Analysis of pesticide residues using various GC/MS systems

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OUTLINE

- ⇨ Multiresidue method: target approach
- ⇨ Multiresidue method: GC part
- ⇨ „Problematic" pesticides: Example #1 Dinocap
- ⇨ „Problematic" pesticides: Example #2 Iprodione
- ⇨ Conclusions

Target analysis of pesticide residues: multiresidue method

⇨ **QuEChERS[#] method:** ***360 pesticides*** in each sample (**without PSA clean-up**)
one extraction procedure for GC-MS and LC-MS measurement ✓

SANCO/12571/2013 ✓

[#] EN 15662:2008 Foods of plant origin - Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE - QuEChERS-method

Target analysis of pesticide residues

⇨ Sample measurement: GC part

GCxGC-TOF with PTV injection

GC-MS/MS with PTV injection

Target analysis of pesticide residues

1. PTV-GCxGC-TOF

LECO Pegasus 4D equipped with:
- consumable-free (CFM) modulator
- no need of liquid nitrogen

Injection technique - PTV	PTV operated in a solvent vent mode **injection volume 10 ul**, vent time 40 sec, vent flow 20 ml/min, temp. 40 C
Columns (GCxGC)	1st dimension **DB-5 MS** (30 m x 0.25 mm x 0.25 um) 2nd dimension **BPX-50** (2 m x 0.1 mm x 0.1 um)
Modulator	modulation period: **5 sec**
TOF-MS	EI ionization, acquisition rate: **50 spectra/sec,** mass range 50-550

Target analysis of pesticide residues

2. PTV-GC-MS/MS

Varian CP-3800 GC/1200L MS:

Injection technique - PTV	PTV operated in a solvent vent mode **injection volume 10 ul**, temperature programme: 45 °C (1 min, CO_2 cooled), 200 °C/min to 280 °C Split ratio: On 50:1 (1 min), Off (2.3 min), On 100:1 (10 min), On 20:1 (to the end of GC run)
Column	VF-5-MS capillary column (30 m x 0.25 mm x 0.25 µm)
MS parameters	EI ionization, ion source temperature: 200 °C, transfer line temperature: 290 °C, collision gas (argon, 2 mTorr)

Example 1: DINOCAP

⇨ Contact Fungicide and Acaricide

⇨ DINITROPHENOL group

⇨ Molecular formula: C18H24N2O6

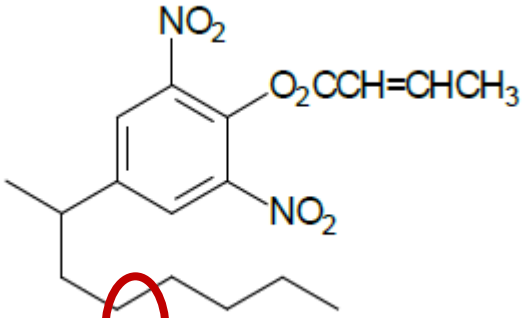
⇨ Molecular weight: 364

⇨ Present in EUPT-SM06
(EUPT for screening methods, green pepper, February 2014)
only 37% Labs identified dinocap in the sample

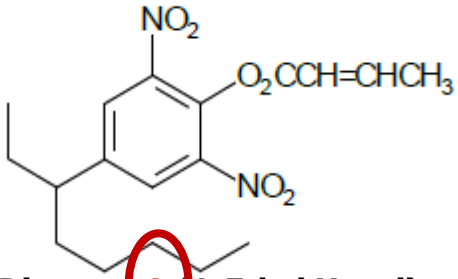
⇨ MRL definition: Sum of dinocap isomers and their corresponding phenols expressed as dinocap

Example 1: DINOCAP

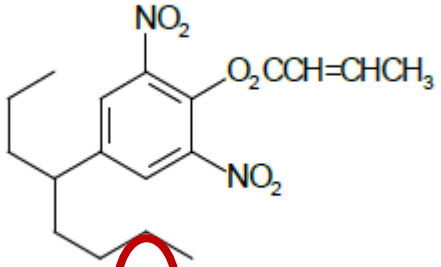
Mixture of isomers



Dinocap-4-(1-Methyl Heptyl)

