

# QDA analysis in pesticide formulations

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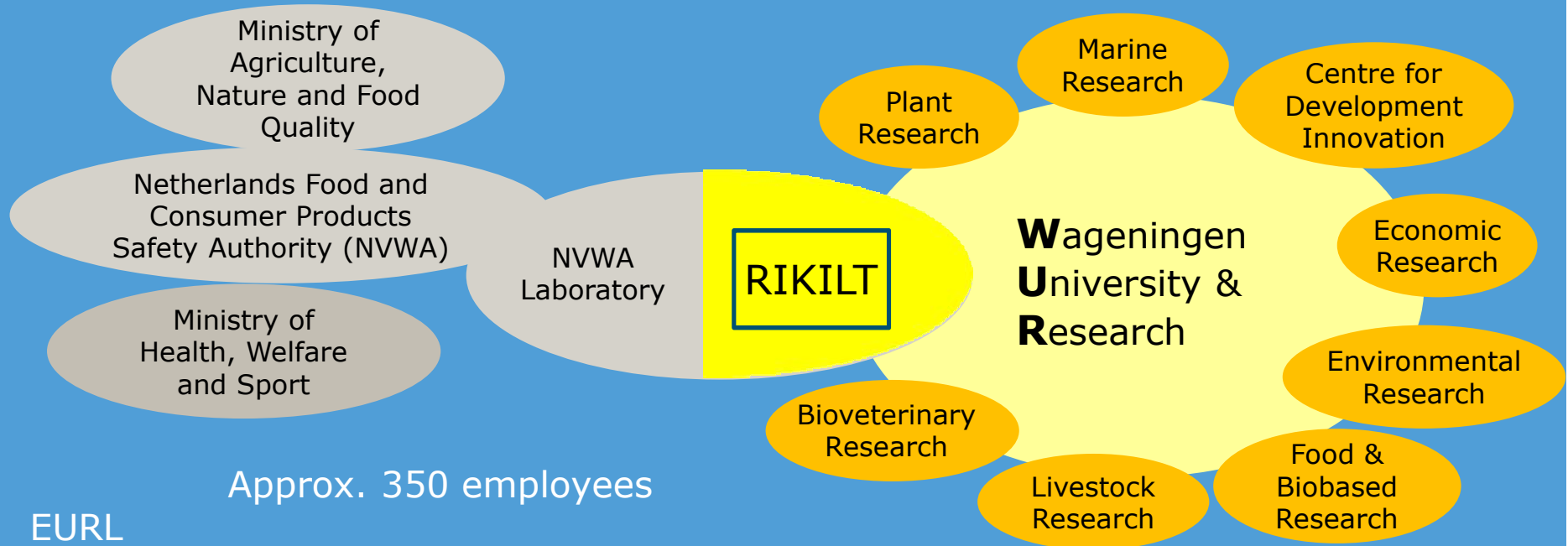




# WFSR (RIKILT)

## WAGENINGEN UNIVERSITY & RESEARCH

# RIKILT Wageningen University & Research



Approx. 350 employees

## EURL

- So called 96/23 legislation: Hormones
- Mycotoxins and plant toxins

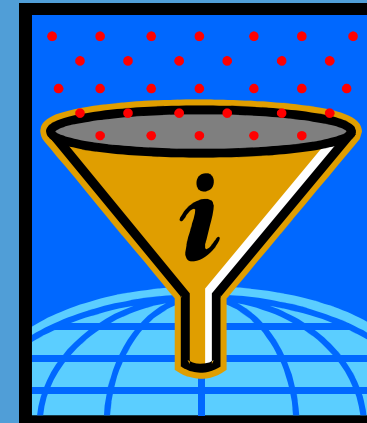
## NRL for >20 other subjects

- ✓ Pesticides (4x)
- ✓ Heavy metals
- ✓ GMO
- ✓ Contaminants (Dioxins, PAHs)
- ✓ and so on..



# Overview

- PPP control: Four fingers approach
- Non chromatographic based methods
- Chromatographic based methods
- QDA analysis
- Summary & conclusions



# PPP full product control

## Four fingers approach

- DG SANTE (“FVO”) audit
- Full product control
- Not possible due to lack of
  - Methods
  - Reference materials
  - (direct access to dossier)
- What’s next?



# Four fingers approach



- Four screening methods:

- FTIR
- NMR
- GC-MS
- LC-MS

- Comparison against:

- Original products
- Actives (pure compounds)
- Other compounds like modifiers, etc.  
(if available)

- Algorithm development

RESULT:

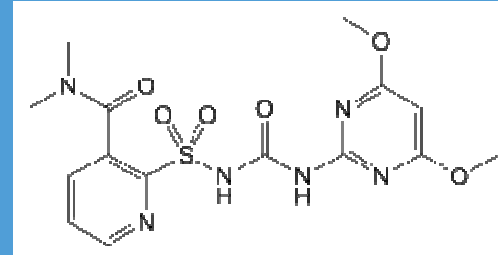


or THUMBS DOWN

# Examples

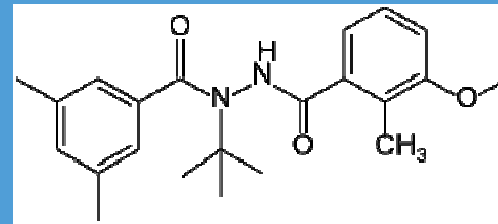
## Nicosulfuron (OD)

- Herbicide
- $C_{15}H_{18}N_6O_6S$
- 410.4 g/mol



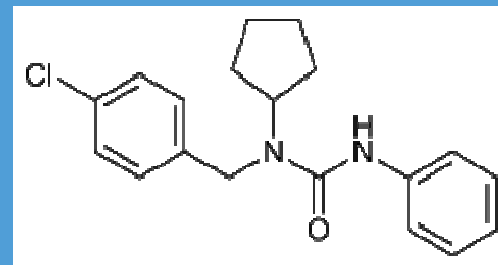
## Methoxyfenozide (SC)

