Low sample flow SESI vapor ionizer.

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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)

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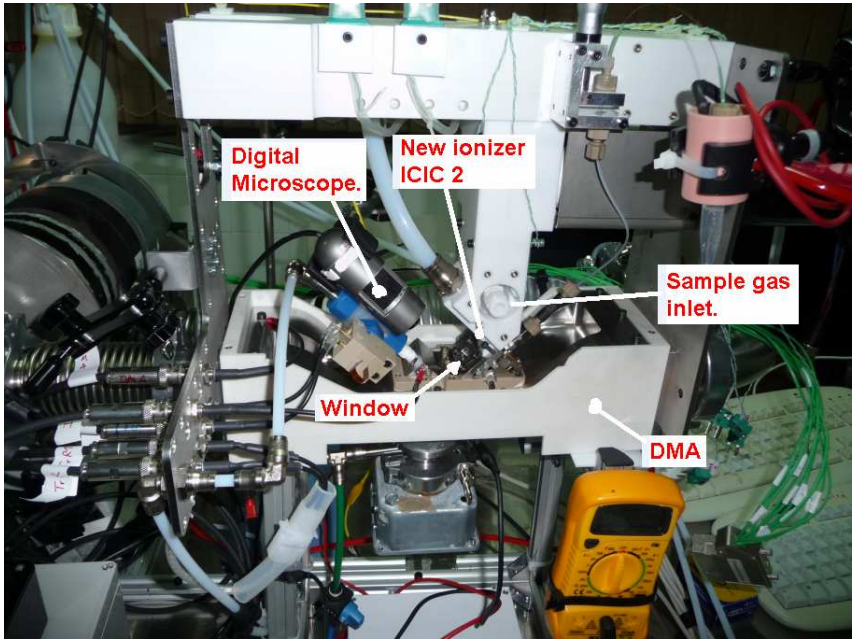
Vapor ionizer development.

- 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.



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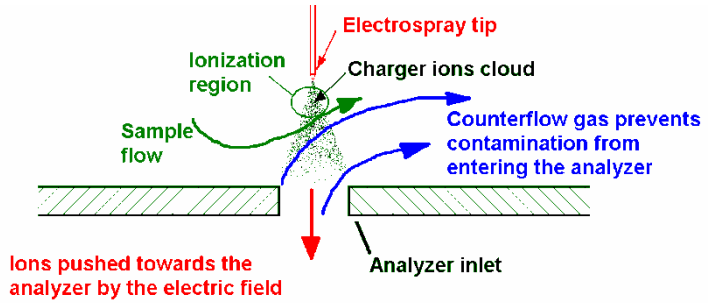
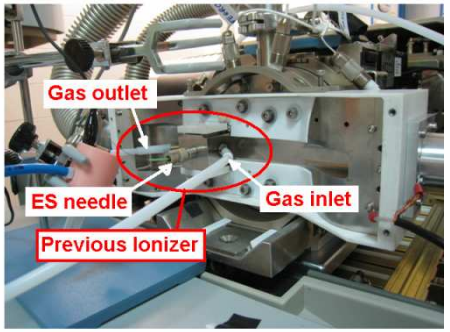
Background, SESI ionization.

- 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).





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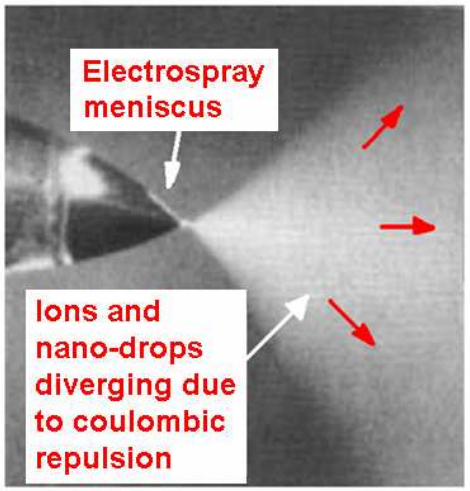
Background, Ion to Vapor concentration ratio.