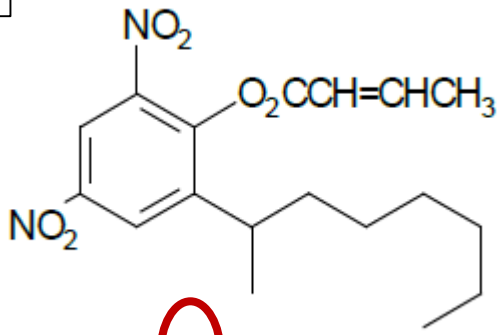


Dinocap-4-(1-Ethyl Hexyl)

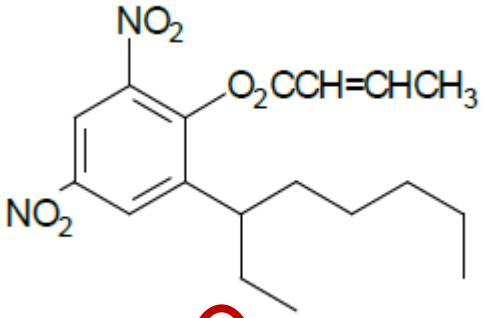


Dinocap-4-(1-Propyl Pentyl)

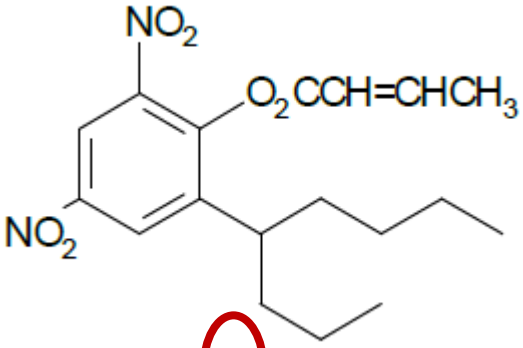
2
1



Dinocap-6-(1-Methyl Heptyl)



Dinocap-6-(1-Ethyl Hexyl)

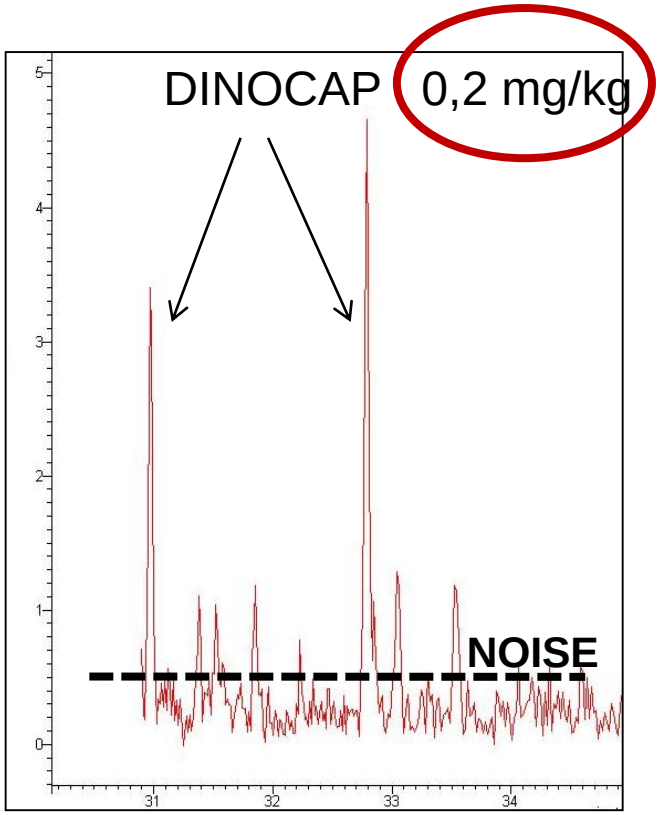


Dinocap-6-(1-Propyl Pentyl)

