



# Applications of advanced instrumental analytical techniques in the field of pesticide formulations

Impurities, illegal, counterfeit,  
spraying solutions and unknown  
samples

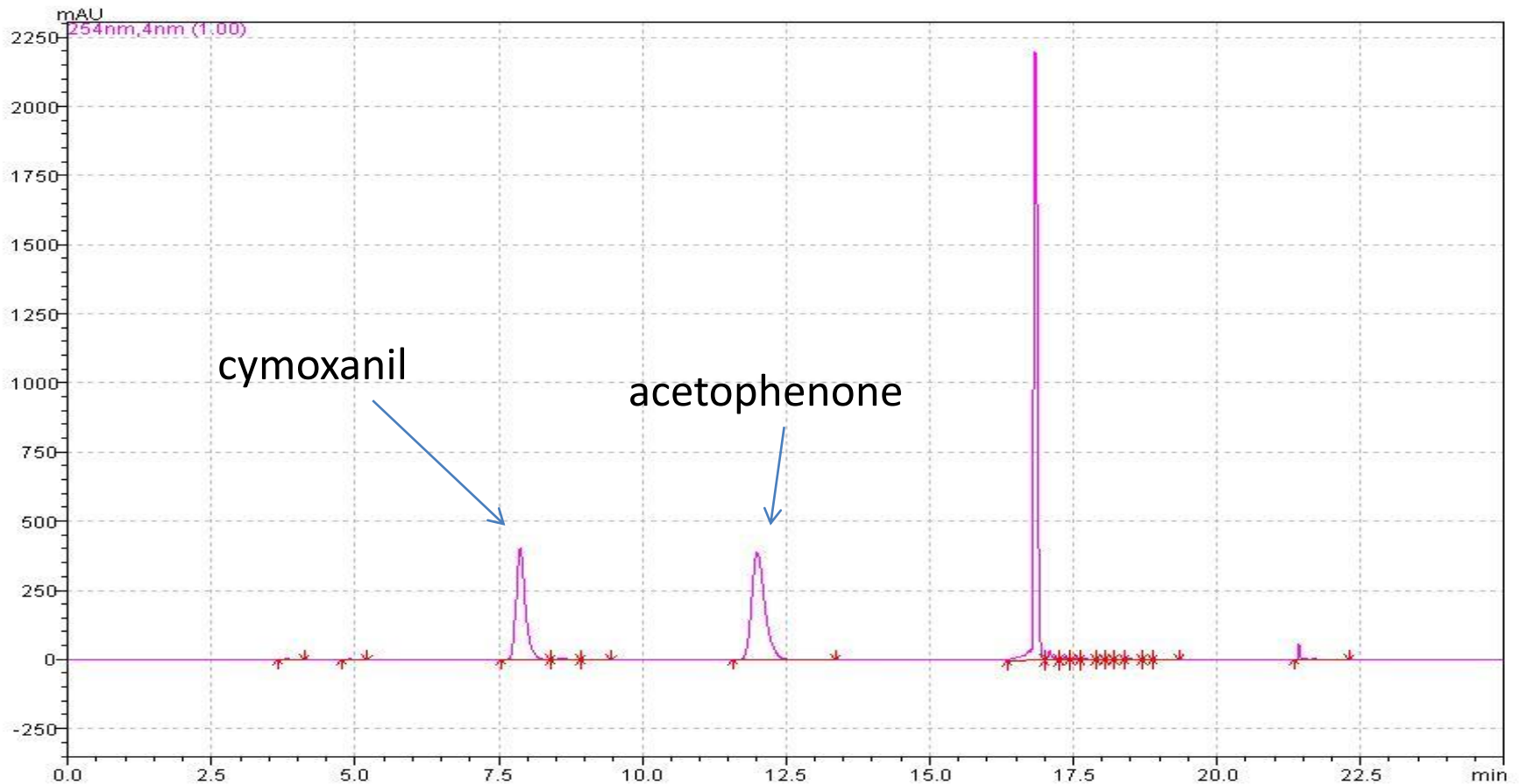
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- Instrumental Analytical Techniques
  - For formulations
    - HPLC-UV
    - GC-FID
  - Determination of
    - active ingredients
    - Impurities

