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 N_2 and clean CO_2 at 0.5 and 5 lit/min, respectively.
*The ionizing electrospray is 0.1% Formic acid in 9:1 Methanol/H_2O.
*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 155ºC.
*We have studied TNT, HMX, DNT, RDX, Pentrite (PENT) and Nitroglycerine (NG).

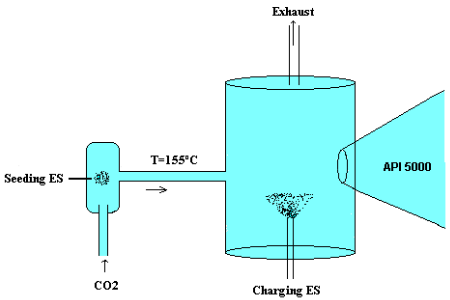

Figure 1. Experimental set up

Table 1: MS² Transitions for Explosive Detection

Explosive	Precursor Ion (m/z)	⇨ Product Ion (m/z)
TNT	226.1 $(M-H)^-$	46.1 (NO_2^-)
HMX	340.9 $(M+HCOO^-)^-$	45.9 (NO_2^-)
DNT	180.9 $(M-H)^-$	45.9 (NO_2^-)
RDX	267.0 $(M+HCOO^-)^-$	46.0 (NO_2^-)
PENT	360.8 $(M+HCOO^-)^-$	62.1 (NO_3^-)
NG	271.9 $(M+HCOO^-)^-$	62.1 (NO_3^-)

RESULTS

*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 $CO_{2,}$ 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 backgroundlimited 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_i within the API-5000: p = signal/(vapor concentration*sample flow rate)/p_i. The best value obtained is $p \sim 10^{-4}$.

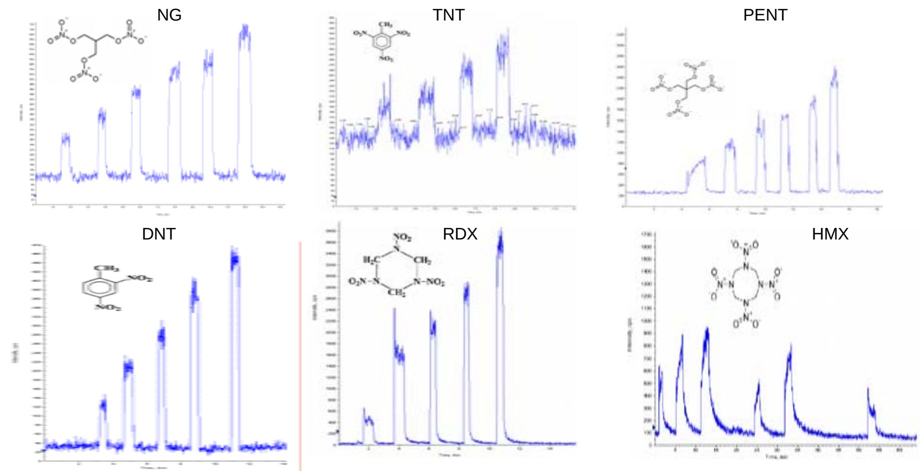

Figure 2: Response of the API 5000 to differents explosive vapors at various concentrations)

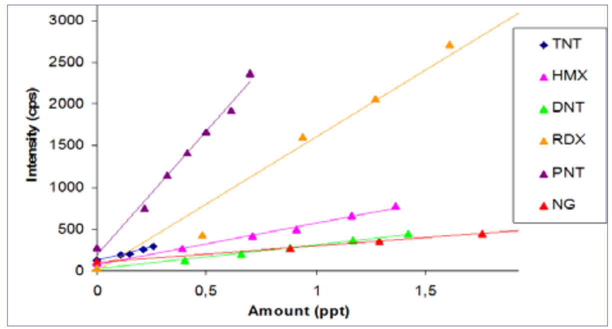

Figure 3: Calibration: MS signal vs. vapor concentration

Explosive	Sensitivity (ion/s/ppt)	LDL (ppt) IUPAC[1]	LDL (ppt) B-99%[2]
TNT	633	0.07	0.018
HMX	494	0.11	0.025
DNT	295	0.12	0.023
RDX	1642	0.07	0.005
PENT	2959	0.04	0.006
NG	197	0.22	0.056

Table 2: Sensivity and Limits of detection

[1] Background mean + 3*(standard deviation) of the blank.
[2] Signal exceeding noise level with 99% probability

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

[1] P. Martinez-Lozano, J. Rus, G. Fernandez de la Mora, M. Hernandez, et al.. JASMS, 20, p. 287,2009