Example 1: DINOCAP

PTV-GC-MS/MS

- ⇨ Difficult identification due to poor intensity of product ions
- ⇨ Ion selected for fragmentation (most intensive) : 69
- ⇨ MS/MS Transitions: 69/41, 69/57
- ⇨ **LOQ: 0,1 mg/kg**
- ⇨ **EU MRL: 0,05 mg/kg for most of products**
- ⇨ Chromatographic interferences



Example 1: DINOCAP

PTV-GCxGC-TOF MS

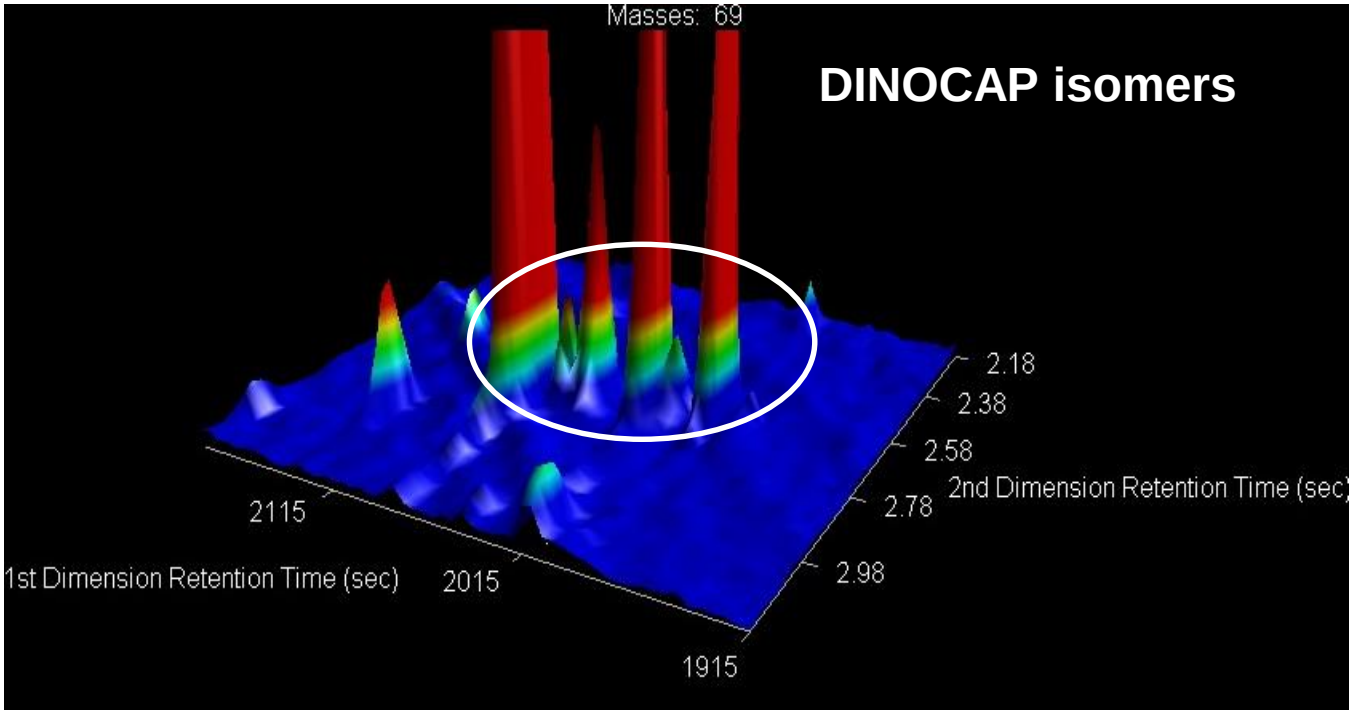
⇨ Improved chromatographic separation (all isomers are separated)

