



Low sample flow SESI vapor ionizer.

G. Vidal¹, M. Macía¹, P. Pinacho¹, J. Blanco¹
¹SEADM S.L.



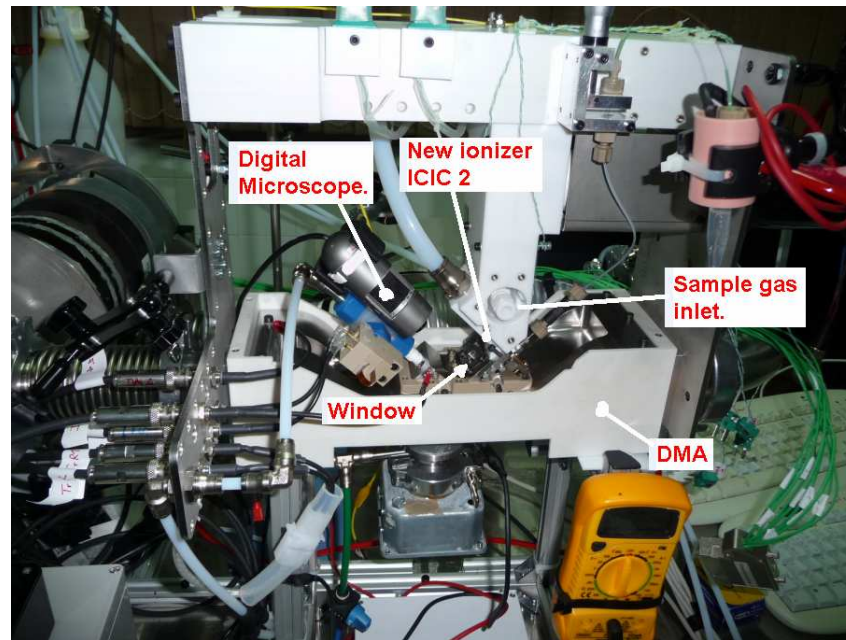
SEADM Overview.

- Spanish R&D micro-business,
- Born in February 2005.
- HW development: Differential Mobility analysis.
 - MAIMS, (Canadeka program, partially funded by the Spanish Ministry of Industry).
 - VEAME, (Avanza).
 - EVA (ADE Line4)
- HW development: Vapor ionizer SESI.
- Applications: Explosive trace detection.
 - AROMA, (Profit & Coincidente).
 - OLFATO, (ADE line 4).
 - DETEV, (Spanish Ministry of Industry).
 - SIMDE, (ADE line 4).
 - CARGO (SEDET).
 - EFFISEC program, (integration program from the First Security Call FP7).
- Applications: Odor medical diagnosis of Cancer.
 - IDOC. (Avanza2)
- Applications: Odor biometrics identification.
 - Nebli (Avanza)
 - EMOCION(Avanza)



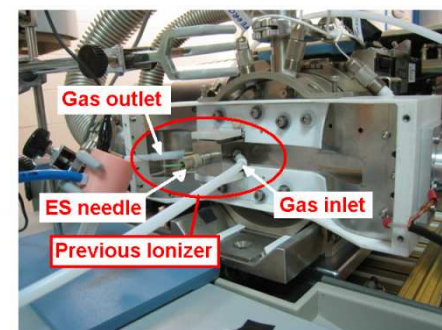
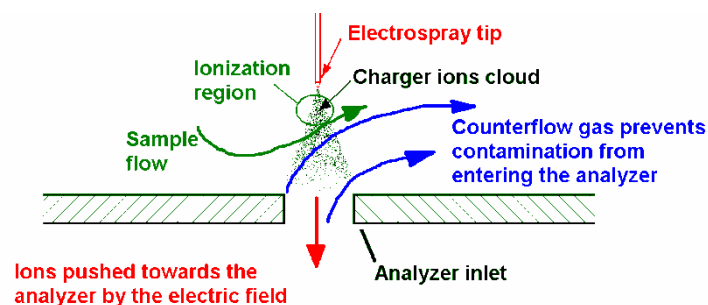
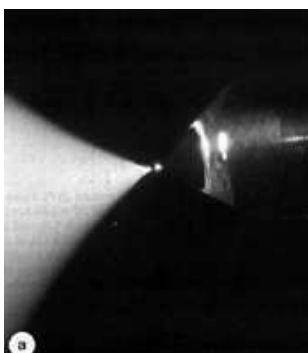
Vapor ionizer development.