- Insecticide
- $C_{22}H_{28}N_2O_3$
- 368.5 g/mol



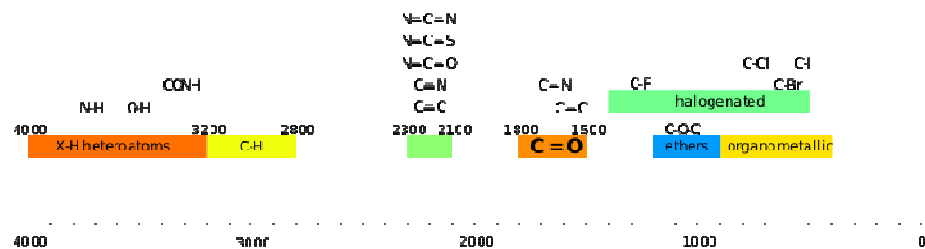
## Pencycuron (SC)

- Fungicide
- $C_{19}H_{21}ClN_2O$
- 328.8 g/mol



# Four fingers: 1. FTIR

- Infrared spectroscopy gives information about the vibration frequencies within a molecule
- Mid infrared  $\lambda = 2.5\text{-}25\ \mu\text{m}$  or  $4000\text{-}400\ \text{cm}^{-1}$
- Complicated spectra, specialist interpretation needed
- Sample can be applied "as is".