⇨ More than 10x increased signal-to-noise ratio

⇨ LOQ: 0,008 mg/kg

⇨ EU MRL:
0,05 mg/kg
for most of products

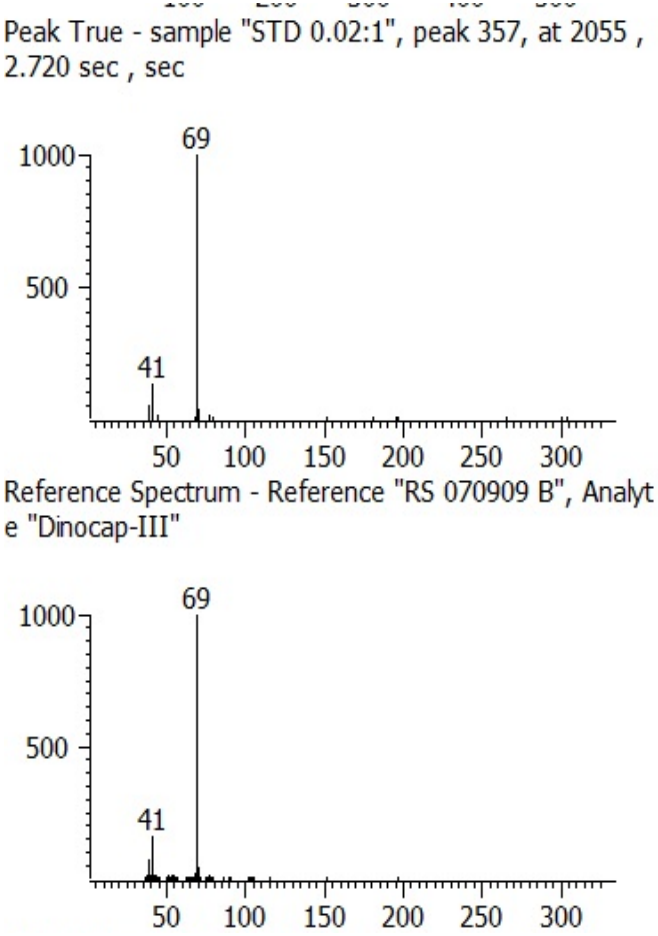
✓



Example 1: DINOCAP

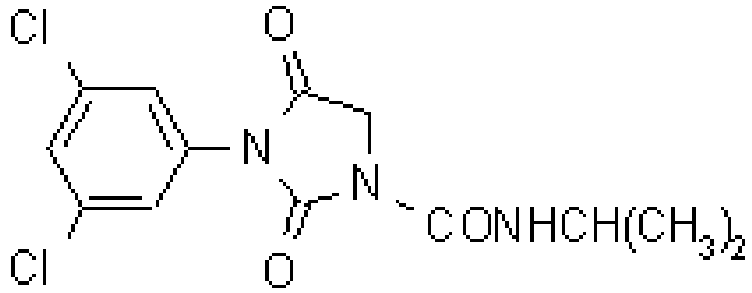
PTV-GCxGC-TOF MS

- ⇨ Improved chromatographic separation
- ⇨ More than 10x increased signal-to noise ratio
- ⇨ LOQ: 0,008 mg/kg
- ⇨ Identification based on Spectral Match (>700), ret.time and presence of dinocap isomers



