GC-APCI-QTOF as an alternative to GC-MS/MS for the wide-scope screening of pesticides in orange

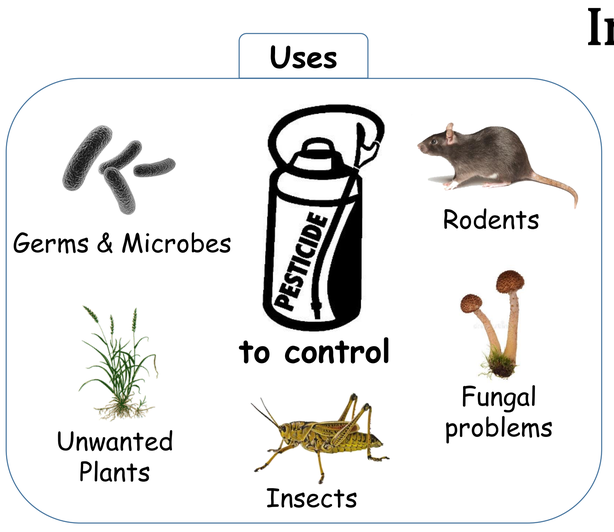
AACD 2018

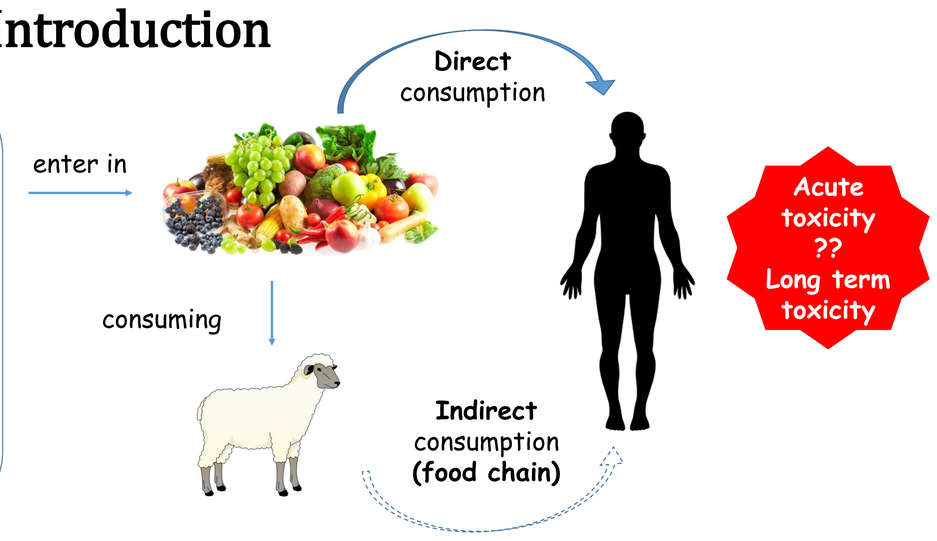
S.E. Kokolakis[1], D.E. Damalas[1], C. Baessmann[2], N.S. Thomaidis[1]

1 Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece
2 Bruker Daltonik GmbH, Fahrenheitstr. 4, 28359 Bremen, Germany

e-mail: ntho@chem.uoa.gr

Introduction

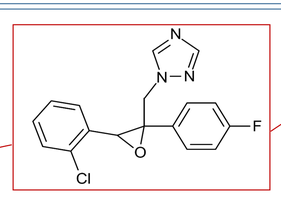




Objectives

- Development of a Database including analytes compatible with GC-APCI-QToF systems.
- Development of a methodology for the wide scope screening of multiclass pesticides in orange
- Analysis of real samples and investigate where the concentration of pesticides is greater
- Highlight the potential of GC-APCI-HRMS as a promising alternative to GC-MS/MS for the determination of pesticides

Database development

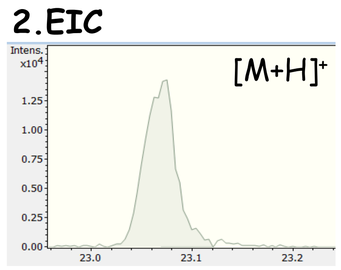


1.Investigation of Ionization:

