

The Power of Low Energy EI Ionisation in GC/Q-TOF MS

Camilla Liscio, Anatune Ltd, Girton, Cambridgeshire (UK).

Introduction

Identification of unknowns is one of the most challenging tasks in analytical chemistry, particularly when dealing with real sample matrices. Differently from LC-MS, GC-MS can rely on the fragmentation pattern information provided by the several spectral libraries available on the market. Nevertheless, this is often not enough, for instance when dealing with isomers or with new unknown molecules. Additionally, Electron Impact (EI) is a hard ionisation technique meaning that often the molecular ion is not present in the spectrum due to the amount of fragmentation generated by the ionisation energy involved.

Being able to generate cleaner spectra with less low mass fragmentation, and a tilt towards the molecular ion, can be extremely beneficial for unknown identification. Conventional EI sources could potentially operate at low electron energy to perform softer ionization and increase the relative intensity of the molecular ion, but this typically results in drastic drop in sensitivity levels. Agilent 7250 Q-TOF is equipped with a low energy EI source with a novel source design based on the High Efficiency Source available on the GC/MSD and GC/QQQ models.

Optimization includes a stronger axial magnet, modified lens geometry and a centred filament design. These changes allow the source to become even more efficient at ionization, trading some efficiency for softness and a tilt towards the molecular ion. Low energy EI spectra show a loss total ion current at lower electron energy values but the efficiency of ionization provides usable levels of sensitivity.

This application note describes optimisation of the low energy EI ionisation on the Agilent 7250 QTOF using design of experiments and showcases two applications benefiting of cleaner spectra and molecular ion information provided by low energy EI.

Instrumentation

Autosampler: Dual head MPS Robotic, USM tool equipped with 10 µL syringe

Modules: Vial tray VT40 2 mL, Large wash station

GC-MS: Agilent GC 7890B coupled to Agilent 7250 QTOF MS, Low energy EI source

Software packages:

- Statistical analysis software JMP® for Design of Experiment data processing
- MassHunter Quantitative Data Analysis for peak integration



Figure 1: GERSTEL Dual Head Robotic MPS on top of Agilent GC 7890B coupled to 7250 Q-TOF MS

Methods

Low Energy E Optimisation using Design of Experiments

Definitive Screening Design (DSD) was used as the model design in the low energy EI optimisation process for factor screening.

GC-MS analysis

Example 1: Separation of Isomers

Inlet: Split Splitless injector

GC: Column: HP-5MS Ultra inert 30 m x 0.25 mm x 0.25 µm

Splitless Mode, Injection Volume 1 µL

Flow: 1 mL/min

GC ramp: 50 °C held for 2 min, 35 °C/min to 300 °C held for 0.9 min

Runtime: 10 min

MS: Auxiliary temperature: 300 °C

Mass range 50-650 m/z

Example 2: Identification of Unknowns

Inlet: Split Splitless injector

GC: Column: HP-5MS Ultra inert 30 m x 0.25 mm x 0.25 µm

Splitless Mode, Injection Volume 1 µL

Flow: 1 mL/min

GC ramp: 50 °C held for 5 min, 10 °C/min to 250 °C held for 5 min

Runtime: 30 min

MS: Auxiliary temperature: 300 °C

Mass range 50-350 m/z

Results and Discussion

The optimisation of the Low Energy EI ionisation conditions using DoE was carried out focusing on the molecular ion intensity as response. The values were generated by Mass Hunter Qualitative Analysis when processing the data. The design required a total of only 17 experiments. Each experiment included sample liquid injection and GC-MS analysis 10 min runtime. Within 3 hours results were available for data processing. The DSD generated a model which highlighted the presence of significant factors and interactions between the factors. Quadratic behaviour was found for Energy. Optimised conditions were chosen to perform application work.

Example 1: Characterisation of Isomers

The optimised settings were applied to the analysis of Farnesol isomers. A solution of two Farnesol isomers in hexane (100 µg/L) was injected and acquired using standard EI mode and optimised Low Energy EI mode. Figure 2 shows the comparison between ionisation modes for one of the targets.

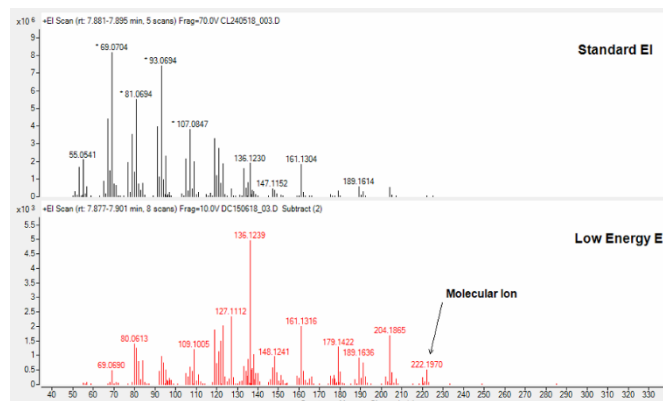


Figure 2: Comparison between Standard EI ionisation and Low Energy EI Ionisation on the Agilent 7250 Q-TOF for one of the Farnesol isomers.