Example 2: IPRODIONE

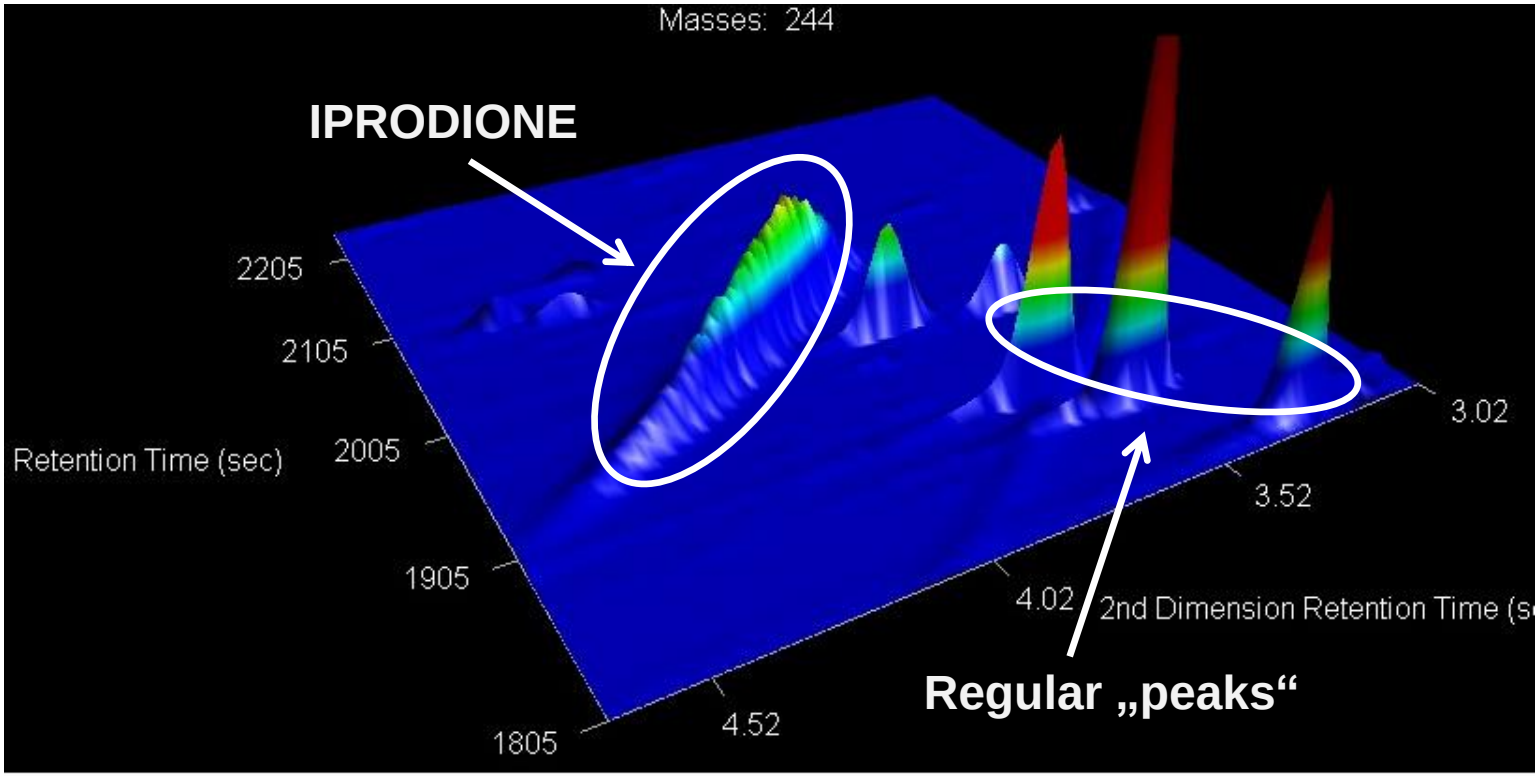
- ⇨ Fungicide
- ⇨ Group of dicarboximide compounds
- ⇨ Molecular formula: C13H13Cl2N3O3
- ⇨ Molecular weight: 330
- ⇨ MRL definition: Iprodione