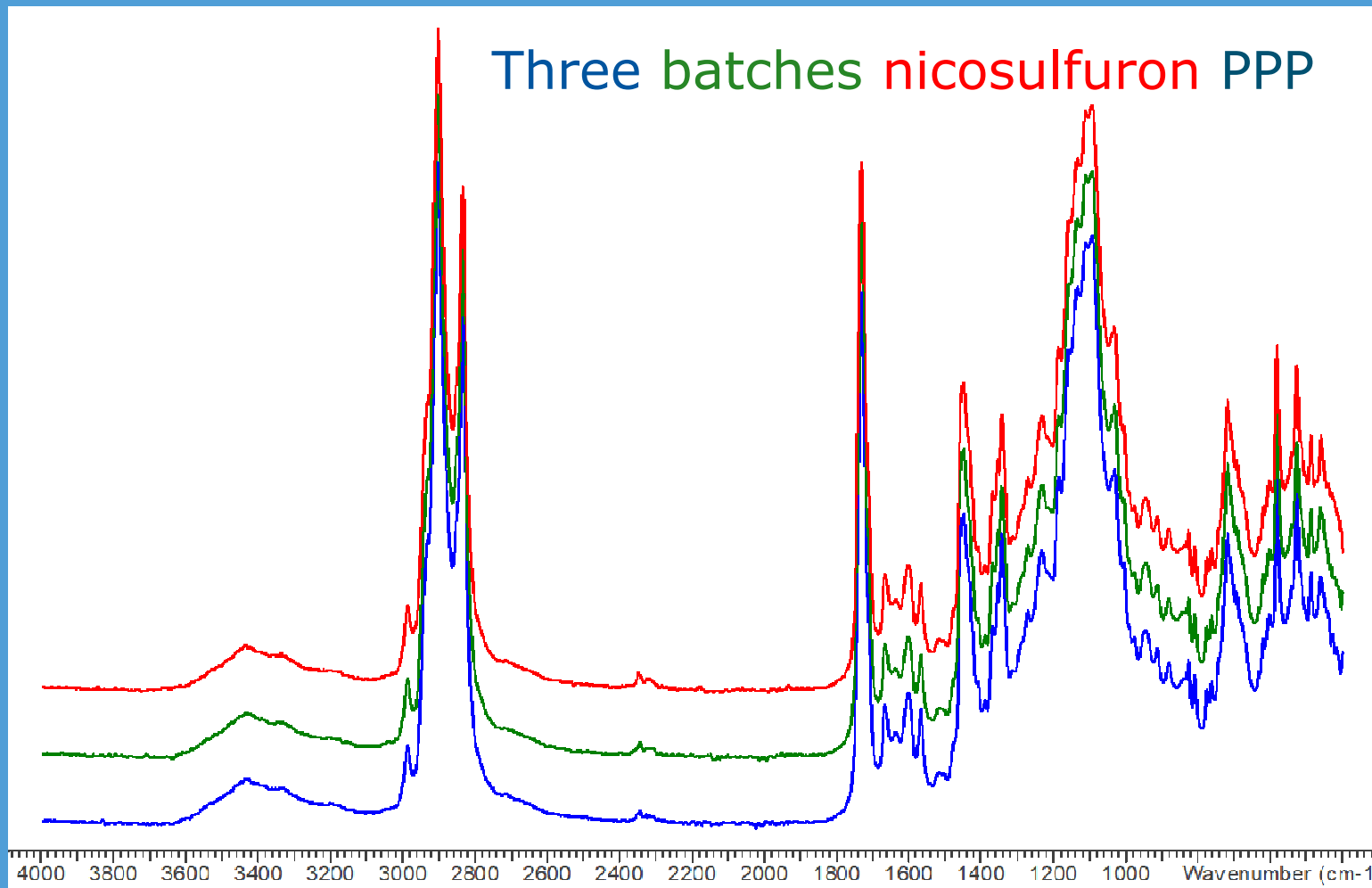


Source: Wikipedia

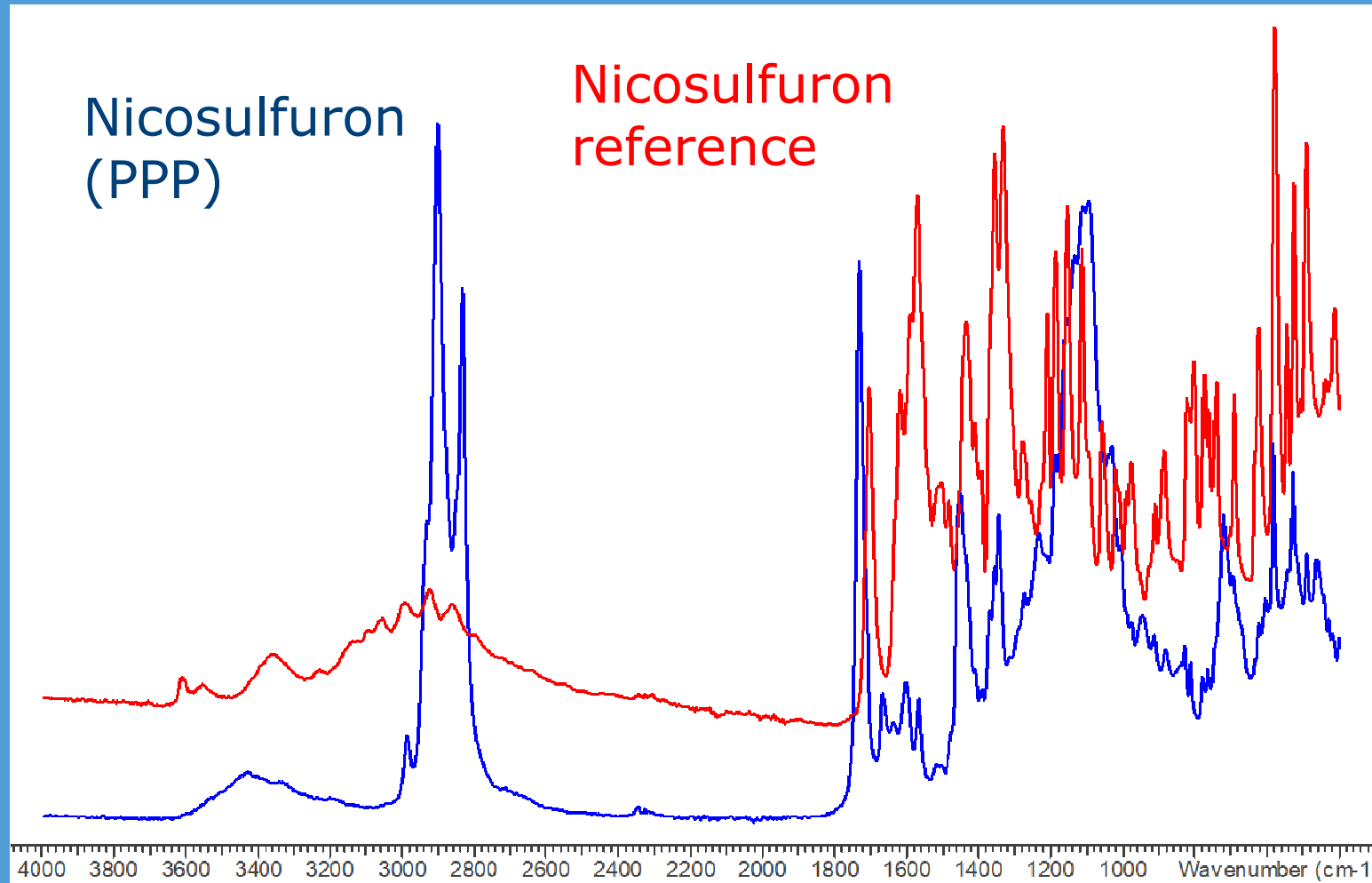




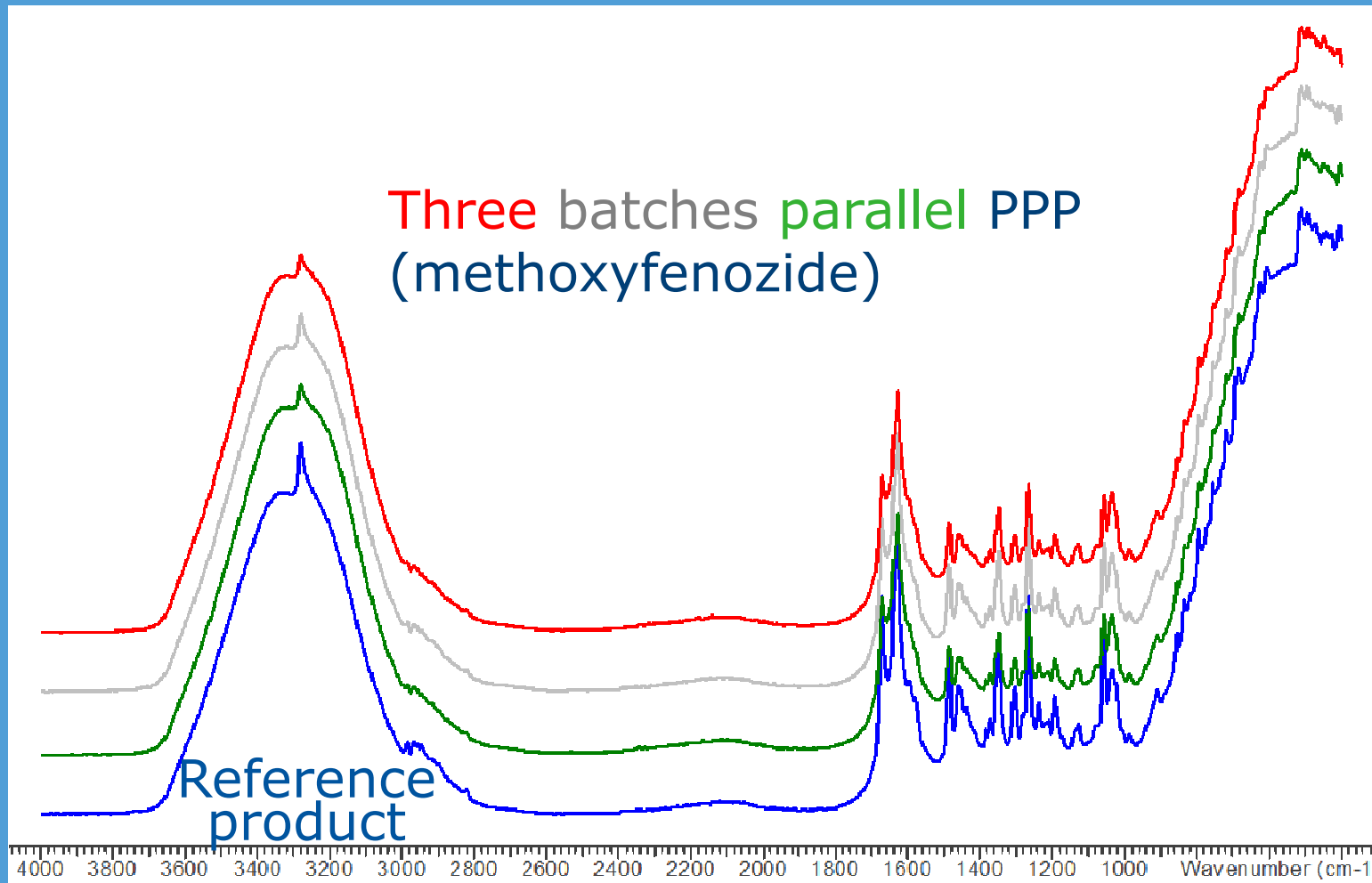
# Example FTIR



# Example FTIR

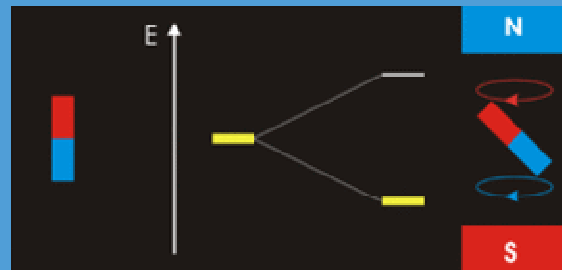


