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Technical note

Contamination from electrically conductive silicone tubing during aerosol chemical analysis

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ABSTRACT

Electrically conductive silicone tubing is used to minimize losses in sampling lines during the analysis of airborne particle size distributions and number concentrations. We report contamination from this tubing using gas chromatography–mass spectrometry (GC–MS) of filter-collected samples as well as by particle mass spectrometry. Comparison of electrically conductive silicone and stainless steel tubing showed elevated siloxanes only for the silicone tubing. The extent of contamination increased with length of tubing to which the sample was exposed, and decreased with increasing relative humidity.

1. Introduction

Airborne particles influence global climate change, regional air quality and public health (Finlayson-Pitts and Pitts, 2000; IPCC, 2007; Seinfeld and Pandis, 1998). While such effects are due to the chemical and physical properties of aerosols, knowledge of their sources, sinks and interactions with climate and biogeochemical cycles is still very incomplete (IPCC, 2007). A critical part of developing the necessary insights is analysis of the chemical composition as well as the particle size distribution and number concentration. Because the particles have a distribution of electrical charges, depending on their size (Hinds, 1982), it is important to have sampling lines that reduce the buildup of static charge and minimize particle loss to the tubing walls. As a result, electrically conductive silicone tubing is used extensively for measuring the physical properties of particles. Indeed, such tubing is recommended for aerosol sampling into particle counters and is also used to interconnect the components of commercial scanning mobility particle sizers.

A variety of techniques have been used to probe the chemical composition of particles. This includes collection on filters and impactors, followed by analysis by standard techniques such as GC or HPLC combined with MS, ESI-MS and FTIR (Chow et al., 2008; Spurny, 1999). More recently, particle MS techniques have been applied (Canagaratna et al., 2007; Sullivan and Prather, 2005; Zelenyuk and Imre, 2005). In most cases, these techniques are paired with measurement of particle size distributions and concentrations. Given that airborne particles often have a complex composition and the chemical constituents are generally present in relatively small concentrations, artifact-free analysis is even more challenging than for some other types of trace chemical analysis where contamination is a common problem (Keller et al., 2008; Manier et al., 2008; Oran et al., 2004; Pattinson and Wilkins, 1989).

We report here evidence for contamination of samples of airborne particles from electrically conductive silicone tubing. For comparison, stainless steel was also examined, as were the effects of tubing length and relative humidity.

2. Experimental

Aerosols were generated from sodium nitrate (Fisher Certified ACS grade, 99.9%) solutions in Nanopure water (Barnstead 18 MΩ cm). Salt solutions were aerosolized using an atomizer (TSI Inc., Model 3076), and dried with two inline diffusion dryers (TSI Inc., Model 3062). The aerosol particles (number concentration 5×10^6 cm^{-3} with geometric mean diameter at 83 nm) then passed through the tubing and were collected on quartz fiber filters (Tissuquartz TM, 37 mm) in 3-piece polypropylene SureSeal air monitoring cassettes (SKC Inc.). The filters had been cleaned by heating in air to 475 °C overnight. Two types of tubing were tested: electrically conductive silicone tubing (Simolex Rubber Corp. or TSI Inc.), and

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stainless steel tubing (Alltech Associates, Inc.). For comparison, ultra zero grade air (Oxygen Services Company, synthetic blend of O_2 and N_2, THC < 0.01 ppm, $H_2O < 2.0$ ppm, CO < 0.5 ppm, $CO_2 < 0.5$ ppm) or humid air (ultra zero air through a Nanopure water bubbler) was continuously flowed at 5 L min^{-1} through various tubing and quartz filters using Leland Legacy sample pumps (SKC Inc.).

The filters were extracted using 2 mL acetonitrile (EMD Chemicals Inc., HPLC grade) with sonication for 10 min in a water bath. The extracts were analyzed using GC–MS (Agilent Model 6850 Series II GC with a DB-5ms column of 60-m length, 0.25-mm internal diameter, and a 0.25-μm film thickness, Agilent Technologies, Inc., with detection using a Model 5975B VL mass selective detector, MSD). The column was temperature programmed as follows: 60 °C, 10 °C min^{-1} to 200 °C (hold for 6 min), then 10 °C min^{-1} to 280 °C (hold for 15 min). The splitless inlet temperature was 280 °C and the carrier gas was He. Electron ionization mass spectra (EI-MS) were recorded at 70 eV ionization energy. The complete scanning mode (SCAN) in the 35–550 m/z range of the GC/MS allowed the identification of compounds by comparison of their mass spectra with the NIST library. Several decamethylcyclopentasiloxane (Aldrich, 97%) solutions (2–40 ng mL^{-1}) were made as standards for quantitative analysis.

Aerosol composition was also analyzed using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research, Inc.). Details of this high-resolution time-of-flight aerosol mass spectrometer are described in the literature (DeCarlo et al., 2006; Drewnick et al., 2005).

3. Results and discussion

Fig. 1a shows a portion of the chromatogram of the filter extract for a sample of dry $NaNO_3$ aerosol passed through 11 ft of electrically conductive silicone tubing or through the same length of stainless steel tubing. Fig. 1b shows the results of filter analysis when dry air passed through the same lengths of tubing. Peaks at retention times of 15.0, 17.2, 18.8 and 22.3 min are observed in both cases. Their corresponding mass spectra are shown in Fig. 2. The compound at a retention time of 15.0 min is identified as tetradecamethylhexasiloxane by comparison to the NIST library, with 94% confidence. Small peaks at 17.2, 18.8 and 22.3 min were not identified by the library but their mass spectra are similar to tetradecamethylhexasiloxane. Hence we also attribute these three unknown compounds to siloxanes. Clearly, either aerosol or air flowing through electrically conductive silicone tubing showed much higher levels of siloxanes than the stainless steel tubing.