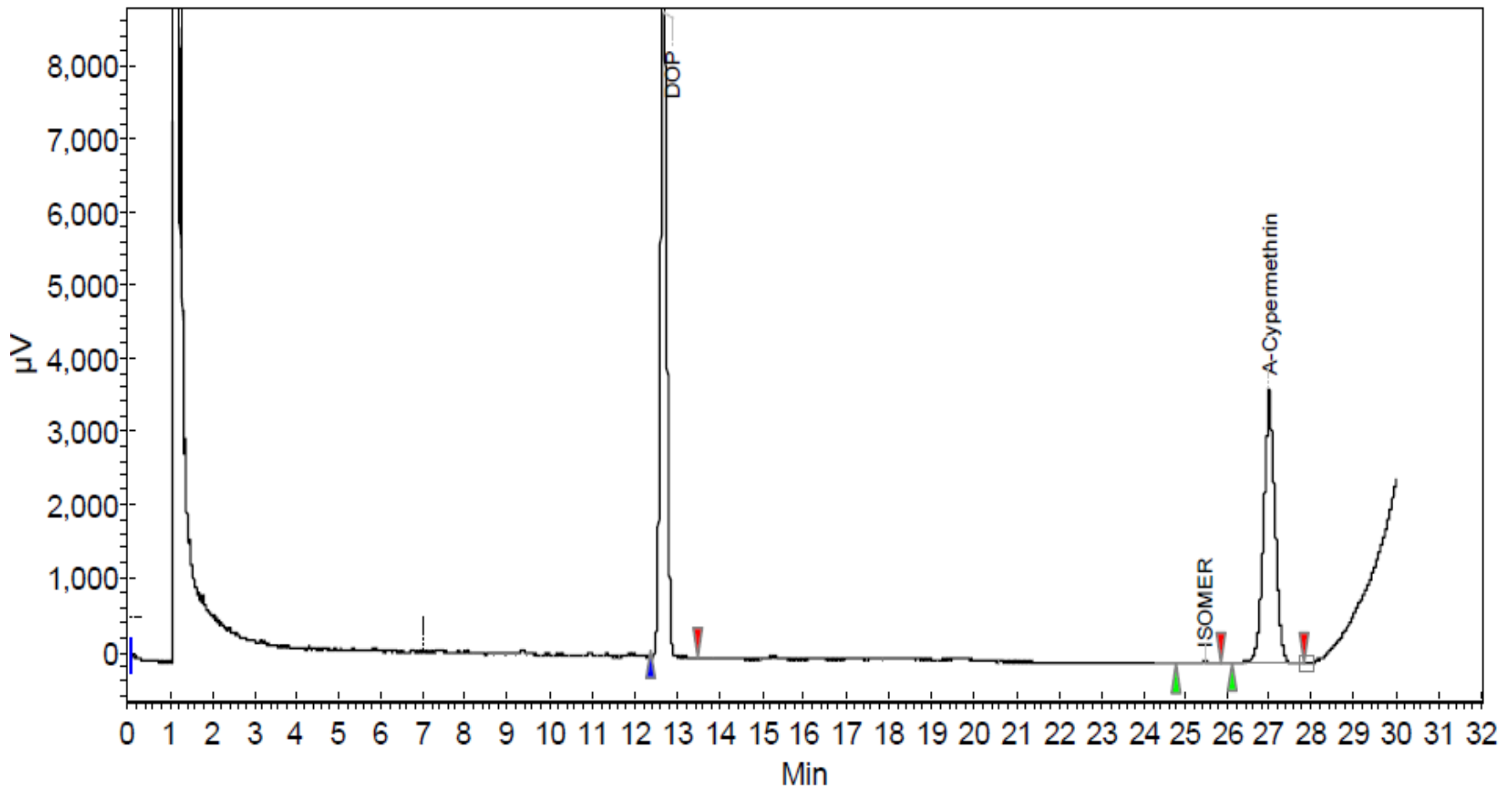


- HPLC-UV: cymoxanil

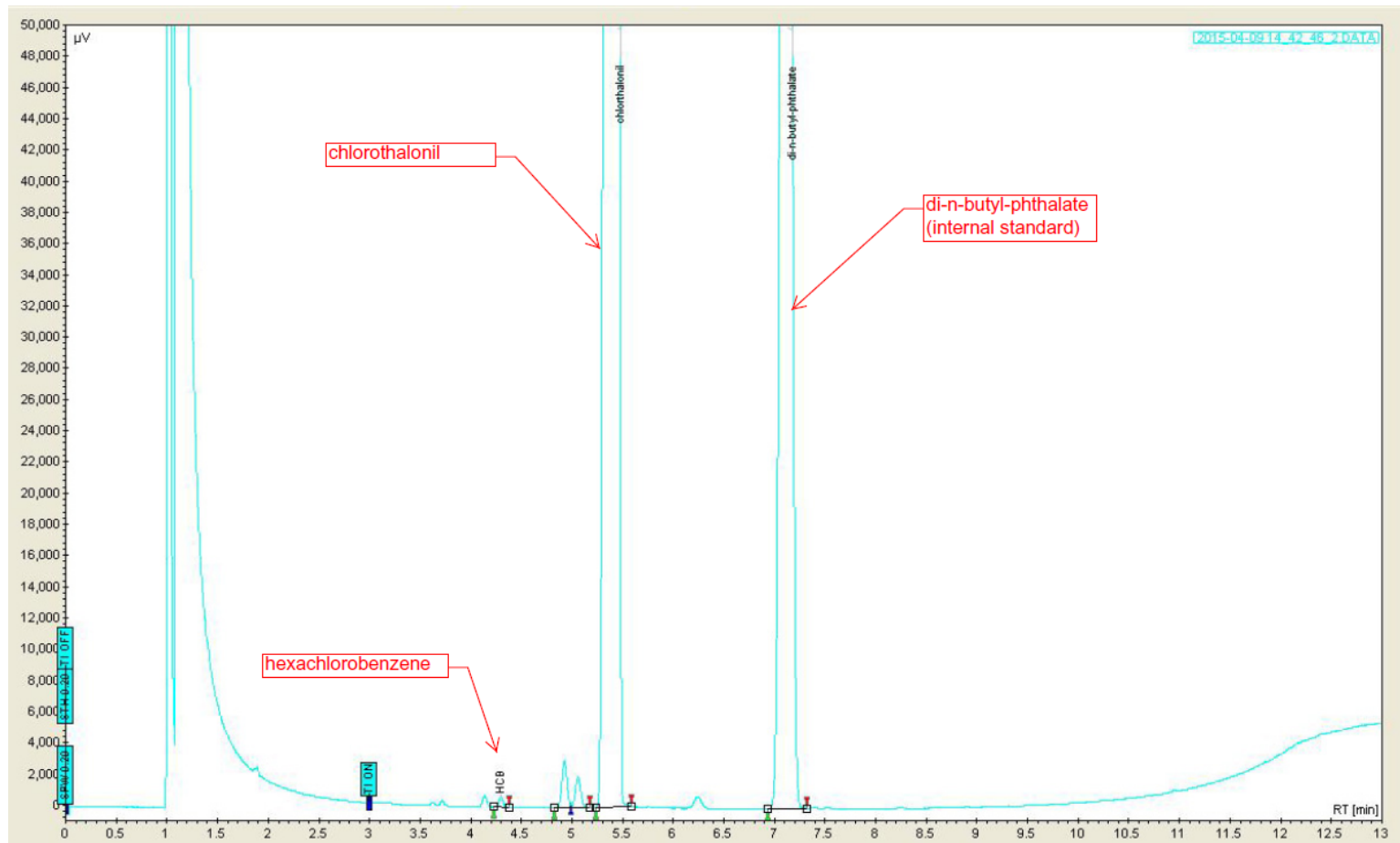




- GC-FID: alpha-cypermethrin



- GC-FID: chlorothalonil





- Advanced Instrumental Analytical Techniques
  - Instrument Configurations
    - LC-MS
    - LC-MS/MS
    - GC-MS
    - GC-MS/MS
  - Extreme cases
    - High resolution MS
    - NMR
    - X-ray electronic microscope
  - Ionization techniques
    - Electrospray Ionisation – Atmospheric Pressure Ionization (ESI-APCI)
    - Electron Ionization- Negative/Positive Chemical Ionization (EI-NCI-PCI)