- 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.



$$n_s = N_s \cdot p_i = N_s \cdot \frac{k_{cs}\varepsilon_0}{Z_s \cdot e}$$

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

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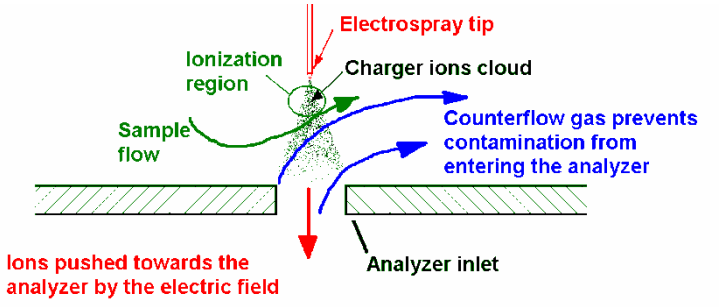
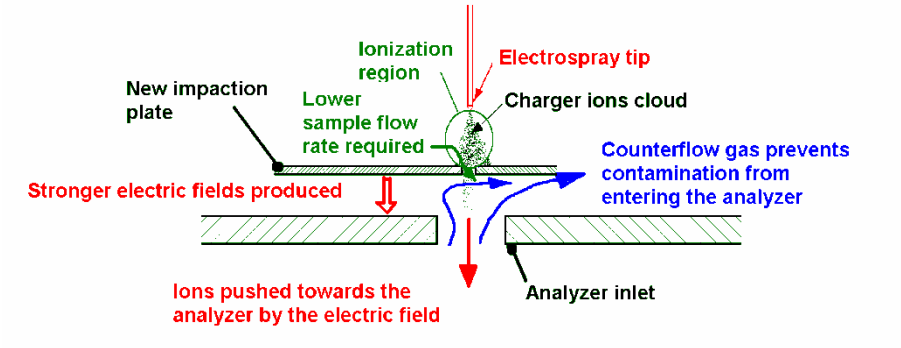
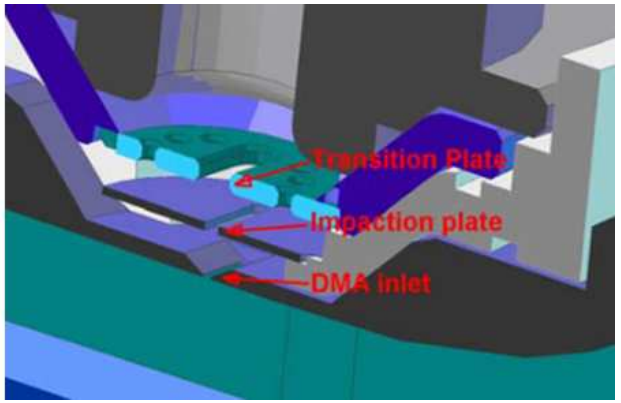
Background, New Ionizer concept.

- 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*







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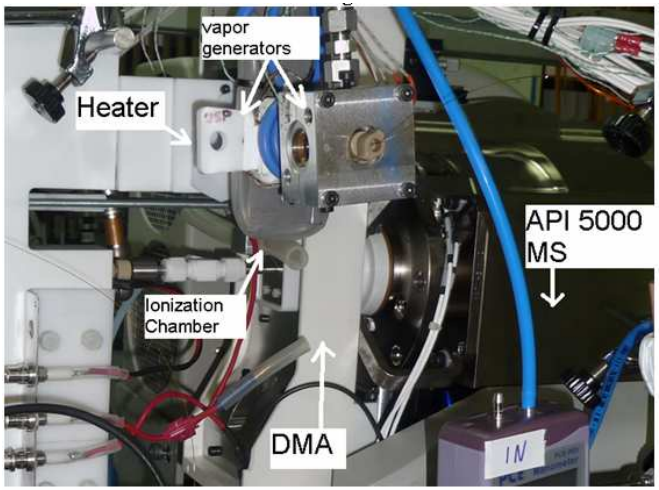
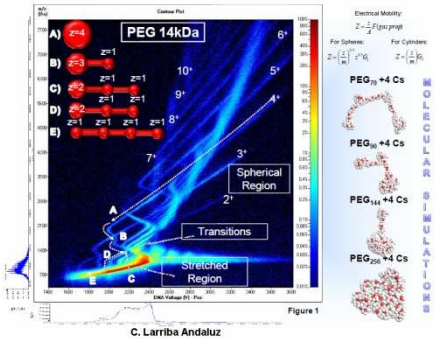
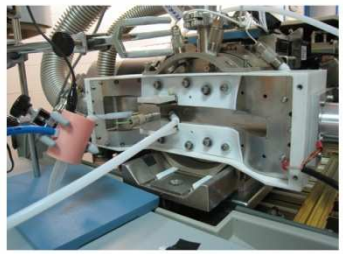
Scope and Methods: DMA-MS.

