Sampling gaseous oxidation products of aromatic compounds in gas/particle separation systems

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In this study we performed a direct comparison between two different ambient air samplers to characterize their performance in sampling oxidized gaseous organic compounds, known as oxidation products of aromatics. We investigated compounds with a variety of functional groups and vapor pressures. A polyurethane foam (PUF) adsorbent and an annular diffusion denuder sampler were operated along with particle filters. In both systems the sampling devices were liquid-extracted, followed by derivatization and analysis by GC-MS. The PUF system works very well for aromatic as well as non-aromatic compounds, whereas the denuder shows smaller collection efficiencies for highly volatile non-aromatic compounds. In addition, the sampling efficiencies in the PUF set-up are in good agreement with the calculated vapor pressures of the compounds and also the particle phase is not affected by most compounds.

Introduction

Hydrocarbons, aromatic and non-aromatic, are abundant organic compounds in the polluted atmosphere, but they are also detected in almost every compartment of the environment. The atmosphere is a well known pathway for transport and also deposition of organic compounds.1 Several polycyclic aromatic hydrocarbons (PAHs), important constituents of the organic matter in the atmosphere, have been identified as carcinogens1,2 or mutagens.3 The environmental fate of volatile organic compounds (VOC) is phase dependent because atmospheric reactions, transport and deposition processes differ for gas and particle phase species.1 Information about phase distribution is required, for example, for strategies to control volatile organic pollutants. Low volatility compounds produced by oxidation reactions of aromatics in the atmosphere-mostly emitted by anthropogenic activities—are among the most important contributors to secondary organic aerosol (SOA) mass.4 Many of these reaction products are distributed between the gas and the particle phase. Particles in the atmosphere have important effects on human health,5 regional air quality6 and climate forcing.7,8

Separation and sampling of gas and particulate organic compounds in the atmosphere require an efficient separation of the two phases. Most phase distribution measurements have been made by determining the concentrations of particulate phase organics on filters and the analysis of gas phase species trapped by adsorbents. Gundel et al.10 used an annular denuder coated with the adsorbent resin XAD-4, which adsorbs organic gas phase species from the air stream before collecting the particles on a filter. Eatough et al.11,12 also used several diffusion denuders to provide the determination of gas and particulate phase VOCs. Another standard method for monitoring VOCs uses samplers equipped with polyurethane foam (PUF) adsorbents. In these types of samplers, air is drawn through a filter to retain the particle phase and then through the PUF to adsorb the gas phase compounds. They have been employed extensively to study VOCs in the atmosphere.13-16 The advantages of PUFs over denuders are easy handling, storage, and transportation, as well as the low cost of the material. PUFs are in general Soxhlet extracted overnight.17 Maddalena et al.17 described also another method where the PUF is compressed to minimize the ratio of mobile phase to specific surface area. The adsorbed compounds are eluted with a solvent to remove the analyte.

All of the currently available separation systems suffer from artifacts by under- or overestimating the gas/particle partitioning. A main sampling artifact is that the gaseous compounds adsorb to particle filters and therefore lead to an overestimation of the particle phase. Pankow et al.18,19 as well as Kirchstetter et al.20 described positive gas adsorption artifacts when using Teflon membrane filters and quartz fiber filters.

We directly compare two common sampling set-ups used for semi-volatile oxidized compounds. The sampling setup with the best collection efficiencies will be later used to characterize smog chamber experiments. In our labs studies are currently underway to determine the SOA and gas phase compounds generated via photooxidation pathways from aromatic compounds. The sampling efficiency is a crucial parameter for determining the compounds in both phases. In this study we performed experiments with a filter/PUF setup and a denuder/filter setup for collecting aromatic and non-aromatic gas phase compounds known to be reaction products of aromatic oxidation. The collection efficiency and the handling of both systems are compared in detail. We show that collecting gas phase compounds works well, without measurable adsorption onto the filters for most of these compounds.

Experimental

Materials and chemicals

The PUFs, the annular denuders as well as the round glass containers for the PUF sampling line were purchased from Maddalena et al.17 described also another method where the PUF is compressed to minimize the ratio of mobile phase to specific surface area. The adsorbed compounds are eluted with a solvent to remove the analyte.