- More specific molecules are bigger.
- But bigger molecules have lower vapor pressure.
- Specific molecules are found in minute concentrations in real environment.
- Sensitivity is crucial for vapor analysis.
- Goal of the development: Increase the sensitivity.



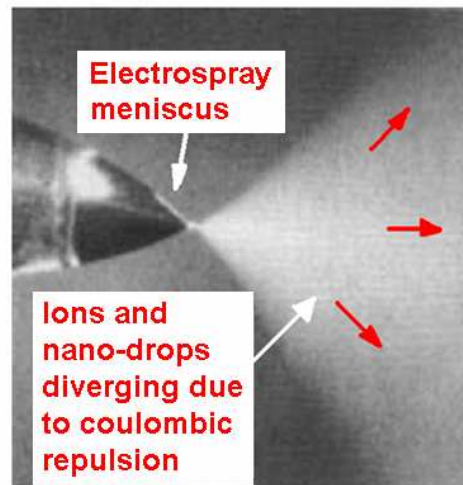
Background, SESI ionization.

- Previous ionizer using ES had record sensitivities (0.02 ppt; E. Mesonero et. al.) of TNT.
- Based on SESI ionization technique:
 - Permits charge transfer reactions at atmospheric pressure.
 - Soft ionization technique.
 - Selective ionization.
 - High ionization efficiency.
- But requires high sample flow rates.
 - Counterflow is required to prevent analyzer contamination.
 - Counterflow dilutes sample and limits ionization efficiency.
 - Requires high sample flow rates (5lpm).



Background, Ion to Vapor concentration ratio.

- ES charger ions transfer their charge to the neutral ions.
- But charger ions also produce coulombic repulsion.
- An equilibrium is reached.
- Concentration of ionized vapors is constant!
- Typical values: $p_i=1e-4$.

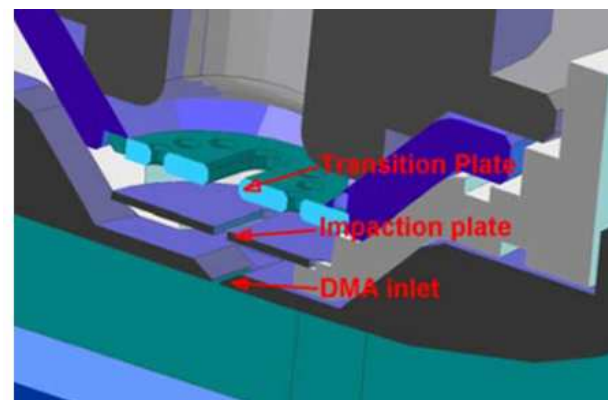
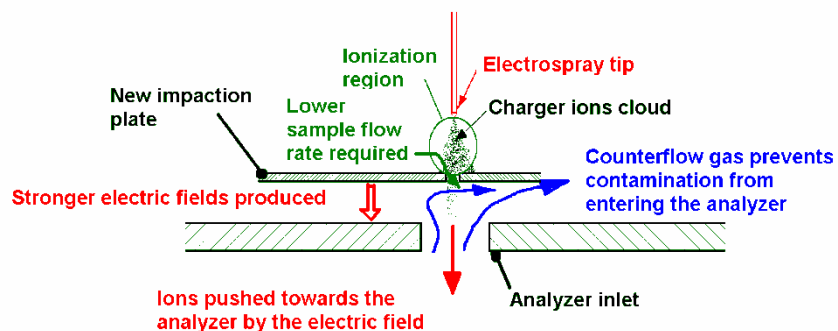
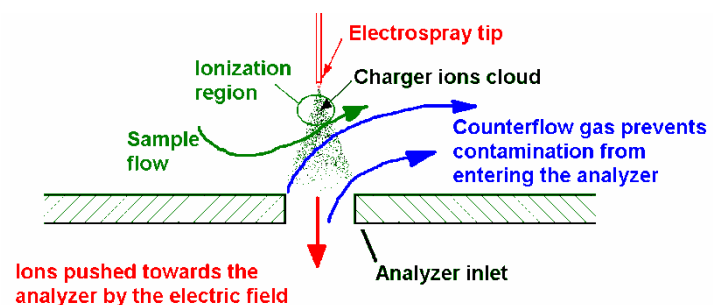


$$n_s = N_s \cdot p_i = N_s \cdot \frac{k_{cs} \epsilon_0}{Z_s \cdot e}$$

- Juan Fernandez de la Mora, Ionization of vapor molecules by an electro spray cloud, *Int. J. Mass Spectrom.*, 300 182-193 (2011)

Background, New Ionizer concept.

