APCI-MS detection of low volatility (ppt) species at room temperature: the advantage of Fenn's droplet-based "electrospray charging"

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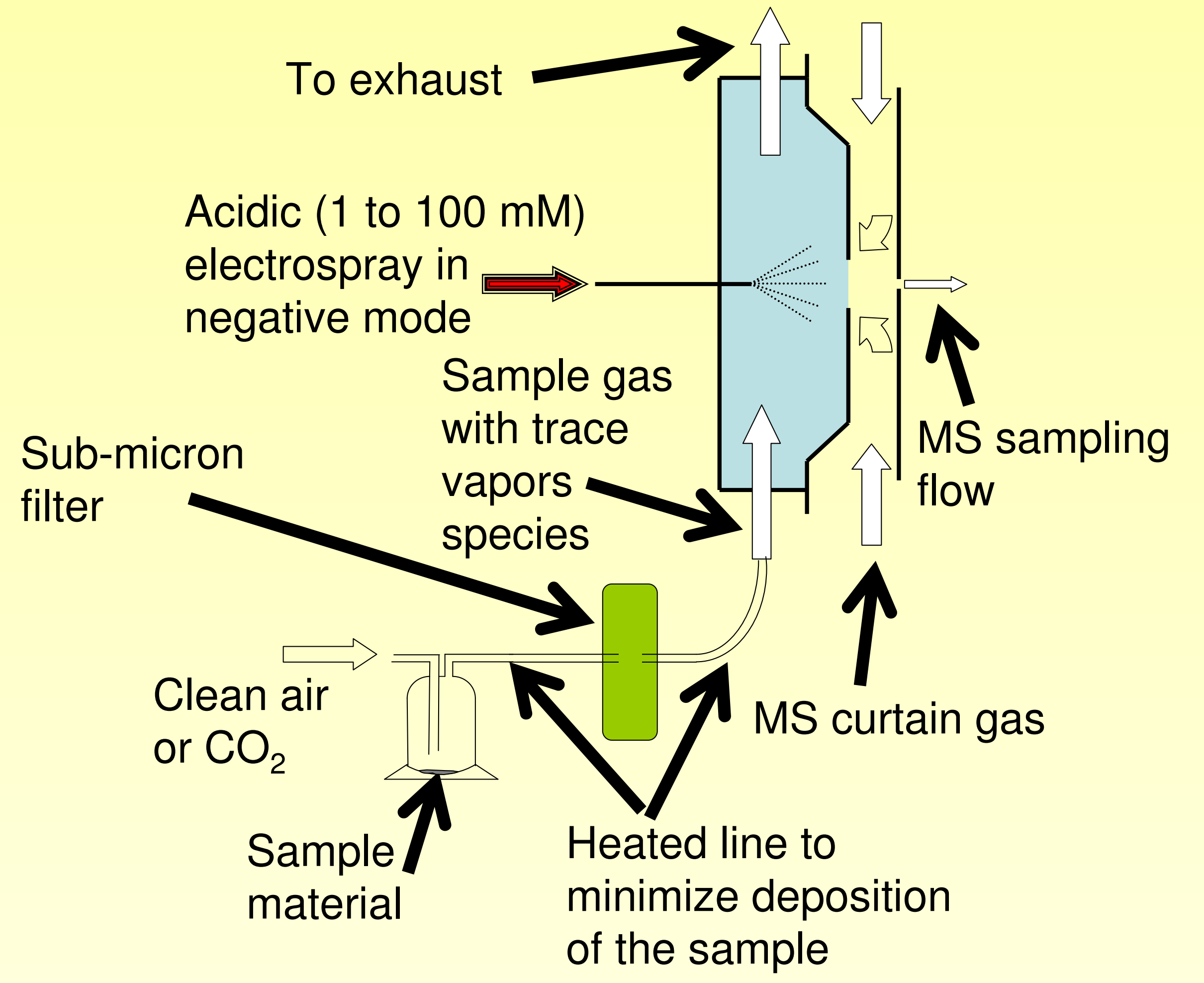
Overview

Several experiments are presented aimed at evaluating the charging efficiency of an electrospray cloud interacting with trace vapor species in a gas, and its potential advantage over charge transfer from ions