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Table 1  Identification parameters for analysis by GC-MS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight</th>
<th>Molecular weight of derivative</th>
<th>Mass for SIM/m/z</th>
<th>Ion for SIM</th>
<th>Retention time/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glyoxal</td>
<td>58.04</td>
<td>448.22</td>
<td>448.22</td>
<td>M</td>
<td>18.94</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>72.06</td>
<td>462.24</td>
<td>265.16</td>
<td>M-197</td>
<td>19.25</td>
</tr>
<tr>
<td>Glyoxylic acid</td>
<td>74.04</td>
<td>383.38</td>
<td>326.27</td>
<td>M-57</td>
<td>14.09</td>
</tr>
<tr>
<td>Pyruvic acid</td>
<td>88.06</td>
<td>397.65</td>
<td>340.54</td>
<td>M-57</td>
<td>15.10</td>
</tr>
<tr>
<td>2,5-Dimethylbenzaldehyde</td>
<td>134.18</td>
<td>232.97</td>
<td>329.27</td>
<td>M</td>
<td>18.27</td>
</tr>
<tr>
<td>2,6-Dimethylbenzoquinone</td>
<td>136.15</td>
<td>331.24</td>
<td>331.24</td>
<td>M</td>
<td>18.72</td>
</tr>
<tr>
<td>6-Nitro-m-cresol</td>
<td>153.14</td>
<td>267.39</td>
<td>210.28</td>
<td>M-57</td>
<td>16.10</td>
</tr>
<tr>
<td>3,5-Dimethylbenzoic acid</td>
<td>150.17</td>
<td>264.42</td>
<td>207.31</td>
<td>M-57</td>
<td>14.70</td>
</tr>
</tbody>
</table>

Molecular weight for derivative is for full derivatization of all functional groups in the molecule. Of the two carbonyl groups in 2,6-dimethylbenzoquinone only one is derivatized with PFBHA.

The compounds used (Fig. 1) are known oxidation products of aromatic hydrocarbons, e.g. of 1,3,5-trimethylbenzene\(^{21-25}\) or toluene.\(^{23}\) They cover a range of volatility from highly volatile to less volatile over several orders of magnitude. The vapor pressure is a critical parameter governing the partitioning of VOCs between the two phases.\(^{24,25}\) Vapor pressure estimates are therefore a useful proxy for gas/particle partitioning. We estimated the vapor pressures at 298 K (Fig. 1) according to Myrdal and Yalkowsky.\(^{26}\) The compounds cover the range from 1.6 \(\times 10^{-8}\) atm for 3,5-dimethylbenzoic acid to 0.39 atm for glyoxal. Compounds with a vapor pressure below 10\(^{-7}\) atm are considered semi-volatile.\(^{27}\) Boiling points-if required—were calculated according to Walters et al.\(^{28}\) from the available melting points. For pyruvic acid the estimated vapor pressure compares well with literature values\(^{29}\) (NIST: 1.7 \(\times 10^{-3}\) atm, estimation: 1.2 \(\times 10^{-3}\) atm for pyruvic acid). The vapor pressure of glyoxylic acid was not calculated, because neither the boiling point nor the melting point was available in the literature. It is likely to be slightly

![Chemical structures and estimated vapor pressures (see text)](image)

**Procedures**

Filters, denuders and PUFs were cleaned before use as follows: the TQFFs (15 mm diameter) were sonicated in toluene for 15 min, air dried in the hood and stored in a glass vial with a Teflon\(^{26}\) cap until use. Each PUF (7.5 cm \(\times\) 2.5 cm) was rinsed twice with deionized water, then sonicated for 15 min with methanol (2 \(\times\)) followed by dichloromethane (2 \(\times\)), then allowed to air dry in a fume hood, and stored in a glass beaker covered with aluminium foil in the dark until use. The denuders are 40 cm long and consist of 5 annular channels with 2 mm spacing. They were cleaned with organic solvents and the sandblasted walls were coated with ground Amberlite XAD-4 (40 \(\mu\)m grain size) using the procedure described by Gundel et al. (1995). XAD-4 was chosen because it is widely used, because of its good adsorption characteristics for volatile organic compounds, and because of its high surface area (725 m\(^2\) g\(^{-1}\)).\(^{10}\)

PALLFLEX Membrane Filters, were from PALL Gelman (Ann Arbor, MI, USA). Chemicals used as standard compounds were either from Sigma-Aldrich or Fluka, solvents (HPLC-grade) as well as tetradecane used as internal standard were from Fluka. All experiments were carried out at room temperature.

