

GC-(NCI)-QTOF approach with accurate mass data processing for determination of 70 pesticides in vegetables

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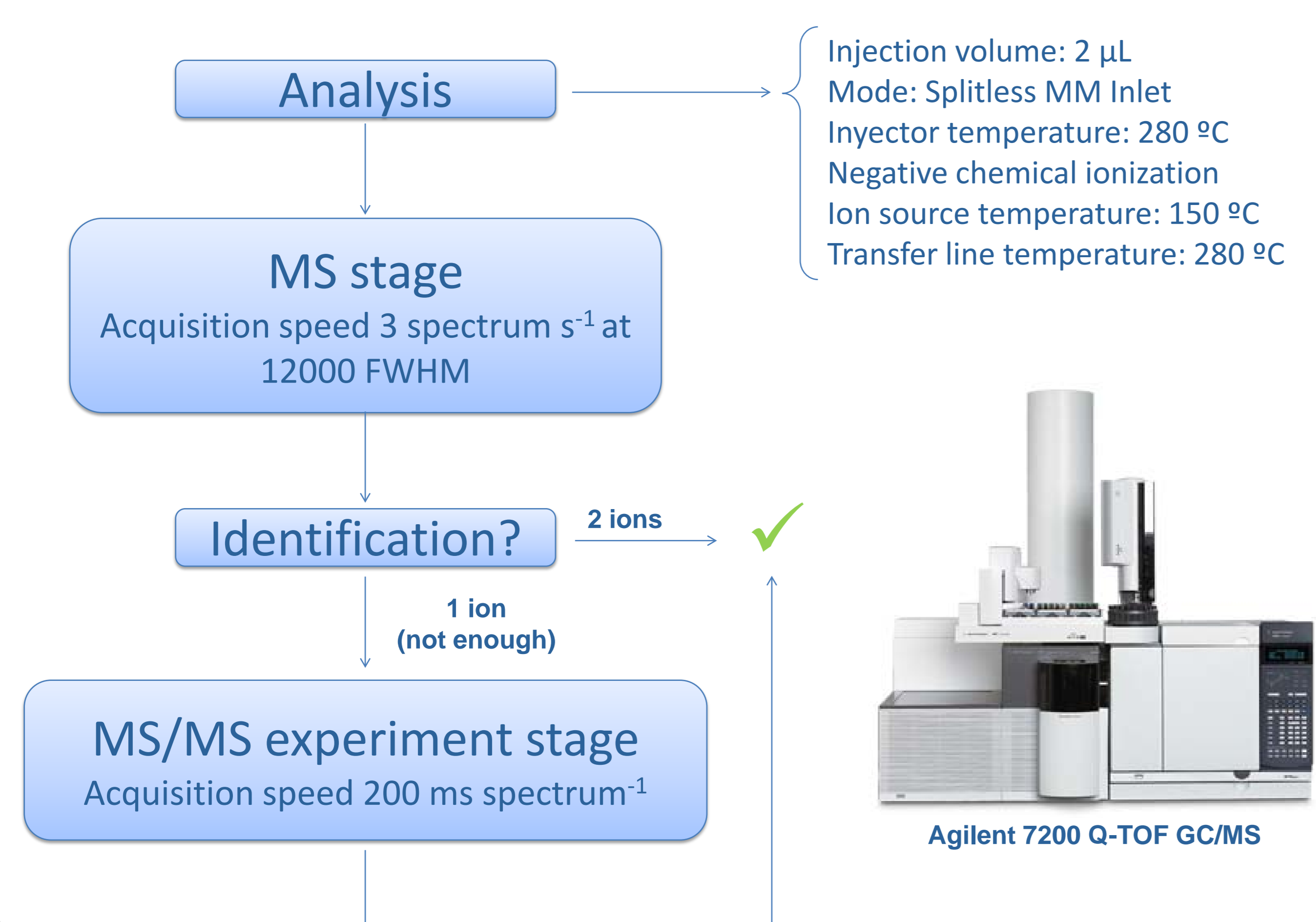
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ABSTRACT