# Example FTIR

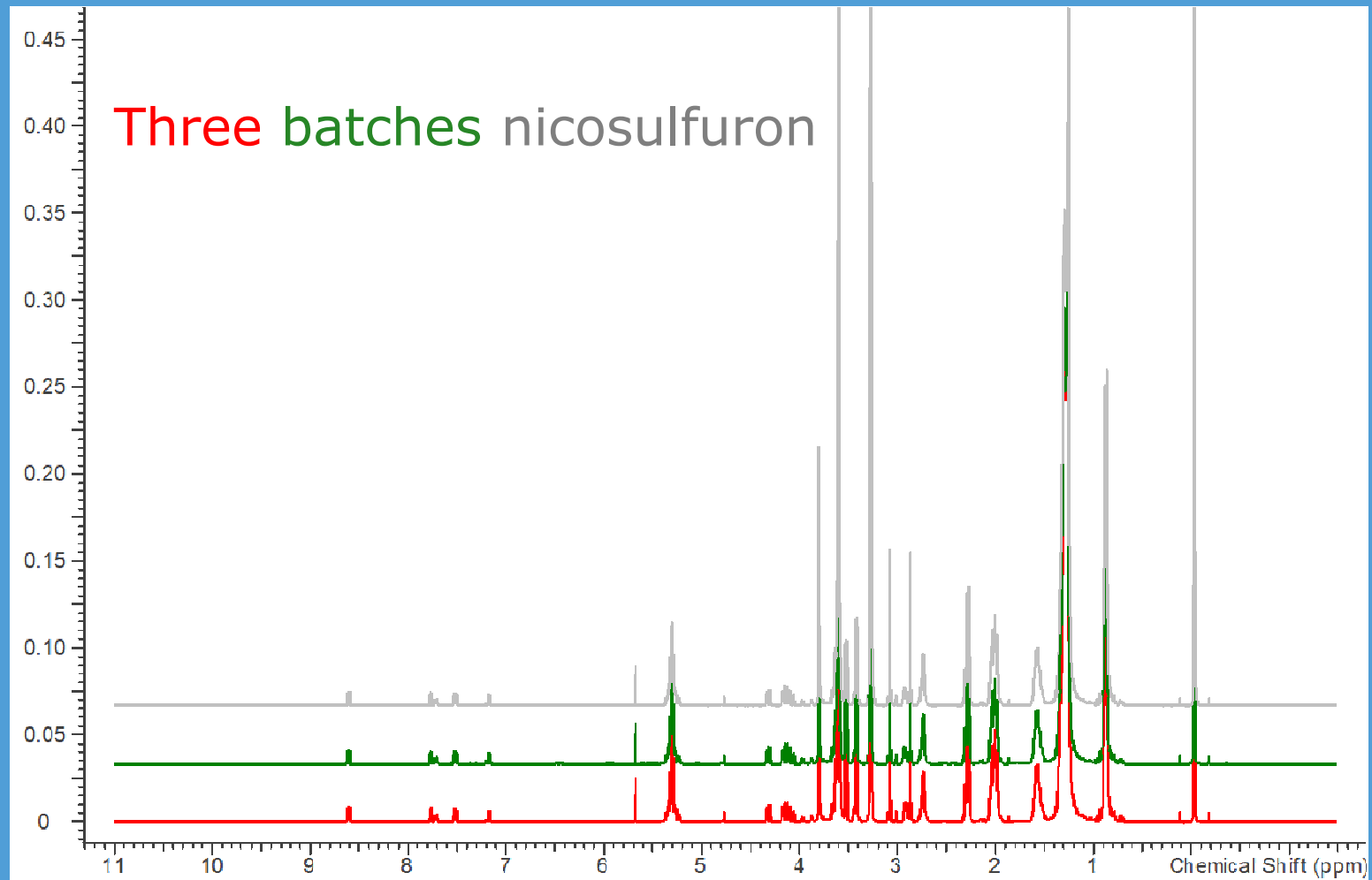


# Four fingers: 2. NMR

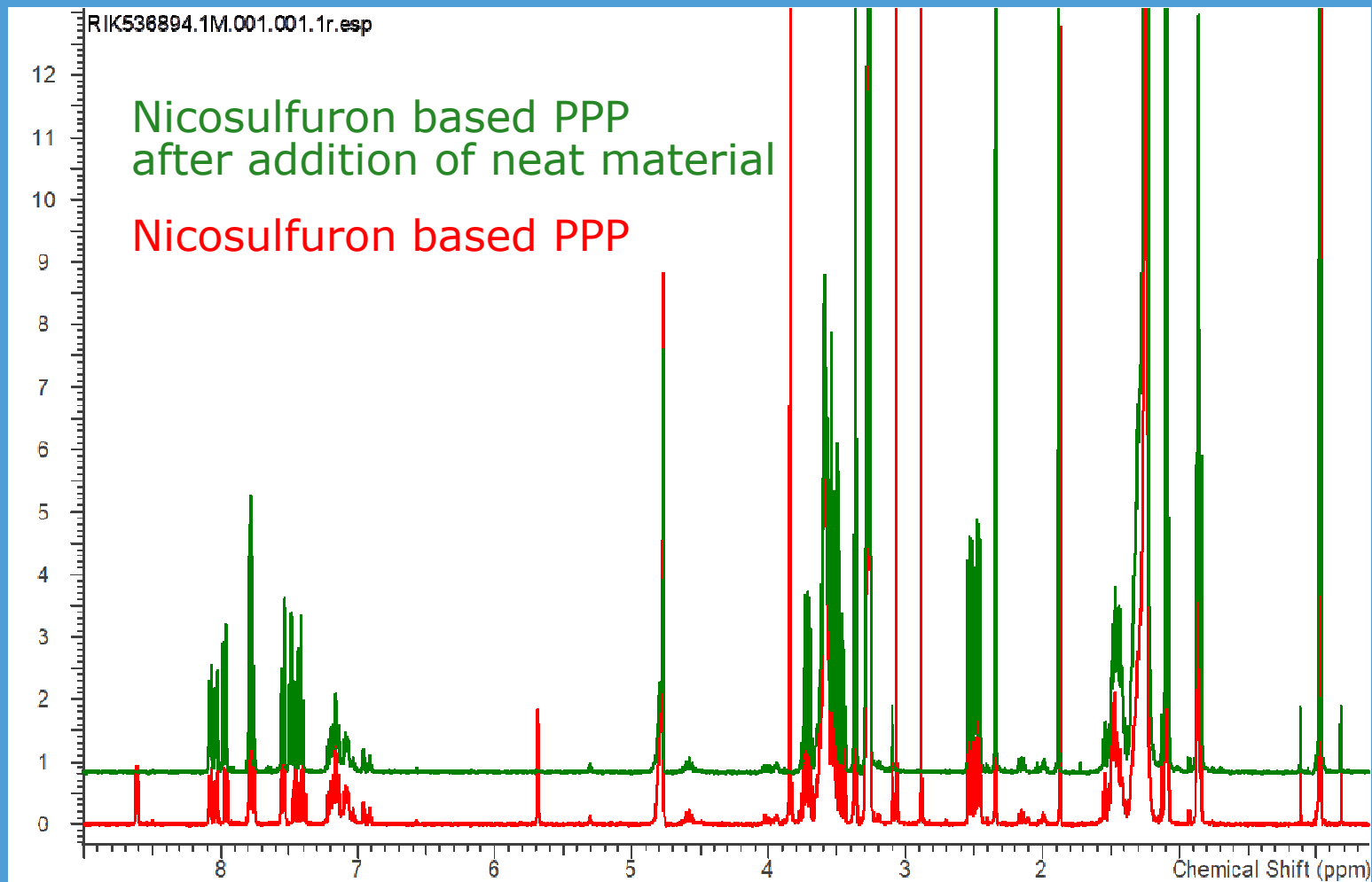
- Isotopes that contain an odd number of protons and/or neutrons
- Most common  $^1\text{H}$  or  $^{13}\text{C}$ ;  $^{31}\text{P}$ .
- Proton NMR most sensitive (use deuterated solvents)
- It gives information about the “surroundings” of an atom in a molecule: molecular structure.