- New ionizer concept separates ionization region and counterflow region.
 - Lower sample flow rates required.
 - Higher electric fields push more ions towards the analyzer.
 - Patent: *Guillermo Vidal de Miguel, "Improved ionizer for vapor analysis decoupling the ionization region from the analyzer", 61/204,996*



Scope and Methods: DMA-MS.

- The Ionizer is a subsystem to be integrated in vapor analyzer comprising:
 - Sample collector/vaporizer
 - Vapor Ionizer
 - DMA-MS Analyzer
- DMA-MS technique increases the selectivity of the analyzer.

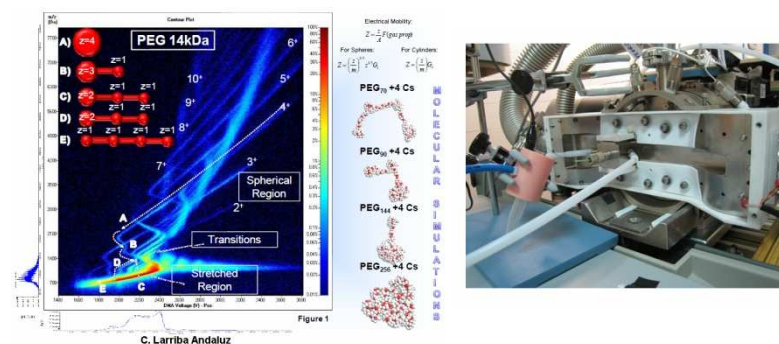
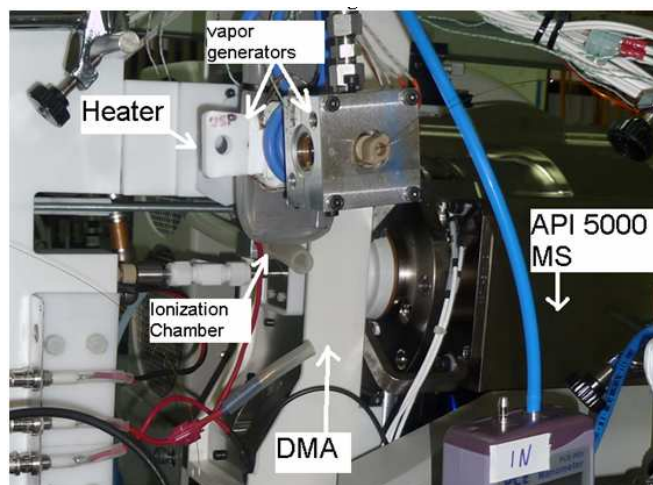
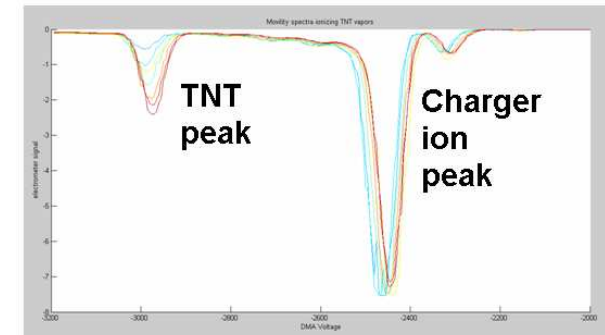
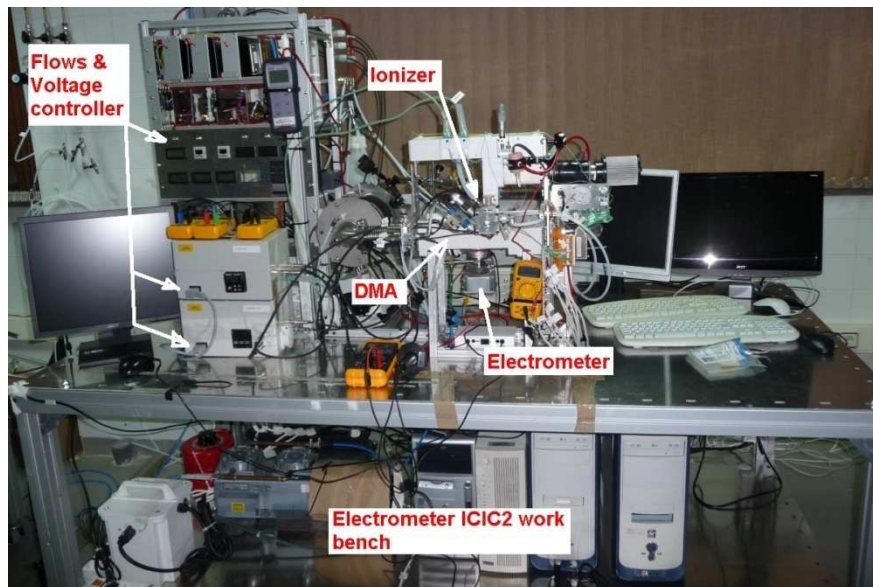