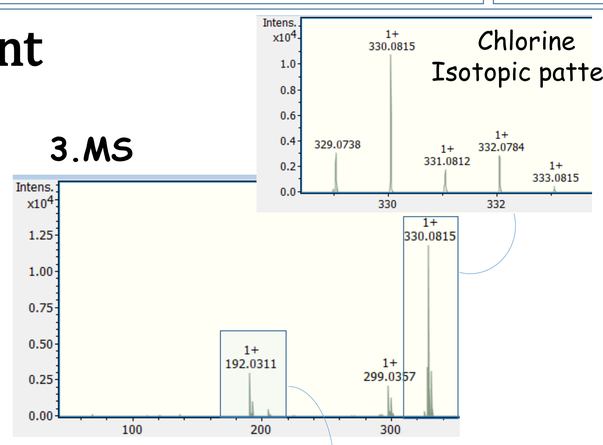
$[M]^+$? $[M+H]^+$? $[M-Cl]^+$? etc

Workflow example

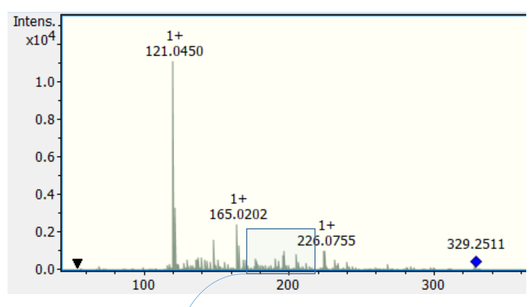
2.EIC



3.MS

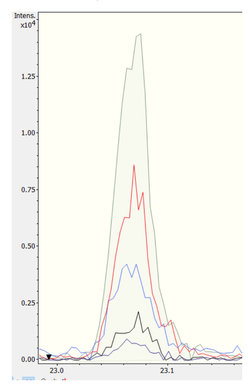


4.MS/MS



Compass DataAnalysis

5.Confirmation of Qualifiers



Precursor ion — Includes information over

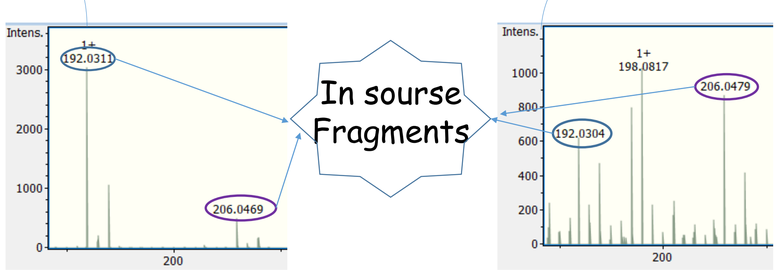
Database

m/z	RT	formula	name	CAS	Qual1	Qual2	Qual3
330.0804	23.13	C17H14ClFN3O^1+	Epoxiconazole	135319-73-2	121.044	192.0282	165.0168
235.0076	21.16	C13H9Cl2^1+	2.4-DDT	789-02-6	318.9424	165.0664	199.0278
180.9373	14.23	C6H4Cl3^1+	a-HCH	319-84-6	172.9632	218.9111	180.9373
366.8541	18.18	C8H9BrCl2O3PS^1+	Bromophos Methyl	2104-96-3	142.9902	352.8402	240.8597
271.095	14.12	C10H24O2PS2^1+	Cadusafos	95465-99-9	158.9658	130.938	130.9382
351.9306	17.60	C9H12Cl3NO3PS^1+	Chlorpyrifos Ethyl	2921-88-2	199.9207	114.9609	209.9416
220.9532	9.76	C4H8Cl2O4P^1+	Dichlorvos	62-73-7	184.9765	144.9818	127.0145
259.8096	9.53	C4Cl6^1+	Hexachlorobutadiene	87-68-3	224.8408	189.8719	140.906
260.8727	13.22	C6HCl4NO2^1+	Tecnazene	117-18-0	202.8759	242.8805	195.9018

>300 Analytes

250 Pesticides
8 FAMEs
26 PAHs
6 PBDEs
7 PCBs
8 PCNs

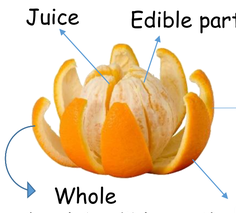
In sourse Fragments



Method

Sample treatment

Compartmentalization



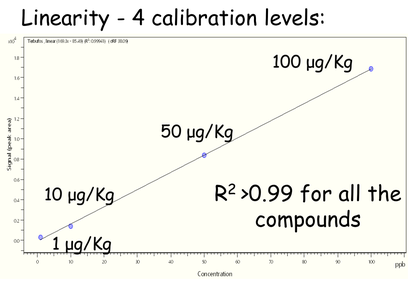
QuEChERS

ACN $MgSO_4$ CH_3COONa → Shaking / centrifuge → $MgSO_4$, C18, PSA → Shaking / centrifuge → Evaporation in N_2 → Reconstitution in n-hexane