# Example NMR



# Example NMR

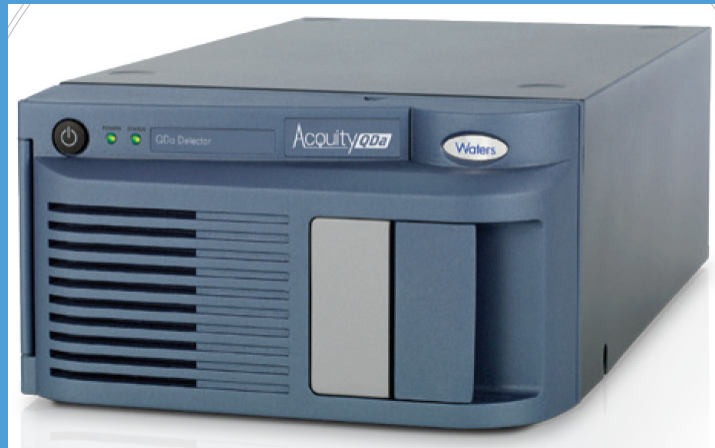


# Four fingers: 3. GC-MS

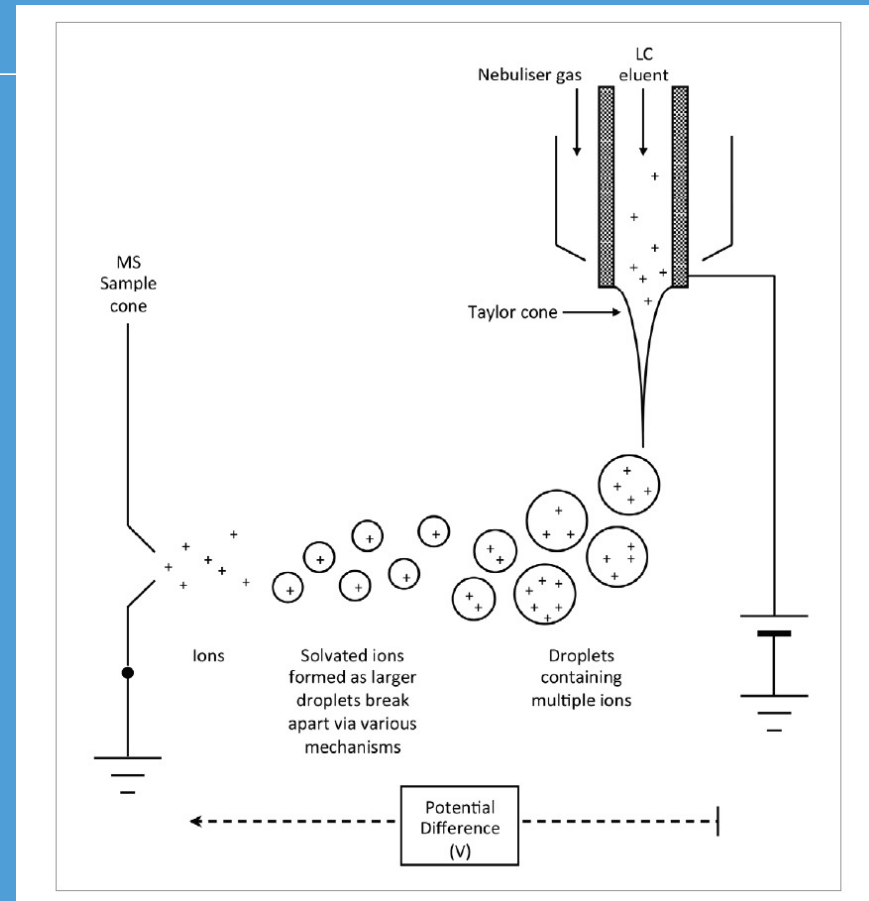
- Under development



# Four fingers: 4. QDA



Source: Waters

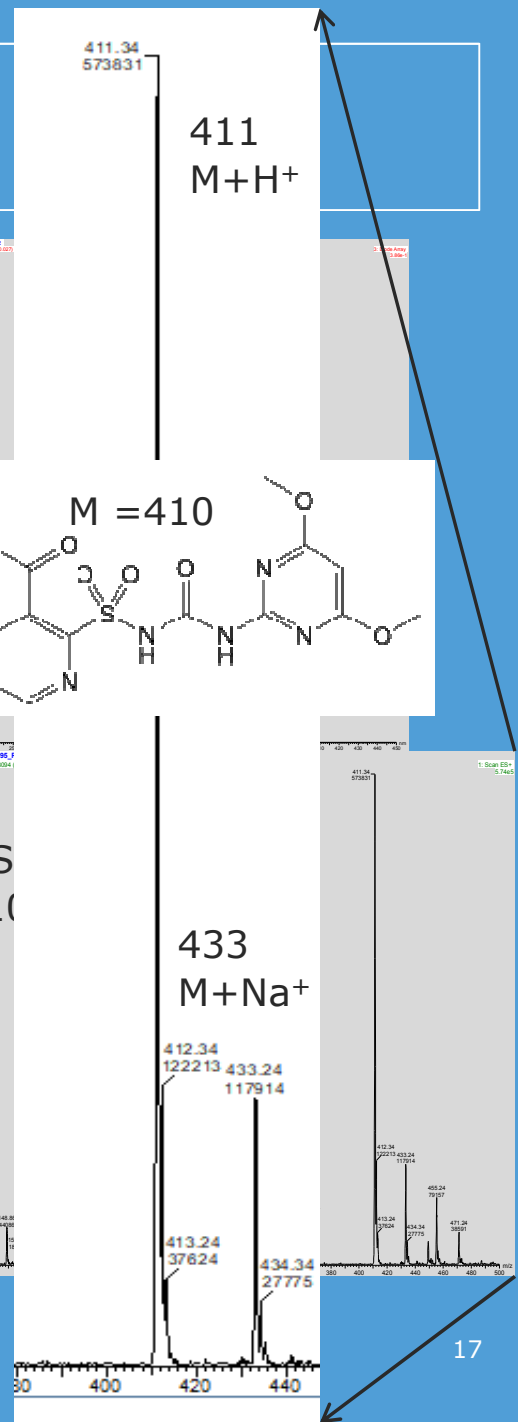
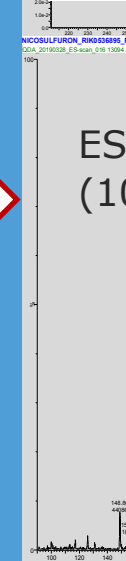
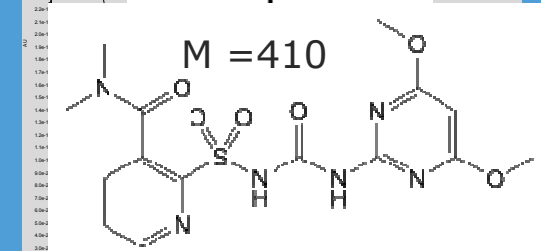
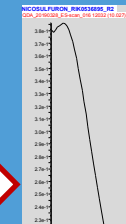
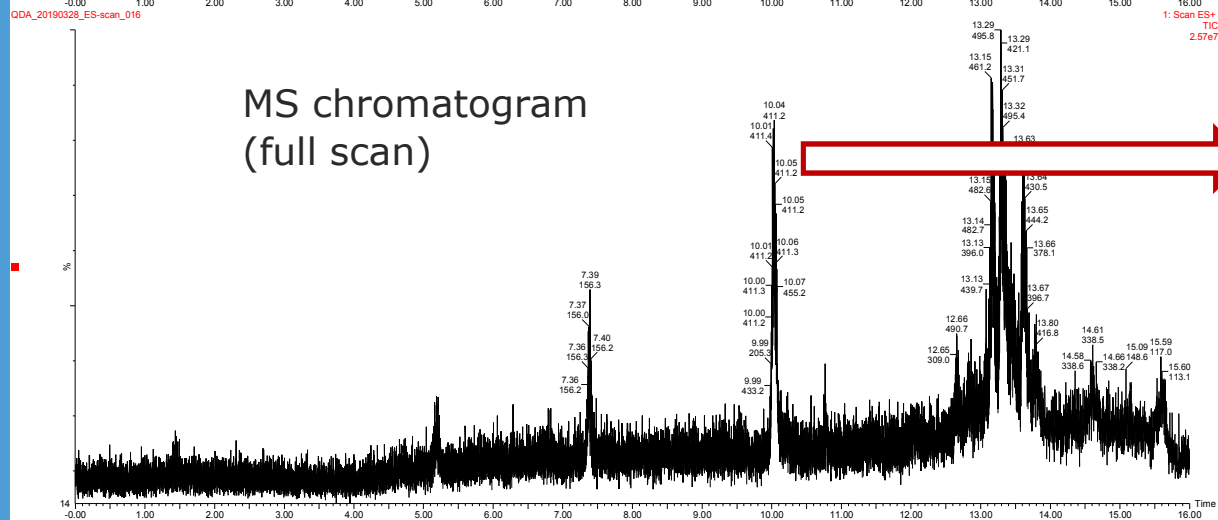
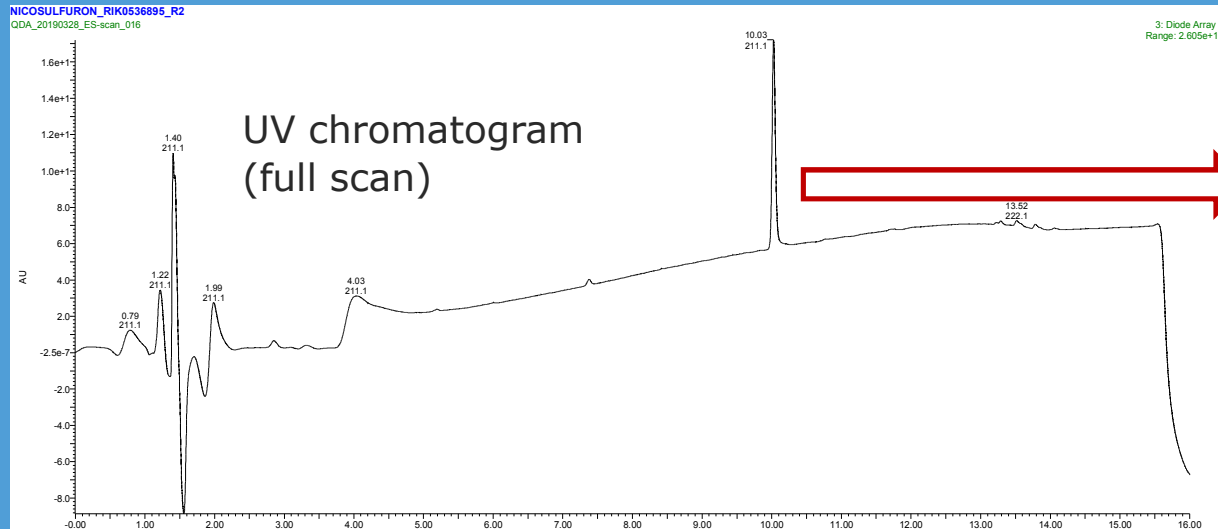


