

COUPLING GC×GC WITH QTOF DETECTION IN MS/MS MODE: A FEASIBILITY STUDY

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The Agilent 7250 QTOF detector delivers high-resolution MS data, tunable ionization energy and MS/MS capability. Accurate-mass spectra with classic ionization can therefore be complemented with soft ionization spectra as well as MS/MS data for identity confirmation of targets and structure elucidation of unknowns. This makes GC-QTOF valuable for challenging applications that demand confident identification in highly complex matrices (e.g. metabolomics, pesticides analysis).

Comprehensive two-dimensional gas chromatography (GC×GC) is the chromatographic method of choice to unravel high sample complexity. Compared to classic GC, GC×GC grants superior separation power and unmatched peak capacity by coupling two different separation mechanism in a single analysis. Co-elutions are avoided or minimized, granting easier identification and more reliable quantification.

Several examples are available for GC×GC in combination with the QTOF used in scan mode as a HRMS-TOF detector. The elevated number of resolved peaks and the clean 2D spectra, in combination with formula generation based on accurate-mass data, allow more precise and informative profiling. However, up to now GC×GC is hardly used in combination with the QTOF in MS/MS mode. Here we investigate the feasibility of GC×GC-QTOF-MS/MS.

Experimental

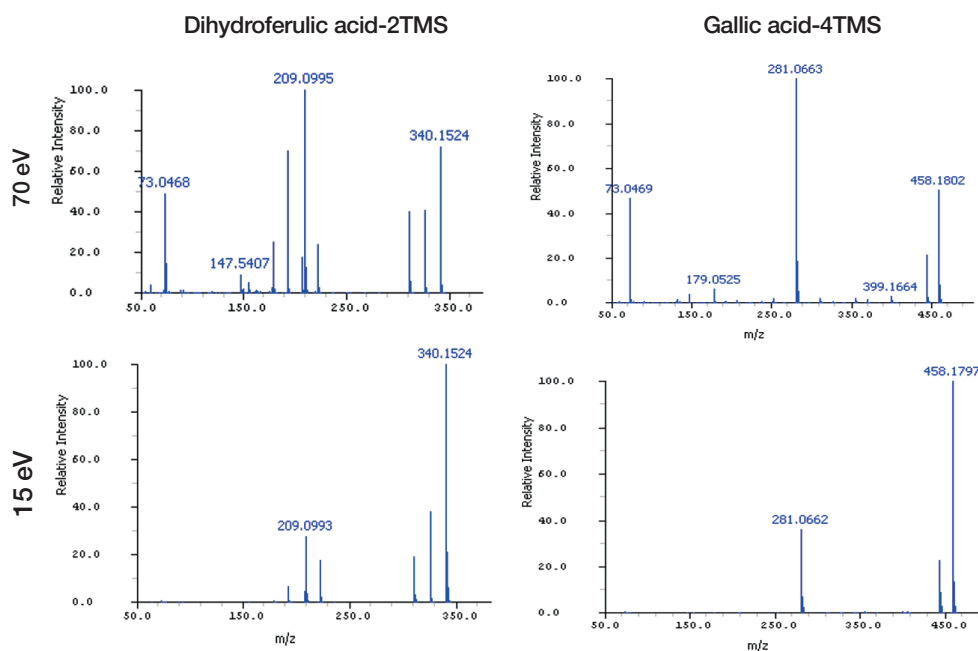
A test mix of Dihydroferulic acid and Gallic acid TMS derivatives at 100 µmol/L is measured on an Agilent 7890B GC with Zoex ZX2 thermal modulator and Agilent 7250 QTOF Detector. All data are displayed and processed using the *GC Image HR* software package.

Results and discussion

Fig. 1 shows the spectra acquired for the two test compounds with classic and soft ionization, respectively. Low-energy ionization reduces fragmentation significantly and the molecular ion become the most abundant fragment. This is interesting to maximize the MS/MS parent ion and thus sensitivity.

Fig. 1

GC×GC-QTOF spectra with hard and soft ionization. Acquisition in scan mode at 50 Hz.