Example 2: IPRODIONE

PTV-GCxGC-TOF MS

⇨ **Chromatographic problems due to higher retention of iprodione**



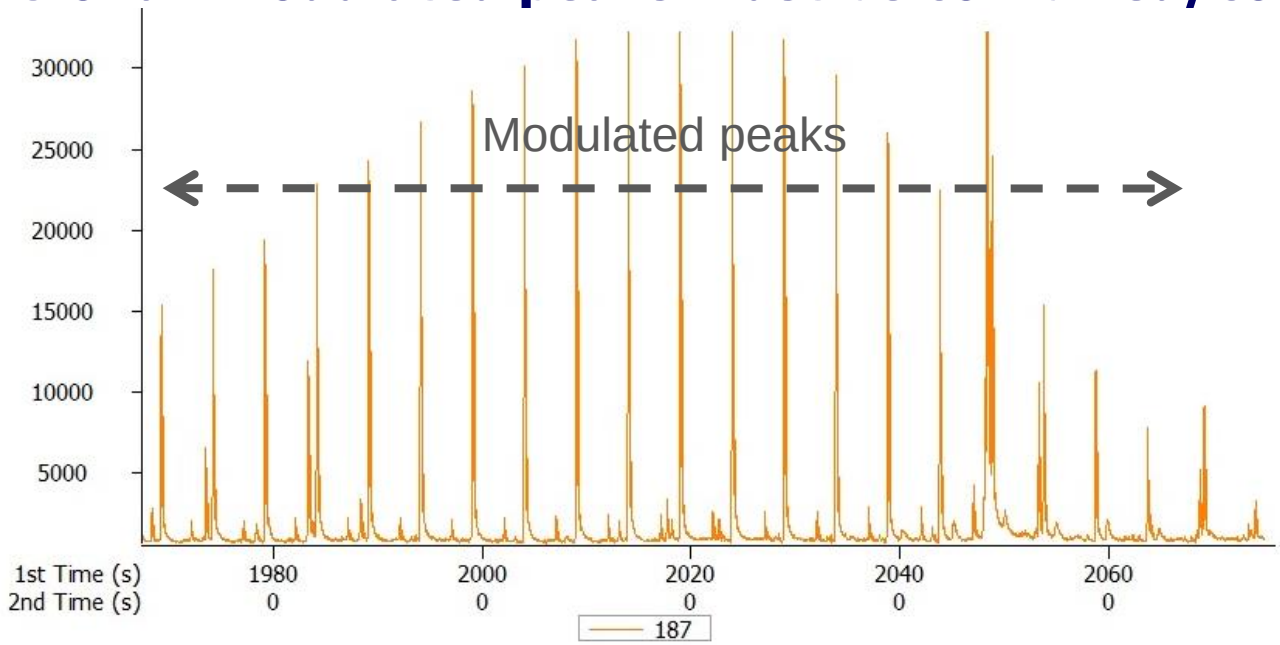
Example 2: IPRODIONE

PTV-GCxGC-TOF MS

⇨ **Chromatographic problems due to higher retention of iprodione**

⇨ **More than 15 modulated peaks of iprodione (for other pesticides usually 2-3 modulated peaks)**

⇨ **AREAS of all modulated peaks must be combined/counted up**



Example 2: IPRODIONE

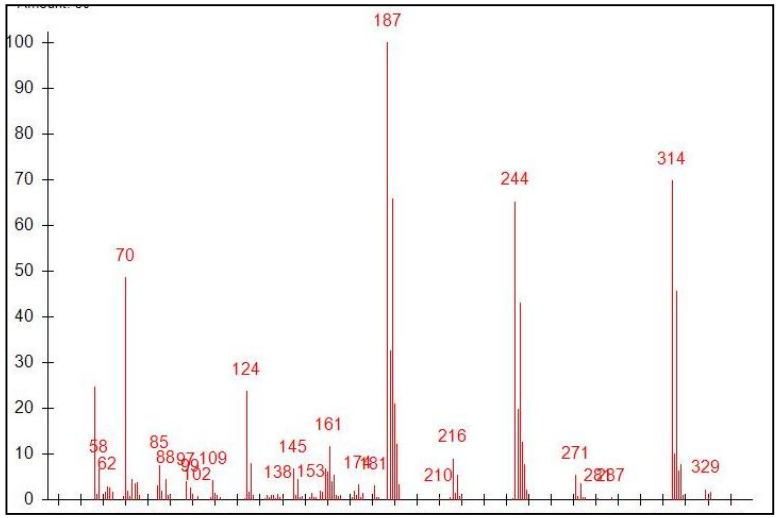
PTV-GCxGC-TOF MS

⇨ Chromatographic problems due to higher retention of iprodione

⇨ More than 15 modulated peaks of iprodione (for other pesticides usually 2-3 modulated peaks)

