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Atmospheric Solids Analysis Probe (ASAP) on a Thermo Fisher LTQ Orbitrap XL

by CM Williams, EPSRC National Mass Spectrometry Service Centre, Swansea University, SA2 8PP, UK
<http://www.nmssc.ac.uk/>

Introduction

The Atmospheric Solids Analysis Probe (ASAP)^[1] allows rapid and sensitive ionisation of samples obtained in solid or liquid forms. It can easily be fitted to any modern mass spectrometer with an atmospheric pressure chemical ionisation (APCI) source.

Experimental methodology

Instrumentation

- Thermo Fisher Scientific LTQ Orbitrap XL (Thermo Fisher Scientific Inc., CA, USA).
- ASAP-MS probe^[1] for Thermo Fisher Ion Max source (In APCI mode).
- All data acquisition, processing and reporting was achieved using Xcalibur v2.0.7.

Materials and Reagents

- Polyethylenimine (PEI) and Cholesterol was purchased from Sigma-Aldrich (Dorset, UK) and made up as per NMSSC Application Note 3^[2].
- Methanol, Dichloromethane and Water were purchased from Fisher Scientific (Loughborough, UK)
- Ammonium Acetate (NH₄OAc, 30mM) was prepared using Ammonium Acetate purchased from Sigma-Aldrich (Dorest, UK) and dissolved in Methanol.
- Samples submitted to the NMSSC.

Method

- Initially, the instrument was tuned and calibrated as per the manufacturer's instructions using electrospray (ESI).
- Tuning was best achieved using ASAP. The technique requires a low tube lens voltage (circa 5 to 10V), in order not to cause fragmentation.
- For ASAP, PEI was used to check the calibration with a vaporising temperature of 250°C and a tube lens voltage of 5V. Ions observed from m/z 190.2 to 663.6 were also used to calibrate (Figure 1).
- Sample was deposited onto a glass melting point tube.
- Any additive was deposited onto the glass capillary at this point using a pipette.
- The melting point tube was placed into the ASAP probe, which was inserted into the source.
- The APCI discharge current was set to 4 µA.
- The sample acquisition was started.

- The APCI vaporiser temperature was raised from ambient temperature to the temperature that vaporised the sample.

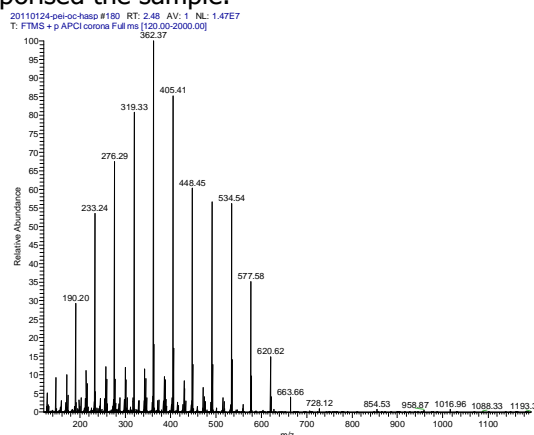


Figure 1: ASAP calibration using PEI.

- The initial setup was checked using cholesterol with the addition of NH₄OAc (Figure 2). M/Z 369 shows loss of -OH, the added NH₄OAc promotes the NH₄⁺ adduct at m/z 404, see expansion in bottom spectrum.

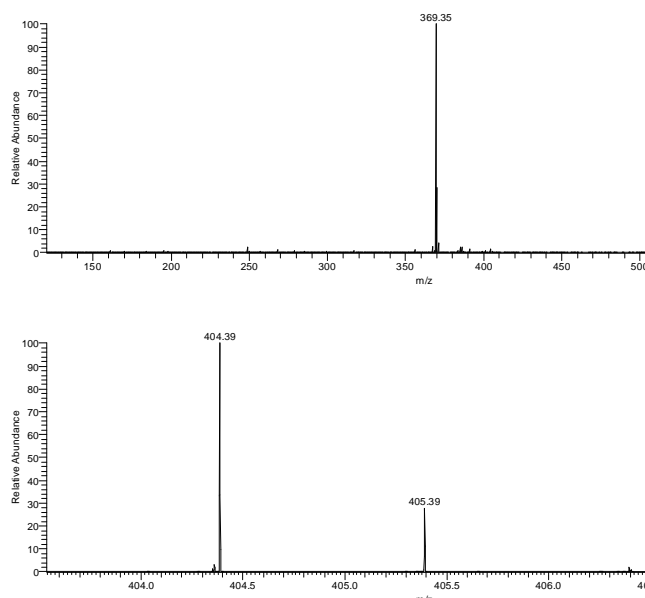


Figure 2: Spectrum showing ASAP analysis of Cholesterol, with the addition of 30mM NH₄OAc in MeOH. Expansion of region m/z 403-407 showing [M+NH₄]⁺, bottom spectrum.

Results and Discussion

- It was found that ASAP was versatile in the types of samples that could be ionised.

- It was able to cope with samples that would have previously been analysed by ESI, APCI, electron ionisation (EI), chemical ionisation (CI) and even fast-atom bombardment (FAB).
- It was possible to influence the ionisation by the use of additives. This can be observed in Figure 3.