Figure printed with permission of the authors: C. Larriba, J. Fernández de la Mora.

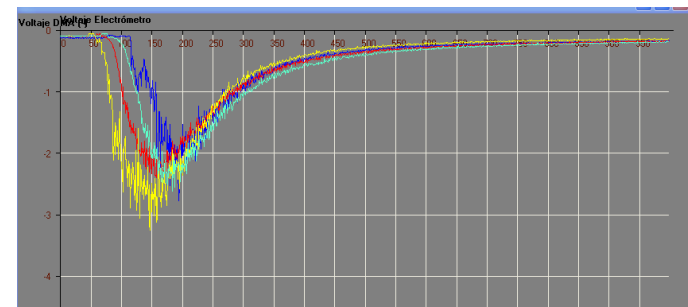
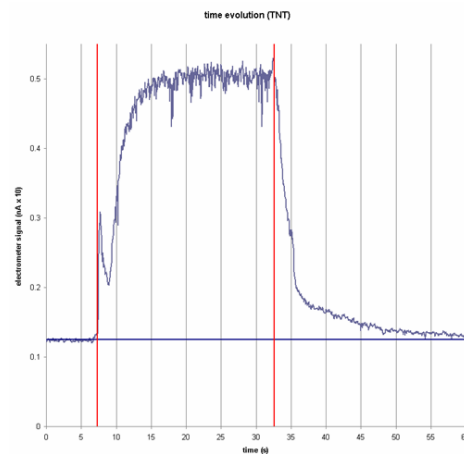
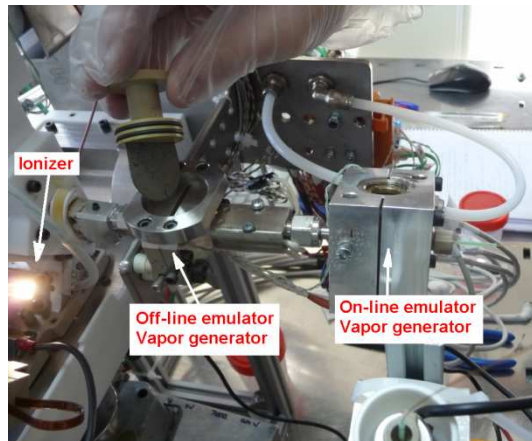
Scope and Methods: Workbench.

- DMA suffices to differentiate charger ions and sample vapor ions.
- Ionizer development test bench comprises:
 - Vapor generators.
 - Vapor ionizer.
 - DMA.
 - Electrometer.



