ATMOSPHERIC PHOTOIONIZATION SOURCE COUPLED TO A DMA-MS FOR THE ANALYSIS OF ATMOSPHERIC NON-POLAR CONTAMINANTS

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Introduction

The rapid detection of ubiquitous gas-phase environmental compounds represents an exciting new application for mass spectrometers equipped with ion mobility interfaces. The integration of thermal desorption methods with differential mobility analyzer (DMA) interfaces and mass spectrometry has enabled the fast and sensitive detection of trace analyte vapors, while often eliminating the requirement for extensive sample cleanup or chromatography. Utilizing a new low-flow Atmospheric Pressure Photoionization (APPI) source, we now demonstrate the detection of various environmental analytes, many of which may be difficult to ionize using alterative methods. Discrete volumes of air containing vehicle exhaust emissions have been analyzed within minutes, demonstrating how cold engine operation may generate significant PAH emissions.

Methods

Sampling: The sampler is capable of flow rates up to 250 L/min. A fibre-glass filter cartridge coated with Tenax adsorbent media is used to collect airborne analyte vapors or particles. Pre-concentration enables enhanced LODs not practical by online methods. Samples can be collected and stored/transported for later analysis.

Thermal Desorber: it is used to rapidly vaporize adsorbed particles from the adsorption filters into a low flow (< 0.3 L/min) nitrogen carrier gas stream. Analyte vapor is carried into the source for ionization and transmission to the DMA-MS analyzer

Field free Atmospheric Photoionization (APPI) ion source: A field-free Atmospheric Pressure Photoionization (APPI) source has been designed specifically for the analysis of gas-phase analytes and airborne particles. The source was designed based upon the geometry of first-generation field-free APPI sources intended for LC-MS applications [1].

Differential Mobility Analyzer (DMA): SEADM´s P5 planar DMA combines a horizontal laminar flow of gas with a vertical electric field between two parallel plates, such that ions of different mobilities penetrating through a first (inlet) slit in the upper plate open up in a fan as they drift toward the other plate (Figure 2); therefore, only a small range of mobilities are sampled through a second (sampling) slit in the lower plate.

Mass spectrometer (MS): A Siex´s API 3200 Qtrap was used for the mass analysis using Multiple Reaction Monitoring mode (MRM).

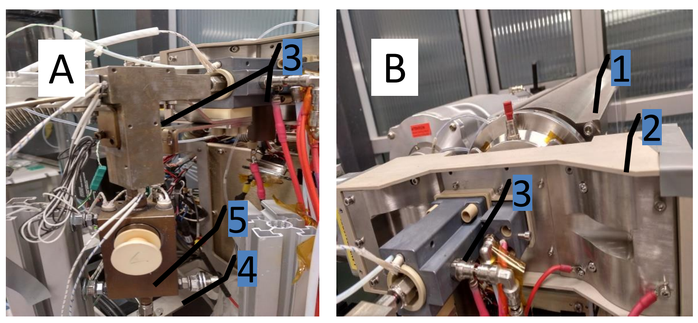

Figure 1. A: Thermal desorber coupled to the APPI ion source. Right. B: APPI ion source coupled to the DMA and the triple quad mass spectrometer. Items: 1. Mass Spectrometer, 2. DMA, 3. APPI Ion Source, 4. Thermal Desorber, 5. Adsoprtion Filter.

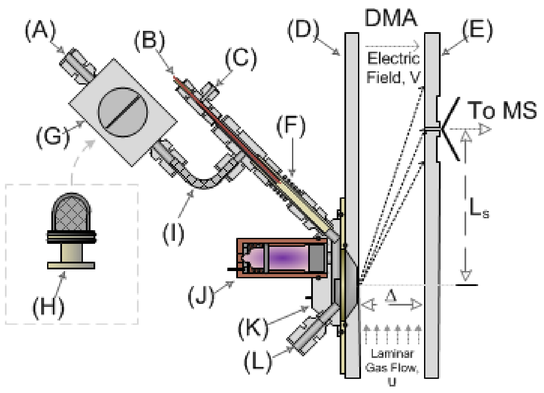

Figure 2. Schematic TD-APPI-DMA-MS/MS system. (a) sample gas inlet, (b) reagent solvent inlet capillary, (c) nebulizer gas inlet, (d) inlet DMA electrode, (e) outlet DMA electrode, (f) heated nebulizer, (g) thermal desorber, (h) Tenax-GR coated fiberglass/stainless steel filter cartridge, (i) heater sample transfer tube, (j) DC Krypton PID lamp, (k) source block, and (l) source exhaust outlet.