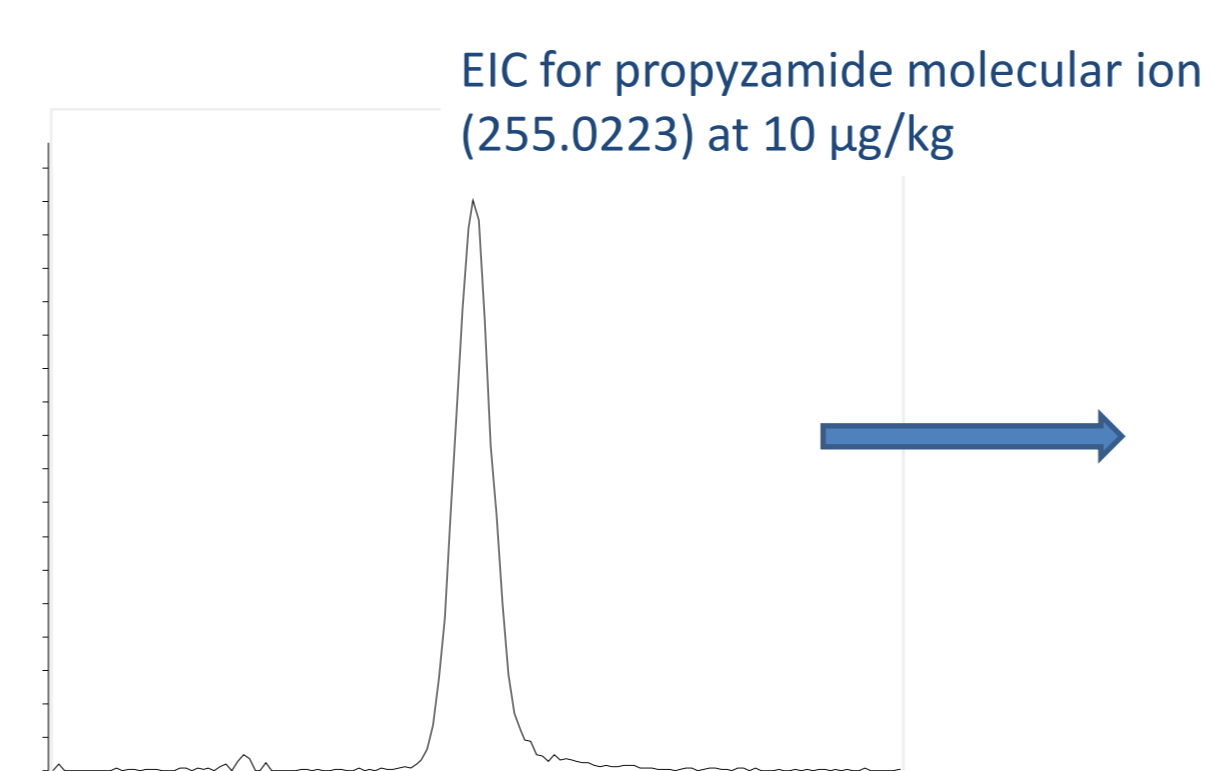
Gas chromatography coupled to high resolution hybrid quadrupole time-of-flight mass spectrometry (GC-QTOF MS), operating in negative chemical ionization (NCI) mode and combining single-stage MS with MS/MS experiment, has been explored for the automated accurate mass analysis of pesticides in fruit and vegetables. Seventy compounds were included in this approach and 50 % of these ones are pesticides not approved by the EU legislation. Detection limits, recovery studies and repeatability were investigated at three concentration levels (1, 5, and 10 $\mu\text{g kg}^{-1}$) for all pesticides. A homemade database was developed and applied to an automatic accurate mass data processing. Mass accuracies of the generated ions were measured. When only one ion was obtained in the single-stage MS, a new criterion for identification was proposed: to use the FS ion and a representative product ion from MS/MS experiment. A total of thirty real samples from Almería market were analyzed and twelve pesticides were detected at different concentration levels in varied matrices.