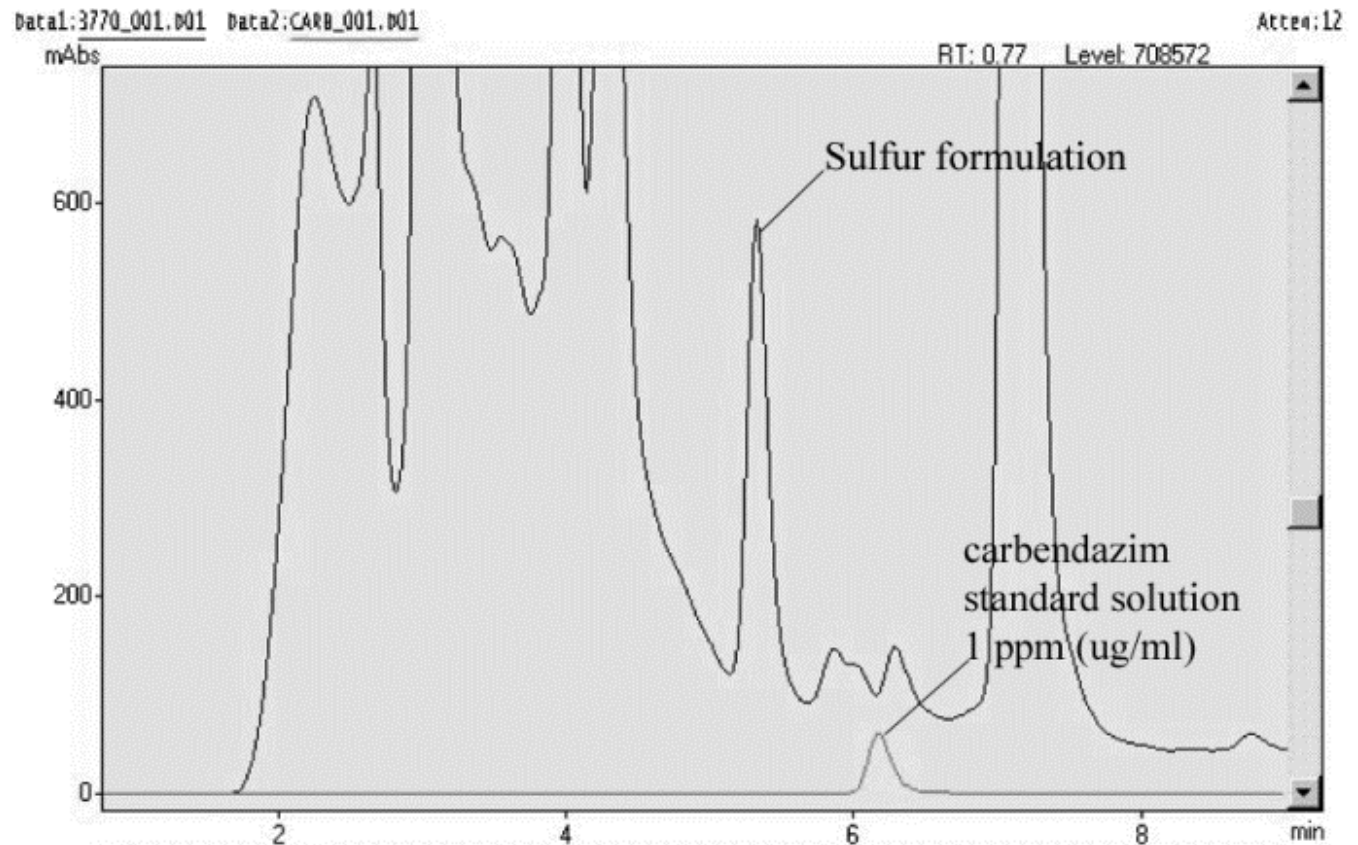
- **Advanced Instrumental Analytical Techniques**
  - Analysis of
    - Samples with strong interference to the target analyte
    - Small concentrations of target analytes
    - Screening-Non target analysis
    - Chromatographic profiling
  - Target analytes
    - impurities –relevant impurities (hexachlorobenzene-nitrosamines)
    - active ingredients (wrong active ingredients, unknown samples, spraying solutions, a.i. that do not resolve chromatographically)
    - Co-formulants