The Low Energy EI spectrum revealed a tilt towards the molecular ion which could not be observed when operating in Standard EI mode. Mass accuracy of 3.7 ppm was obtained for the molecular ion.

Figure 3 shows the comparison between the spectra of the two isomers when using Standard EI and Low Energy EI, respectively. The spectra show differences in the relative intensity of the fragments for the two isomers.

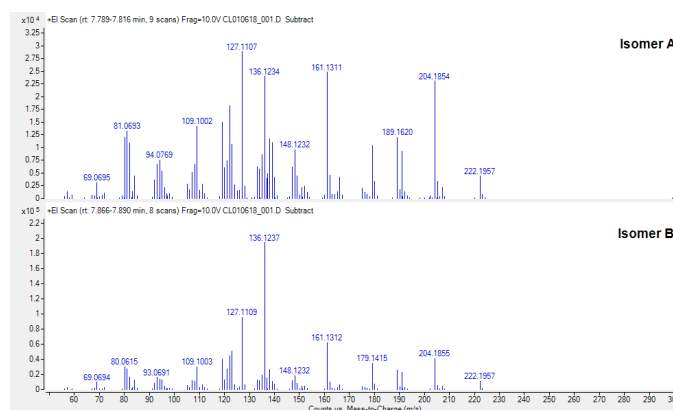


Figure 3: Comparison of Low Energy EI spectra for the two Farnesol isomers.

Example 2: Identification of Unknowns

A combination of Standard EI, Low Energy EI Scan, and Targeted MS/MS spectra was used to help with the characterisation of unknown peaks present in a customer sample. For the acquisition of Low Energy EI spectra, conditions optimised by design of experiments were used.

Figure 4 shows the comparison of the MS spectra obtained for one of the target unknowns in Standard EI, Low Energy EI Scan and Targeted MS/MS, respectively.

optimized conditions tilted significantly fragmentation pattern towards the molecular ion increasing confidence in unknowns' identification.

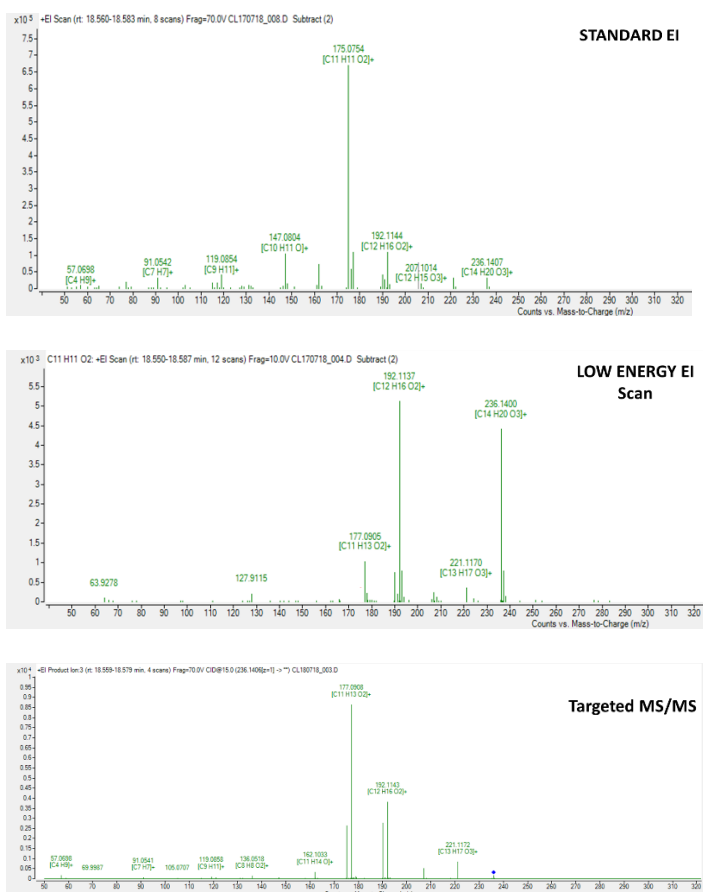


Figure 4: Comparison between Standard EI (top), Low Energy EI Scan (middle) and Targeted MS/MS for one of the target unknowns.

The Low Energy EI acquisition significantly tilted ionisation towards the molecular ion, allowing its confirmation. The Targeted MS/MS spectrum using the confirmed molecular ion as precursor ion, showed comparable fragments to the standard EI spectrum.

Proposed molecular formula for the unknown compound gave mass accuracy of 2.6ppm and Score of 96.4.

Conclusions

The use of design of experiment to optimize the Low Energy EI parameters provided very good understanding of the process and the factors affecting it. This allowed to find the optimal conditions for the best analytical performance. The