline after *n*-C₂₄, *n*-C₂₈, and *n*-C₃₀ in Silcosteel-treated stainless steel, deactivated fused silica, and Siltek-treated stainless steel transfer lines, respectively. Thus, quantitative recovery at 320 °C of compounds with vapor pressures less than about 3×10^{-8} Pa is not expected in valveless SVOC thermal desorption systems that use Siltek-treated stainless steel transfer lines and fused silica or quartz wool as preconcentration substrates.

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1. Introduction

Many organic substances associated with aerosols are semivolatile and thus are distributed in the atmosphere between the vapor and particle phases [1–6]. Quantitative organic molecular analyses of semivolatile organic compounds (SVOCs) are needed to (1) investigate atmospheric chemistry and air quality [7], (2) evaluate effects of Earth's climate on radiative forcing [8,9], (3) reconcile sources of atmospheric organic matter [10,11], and (4) assess risks to human and environmental health from materials such as persistent bioaccumulative toxic compounds [12] and fine particles [13–17].

Thermally extracting whole samples of atmospheric aerosols into a gas chromatograph (GC) is an effective analytic method for determining organic molecular composition [18,19]. However, recovery of polar molecules and nonpolar organic com-

pounds with more than 26 carbon atoms with this technique may not be quantitative [20]. In addition, the polyurethane foam and XAD-2 resin currently used in air samplers to capture vapor-phase SVOCs [21,22] are not amenable to thermal desorption. Recently developed air samplers instead use diffusion denuders fabricated from a bundle of fused silica capillary columns coated with 100% dimethylpolysiloxane to adsorb the organic vapors and to allow the particles to pass through to a filter, where they are collected [23–26]. The organic compounds are then thermally extracted from the denuder and filter into a GC for analysis.

Vapor pressures of the SVOCs are much lower than the vapor pressures of volatile organic compounds (VOCs) and thus thermal transfer of SVOCs in analytic systems is difficult. Analytic systems for VOCs typically contain a preconcentration substrate and switching valve [see, e.g., 27]. To prevent adsorptive losses of high-molecular weight substances, SVOC analytic systems have been designed without valves and analytes are instead preconcentrated on the cooled head of the analytic column in the GC [18]. However, to prevent excessively high column head pressures in systems without preconcentration inlets, gaseous

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flow rates during thermal desorption are typically restricted to 100 mL min^{-1} or less. Recently, a valveless, whole-sample analytic system for SVOCs has been reported [24–26]. The analytic system includes a thermal extraction module, an open-tubular capillary to transfer the analytes to the GC, and a programmable temperature vaporization (PTV) inlet to concentrate the analytes from the carrier gas stream and inject them onto the analytic column. The thermally extracted analytes are preconcentrated in the GC inlet because gaseous flow rates during extraction are typically $500\text{--}750 \text{ mL min}^{-1}$ making on-column preconcentration infeasible [25]. Thus, quantitative transfer of analytes through the open-tubular capillary to the GC inlet and quantitative thermal extraction of SVOCs from the preconcentration substrate (e.g., Tenax-TA) are essential.

Whole-sample analysis eliminates extraction of the collection substrate with an organic solvent. In addition, if two-dimensional GC (2D-GC) is used as the analytic tool, preanalytic separation of the sample extract into organic compound classes by liquid/solid chromatography is unnecessary for some sample matrices [28–30]. Eliminating tedious sample preparation steps enables high-throughput analyses with improved analyte recoveries and greater sensitivities. Thus, a whole-sample analytic scheme for SVOCs allows extensive temporal and spatial characterization of the organic molecular composition of the atmosphere with significant savings in analytic costs.

We evaluated the performance of a preconcentration inlet and four open-tubular capillaries as transfer lines for a whole-sample analytic system that uses valveless thermal extraction of SVOCs from denuders and aerosols. An homologous series of *n*-alkanes was selected as the performance test mixture because these compounds occur in the atmosphere with a broad range of carbon atoms (11–36), and they are nonpolar [2,31]. Thus, transfer of the *n*-alkanes through the capillaries would be affected mostly by temperature and essentially dependent on compound vapor pressure. Polar substances, which compose a significant fraction of atmospheric organic matter, are difficult to recover by thermal extraction. In addition, they are not effectively transferred through analytic systems without chemical derivatization of the polar moieties. If thermal transfer of the *n*-alkanes through the analytic system is not effective, the technique is similarly expected to not be effective for polar substances that are derivatized.