- 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.







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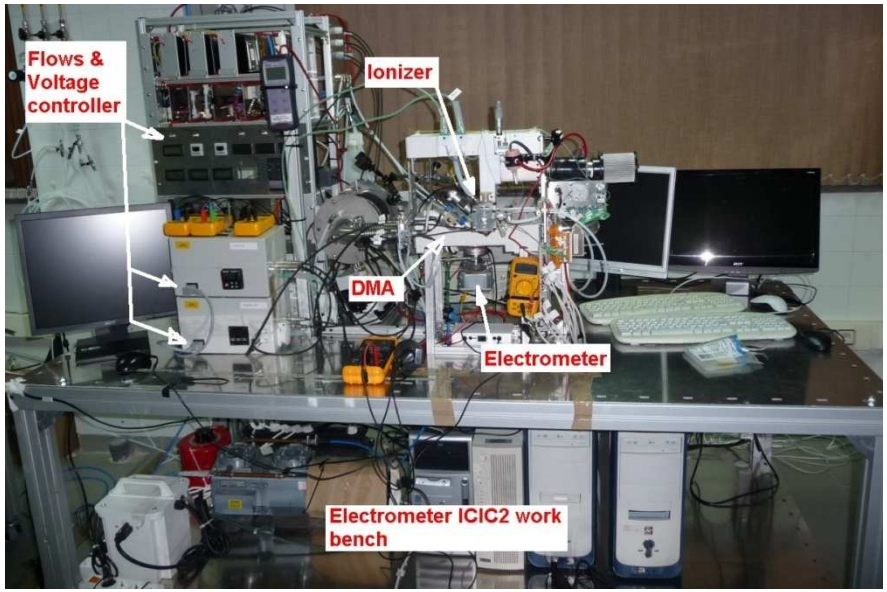
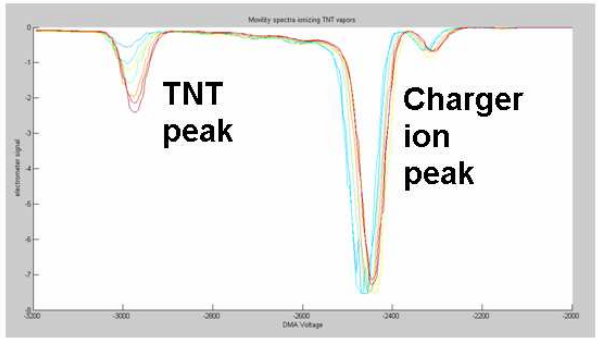
Scope and Methods: Workbench.

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





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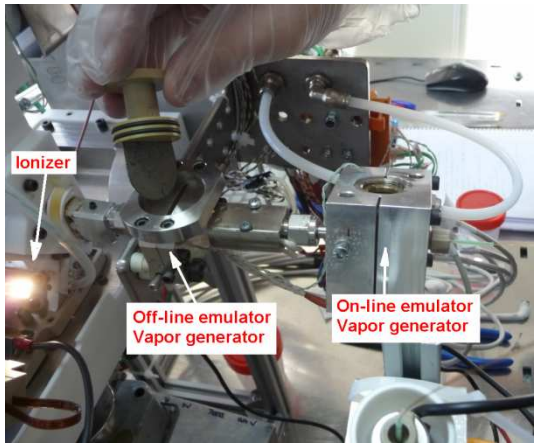
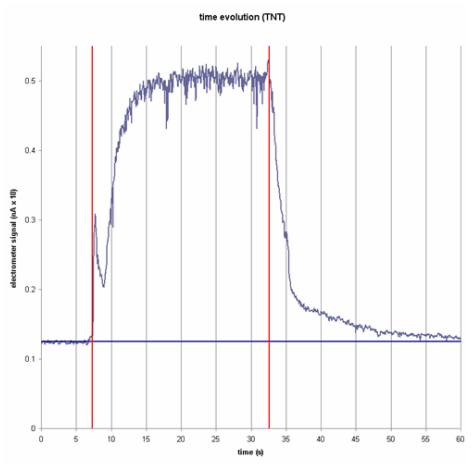
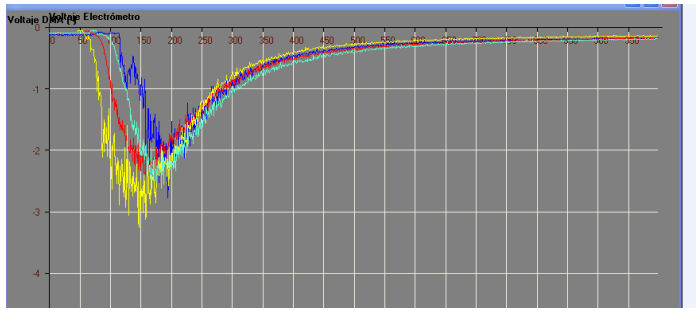
Scope and Methods: Vapor generators.