Introduction

- ES has been used primarily as a source of solution ions, but electrospray drops have also great potential for ionizing species on surfaces (DESI) or in the gas phase. The later approach involves the interaction of trace vapor species in a gas (generally at atmospheric pressure) with an electrospray cloud. Fenn and colleagues and Hill and colleagues have indicated that vapor capture and charging occurring at the charged drops is probably a more effective charging agent than transfer of charge from individual ions to neutral vapors, but this point remains ambiguous.
- Combined charging and ion transmission-detection probabilities *($p = p_{ch} \cdot p_{trans}$)* are estimated by dividing the measured ion count rate by the number of molecules the saturated vapor would hold in the sample flow, which in the case of PETN (18 ppt vapor pressure at room temperature) is $457 \cdot 10^9$ molecules per liter. Therefore the measured p is a lower limit to the actual probability since the vapors tend to be diluted below that saturation limit

Experimental Setup

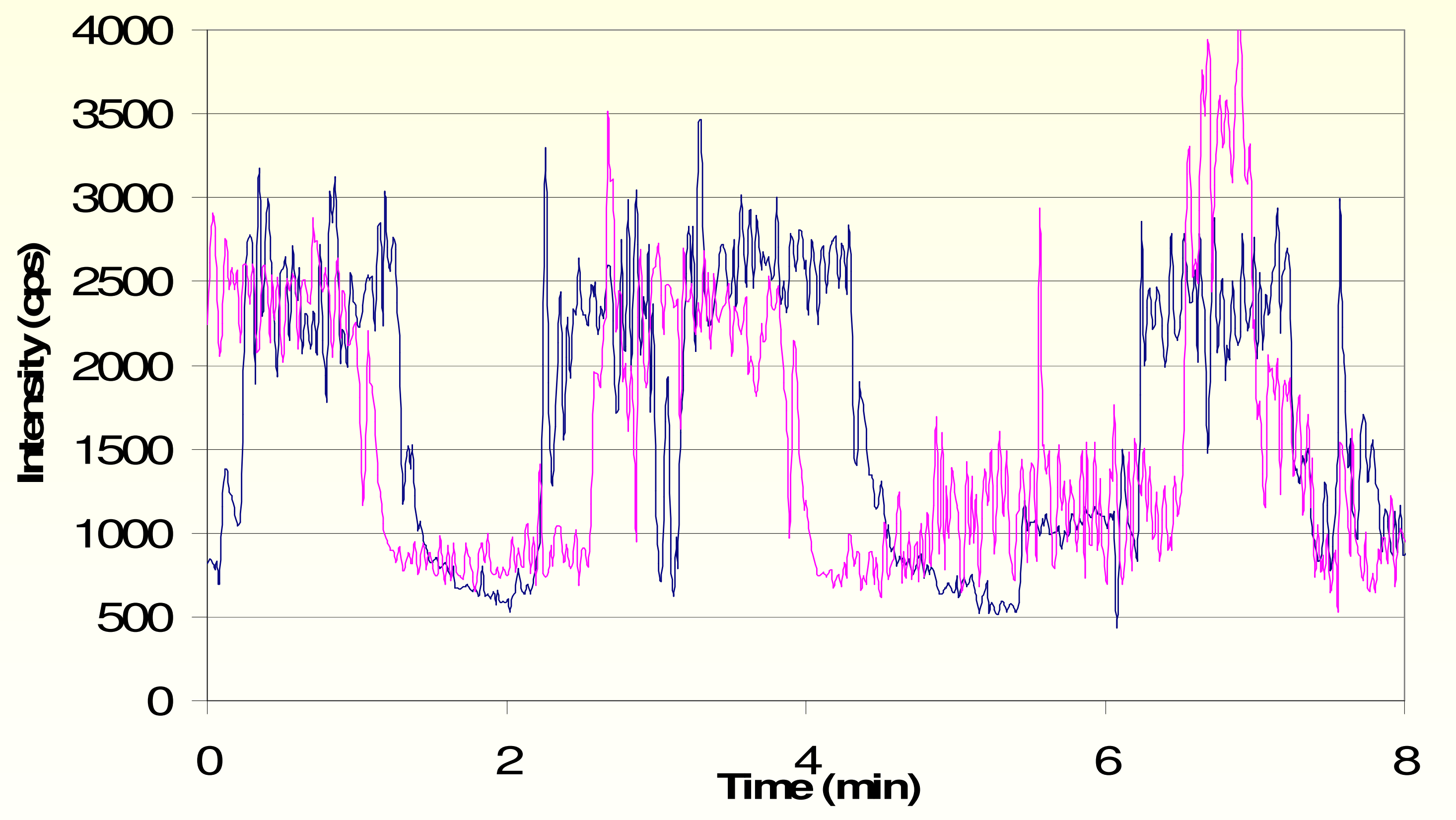


Sensitivity in a Sciex's API 365 to PETN in CO_2

- A signal of about 1300 cps over the background is obtained when 13 l/min of CO_2 are passed through the flask with 1 µg of PETN and then filtered
- This yields a detection probability of $p \sim 0.3 \cdot 10^{-6}$