2. Experimental

The PTV inlet (CIS-4; Gerstel, Baltimore, MD, USA) of a Model 6890N GC with a flame ionization detector (FID; Agilent Technologies, Palo Alto, CA, USA) was used as the preconcentration module. Liquid nitrogen cooling of the PTV inlet allows analyte preconcentration over a wide range of temperatures. Fused silica and quartz wool (Alltech, Deerfield, IL, USA) were selected as inlet packing materials because they were expected to release fewer organic substances upon thermal desorption than organic polymers like Tenax-TA. Also, $\text{C}_2\text{--}\text{C}_{12}$ VOCs that are preconcentrated on fused silica wool are completely recovered by thermal extraction [32]. An *n*-alkane calibration mixture (Restek, Bellefonte, PA, USA) containing

n- C_9 and even-numbered $\text{C}_{10}\text{--}\text{C}_{36}$ *n*-alkanes, each at a concentration of $1000 \mu\text{g mL}^{-1}$ in dichloromethane, was diluted to $10 \mu\text{g mL}^{-1}$ for use as a performance evaluation standard. To evaluate the packing materials, $1 \mu\text{L}$ aliquots of the standard were injected by syringe, through the septum head of the PTV inlet using the hot needle, solvent flush technique. This particular injection method was used to quantitatively inject the highest-boiling homologs of the *n*-alkane mixture.

Open-tubular capillaries ($33 \text{ cm} \times 530 \mu\text{m ID}$) selected for the investigation included the following: Siltek- and Silcosteel-treated stainless steel (Restek), Silcosteel-treated stainless steel coated with a $0.25\text{-}\mu\text{m}$ -thick film of 100% dimethylpolysiloxane (MXT-1; Restek), and deactivated fused silica (Alltech). The outer surfaces of pre-cut Siltek- and Silcosteel-treated stainless steel capillaries were treated by the Siltek and Silcosteel processes (Restek), respectively, to passivate all heated surfaces that might contact the analytes. An injection system was fabricated to test the transfer lines (Fig. 1). A septum injector nut (Valco Instruments, Houston, TX, USA) was connected to the top port of a Siltek-treated 0.159-cm union tee (Parker Instrumentation, Huntsville, AL, USA) by a short length of Siltek-treated stainless steel tubing ($760 \mu\text{m ID}$). Siltek-treated fittings were used in the fabricated injection system because thermal cracking of *n*-alkanes was observed in preliminary tests that used Silcosteel-treated fittings heated to 250°C . Responses of low- and high-molecular weight *n*-alkanes that were injected through Silcosteel-treated fittings were elevated and diminished, respectively. Apparently, the rough surfaces of fittings are ineffectively passivated by Silcosteel treatment, which deposits a thinner coating than Siltek treatment. The bottom port of the tee was connected to the transfer lines by a $13 \text{ cm} \times 760 \mu\text{m-ID}$ section of Siltek-treated stainless steel tubing with a $0.159 \text{ cm} \times 0.079 \text{ cm}$ stainless steel reducing union (Valco Instruments). To establish an inert connection between the transfer line and the injector, the capillary was inserted through the reducing union and directly into the short Siltek-treated stainless steel tubing to a depth of 1 cm. The injection system was placed in a valve oven (Valco Instruments), and the transfer line was located in $28 \text{ cm} \times 0.56 \text{ cm-ID}$ stainless steel tubing wrapped with heating tape. Both heated zones were maintained at 320°C and monitored with thermocouples. An auxiliary source of helium at 343 kPa that entered the side port of the tee was maintained at 26 mL min^{-1} with a mass flow controller (MKS Instruments, Andover, MA, USA). We used a syringe with a 7.62 cm needle to release the analytes directly into the Siltek-treated stainless steel tubing that was connected to the bottom port of the tee. The syringe injection technique combined the hot needle and solvent flush approaches.

The transfer line entered the PTV inlet through a custom-made 316 stainless steel block that replaced the septum head. A 0.8-mm stainless steel nut and ferrule combination (Valco Instruments) was used to make a leak-tight connection between the transfer line and the block, which was wrapped with heating tape, maintained at 320°C , and monitored with a thermocouple. The stainless steel block included a connection for the GC carrier gas and thus, the electronic pressure control (EPC) system of the GC could be used to maintain column head pressure when flow

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