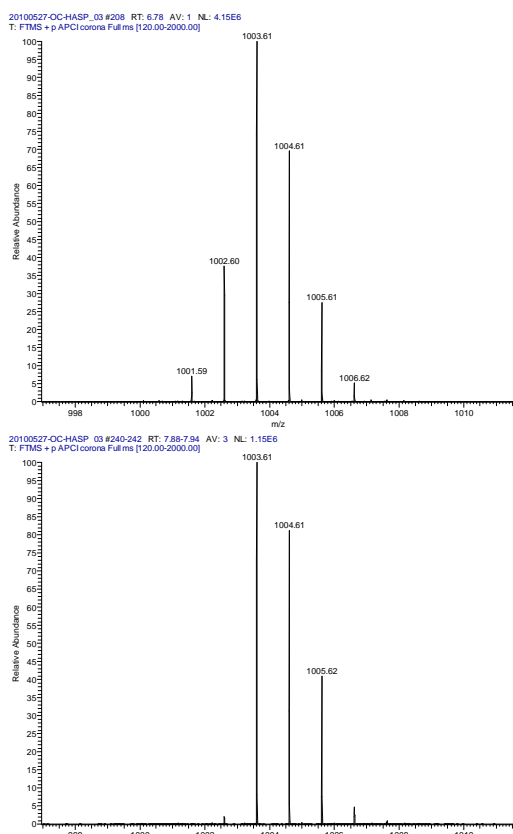


Figure 3: Spectrum showing sample ionised with no additives (EI type), top, and sample ionised with the addition of 30mM NH₄OAc (CI type), bottom.

- It was important to keep a low tube lens voltage to minimise fragmentation of the M^{•+}, [M+H]⁺ or [M+NH₄]⁺ ion.
- The exception to this was when the sample was 1) of high molecular weight and 2) required a high vaporisation temperature. When these two conditions were satisfied it was found that the tube voltage could be increased in order to observe the (pseudo-) molecular species.
- There are two modes of ionisation: Charge transfer and Proton Transfer.
- The presence of water vapour can lead to an apparent [M+16]⁺, found to be [M+O]⁺, caused by consecutive reactions.
- Hydrocarbons, usually analysed by EI and giving a radical molecular ion, M^{•+}, gave rise to a pseudo-molecular species [M+H]⁺ without any additives, Figure 4.
- It was found that there was no difference between calibrating in ESI or ASAP using this instrument. It was important to observe that no ions were missing during the calibration routine.
- There was no difference in the analysis from using sealed or open ended glass capillaries.
- It was noted that sealed glass capillaries did emit background ions as the temperature increased. It

may, therefore, be necessary to pre-heat sealed glass capillaries before the sample is deposited.

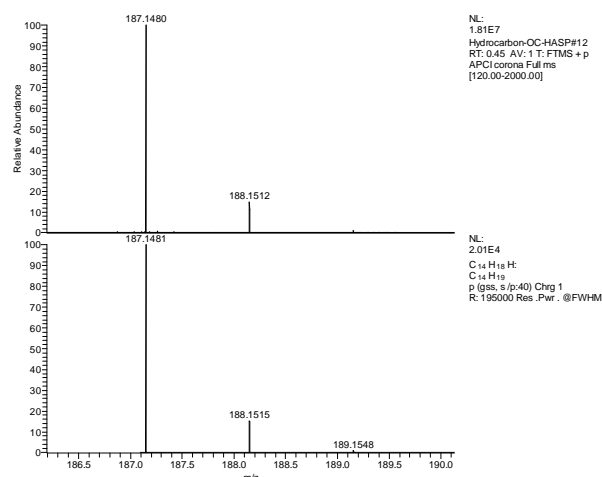


Figure 4: Spectrum showing hydrocarbon of formula C₁₄H₁₈, top, with theoretical isotope pattern, bottom. The ion observed was the protonated [M+H]⁺.

Conclusion

- Sample preparation was rapid.
- Sample acquisition was rapid, no more than a few minutes.
- The method was found to be sensitive.
- Ability to analyse solids.
- Can ionise samples in both negative and positive modes.
- The use of additives, or modifiers, drove the ionisation towards a favoured ion, e.g. [M+H]⁺, which avoided confusion when interpreting data when both the radical molecular ion and pseudo-molecular ions were initially observed.
- Under controlled conditions, zero-carryover can be observed.
- Samples that previously ionised poorly using the Advion TriVersa Nanomate (Advion Biosciences Inc., NY, USA) often gave enhanced ionisation using ASAP. The expected ion was now the base peak, with very little background.
- ASAP can ionise non-polar samples.
- Common API background ions are still observed using ASAP.
- The use of ASAP on the LTQ Orbitrap XL provides a means of performing EI/CI type experiments on this instrument; a feature greatly welcomed.

Acknowledgements

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- The users of the EPSRC NMSSC for the copious amounts, and varieties, of samples to use with the ASAP technique.

References

- [1]. M&M Mass Spec Consulting LLC, Delaware, USA <http://www.asap-ms.com>
- [2]. NMSSC Application Note 3 http://www.nmssc.ac.uk/ms_app_notes.html