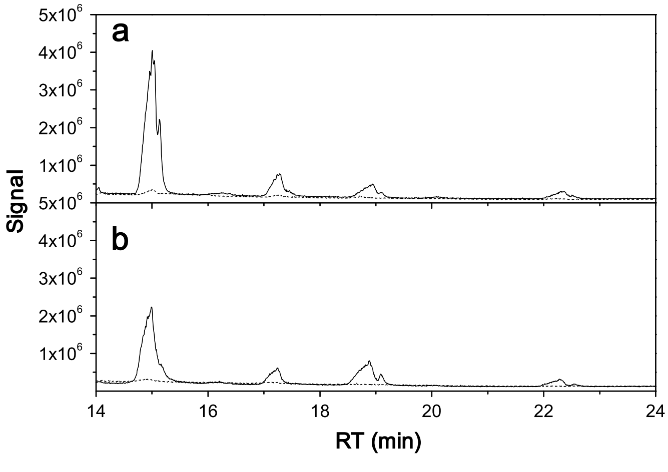

Fig. 1. Chromatogram of filter extract for samples that had passed through 11 ft of electrically conductive silicone tubing (solid line) or through 11 ft of stainless steel tubing (dashed line): (a) dry $NaNO_3$ aerosol; (b) dry air.

Siloxanes are widely found in laboratory and ambient air, plastic bags and boxes, crimp-cap vial closures, microfluidic devices and siliconized rubber stoppers, and thus are often observed as contaminants in various mass spectrometry analyses (i.e. electrospray ionization or atmospheric pressure ionization mass spectrometry, matrix-assisted laser desorption/ionization and laser desorption/ionization mass spectrometry, and time-of-flight secondary ion mass spectrometry) (Apicella et al., 2004; Guo et al., 2006; Pattinson and Wilkins, 1989; Pavanetto et al., 1991; Ryssel et al., 1993; Schlosser and Volkmer-Engert, 2003; Sung et al., 2003; Vickerman and Briggs, 2001). Siloxanes have also been detected in airborne particles, even in Arctic aerosols (Chandramouli and Kamens, 2001; Latimer et al., 1998; Weschler, 1981). However, the dramatic difference in the amounts seen using the electrically conductive silicone versus the stainless steel tubing (Fig. 1) establishes that the silicone tubing is a significant source of siloxane contamination in the filter samples.

The mass spectrum of a $NaNO_3$ aerosol that had passed through the electrically conductive silicone tubing was also directly measured using an aerosol mass spectrometer. Peaks were observed at m/z 73, 147, 207, 221, 267, 281, 327, 341, 355, 401, 415 and 429. Some of the observed mass peaks (m/z 73, 147, 207, 221 and 281) are consistent with previous analyses of soot particles in which these peaks were also assigned to contamination from electrically conductive silicone tubing (Schneider et al., 2006). High-resolution mass spectra confirmed some ions as fragments of siloxanes: $[(SiOC_2H_6)_n(Si(CH_3)_3)]^+$ with $n = 1, 2, 3, 4$ at 147.066, 221.085, 295.104, and 369.123 amu, respectively; and $[(SiOC_2H_6)_n(SiOCH_3)]^+$ with $n = 2, 3, 4, 5$ at 207.033, 281.052, 355.070, and 429.089 amu, respectively. Schneider et al. (2006) had assigned the m/z 147, 221 and 295 peaks in low-resolution AMS measurements as $[(SiOC_2H_6)_n(SiOC_2H_5)]^+$, however, our high-resolution AMS shows them to be due to fragments of the type $[(SiOC_2H_6)_n(Si(CH_3)_3)]^+$ where $n = 1$, 2 and 3.

Confirmation of mass peaks due to siloxanes can be accomplished in some cases without high-resolution mass spectrometry by taking advantage of the silicon isotopes. ^{30}Si represents 3.1% of naturally-occurring silicon, with ^{28}Si representing 92.2%. The intensity of $[M + 2]$ can therefore be used to confirm the attribution of a peak at [M] as a silicon-containing species. For example, if the peak at 207 is due to $(SiOC_2H_6)_2(SiOCH_3)^+$, the ratio of m/z 209–207 should be ~10%. Likewise if the peak at 281 is due to $[(SiOC_2H_6)_3(SiOCH_3)]^+$ the ratio of m/z 283 to m/z 281 should be ~12%. For higher MW peaks that have more silicon atoms, the ratios of $[M + 2]$ to [M] should be even larger. This method can be applied to low-resolution AMS data and GC–MS electron ionization mass spectra as long as there are no interfering contributions from other fragments.

The siloxane contamination is likely due to off-gassing from the silicone tubing surface. It was also observed in acetonitrile that had flowed through the tubing. Previous studies showed partitioning of siloxanes between the gas phase and surfaces (Chandramouli and Kamens, 2001; Latimer et al., 1998). The vapor pressure of a polydimethylsiloxane of approximately 18 siloxane units is $\sim 10^{-6}$ Pa (Weschler, 1981), so it is reasonable that they appear on quartz filters and aerosol when the sample passes through the silicone tubing.

The extent of contamination is dependent on tubing length and relative humidity Table 1 summarizes the results of several experiments in which these were varied. As expected, the amounts of siloxanes increase with the length of the tubing since longer tubing gives larger contact surface area as well as longer contact time. Additionally, the amounts of siloxanes decrease as the relative