Validation of a qualitative screening method for pesticides in fruits and vegetables by GC-(APCI)QTOFMS

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Background

GC with full scan MS is a powerful approach for wide-scope screening of pesticides and contaminants. Nominal resolution MS has been mostly used for this purpose so far. High resolution/accurate mass TOF is a more recent development offering a higher selectivity.
Dedicated GC-MS systems involve electron ionization (EI) typically resulting in a strong fragmentation. This prohibits a straightforward detection of analytes in the raw data through their (pseudo)molecular ion and is a serious drawback in detection of unknowns.
Recently, atmospheric pressure chemical ionization (APCI) has become available as an alternative option to couple GC to MS. This results in much less fragmentation compared to EI, and provides access to a range of existing MS systems initially developed for LC-MS.

Objective

- Investigate the potential of APCI as an alternative to EI in GC
- Apply GC-(APCI)QTOF MS instrumentation for screening and identification of pesticides in fruits and vegetables.
- Validate a qualitative screening method for 150 pesticides in various commodities according to SANCO/12495/2011.
- Establish the screening detection limit (SDL) for each of the pesticides studied and the number of false positives.

Experimental

- Extraction: QuEChERS
- Solvent switch to toluene
- Final extract: 3.33 g/mL
- Injection: 1 µL splitless
- GC: 7890A (Agilent);
- 30 m x 0.25 mm ID, 0.25 µm DB5MS
- Source: APCI (proton transfer promoted by water vapour)
- MS: quadrupole time-of-flight MS (Xevo G2-QTOF, Waters), Resolving power 18,000 (@ m/z 556 FWHM)
- Acquisition: m/z 50-650, scan speed 2.5 scan/sec
  alternating scans: low collision energy and energy ramp (MS^E)
- Data Processing: Chromalynx XS (Waters)

Results

Screening based on molecular ion searching

In APCI molecular ions and/or protonated molecules are highly abundant, in contrast to EI.

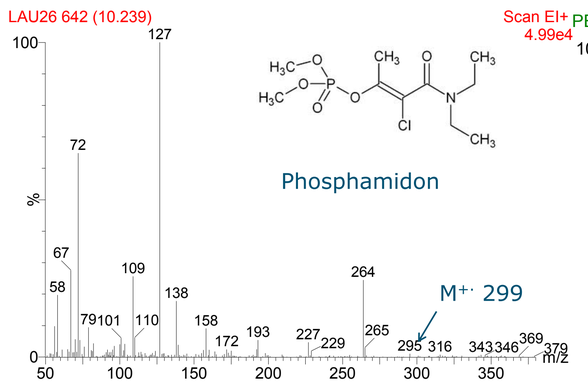

Figure 1. GC-EI-MS spectrum

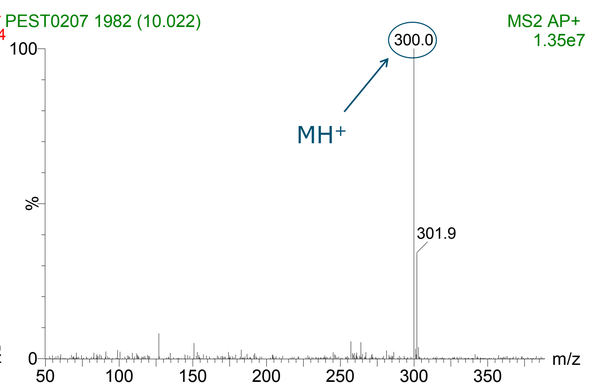

Figure 2. GC-APCI-MS spectrum

Qualitative screening method validation

- Validation set: 10 commodities (tomato, lettuce, cucumber, pepper, oranges, grapes, peach, apples, cauliflower and carrots)
- Samples spiked in duplicate at 0.01, 0.05 and 0.20 mg/kg
- 150 pesticides (organochlorine, organophosphorus, pyrethroids, etc)

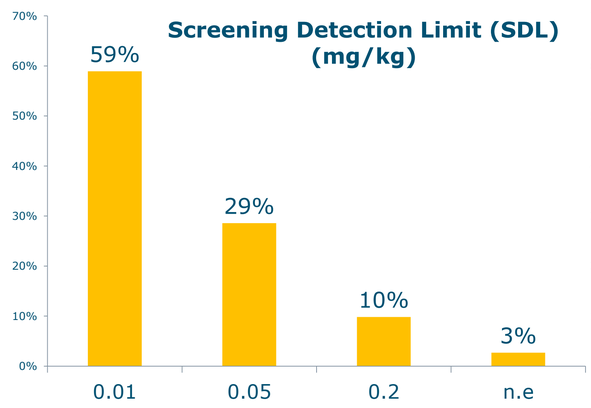

Figure 3. Screening based on $[M+H]^+$, Δmass ± 5 ppm; ΔRTdatabase ± 0.2 min
Blanks: 80 detects out of 150x10 pest./matrix combinations, all but one < 0.01 mg/kg.

