A Universal Low-Flow Secondary Electrospray Ionizer: High Sensitivity Volatile Analysis on Pre-existing MS Instruments

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1. Overview

- Secondary Electrospray Ionization (SESI) in tandem with Atmospheric Pressure Ionization Mass Spectrometry (API MS) has achieved sensitivities in the sub-ppt range for polar vapors [1-7].
- Low-flow SESI (LFSESI) was developed in tandem with a Differential Mobility Analyzer, and in explosive detection applications reached sensitivities at the sub-ppt range [8-9].
- However, it is only available for dedicated applications. We therefore developed an add-on Universal Low-Flow SESI which can be coupled to a pre-existing MS [10].
- This device consists basically on a heated asymmetric LFSESI chamber which is coupled to the MS atmospheric pressure interface. A 2-μm micrometric positioning system provides fine mechanical alignment between the LFSESI and the MS inlet capillary. Also, the axial position of the electrospray tip can be optimized manually. Figure 1 shows the LFSESI coupled to an MS.

2. Benchmarking

- LFSESI performance benchmarked against a “standard” SESI source [10]. We delivered precise amounts of target vapor species and measured the resulting mass spectral signal intensity. Figure 2 shows the setup.
- Electrospray solutions of the species of interest dissolved in H2O were mixed with a controlled flow of clean nitrogen. The electro spray generator and the clean nitrogen line were heated up to 100°C. The temperature of the ionization source was set at 85°C (PID controlled), limited by the charging agent (PH3-formic acid 0.1%) boiling point.
- Inlet capillary temperature was set at 200°C. Voltages, mechanical alignment and electrospray tip axial position were optimized prior the experiments.

3. Drugs detection

- SESI-MS has shown promise to investigate the in vivo pharmacokinetics of injected drugs in mice [11].
- LFSESI performance tested towards vapors of common drugs: Melatonin, Propolis, Aetaminophen, Pentobarbital and Midazolam. Sample flow set at an optimal value of 0.2 L/min.
- Figure 4 shows that the system was able to detect these drugs from concentrations of tenths of ppt in the gas phase, with a linear response across three orders of magnitude.
- Such low concentrations are deemed to be necessary to be detected in exhaled breath of small animals such as mice.

4. Light-induced plant metabolism

- Plants release VOCs as part of their own metabolism or to send warning messages to other plants [12]. SESI-MS can be used to decipher the language of plants [13]. Experiments with begonia show more than 1000 different compounds detected.
- Figure 7 shows the set-up to analyze plant VOCs. Figure 7 shows the temporal evolution along two days of some basic plant VOCs related with photosynthesis.

5. Real time breath analysis

- The LFSESI was used for real time breath analysis, a technique more suitable for diagnostic purposes [14] than Exhaled Breath Condensate. High volatile aldehydes (less than six carbon atoms) were detected. Figure 8 shows detection of aldehydes in exhaled breath with the LFSESI.

6. Conclusions

- The LFSESI ionizer outperforms standard ionizers by a factor of 5 in terms of ionization efficiency.
- This add-on can be virtually interfaced with any commercial API-MS without any modification of the latter.
- As a result, pre-existing mass spectrometers can be deployed for the sensitive and real-time analysis of trace gases.
- We provide some examples of application for the universal LFSESI on the detection of drugs, suggesting that such system can be suitable for real-time pharmacokinetic studies, real time breath analysis or deciphering the language of plants by analyzing their released VOCs.

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9. References