## Samples with strong interference to the target analyte

### Carbendazim in sulphur formulations (organic farming)

**HPLC-UV  
analysis**



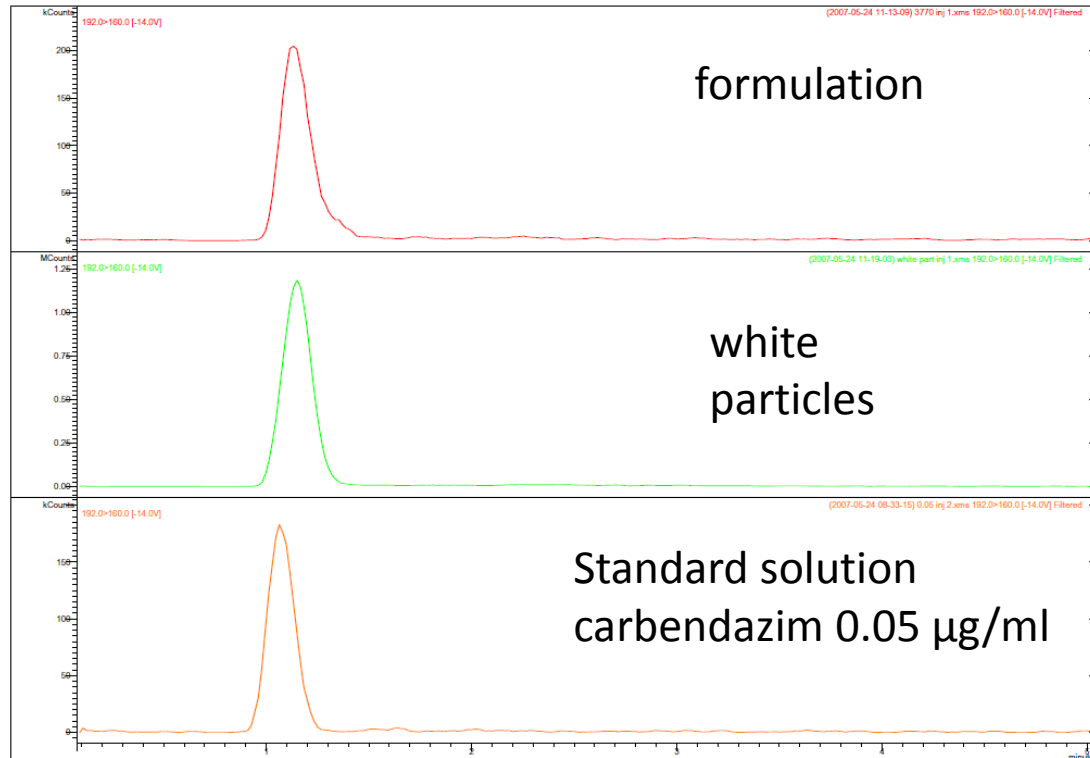




## Samples with strong interference to the target analyte

### Carbendazim in sulphur formulations (organic farming)

LC-MS/MS  
analysis  
(192>160)





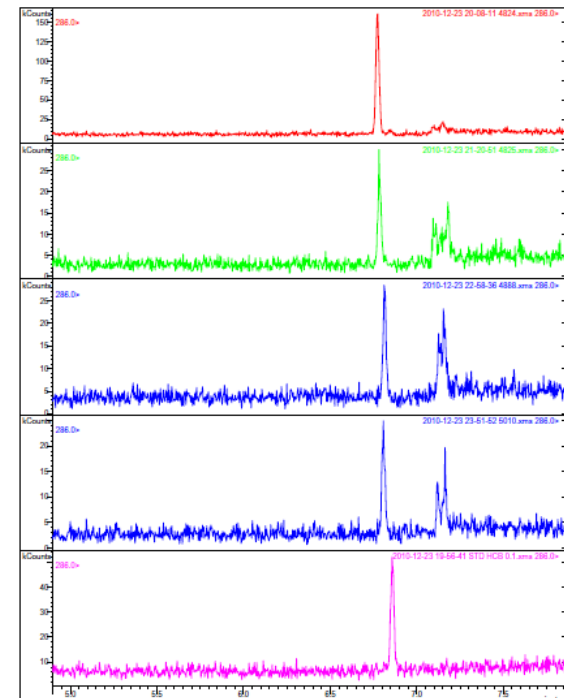
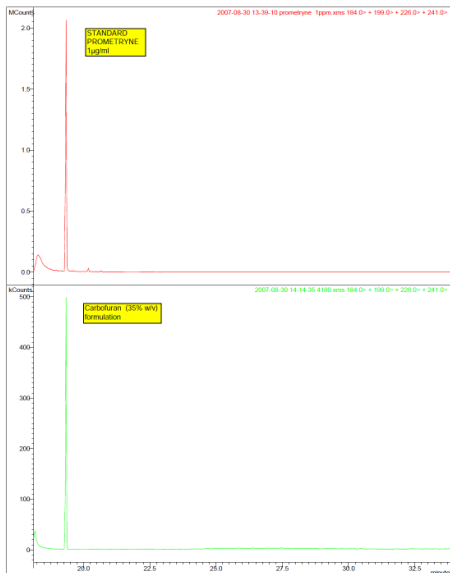
- Small concentrations of target analytes
  - active ingredients
    - Non-registered/wrong-irrelevant active ingredients
  - Relevant impurities
    - Confirmation and/or quantification



# Small concentration of targeted analytes

## Low-quality PPP

- Wrong active ingredient present in the formulation
- Herbicide in insecticide: prometryne found in trace amounts in insecticide formulation (GC-MS/MS)
- Relevant impurity: hexachlorobenzene in chlorothalonil (limit 0.04 g/kg)
- Application of FAO GC-MS method





