

VAPOR DETECTION AT 1 PPT WITH SECONDARY ELECTROSPRAY IONIZATION (SESI) AND A SINGLE QUADRUPOLE MS

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QuickTime™ and a decompressor are needed to see this picture.

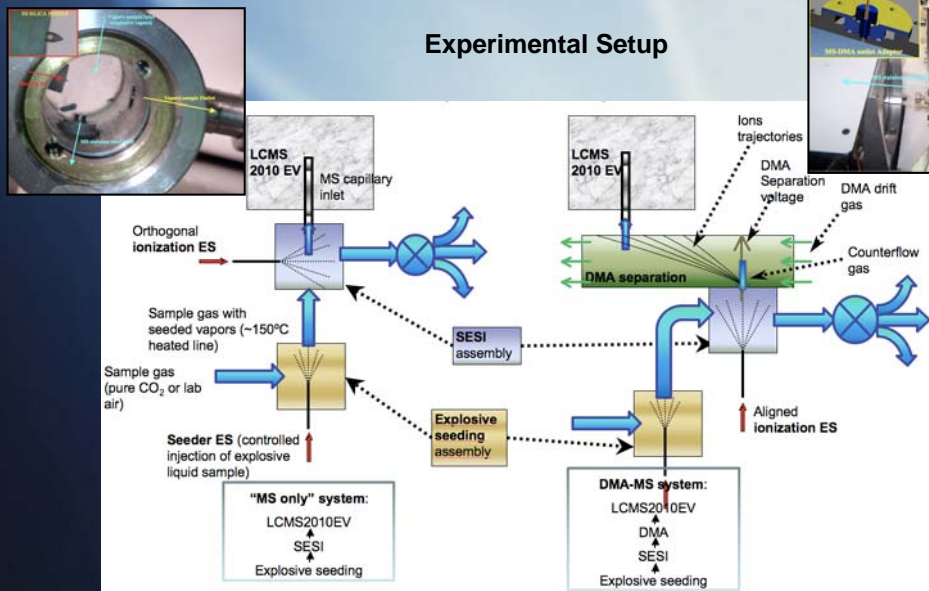
Overview

Several experiments are conducted in order to study the detection of explosive vapors in an IMS-MS system relying on secondary ES ionization (SESI). A single quadrupole MS and its combination in tandem with a differential mobility analyzer (DMA-MS) are compared in a controlled lab atmosphere and in a real scenario.

Introduction

- ❖ SESI coupled to several tandem MS achieves lowest detection limits (LDL) better than 1 ppt for explosive vapors [1]
- ❖ Earlier work based on high-end tandem MS systems extended here to single quadrupole MS: Shimadzu's LCMS-2010 EV.
- ❖ Also a commercial Differential Mobility Analyzer (SEADM), optimized for coupling to LCMS-2010EV [2] has been added into a tandem SESI-DMA-MS configuration for noise reduction studies.

Experimental Setup

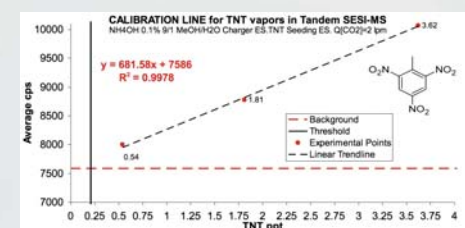
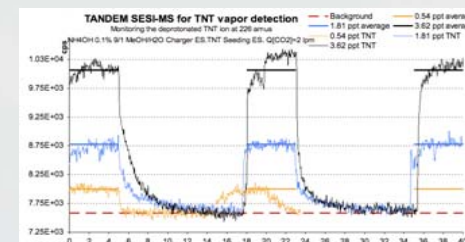
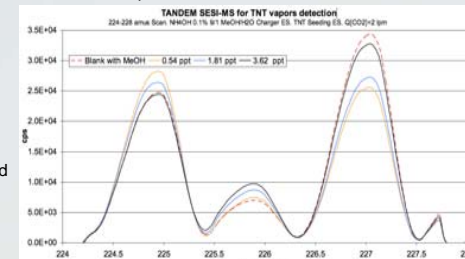


Methods

- ❖ In order to vaporize controlled quantities of explosive into the heated sample gas flow we follow [1]
- ❖ SESI source system (left photograph):
 - o It includes a sharpened silica capillary to form the ES
 - o Dilute solution of Formic acid or NH₄OH in 9:1 Methanol/H₂O (negative mode) as charging ES
 - o ES orthogonal to the inlet stainless steel MS capillary and no counterflow is used for tandem SESI-MS
 - o Sample vapors are heated through the line, SESI-ionized and monitored in the MS usually as deprotonated ions
- ❖ The DMA [2] is rigidly supported on the MS and the DMA sample outlet is directly connected to the MS sampling capillary (right photograph).

Results

- ❖ Best results with tandem **SESI-MS-alone system**:
 - o With clean CO₂ as carrier gas (2 lpm sampled into the SESI source):
 - Seeded with 0.5 ppt of TNT vapors
 - Deprotonated TNT clearly detected with an inferred **LDL of 0.20 ppt**
 - o With ambient air as carrier gas (2 lpm sucked into the SESI source):
 - Deprotonated TNT detected with an inferred **LDL of 1 ppt**
 - This decrease is probably due to the higher background from volatiles in the lab
 - Mixing a small flow of clean CO₂ into the sampled flow favors the negative ionization process thus improving the LDL
- ❖ Results with tandem **SESI-DMA-MS system**:
 - o Not yet improved LDL over the MS-alone system
 - o Other explosives such as PETN, NG, RDX and DNT have been successfully detected as well
 - o Real scenarios have been tested:
- ❖ Biological applications with tandem SESI-DMA-MS have also been explored:
 - o Ion mobility classification of peptides and its equimolar mixtures:
 - Bradykinin, (Glu1)-Fibrinopeptide B, Leucine Enkephalinamide diluted in 50% Acetonitrile + 0.5% formic acid
 - DMA settings: CO₂ seath flow, Q_{counterflow}=1 lpm and positive ionization
 - o Different charge states are identified
 - [Bradykininⁿ⁺ +H]: n=2 and n=3
 - [Glu1ⁿ⁺ +H]: n=4
 - [Leuⁿ⁺ +H]: From n=1 to n=4
 - o Concentrations as low as 0.01 μM were achieved



Figures 3-5: best detection results, TNT vapors detection, when seeded on clean CO₂ and sampled by the SESI-MS system. **Top**: average mass spectrum around the deprotonated TNT mass (226 Da). **Middle**: TNT detection (MS signal at 226 Da) upon seeding different TNT concentrations in the sample. **Bottom**: calibration line for these results

CONCLUSIONS

- ❖ Lower detection limits better than 1 ppt for TNT explosive vapors are achieved on a single-quadrupole MS-based system
- ❖ SESI-DMA interface requires modifications in order to increase the ionization probability and therefore improve the LDL
- ❖ Real explosives samples have been successfully detected and identified in real time with tandem SESI-MS and SESI-DMA-MS

REFERENCES

[1] P. Martinez-Lozano, J. Rus, G. Fernandez de la Mora, M. Hernandez et al. JASMS 09, 20, 2, 287-294
 [2] J.Rus, D. Moro, J.A. Sillero, J.Freixa et al. Poster 042, Annual ASMS conference, 1-6 June 2008.