⇨ Full mass spectra ✓

⇨LOQ: 0,008 mg/kg, comply with EU MRLs ✓



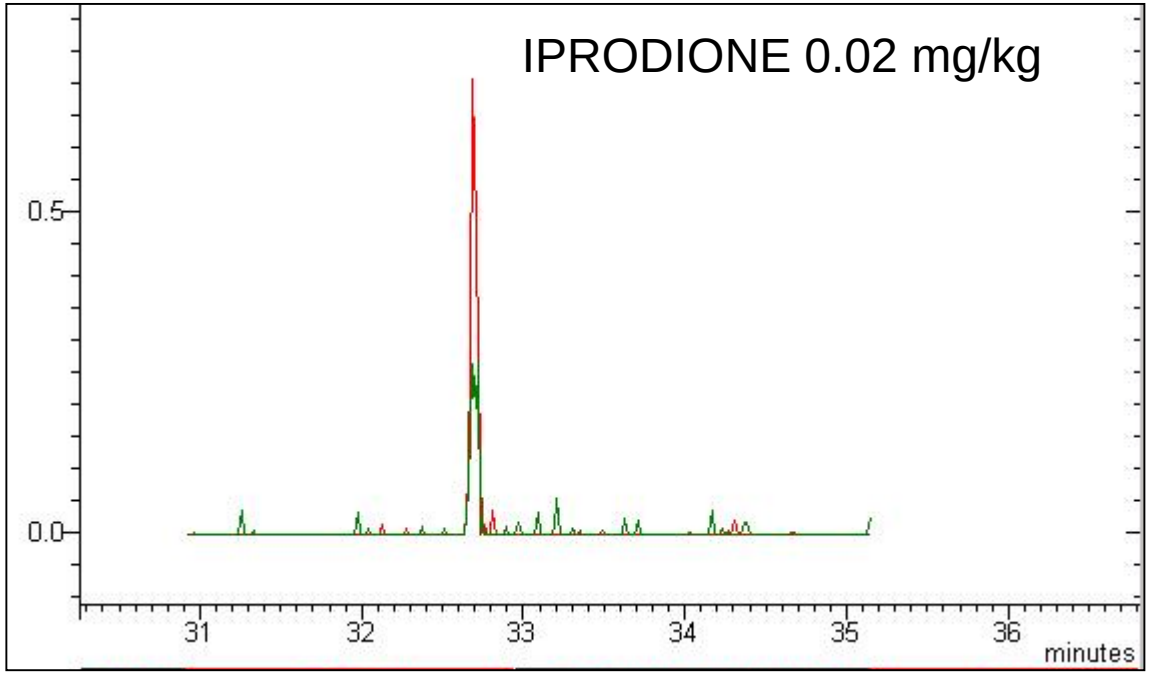
Example 2: IPRODIONE

PTV-GC-MS/MS

⇨ **Ion selected for fragmentation: 314**

⇨ **MS/MS Transitions: 314/271, 314/245**

⇨ **LOQ: 0,008 mg/kg, comply with EU MRLs** ✓



Conclusions

PTV-GCxGC-TOF

⇨ Improved separation (most of pesticides)

⇨ Enhanced sensitivity

⇨ LOQs < 0,01 mg/kg

⇨ Non-target screening

⇨ Full Mass Spectra – Unique identification of compounds

⇨ Retrospective data analysis

Conclusions

PTV-GC-MS/MS

- ⇨ **Better peak shape (for some compounds)**
- ⇨ **Easier data evaluation**
- ⇨ **LOQs < 0,01 mg/kg (for most of compounds)**
- ⇨ **Chromatographic interferences (for some matrices)**

PTV-GCxGC-TOF ⟺ **PTV-GC-MS/MS**

Complementary methods

Thank you for your attention !