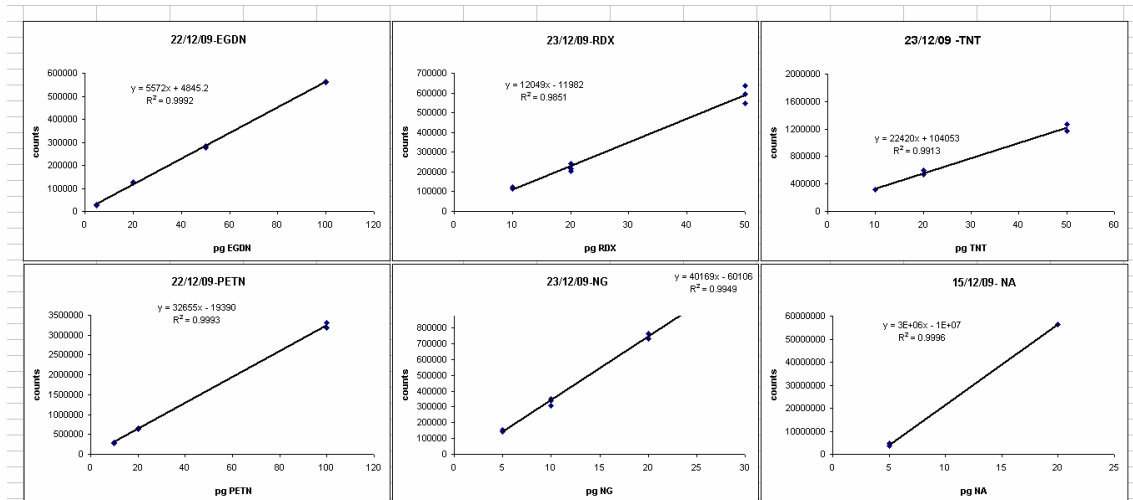
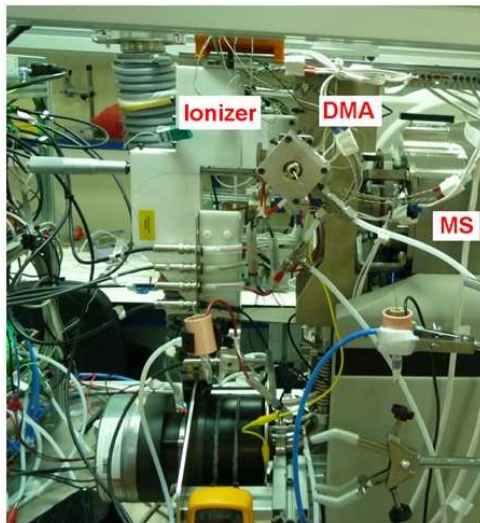
Scope and Methods: Vapor generators.

- Secondary electrospray Vapor generator. (On-line emulator)
 - Solution of sample is electro-sprayed
 - Nano-drops are mixed and evaporated within the sample flow.
 - Sample flow carries vapors towards the vapor ionizer.
 - Permits controlling the concentration of vapor dilution.
- Desorber (Off-line emulator)
 - Solution of sample is pipetted on a metallic mesh.
 - The mesh is introduced in a heated desorber and sample is vaporized.
 - Sample flow carries the vapors towards the vapor ionizer.
 - Permits controlling total amount of available sample.



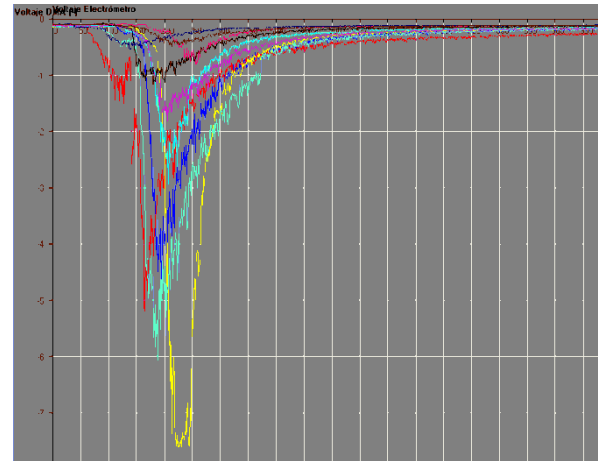
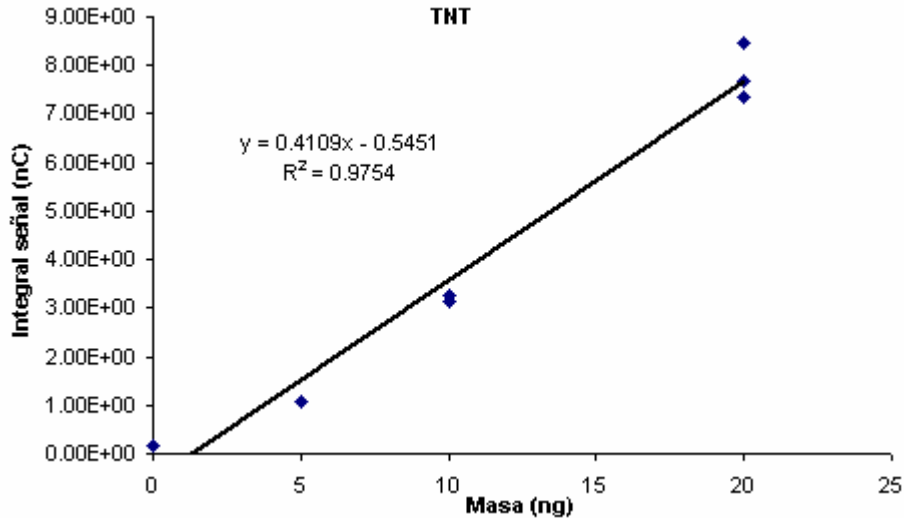
Prototype progression; ICIC1.