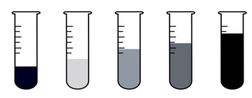
Extraction — Cleaning — Reconstitution

Validation

Linearity - 4 calibration levels:



mix 73 compounds → 70 Pesticides, 3 IS



2 standard addition levels → 2 ppb, 10 ppb

Analysis GC-APCI-QToF

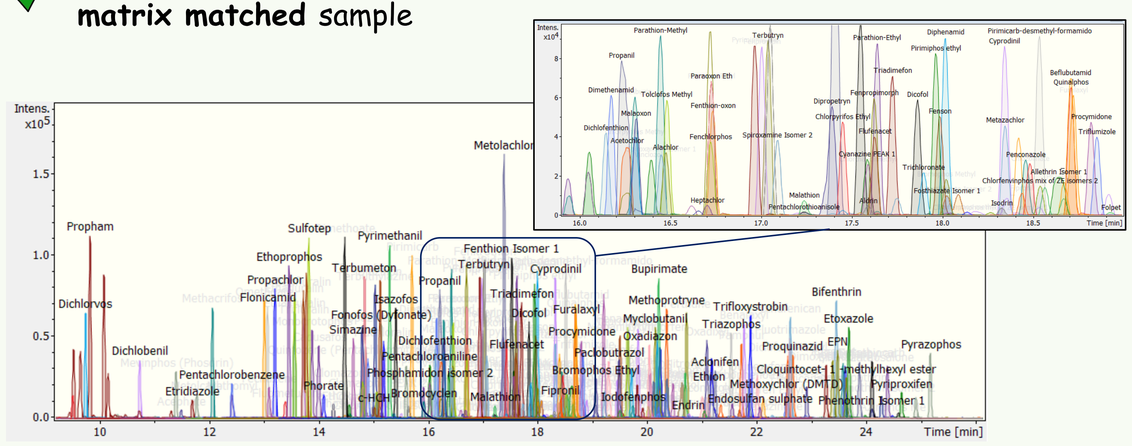
456-GC

APCI II source

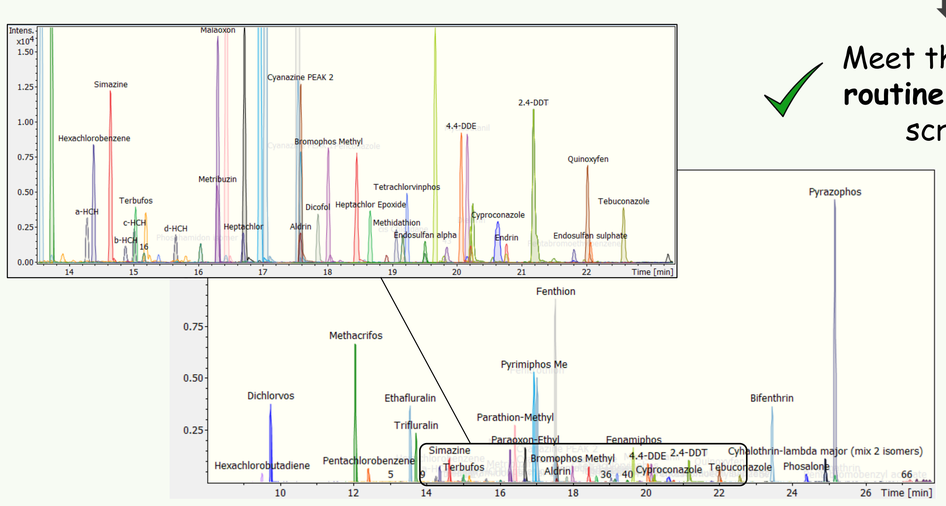
maXis impact

Method performance

✓ **250/250** pesticides were detected at **100 µg/Kg** **matrix matched** sample