- 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.







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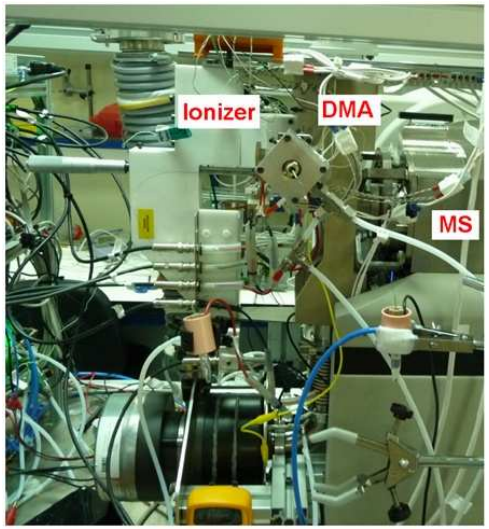
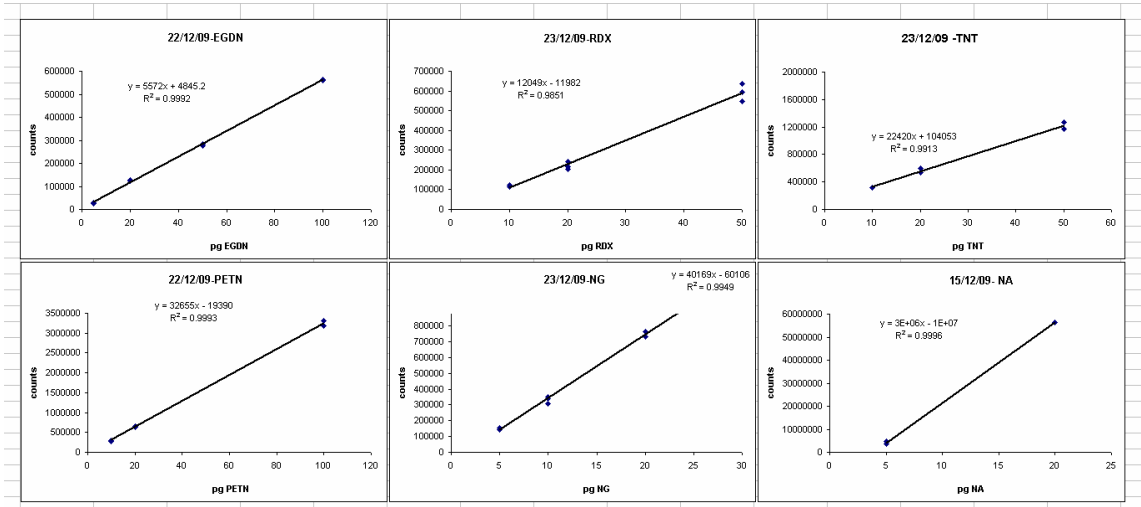
Prototype progression; ICIC1.