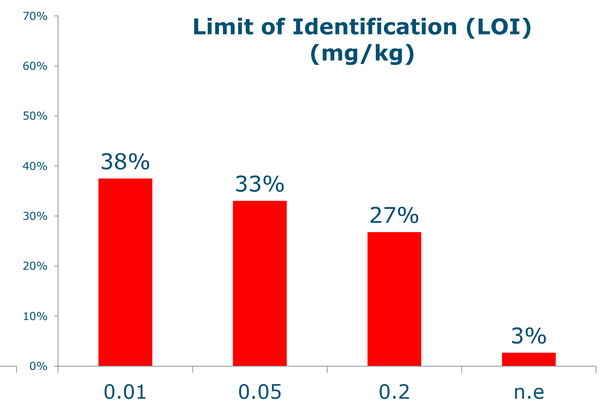

Figure 4. Identification based on presence of $[M+H]^+$ plus fragment ion(s), Δmass ± 5 ppm; ΔRTdatabase ± 0.2 min, ion traces should coincide.

Example chromatograms and spectra

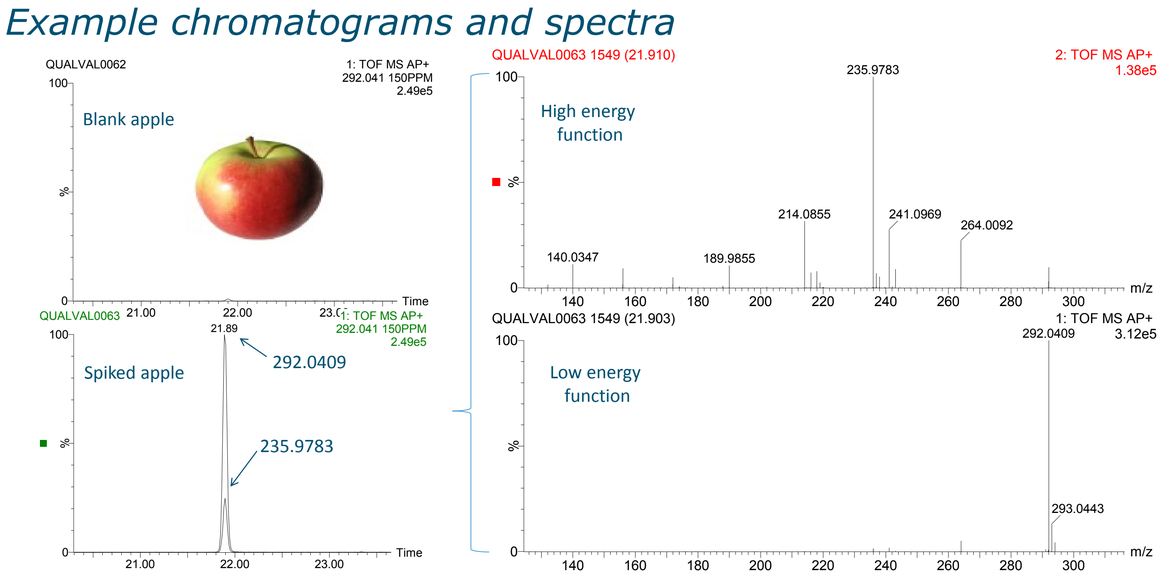

Figure 5. Parathion-ethyl in apple 0.01 mg/kg

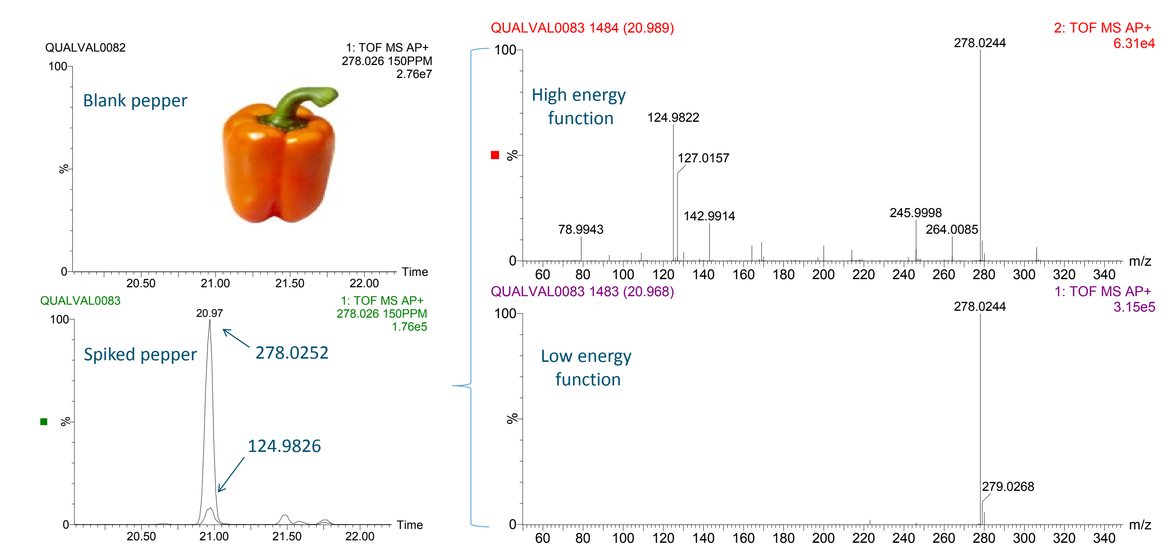

Figure 6. Fenitrothion in pepper 0.01 mg/kg

Conclusions

- GC-(APCI)QTOF MS is suited for rapid wide-scope screening and identification of pesticides in fruits and vegetables
- SDLs established were between 0.01 and 0.05 mg/kg for most pesticides studied

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