**Instrumentation**

Samples were analyzed using a HP model 5890 Series II Gas Chromatograph interfaced to a HP Model 5971A quadrupole mass selective detector (MSD). The GC was equipped with a split/splitless injector. The injector was run in the splitless mode and the pressure was set to 54 kPa. The GC was equipped with an Optima 6-6 capillary column (30 m \(\times\) 0.25 mm, 0.25 \(\mu\)m film thickness) from Macherey-Nagel (Oensingen, Switzerland). The mobile phase was He with a flow velocity of 34.4 cm s\(^{-1}\). The temperature program of the column was isothermal at 50 \(^\circ\)C for 0.1 min, 12 \(^\circ\)C min\(^{-1}\) ramp to 190 \(^\circ\)C, 15 \(^\circ\)C min\(^{-1}\) to 300 \(^\circ\)C and isothermal at 300 \(^\circ\)C for 1 min. The injector and detector temperatures were 250 \(^\circ\)C and 300 \(^\circ\)C, respectively, and the injection volume was 1 \(\mu\)l. The MSD was run in selective ion monitoring (SIM) mode (Table 1) for quantifying analytes, and total ion current for qualitative identification.
Sampling experiments

A first set of experiments was performed with only gas phase compounds present in the sampling system. For the experiments with the two sampling setups (Fig. 2) a ≈ 0.1 m³ bag made of FEP-Teflon® was used, a so-called pillow bag. The bag was cleaned by filling it with N₂ and evacuating it with a pillow bag. All compounds are gaseous higher than the vapor pressure of pyruvic acid. Both aromatic and non-aromatic compounds are represented in the selection, which includes aldehydes, ketones, carboxylic acids and nitro-compounds, covering a variety of functional groups. Prior to the experiment, test runs were performed for all compounds with the GC-MS to standardize the analysis and to validate the mass selection in the SIM mode.

Results and discussion

Fig. 3 shows the distribution of the gaseous compounds in percent between TOFF and two PUFs (A) and three denuders (B), respectively. Five experiments for each sample line were performed and the averages with the standard deviations are shown. 6-nitro-m-cresol was only measurable in 3 experiments. For the quantitative analysis the ratio of the peak areas of the compounds and the internal standard was calculated. The total amount recovered in the system was set to 100% for each compound. We did not measure the absolute recoveries for the compounds sampled on a PUF or denuder, because the main focus of this study is on the distribution of the compounds chosen between the sampling devices, not possible losses (e.g., to the wall) due to the use of the pillow bag. All compounds are gaseous and are expected to adsorb mostly on the first PUF or denuder, unless undesired adsorption to the filter material occurs.

In the filter/PUF experiment PUF 1 and the denuder immediately after sampling and to the filter together with the acetonitrile before sonication.

The extracts were allowed to react with PFBHA overnight (16–20 h) at room temperature. The next day the volume of the solutions was minimized by using a rotary evaporator and then almost blown to dryness in an N₂-stream. MTBSTFA was added and after ca. 1 h of reaction time at room temperature the solutions were ready for the GC-MS measurement. For integration of the peaks in SIM mode the most significant fragment ions were used as listed in Table 1. Derivatization with PFBHA for carbonyls leads to a fragment of the PFBHA derivatisation agent [CH₂C₆F₅]⁻ at m/z = 181, which makes it easy to identify. For compounds with carbonyl groups the fragment M-197, which results from loss of [OCH₂C₆F₅]⁺, was also used for identification. Molecules derivatized with MTBSTFA generally produce fragments at M-37 due to the loss of [C₆H₄CH₃]⁺, 2,5-Dimethylbenzoquinone was derivatized with PFBHA only once, although it carries two carbonyl functionalities.
1.6 very different (estimated 0.39 atm and glyoxal and 3,5-dimethylbenzoic acid is most likely reason. The volatility of to the TQFF surface seems to be the sampling artifact. Therefore adsorption which could result in a positive compounds might have partitioned, organic phase into which these components only small amounts as estimated from the structure. For all 