- 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.*





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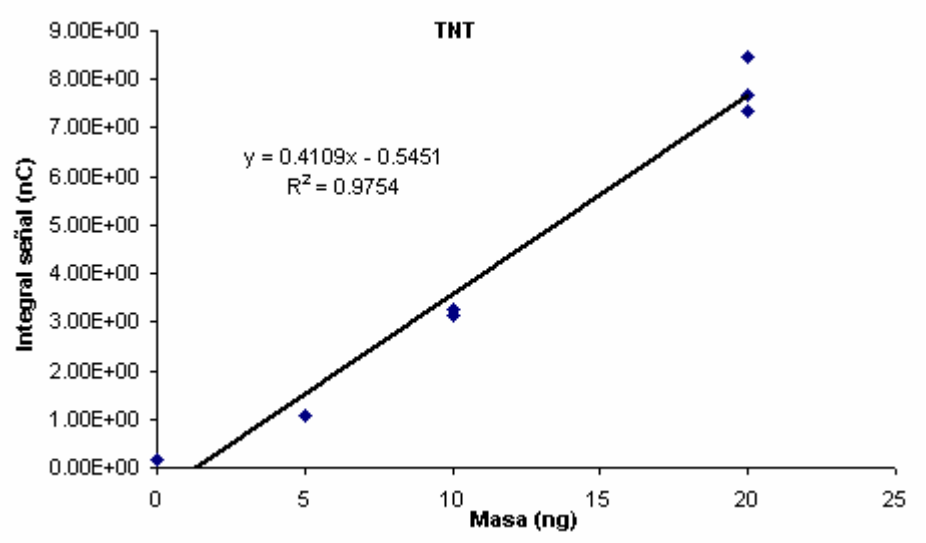
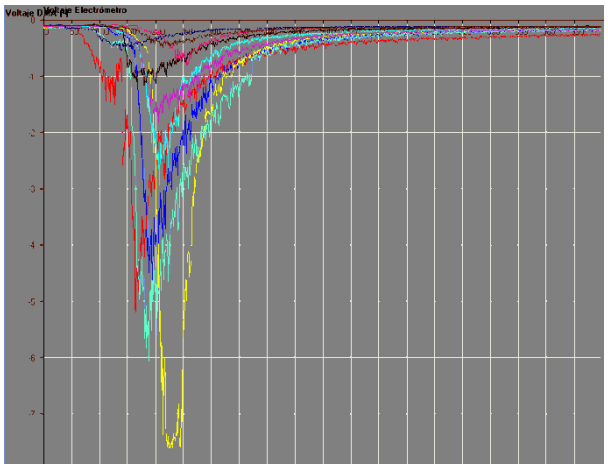
Gain and Ionization efficiency; ICIC1.

- 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 nC/ng.
- Ionization efficiency:
  - P=1e-3; One ion per 1000 molecules. ($P=p_i \cdot Q_{ions}/q_{sample}$)





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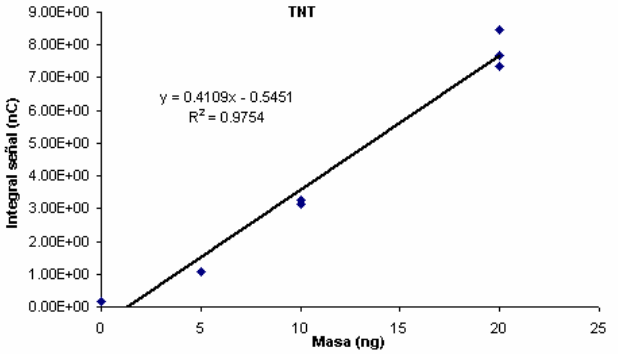
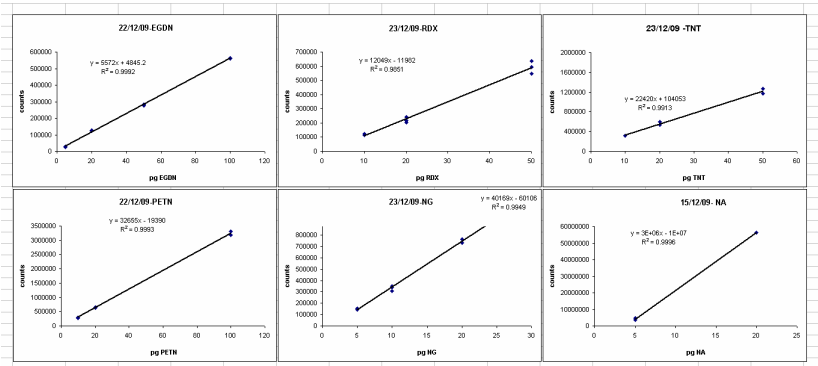
Sensitivity: ICIC1+DMA+API5000(MS-MS).