OPERATIONAL PARAMETERS and WORKFLOW

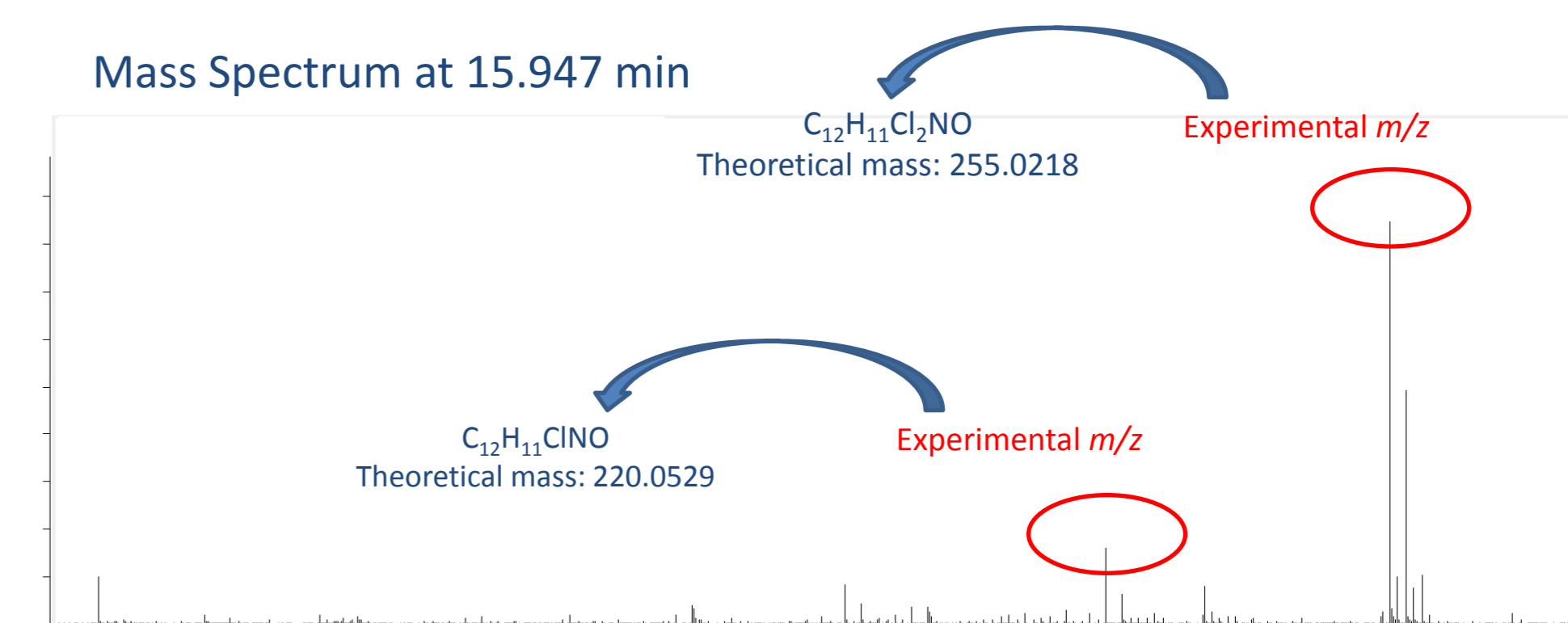


PROCESSING METHOD

Building the homemade database

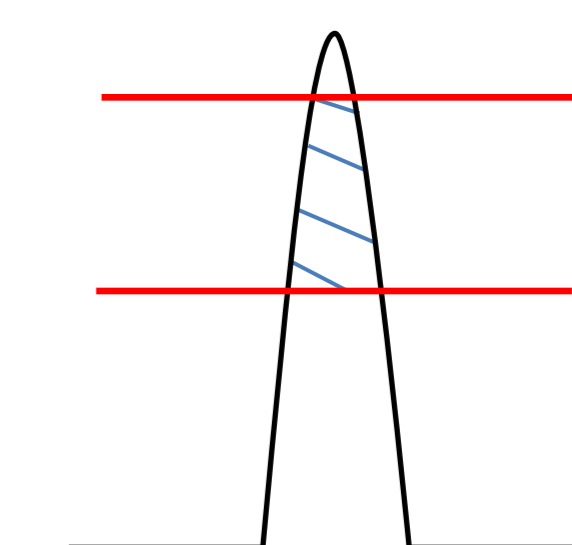