## – Screening-Non target analysis

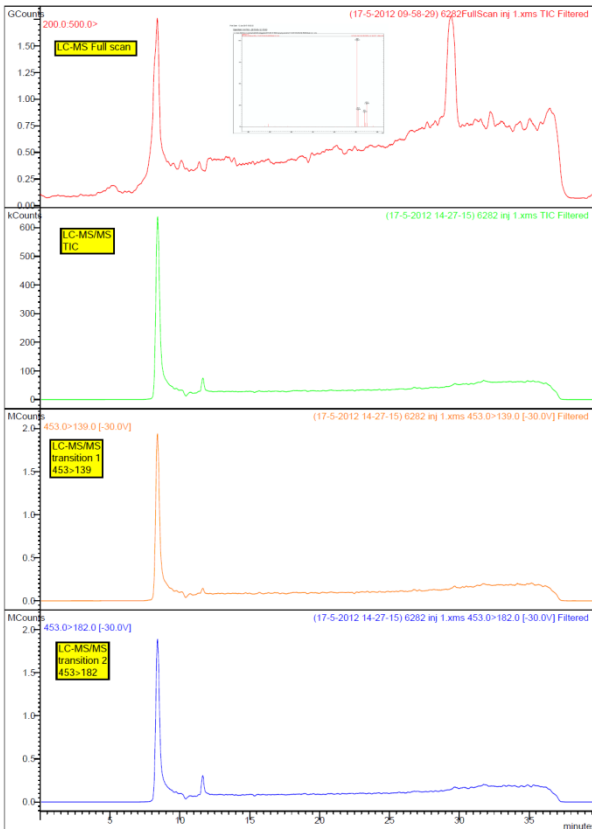
- Identification of compounds in
  - spraying solutions that caused damage
  - samples with small amounts of a second active ingredient
  - Unknown-unlabeled samples
- GC-MS (libraries)
- LC-MS (molecular ion)



# Non target analysis

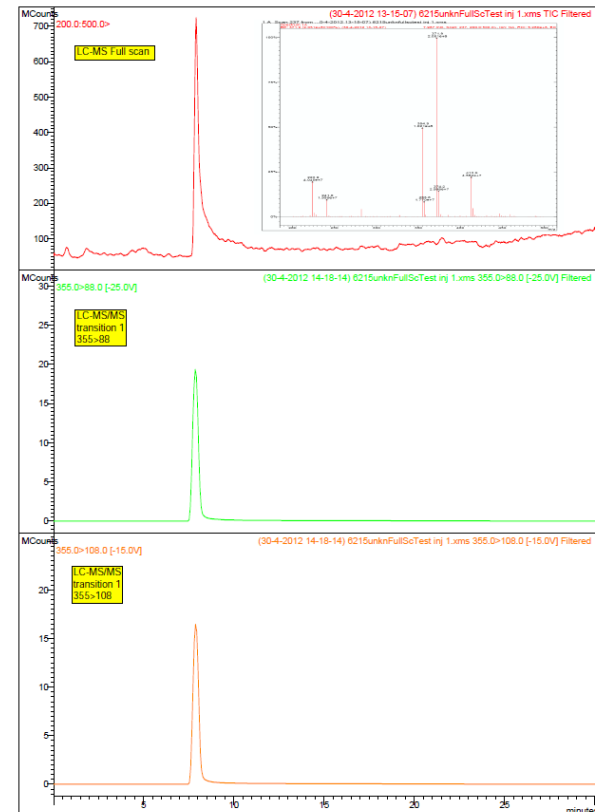
## Spraying solutions

- Caused damage
- Traces of foramsulfuron were detected with LC-MS and confirmed with LC-MS/MS



## Illegal-unknown formulations

- Unregistered thiodicarb formulation with no label
- Detected with LC-MS and confirmed with LC-MS/MS