- 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.



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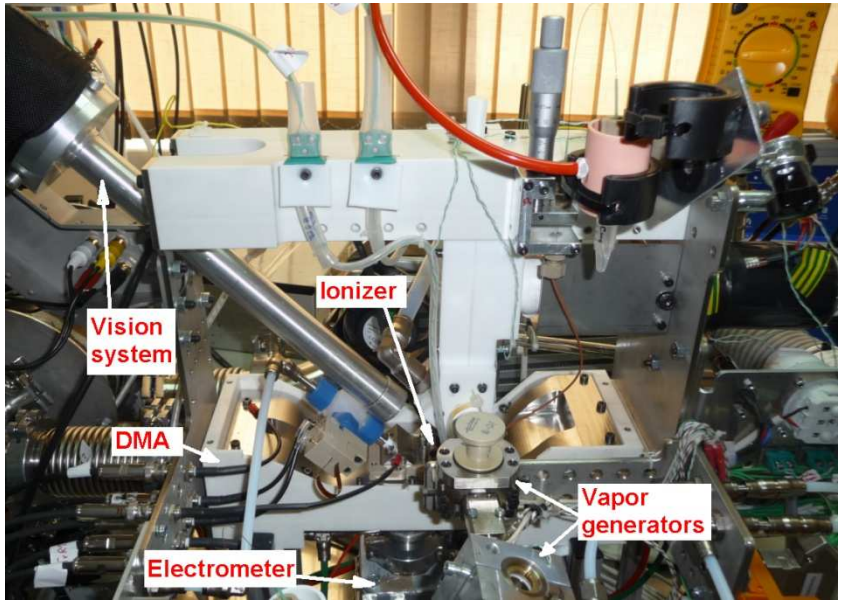
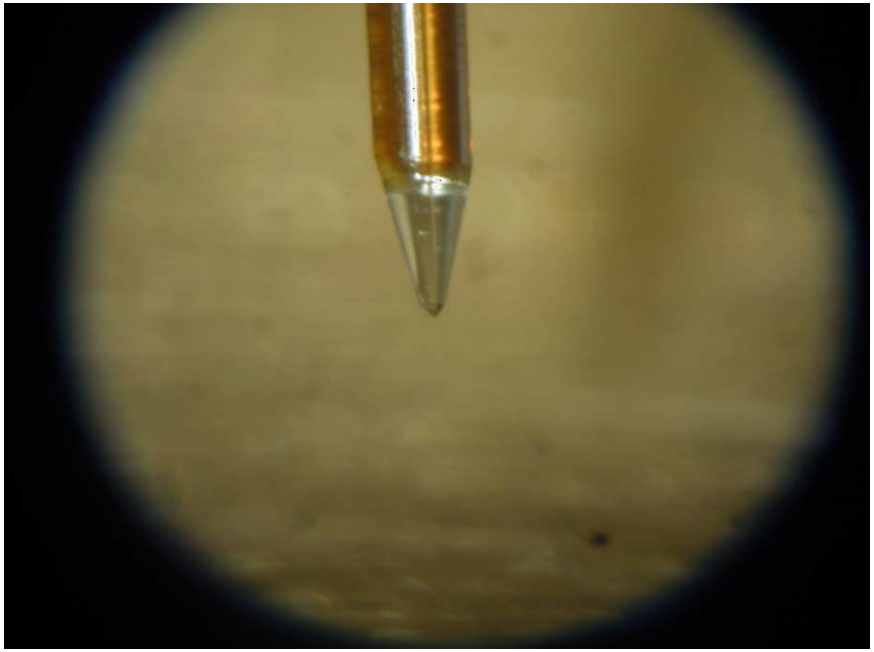
Latest developments; ICIC2.

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





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Conclusions.

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

$$n_s = N_s \cdot p_i = N_s \cdot \frac{k_{cs}\varepsilon_0}{Z_s \cdot e}$$

- *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~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.

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Thanks for your attention!

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