SECONDARY ELECTROSPRAY IONIZATION (SESI) DETECTION OF EXPLOSIVE VAPORS BELOW 0.02 PPT ON A TRIPLE QUADRUPOLE WITH AN ATMOSPHERIC PRESSURE SOURCE

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OVERVIEW
We ionize ambient vapors with secondary electrospray ionization (SESI) relying on charged electrospray drops. We analyze the vapors with Sciex’s API-5000 triple quadrupole MS (the API-5000). Here we focus on the lowest detection limits (LDL) achievable with various explosives. We also infer quantitatively SESI ionization probabilities of explosives.

INTRODUCTION
We have recently reported [1] an ability to sense SESI ionized explosive vapors with various MS instruments. The data reported for the API-5000 showed the best LDL: (0.2 ppt for TNT and PETN), yet were based on measurements taken over a brief visit to the Sciex lab in Toronto. We now extend these studies with a better SESI source and an improved analytical method.

METHODS
*An electrospray chamber was attached to the curtain cone of the API-5000, with the sample gas coaxial with the cone and orthogonal to the negative electrospray needle (Figure 1).
*The curtain and sample flows were N₂ and clean CO₂ at 0.5 and 5 lit/min, respectively.
*The ionizing electrospray is 0.1% Formic acid in 9:1 Methanol/H₂O.
*The explosive vapor sample is produced by electrospraying a known flow rate of a dilute explosive solution into a carrier gas.
*The sample gas lines were heated to 155°C.
*We have studied TNT, HMX, DNT, RDX, Pentrite (PENT) and Nitroglycerine (NG).

RESULTS
We have studied different MS-MS transitions of explosives, with favorable conditions shown in Table 1.

Table 1: MS² Transitions for Explosive Detection

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Precursor Ion (m/z)</th>
<th>Product Ion (m/z)</th>
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<tbody>
<tr>
<td>TNT</td>
<td>226.1 (M-H)</td>
<td>46.1 (NO₂⁻)</td>
</tr>
<tr>
<td>HMX</td>
<td>340.9 (M+HCOO⁻)</td>
<td>45.9 (NO₂⁻)</td>
</tr>
<tr>
<td>DNT</td>
<td>180.9 (M-H)</td>
<td>45.9 (NO₂⁻)</td>
</tr>
<tr>
<td>RDX</td>
<td>267.0 (M+HCOO⁻)</td>
<td>46.0 (NO₂⁻)</td>
</tr>
<tr>
<td>PENT</td>
<td>360.8 (M+HCOO⁻)</td>
<td>62.1 (NO₃⁻)</td>
</tr>
<tr>
<td>NG</td>
<td>271.9 (M+HCOO⁻)</td>
<td>62.1 (NO₃⁻)</td>
</tr>
</tbody>
</table>

Figure 1. Experimental setup

*We have studied different MS-MS transitions of explosives, with favorable conditions shown in Table 1.

*LDL shown in Table 2 with clean bottled gases, with similar results obtained in CO₂, nitrogen or air. LDL for vapors are 50 times better than in prior studies.

*The background in bottled gas is typically 100 ion counts/s (Fig. 3) with standard deviation of 40 cps (figure 2).

*The background in laboratory air is typically 1000 ion counts/s with standard deviation of 40 cps, showing that LDL is background limited under practical conditions.

*The ionization probability p of SESI has been determined based on single MS mode, and on a prior measurement of ion transmission efficiency p within the API-5000: p = signal/(vapor concentration*sample flow rate)/p. The best value obtained is p ~ 10⁻⁴.

CONCLUSIONS
*Selective detection of samples containing TNT, HMX, DNT, RDX, PENT and NG.

*Detection limit, linearity and speed response of the API 5000 for detecting explosive vapors are determined.

*LDL found for ambient volatiles 50 times better than the best previously reported. Limited by background.

*Measured SESI ionization probability of explosives is below 10⁻⁴.

REFERENCES