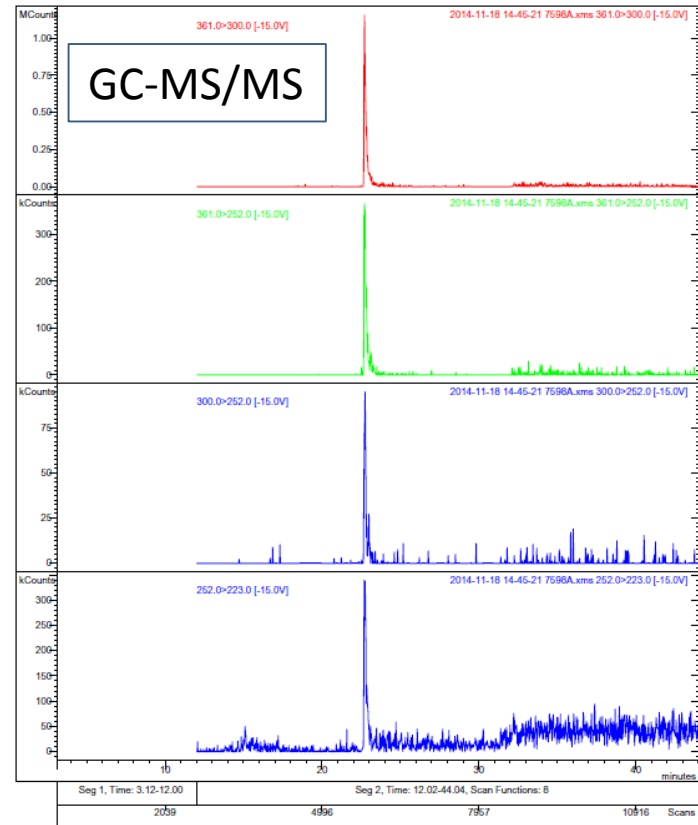
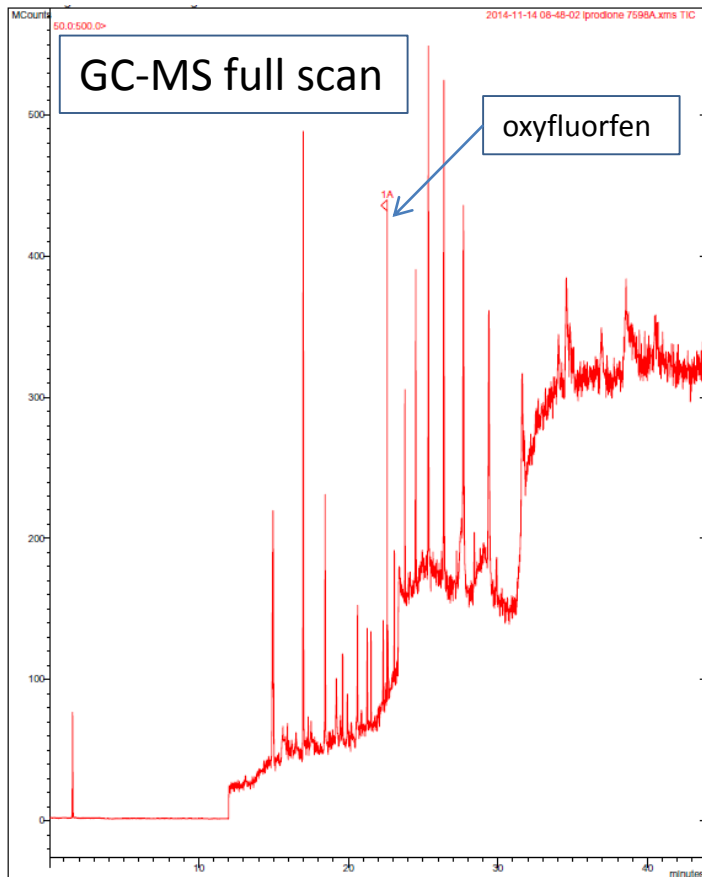


# Non target analysis

## Low-quality PPP

Sample with small amounts of a second active ingredient

– Herbicide in fungicide: oxyfluorfen found in sample of fungicide formulation (GC-MS/MS)