- New **Vapor ionizer ICIC 1** developed and tested.
 - Allows using low sample flow rate
 - **0.4lpm** Offline operation.
 - **0.05lpm** Online operation.
 - Delivering **4lpm** ionic flow rate.
 - Reduces contamination and memory effects.
 - *ICIC1 is easily contaminated and requires frequent maintenance.*



Gain and Ionization efficiency; ICIC1.

- Increases the sensitivity of the system by a factor of **5 to 20** compared with previous state of the art vapor ionization chambers.
- Gain measurements.
 - amount of TNT on the vapor generator vs. charge received at the electrometer:
 - $G=0.4 \text{ nC/ng}$.
- Ionization efficiency:
 - $P=1e-3$; One ion per 1000 molecules. ($P=p_i \cdot Q_{ions}/q_{sample}$)

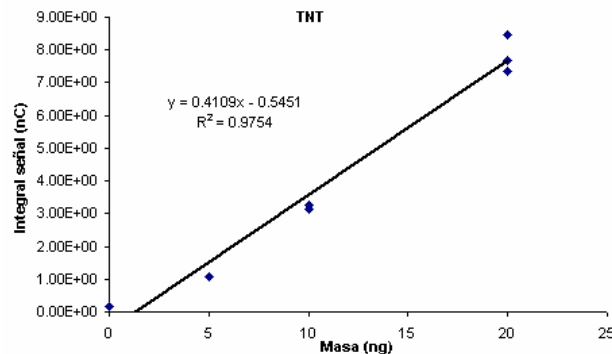


Sensitivity:

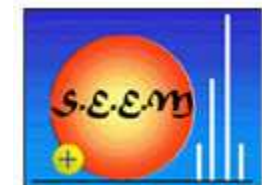
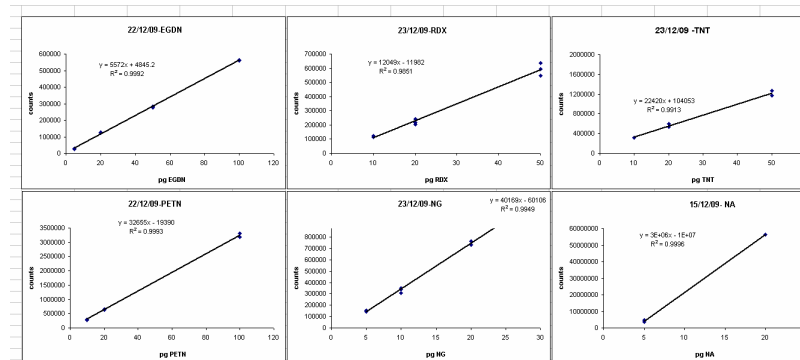
ICIC1+DMA+API5000(MS-MS).

- System has been further integrated with an API 5000. Gain was also measured after fragmentation in MRM mode ($2.2 \cdot 10^4$ ions/pg; A. Peira).
- Online detection limit: **2e6 molecs/s**. Measured using secondary ES2 vapor generator.
 - 20 Times beeter than previous experiments by E. Mesonero (**4e7 molecs/s**).
 - Those experiments used single Quad MS mode (API5000). Maximum transmission, poor selectivity.
 - While new detection limit is measured at DMA-MS-MS mode.
 - More sensitive and more selective
- Transmission of ICIC1-DMA system is known. $G=0.4nC/ng.(2.5 \cdot 10^6$ ions/pg)
- Estimated API 5000 Transmission: ~1%