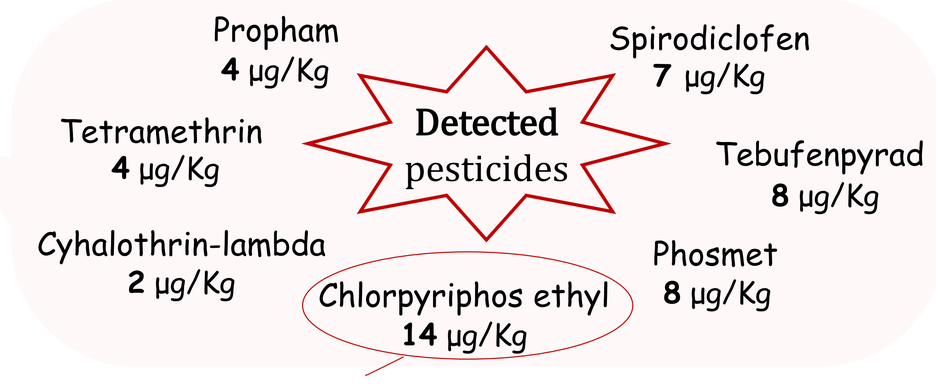


✓ **70/70** pesticides were detected at **10 µg/Kg spiked** sample



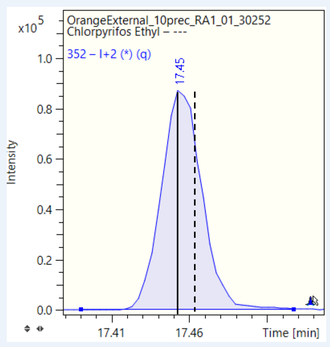
✓ Meet the **needs** of **routine** pesticides' screening

Results

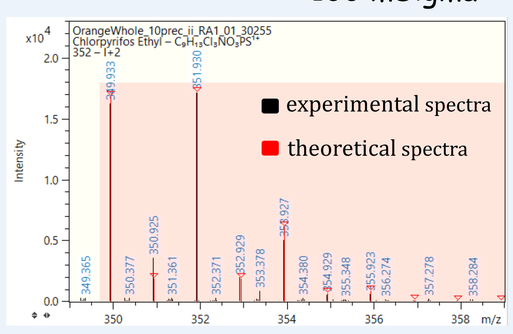


Identification example TASQ 1.4

ΔRT: < 0.1 min

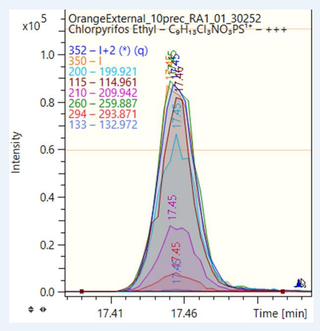


Δm/z: < 5 mDa



Isotopic Profile < 100 mSigma

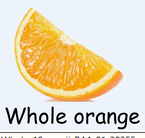
>2 Qualifier ions



Compartment-dependent $C_{pesticides}$

Higher pesticides' concentration in the peel than in other parts of the orange

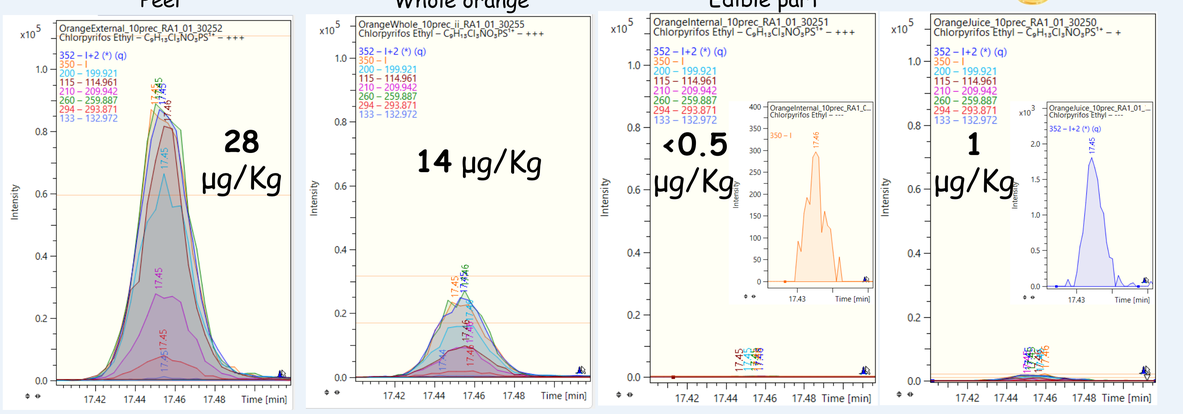
Peel



Whole orange

Edible part

Juice



Conclusions

A comprehensive database with Rt, MS and MS/MS information for > 300 compounds was established

GC-APCI-QToF proved a suitable platform for routine pesticide residues' analysis

Significant differences in the concentration of pesticides were observed in the different parts of orange