Manual assignment of theoretical masses of the ions

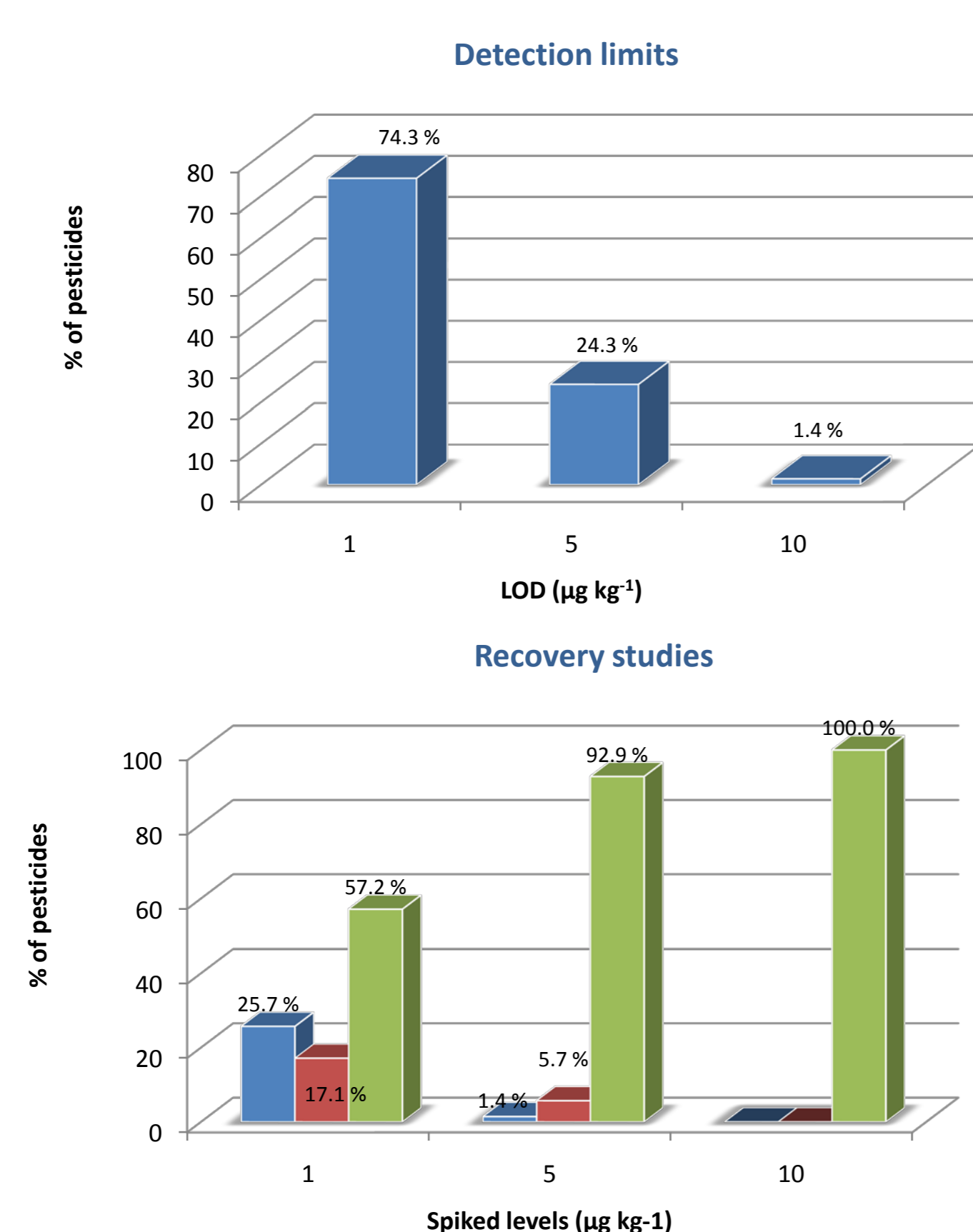


Searching parameters

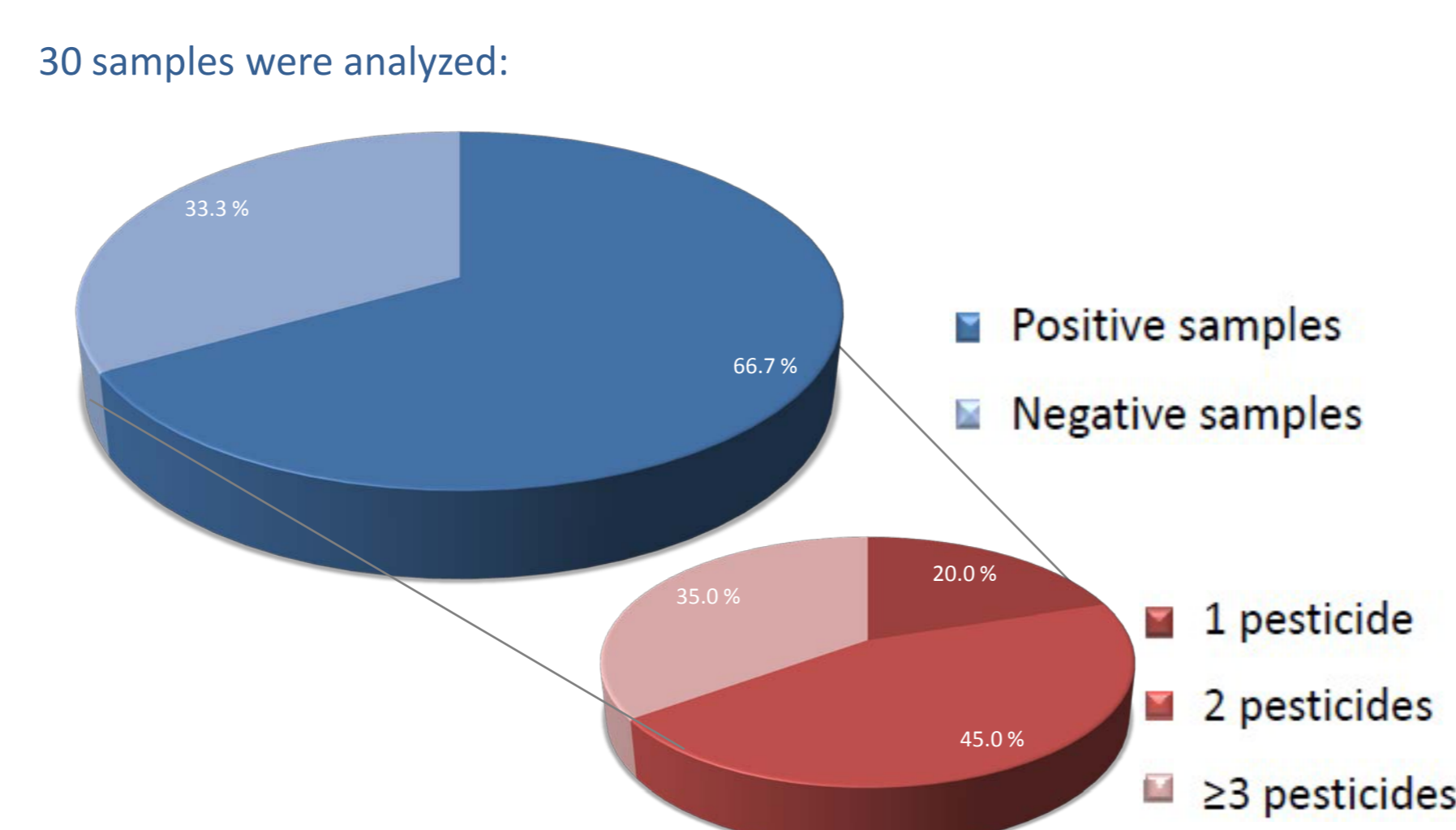
- Masses tolerance: ± 10 ppm
- Retention time tolerance: ± 0.2 min
- Extract EIC and cleaned spectrum
- Exclude if above 10 % of saturation
- Average scans > 50 % of peak height
- Extract MS/MS spectrum per CE with precursor tolerance ± 10 ppm