Several parameters need careful optimization to achieve informative MS/MS data with suitable chromatographic resolution and sensitivity in GC×GC. For instance:

- The option to acquire also full spectra next to MS/MS data is disabled to maximize the number of scans across the peaks.
- The precursor dwell time, which is reversely proportional to speed, is kept small (at the cost of sensitivity) to avoid undersampling.
- To counterbalance, the quad resolution window (“MS1 Res”) is preferably set on wide. With GC×GC the chance of co-elution is greatly reduced, so high selectivity at the quads is not likely to be a key factor.

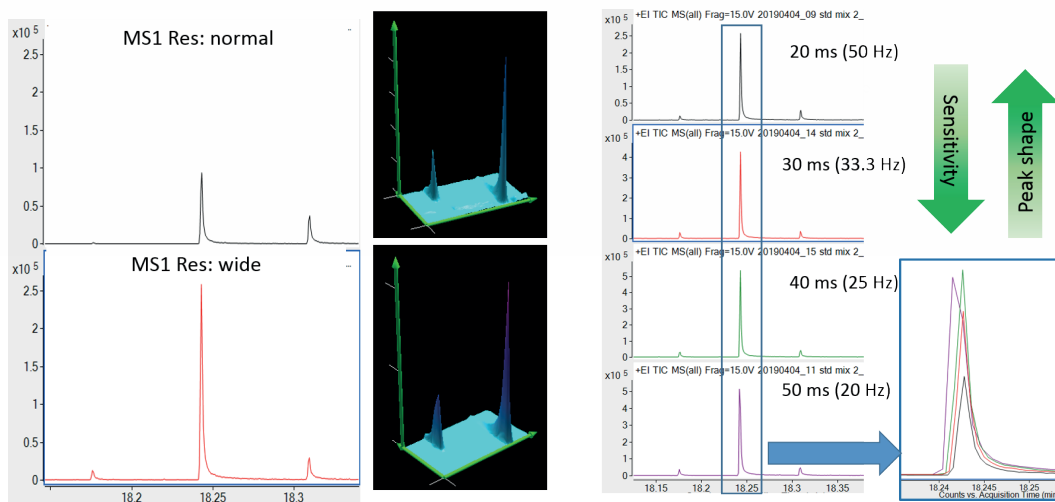
Fig. 2 shows examples of how these settings impact performance. As can be seen, by optimizing the settings as described above it is possible to generate a satisfactory number of points across the sharp modulated peaks. As expected a very short dwell time grants the best peak shape, with larger dwell values sensitivity is improved but the peak is under-sampled and therefore suitable only for qualitative purpose.

Fig. 2

LEFT:
raw data and 3D view for MS/MS peaks with dwell time 20 ms and different quad resolution settings.

RIGHT:
MS/MS peaks with different dwell time values.

IONIZATION ENERGY: 15 eV, MOLECULAR IONS SELECTED AS PRECURSORS, COLLISION ENERGY: 15 eV, TOF ACQUISITION AT 50 Hz.



These results convincingly show the feasibility of operating the QTOF in MS/MS mode also coupled to GC×GC. This feature can be a powerful profiling tool to complement two-dimensional chromatograms and HRMS and their excellent selectivity in order to achieve even more confident identification and determine structures of unknowns.


Data visualization and processing can be performed directly on the 2D image with GC Image, which for instance enables MS/MS library search. In addition, it is possible to use the classic MS/MS workflow based on MassHunter Qualitative Analysis and Molecular Structure Correlator on the raw data.


CONCLUSION

- Agilent’s 7250 QTOF provides high resolution, accurate mass, soft ionization and MS/MS capability. These features are generally used in GC-QTOF for advanced identity confirmation and structure elucidation.
- GC×GC can be used with the QTOF in MS/MS mode. Careful optimization allows to obtain good MS/MS data, also for the sharp modulated peaks.
- GC×GC-QTOF with soft ionization-MS/MS can be a very powerful tool for identification of targets and unknowns with enhanced confidence and selectivity.

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