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

Juan A. Sillero[1,2]; Juan Rus[1]; Juan Fernandez De La Mora[3]

[1]SEADM, Boecillo , Spain ; [2]Polytechnic University of Madrid, Madrid, Spain; [3]Yale University - Mechanical Engineering Department, New Haven, CT

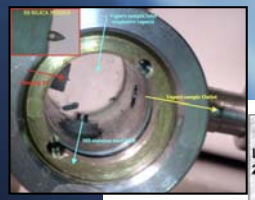
Overview

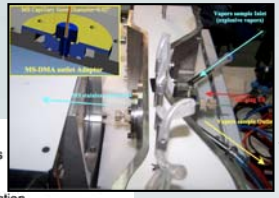
Several experiments are conducted in order to study the detection of explosive vapors in an IMS-MS system relying on secondary ES ionization (SESI). A single quadrupole MS and its combination in tandem with a differential mobility analyzer (DMA-MS) are compared in a controlled lab atmosphere and in a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

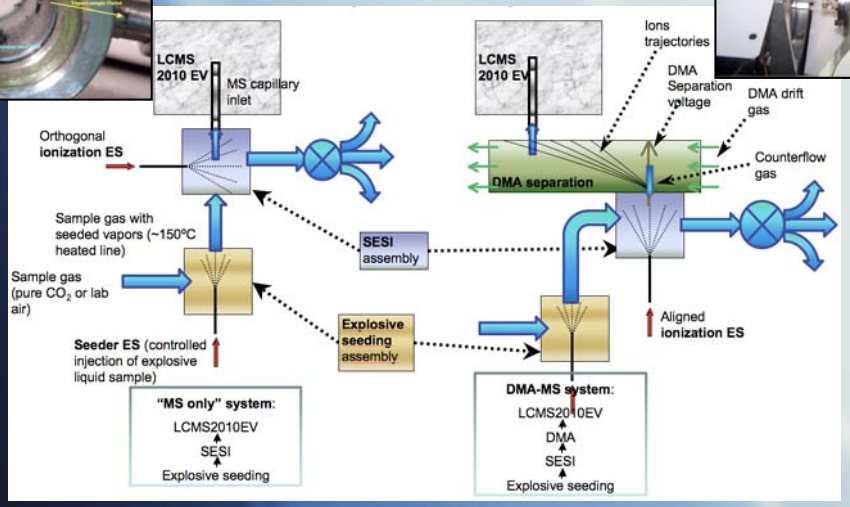
Introduction

- 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





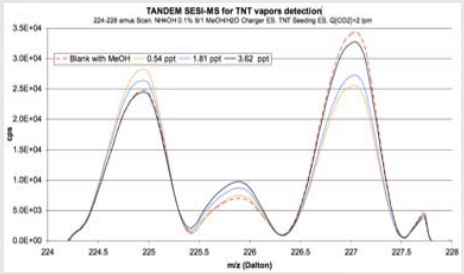


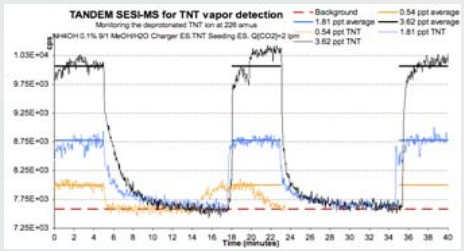
Methods

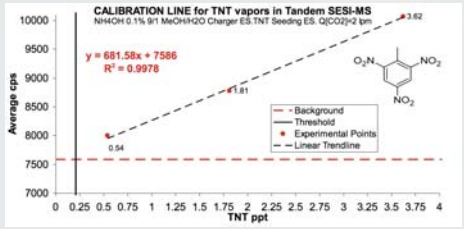
- In order to vaporize controlled quantities of explosive into the heated sample gas flow we follow [1]
- SESI source system (left photograph):
  - o It includes a sharpened silica capillary to form the ES
  - o Dilute solution of Formic acid or NH4OH in 9:1 Methanol/H2O (negative mode) as charging ES
  - 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 mobiliby clasification 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
    - [Bradykinin^{n+} +H] : n=2 and n=3
    - [Glu1^{n+} +H] : n=4
    - [Leu^{n+} +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. Hernadez 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.