## –Co-formulants and solvents

- Chromatographic profile

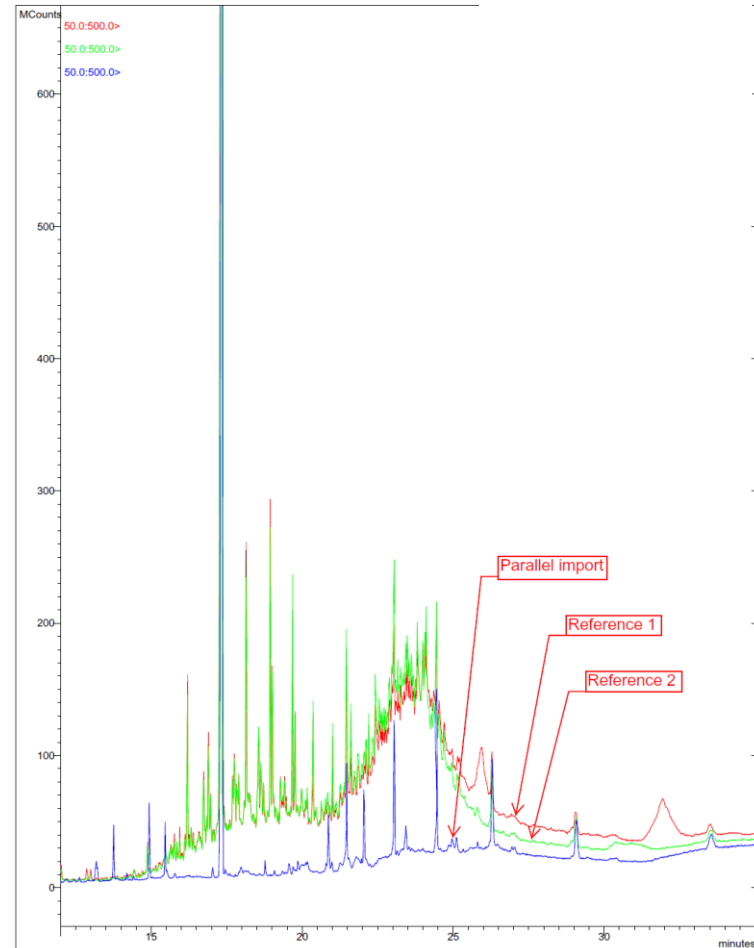
- GC-MS

- LC-MS



# Chromatographic Profiling

**Co-formulants and solvents**  
**Chromatographic profile comparison**

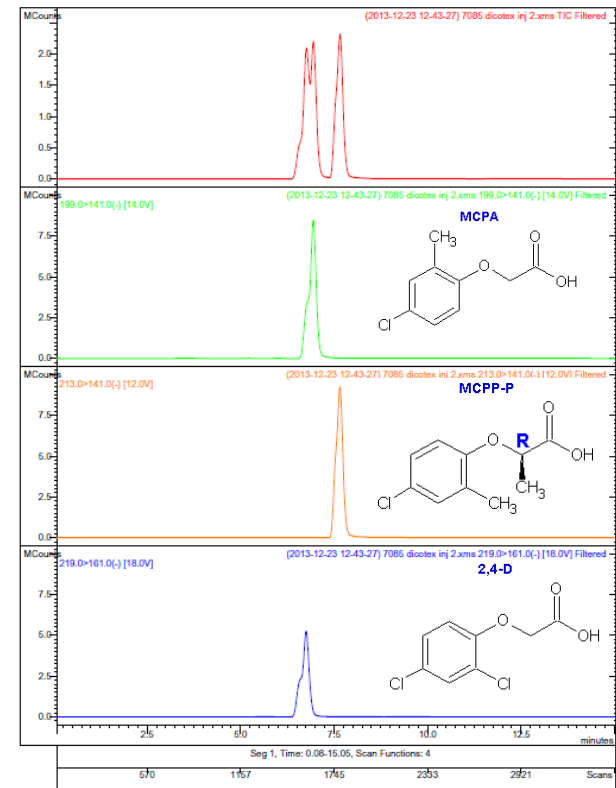
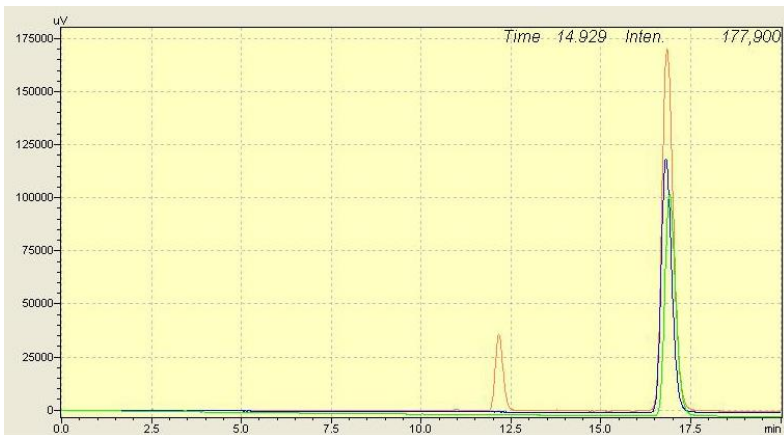






# Determination with LC-MS/MS of PPP active ingredients that do not resolve chromatographically

MCPA   
2,4 D   
Sample 





## Conclusion

PPP  
Market

- Demanding Legal Framework
- Increasing number of “out of the ordinary” samples



Laboratory

- Modern analytical equipment
- Application of advanced analytical techniques



THANK YOU FOR YOUR ATTENTION!

ANY QUESTIONS?