PETN·CH_3COO^- +/- 0.5 amu signal in time

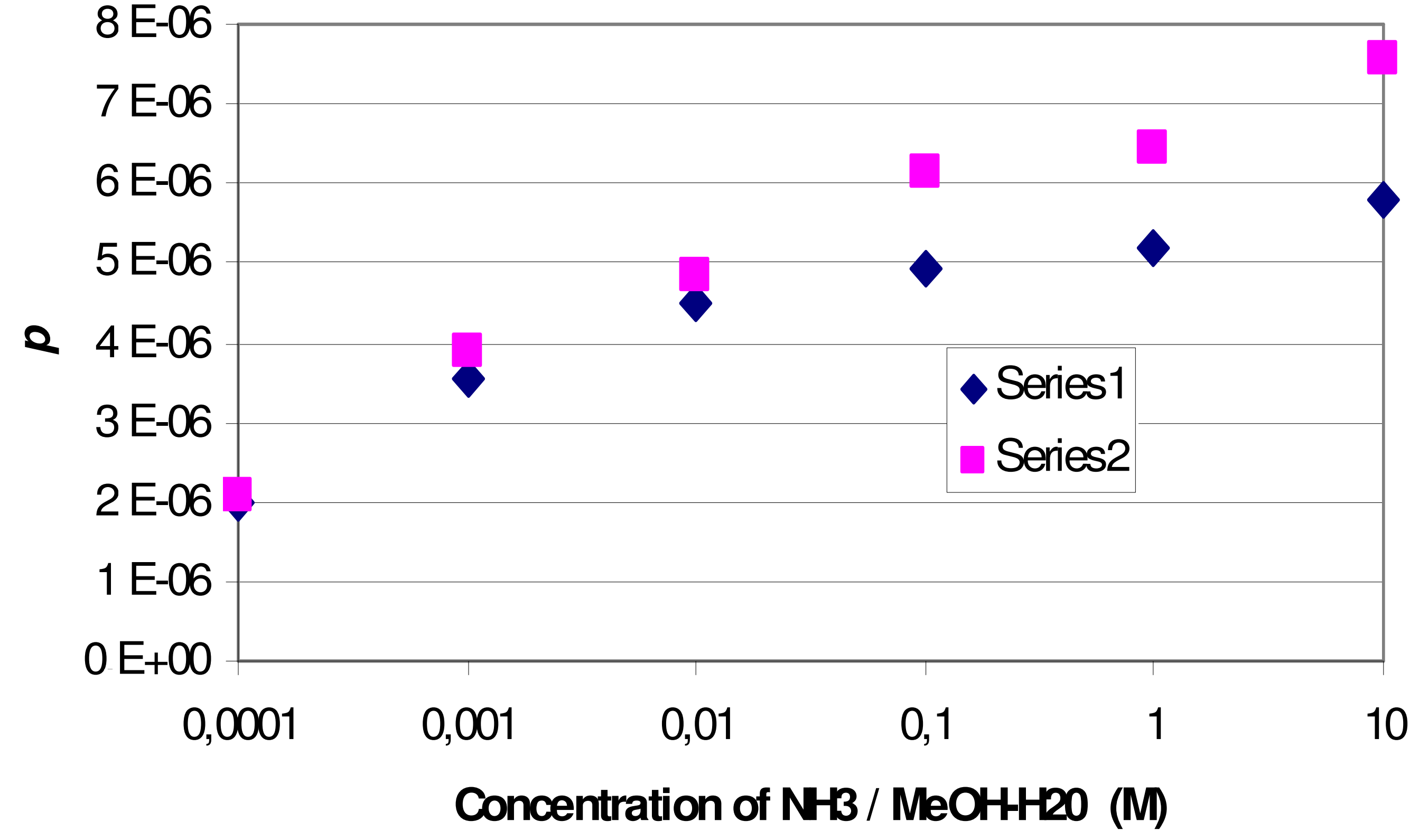
Drops in signal are due to decrease of the CO_2 flow through the flask from 13 to 4 l/min



Sensitivity in a Sciex's API 365 to PETN in air without filter

- Tests carried out without a filter yield much higher signals and detection probabilities, indicating either that some of the signal is due to particles, or that the filter is interacting with the trace vapors and retaining them
- 5 l/min of lab air flowed through the flask with the PETN sample (10 µg)

Combined detection probability based on PETN·CH_3COO^- signal received, as a function of the concentration of ammonia in the electrospray