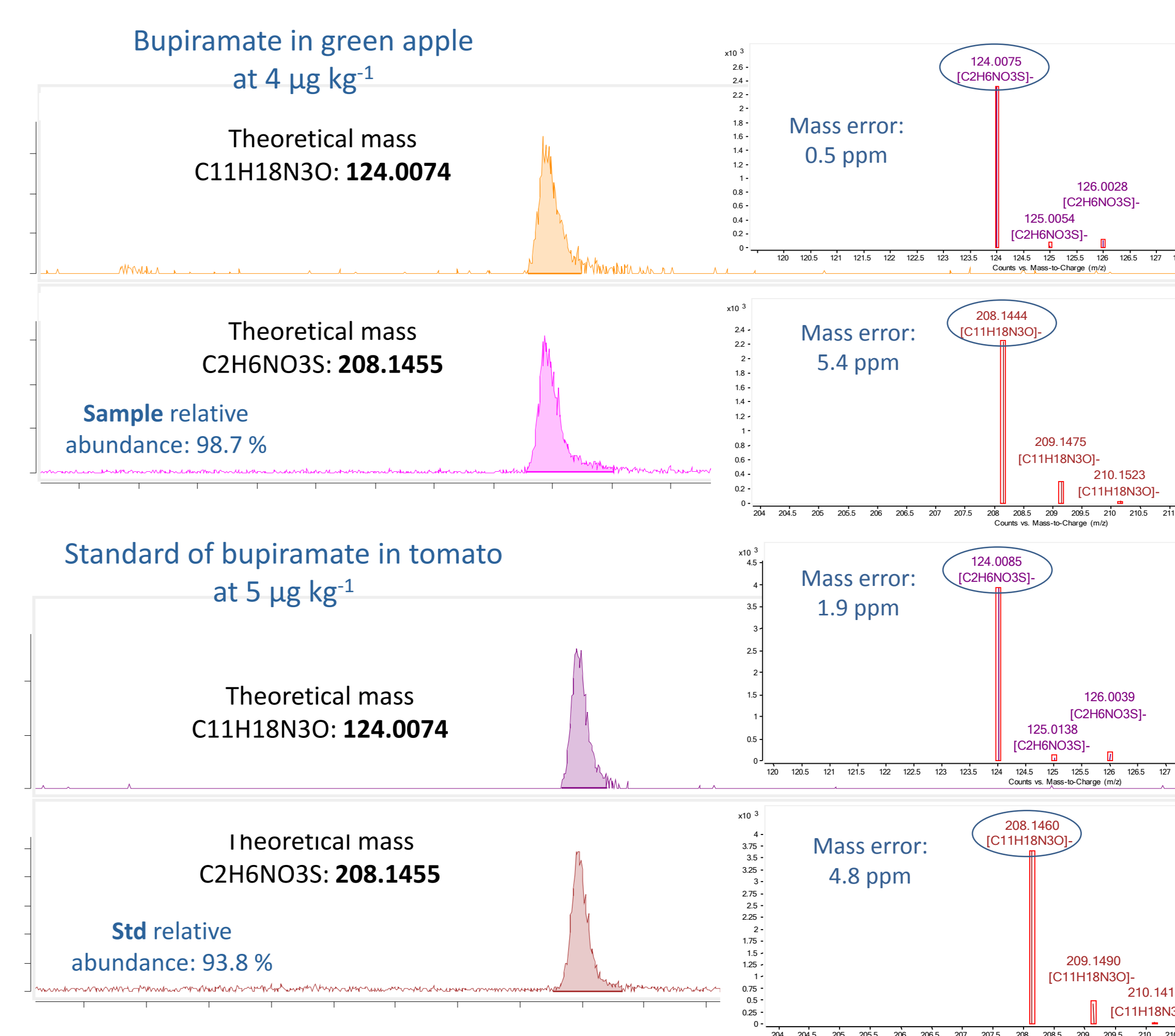
RESULTS AND DISCUSSION



Automatic search in real samples



- Repeatability was also evaluated, obtaining RSDs < 15 % at 5 $\mu\text{g kg}^{-1}$ and RSDs < 20 % at 20 $\mu\text{g kg}^{-1}$



CONCLUSIONS

- A multiresidue acquisition and processing method has been validated for the simultaneous quantification of 70 pesticides in fruit and vegetables.
- Providing very low LODs (75.7 % of pesticides had a LOD ≤ 1 $\mu\text{g kg}^{-1}$) is the main advantage of GC-QTOF operated in negative chemical ionization due to its high sensitivity and selectivity.
- Data obtained for anions generated by NCI afforded mass accuracies within 5 ppm for most ions generated.
- Thirty samples from Almería market were analyzed, where chlorpyrifos, bupiramate and iprodione were the most commonly-found pesticides with mass accuracies consistently below 5 ppm in at least one diagnostic ion.
- From the results obtained, the combined use of HRMS and NCI promise to be a useful tool for analyze samples containing pesticides residues at very low concentration and ensure the absence in case of ecologist samples.