-Electrometer bench data

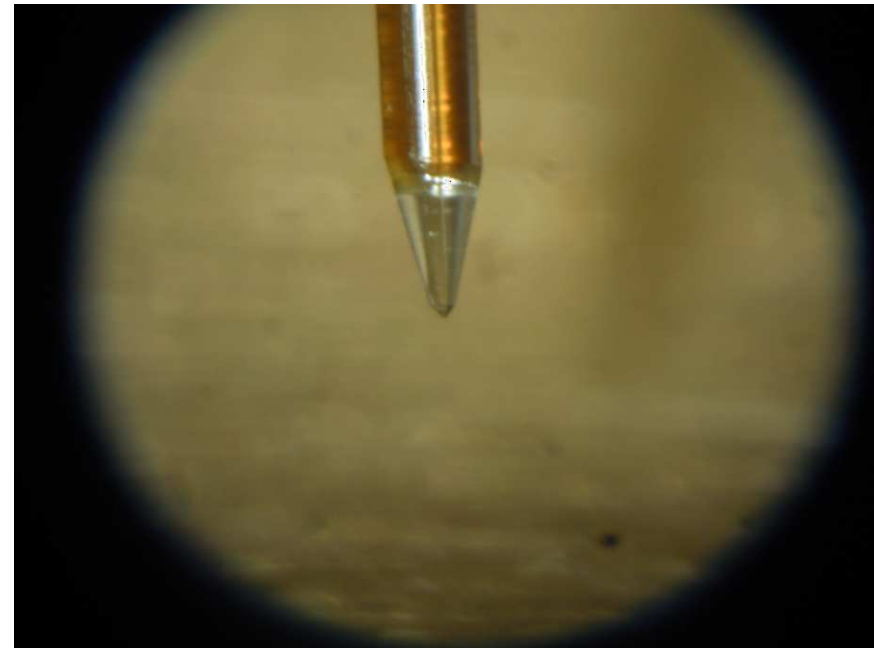
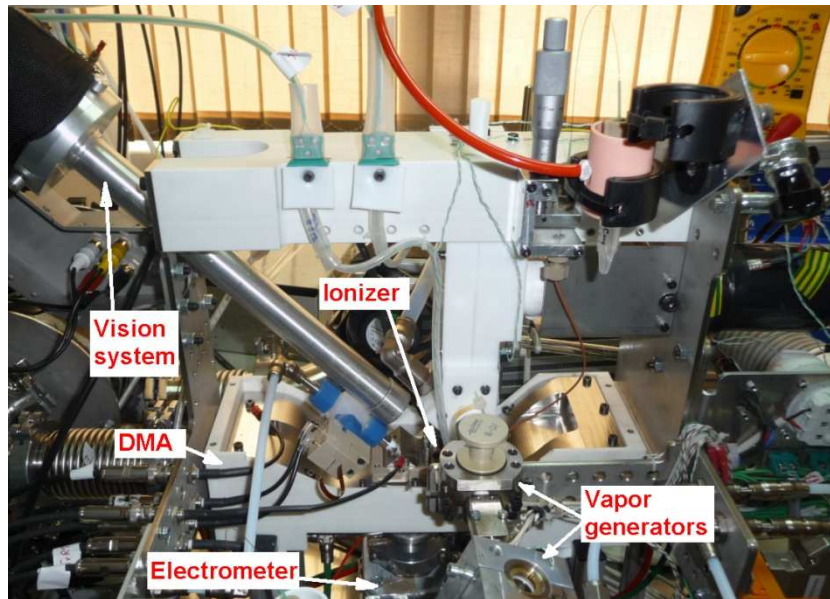


- DMA-MS-MS Data.



Latest developments; ICIC2.

- New **Vapor ionizer** ICIC 2 developed; currently under test.
 - Electro spray oriented at 45°.
 - Electro spray vision system.
 - Similar Gain as ICIC1.



Conclusions.

- *Ion to Vapor concentration ratio is theoretically limited and can't be higher than $p_i \sim 10^{-4}$:*

$$n_s = N_s \cdot p_i = N_s \cdot \frac{k_{cs} \epsilon_0}{Z_s \cdot e}$$

- *However, ionization efficiency can overcome easily this limitation by:*
 - *Reducing the required sample flow rate.*
 - *While producing high ionic flow rates (Electric field induced velocity)*
- *Current prototype performance: $P \sim 10^{-3}$.*
 - *One order of magnitude more efficient than previous most efficient SESI ionizer.*
 - *Still can be improved over tree orders of magnitude.*
 - *ICIC1 coupled to DMA-MS system.*
- *New prototype ICIC2 being optimized; interfaced with DMA.*



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- The complete SEADM team.





Thanks for your attention!

Contact:
Guillermo Vidal
SEADM; Head of the R&D team.
Guillermo.vidal@seadm.com
+34 983 130 154