Results

The concentration of PAHs with formula $C_{20}H_{12}$ was measured under different conditions. $C_{20}H_{12}$ PAHs includes at least the following isomers: B[a]P, B[e]p, B[k]F, B[j]F,B[b]F, B[a]F and Perylene. Given the similar ion mobilities exhibited for each isomer and the sheer number of potential isomers (at least 7), it was not possible for the DMA to resolve them according to mobility - nor was it possible for the mass analyzer utilized in this study to distinguish between the isomers.

$C_{20}H_{12}$ PAH concentration in air was measured in the vicinity of a diesel engine van .

Three different air samples, of 2000 L in volume, were taken at 0.5 m height and 1.5 m of distance in the following sequence: (i) before starting the engine, (ii) 10 minutes after engine starting, (iii) 20 minutes after the engine starting. Results are shown in Figure 3. When the engine has not reached its working temperature (sample 2) the $C_{20}H_{12}$ PAH concentration is four times larger than the concentration with the engine turned of (sample 1). The third sample, with the engine working at its nominal temperature, gave a concentration two times lower than sample 2.

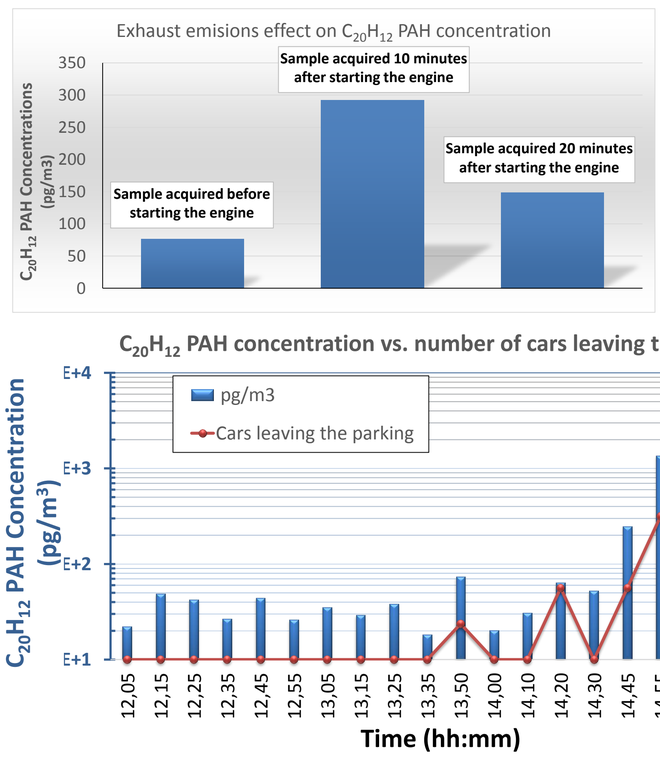

Figure 3. Effect of diesel engine van emissions on $C_{20}H_{12}$ PAH concentration in air samples taken 1.5 meters away from the vehicle.

Airborne $C_{20}H_{12}$ PAH concentration within an underground parking facility throughout three hour period.

1900 Litres of air were sampled at consecutive 10 min intervals in the middle position of the parking (see Figure 4). Figure 5 shows the change in $C_{20}H_{12}$ PAH concentration and car traffic with time. There is a clear correlation between the car departure and the increase of airborne PAH concentrations.

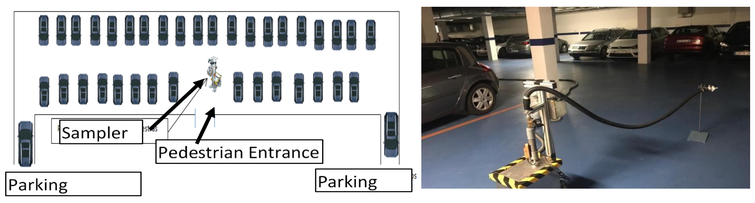

Figure 4 Left. Sampling layout within the parking. Right. Photograph taken during one of the samplings

Figure 5. Airborne $C_{20}H_{12}$ PAH concentration in air within an underground parking facility vs. number of cars leaving the parking.

Conclusions

We have demonstrated the performance of a low-flow APPI source coupled to a DMA-MS instrument enabling the rapid detection of non-polar PAHs.

The proposed set-up has been tested monitoring in real time the airborne $C_{20}H_{12}$ PAH concentration within an underground parking facility throughout a three hour period, showing a good correlation between the car traffic and the increase in PAH concentration.

Acknowledgements

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[1] Robb, D. B.; Covey, T. R.; Bruins, A. P. Anal. Chem. 2000, 72, 3653-3659.