phase of all compounds. 89–100% of pyruvic acid and all four aromatic compounds are found on PUF 1, whereas on PUF 2 only negligible amounts were measurable (Fig. 3A). The most volatile compounds (e.g. glyoxal, methylglyoxal and glyoxylic acid) are also found on PUF 2, assuming that glyoxylic acid has a vapor pressure value between methylglyoxal and pyruvic acid as estimated from the structure. For all components only small amounts (0–2.2%) were found on the filter, except for glyoxal and 3,5-dimethylbenzoic acid (9.5% and 10.5%, respectively), showing that adsorption for most of these compounds to the filter material is negligible. The filters were cleaned prior to use, i.e. there was no organic phase into which these compounds might have partitioned, which could result in a positive sampling artifact. Therefore adsorption to the TQFF surface seems to be the most likely reason. The volatility of glyoxal and 3,5-dimethylbenzoic acid is very different (estimated 0.39 atm and 1.6 x 10^-5 atm, respectively), which excludes the possibility of adsorption to the filter due to similar vapor pressures. At standard conditions glyoxal exists as a mixture of different oligomers31 thus lowering significantly the vapor pressure as calculated for the monomer, which could explain the adsorption on the filter. The low volatility of 3,5-dimethylbenzoic acid is likely the reason for its adsorption on the filter. The total amount found on the filters was very low for all compounds, producing only small peaks in the chromatograms, which in turn resulted in a lower signal-to-noise ratio than for the PUF samples. In addition, in the PUF samples the response for compounds 1, 2 and 3 was small (up to 200 x smaller) compared to all others. This is the reason for the higher standard deviations for 1, 2 and 3.

Fig. 3B shows the distribution between three denuders and a TQFF. It is expected that most of the compounds are adsorbed by D1 and significantly less on D2; TQFF and D3 are expected to be empty, if no sampling artifacts occur. Basically, the same observation as for the PUF system also applies here. Note the appearance of 1, 2 and 3 on all the three denuders as well as 1 and 2 on the filter. The collection efficiency of the denuders is noticeably better for aromatic (91%) than for non-aromatic compounds (43%) used in this study. This is possibly due to the lower vapor pressures of the aromatic compounds used here. In addition, the coating for the denuders (XAD-4) is an apolar, hydrophobic polystyrene granulate, improving the affinity of the aromatics to the coating. In contrast, the non-aromatic compounds (1–4) are retained much less by the denuders and therefore also found on D2 and D3 in significant amounts.

D3, used as a back-up denuder, is not expected to show any signal, but due to high volatility of some compounds, breakthrough after D1, D2 and TQFF may occur. This was indeed found for glyoxal (12.3%), methylglyoxal (20.9%) and glyoxylic acid (6.0%), the three most volatile compounds. All four aromatic compounds showed no signal on D3 as expected.

Comparing Fig. 3A and 3B, both systems are able to collect the aromatic compounds and pyruvic acid with high efficiencies. However, the non-aromatic, more volatile compounds, glyoxal, methylglyoxal and glyoxylic acid are clearly retained better by the PUF system. Whereas for the PUF system a clear difference from PUF 1 to PUF 2 is observed, this is not true for D1 and D2 for these three compounds. Therefore the PUF system can be recommended as the preferred system to collect gas phase oxidation products of aromatic compounds.

In an additional set of experiments it was investigated whether particle filters loaded with organics would cause a change of the separation efficiency of the PUF/filter system for gaseous compounds. The particle filters were coated either sebacic acid (C_{10}H_{18}O_{4}), a long-chain dicarboxylic acid, or benzo(phenanthrene (C_{20}H_{12}), respectively, as surrogates of polar and apolar aerosol components. None of the 8 compounds could be detected on the coated filters. Therefore we can conclude that there is no sampling artifact, i.e., even high filter loadings will not affect the gas/particle separation of aromatic oxidation products due to additional gas adsorption to the collected organic aerosol when using a filter/PUF system.

Fig. 3 Distribution in percentages of 8 compounds (see Fig. 1) after sampling and analysis with GC-MS. The solid bars denote the mean values, the error bars the standard deviation. A: results from the PUF-line. B: results from the denuder-line. Sorted from left to right with decreasing vapor pressures.
Conclusions

Two air-sampling systems (denuder-filter and PUF-filter) were compared for collection efficiency of oxidized compounds. We could show that the PUF system is preferable to the denuder set-up for compounds with vapor pressures over the range of $1.6 \times 10^{-8}$ atm to 0.39 atm. For the semi-volatile compounds both systems were comparable, but the most volatile compounds were better retained on the PUFs than on the denuders. An advantage is also the easy handling and the lower cost of polyurethane foams. In addition, the adsorption to the TQFF placed before the PUFs is negligible for most of the investigated compounds.

Acknowledgements

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References