An Improved BPE-DNPH Cartridge for the Simultaneous Determination of Ozone and Carbonyls

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The BPE-DNPH cartridge is a patent pending, dual-bed sampler for the simultaneous determination of airborne ozone and carbonyls. Each of the sampling beds consists of reagent-impregnated silica particles. The first bed contains trans-1,2-Bis(2-pyridyl)ethylene (BPE) while the second bed contains 2,4-dinitrophenylhydrazine (DNPH). In the sampling stream, the cartridge is configured such that air is first drawn through the BPE bed and then through the DNPH. Ozone reacts with BPE to form pyridine-2-aldehyde. Airborne carbonyls (aldehydes and ketones) pass unimpeded through the BPE to the second bed where they react with DNPH to form carbonyl DNPhydrazone. These chemical reactions are outlined in Figure 1. Following air sampling, the cartridge is eluted with solvent. It is during this stage that the pyridine-2-aldehyde (derived from ozone) comes into contact with residual DNPH to form its own carbonyl DNPhydrazone derivative. The resulting solution is analyzed by HPLC in order to measure all of the hydrazones and determine the amounts of captured ozone, aldehydes and ketones.

The BPE portion of the sampler provides the functions of both ozone measurement and ozone scrubbing. Thus, a traditional potassium iodide cartridge to remove potential interference by ozone is not needed.

Improvements

In collaboration with a leading research group in Japan (1), we have developed and studied extensive improvements to the BPE-DNPH cartridge. Originally, trans-1,2-Bis(4-pyridyl)ethylene (4-BPE) was used as the ozone-capture reagent. However, we have found that the alternative isomer, trans-1,2-Bis(2-pyridyl)ethylene (2-BPE), offers several advantages. These include:

1. Better solubility of pyridine-2-aldehyde DNPhydrazone in acetonitrile/DMSO mixtures – More product derived from the reaction with ozone is eluted from the cartridge with less solvent.
2. Faster reaction with ozone and less dependence on atmospheric moisture – Implications are discussed below.
3. Faster reaction between pyridine-2-aldehyde and DNPH – Less wait time is required between cartridge extraction and HPLC injection. Addition of phosphoric acid to the extraction solvent increases the reaction rate even more.
4. Better HPLC peak shape of pyridine-2-aldehyde DNPhydrazone – Lower concentrations of ammonium acetate in the mobile phase are required.

Advantage 2 is the most critical and is presented here in more detail. In the laboratory, under conditions of controlled humidity, a 147 ppb concentration of ozone was measured using BPE-DNPH cartridges containing either 2-BPE or 4-BPE. The results are shown in Figure 2. From this data it is clear that 2-BPE reacts much more efficiently with ozone than 4-BPE. With 2-BPE, a consistent ozone concentration is measured following less than an hour of sampling. Alternatively, 4-BPE requires several hours of sampling before the measured ozone concentration no longer increases.

At 0% relative humidity (RH), the efficiency of the reaction with 2-BPE is 70% (103/147). Meanwhile, the reaction efficiency is only 55% (81/147) with 4-BPE at 0% RH. Both isomers of BPE exhibit greater reactivity toward ozone in the presence of higher levels of atmospheric moisture. 2-BPE exhibits a maximum reaction efficiency of 84% (123/147) at 32% RH and is clearly less dependent on atmospheric moisture.
Figure 2. Reactivity of Ozone with 2-BPE or 4-BPE at Various Relative Humidities

Figure 3. Pyridine-2-aldehyde and Other Carbonyl 2,4-DNPhydrazones from Laboratory Air Sample

Table 1. Conversion Factors for Ozone Measurements (Actual Ozone = BPE-DNPH Measured Ozone x Conversion Factor)

<table>
<thead>
<tr>
<th>% RH</th>
<th>Conversion Factor</th>
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<tbody>
<tr>
<td>0-10</td>
<td>1.39</td>
</tr>
<tr>
<td>10-20</td>
<td>1.30</td>
</tr>
<tr>
<td>20-30</td>
<td>1.22</td>
</tr>
<tr>
<td>&gt;30</td>
<td>1.19</td>
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moisture than 4-BPE. Above 18% RH, the ozone reaction efficiency of 2-BPE is in the narrow range of 80-84%. Based on these findings, the conversion factors for the 2-BPE/DNPH cartridge listed in Table 1 are recommended.

Method

The improvements to the BPE-DNPH cartridge culminate with the method and chromatogram depicted in Figure 3. Figure 4 demonstrates good correlation between outdoor ozone concentrations measured with the BPE-DNPH cartridge and data for the same time-period reported by local air monitoring stations.

Reference