Chiral and Achiral Profiling of a Pesticide Formulation Using the ACQUITY UPC2 System and the ACQUITY QDa Detector

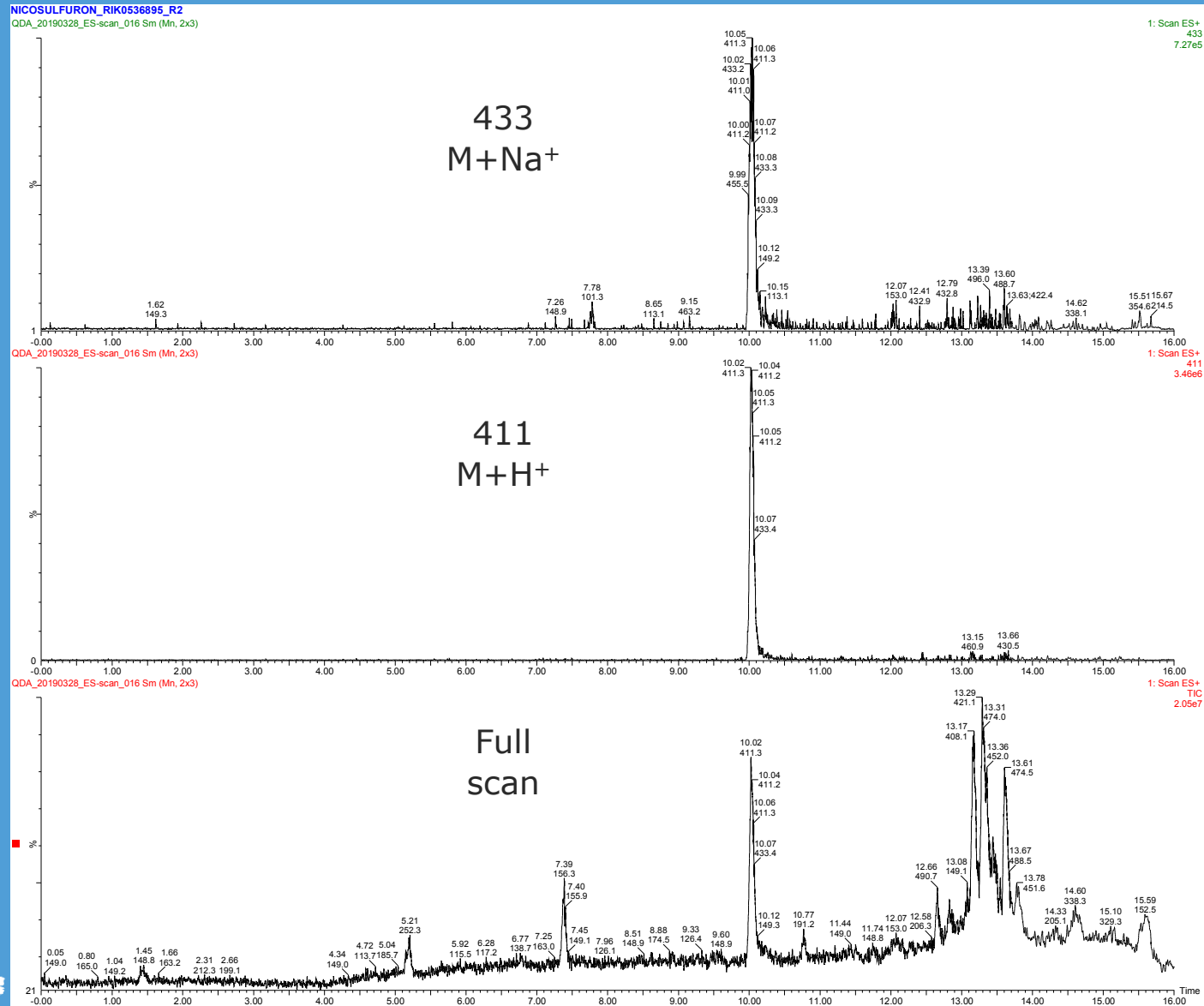
<https://www.waters.com/webassets/cms/library/docs/720004977en.pdf>



