TP 018

DPiMS-MS (PESI) combined with vacuum differential mobility spectrometry for rapid forensic analysis.

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1. Introduction

- Ambient ionisation (AI) mass spectrometry techniques facilitate rapid turn-around of samples, often in a walk-up format with limited sample preparation, with obvious benefits for forensic applications.
- The absence of a chromatographic separation enables sub-minute data acquisition. However, this comes with the cost of greater chance of problems with chemical noise and/or interference between isomeric/isobaric compounds.
- One way to remove chemical noise and to separate interfering compounds is to add an ion mobility separation to the method.
- Here we implement a novel low pressure differential mobility on a DPiMS-8060 (PESI) system and demonstrate performance for steroids and small molecule drugs in saliva.

2. Methods

A prototype vacuum differential mobility spectrometry (vDMS)[1] device was installed on a Shimadzu DPiMS-8060 (PESI) triple quadrupole mass spectrometer. The vDMS is situated between the desolvation line and the Qarray and operated at 33 mbar. vDMS fields are expressed in Townsend (Td) – a unit of reduced electric field.

Data acquisition and analysis was performed using LabSolutions (v5.97), PESI MS solution and software developed in house.

Compounds cortisol, acetaminophen and metformin were dissolved in a range of solvents (solvent selection has previously been shown to have a strong effect on vDMS separation) or artificial saliva.

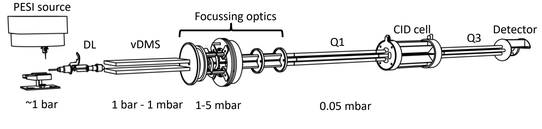

Fig. 1 Prototype vacuum differential mobility spectrometry (vDMS) DPiMS-8060 (PESI) triple quadrupole mass spectrometer

3. Results

- As a proof of principle, Acetaminophen, Metformin and Cortisol were studied in artificial saliva. For Acetaminophen, an interfering species from the solvent (MetOH/formate) was resolved at moderate Ed/N. For Metformin, a single species was observed. The remaining data presented in this poster are for Cortisol.

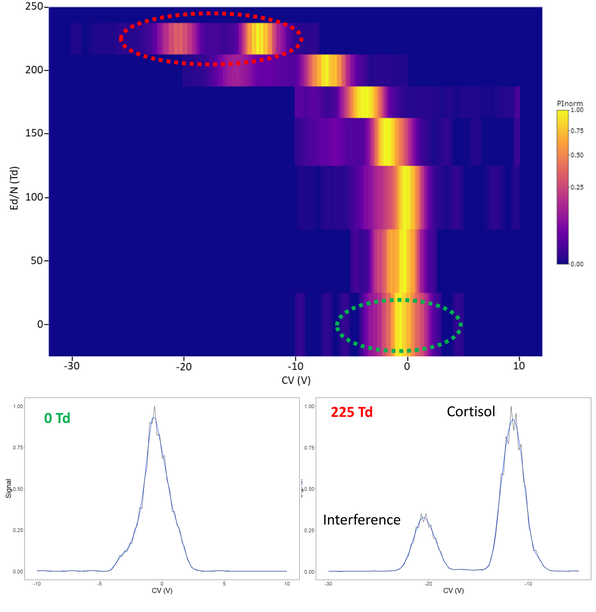

Fig. 2 vDMS separation of cortisol and interference at high field. (a) EcN/EdN plot for 363 m/z. (b) Extracted EcN plot at high field (225 Td). (c) Extracted EcN plot at low field (0 Td).

- Scanning EdN (dispersion field) and EcN (correction field) reveals an isobaric interference for cortisol (**Fig. 2**). Without vDMS separation or at low field, the interference is not resolved. At high field (≥150 Td) the interfering species is baseline resolved.
- By applying fixed EcN/EdN settings the cortisol ions can be isolated from the interfering species. When operated in such a targeted mode specific ion species can be selected for transmission. This is demonstrated in **Fig. 3**.
- Artificial saliva spiked with cortisol was analysed by full scan MS. Without vDMS applied many species are observed across the mass range. When specific vDMS settings for transmission of cortisol are applied the other peaks are removed. Note that adducted cortisol species are retained.

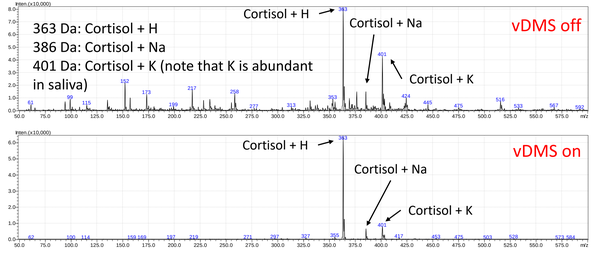

Fig. 3 Full scan MS data for cortisol spiked in artificial saliva (a) without vDMS and (b) with vDMS applied.

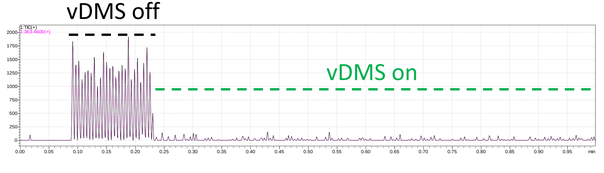

Fig. 4 Chromatogram for 363 m/z in blank artificial saliva with vDMS off and vDMS applied as indicated.

- Blank artificial saliva generates signal in the chromatogram for 363 m/z. This could lead to false positive results and/or problems with the calibration. Applying the specific vDMS conditions for transmission of cortisol removes this background signal (**Fig. 4**).

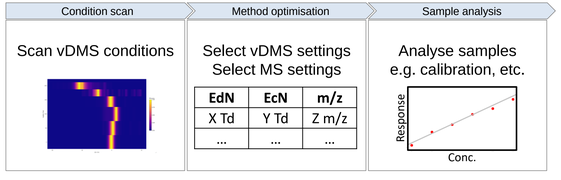

Fig. 5 Generic method development outline for vDMS enabled DPiMS-MS (PESI) methods.

- A generic method development pathway for vDMS enabled DPiMS-MS (PESI) assays is presented in Fig. 5. Whereas for LC-vDMS-MS methods the solvent must be carefully considered due to the impact of solvent vapor on vDMS performance[2], in the case of vDMS enabled DPiMS-MS (PESI) preliminary data shows no impact from the solvent (presumably due to extremely low transfer of solvent to the MS). Therefore, only the physical characteristics of the vDMS need to be considered (waveform, pressure).

4. Conclusion

- These results demonstrate the potential of vDMS to enhance AI-MS by removing chemical noise and separating isobaric species.
- DPiMS-vDMS-8060 (PESI) retains the high acquisition speed of PESI while adding an additional dimension of separation.
- The additional selectivity may lower the LOQ and reduce false positives.
- vDMS-MS methods can be applied in a wide range of complex matrices (e.g. urine, plasma).

References
1) Anal. Chem., 90, 1, 936–943 (2018), Shvartsburg *et al.*
2) Anal Bioanal Chem 414, 7243–7252 (2022), Girard *et al.*

The authors declare no competing financial interest.