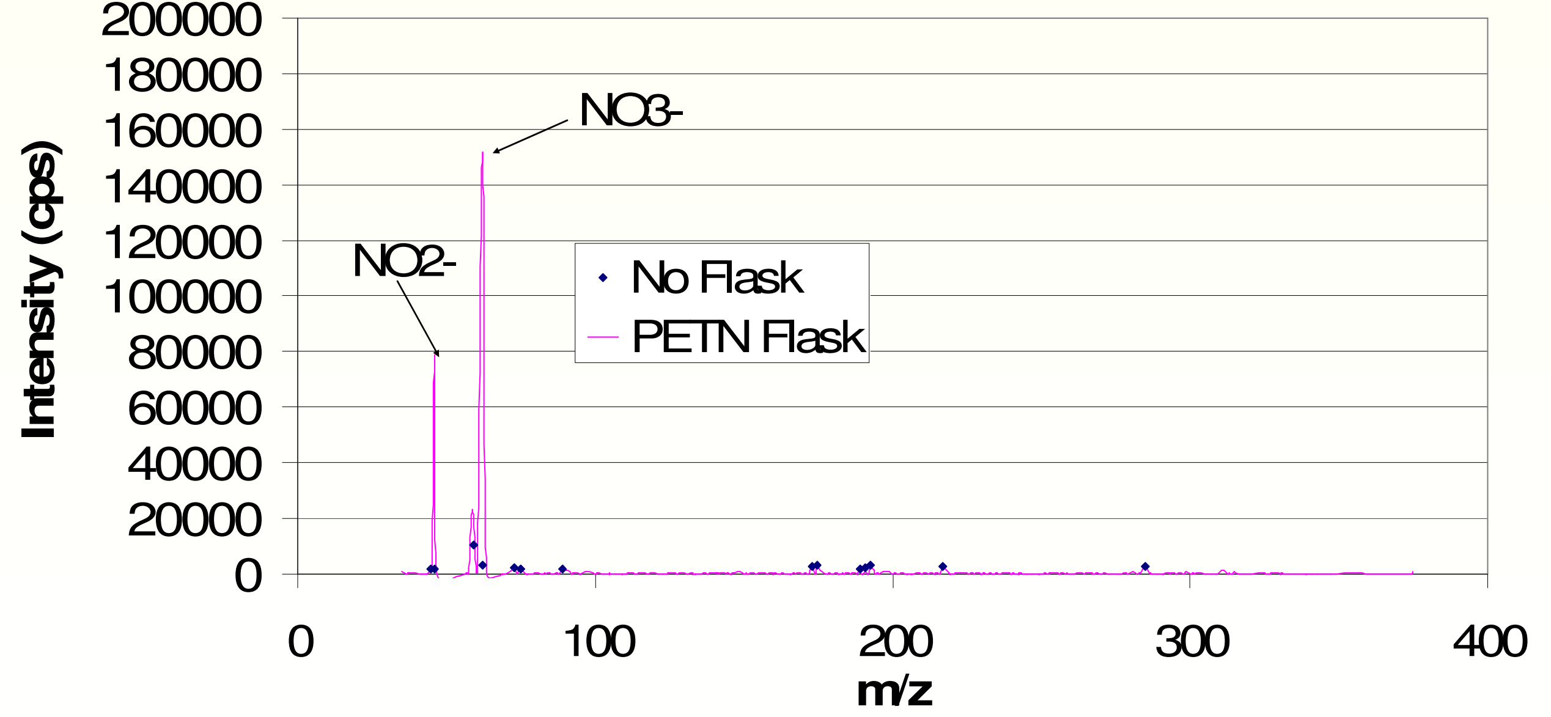


- Contamination of the system with acetic acid yielded PETN·CH_3COO^- as dominant ion

Sensitivity in a Sciex's API 5000 to PETN in air

- 2 l/min of clean air flowed through the flask with the PETN sample
- Fragmentation spectrum shows NO_3^- and NO_2^- as the main fragmentation products from the PETN·CH_3COO^- parent ion (electrospray buffer is CH_3COOH)
- Total signal increase of these products is of about 10^5 cps. This yields a detection probability of $p \sim 6 \cdot 10^{-6}$. However, no filter was used, so part of this signal may be associated to microparticles entrained from the flask by the flow

Fragmentation spectrum of PETN·CH_3COOH-



Conclusions

API-MS is sufficiently sensitive to detect PETN saturated in air at room temperature

Quantitative determination of detection probability is difficult due to particle entrainment and vapor interaction with filters, but a provisional value $p = 0.3 \cdot 10^{-6}$ is obtained