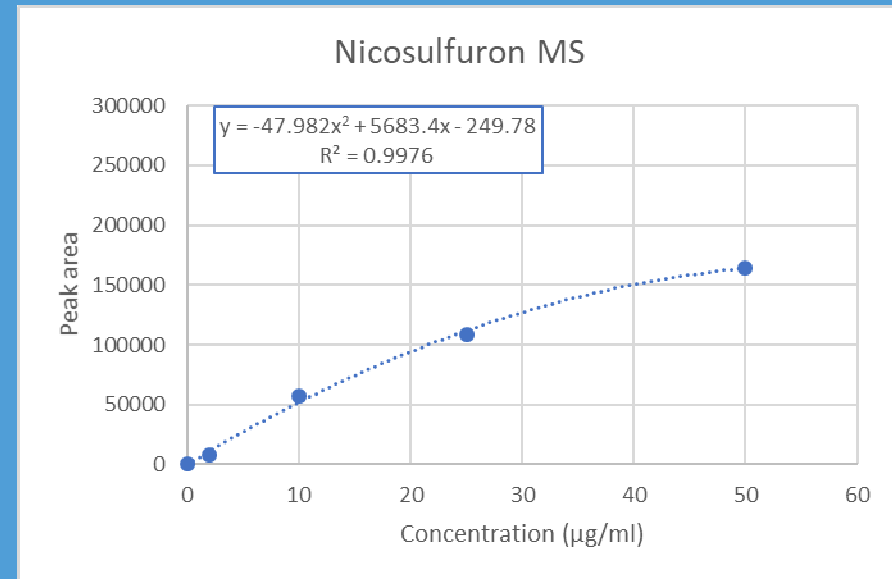
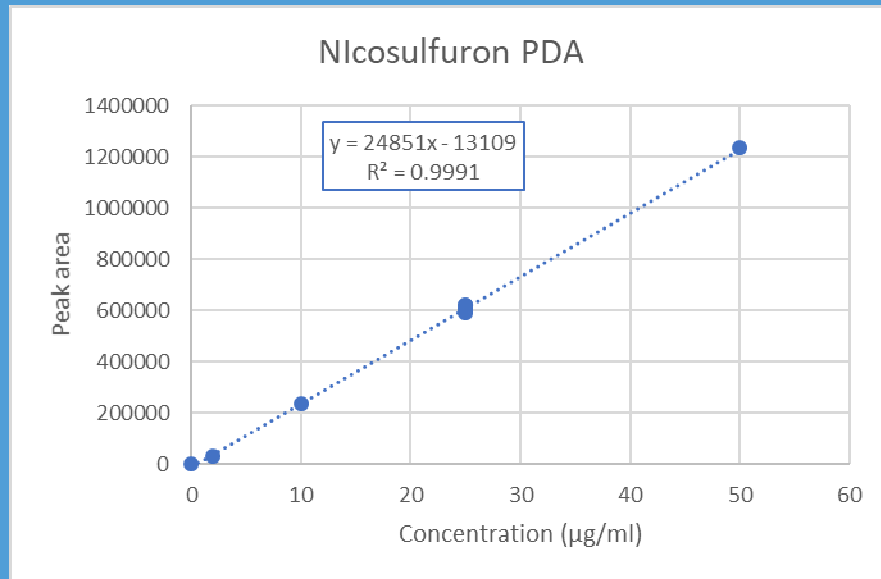
# Nicosulfuron based PPP (OD)



# Nicosulfuron based PPP (OD)



# Nicosulfuron Quantitation

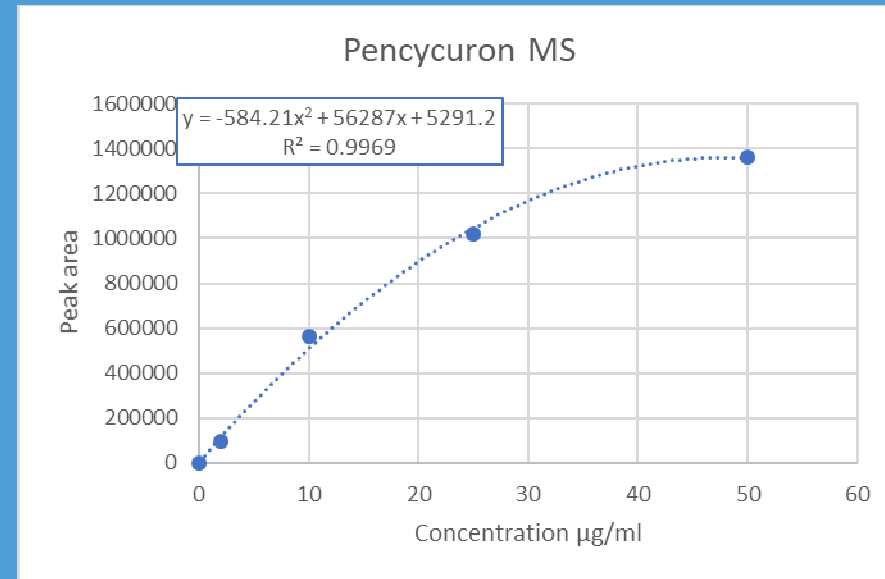
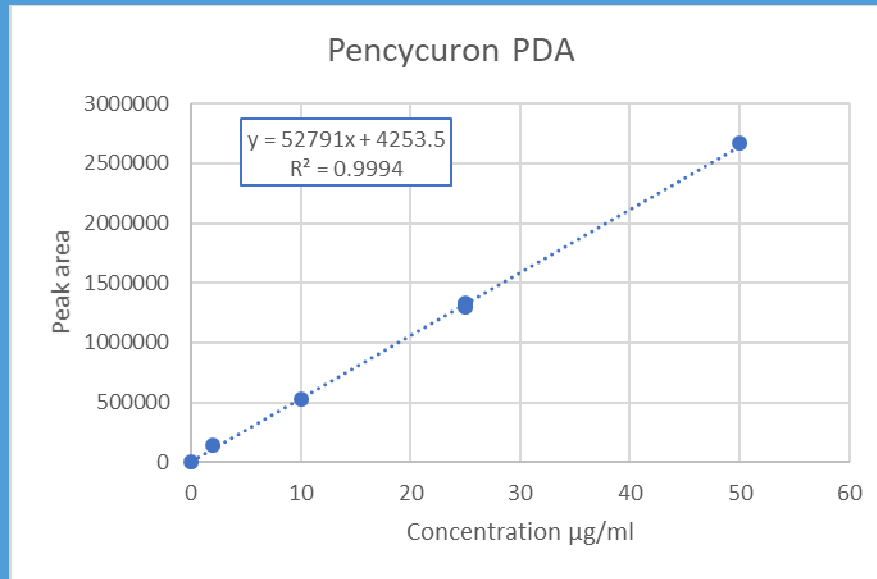


Calculated 63 g/l  $\pm$  0.32%

Calculated 100 g/l  $\pm$  60%

Target 60 g/l (54-66 g/l)

# Pencycuron quantitation

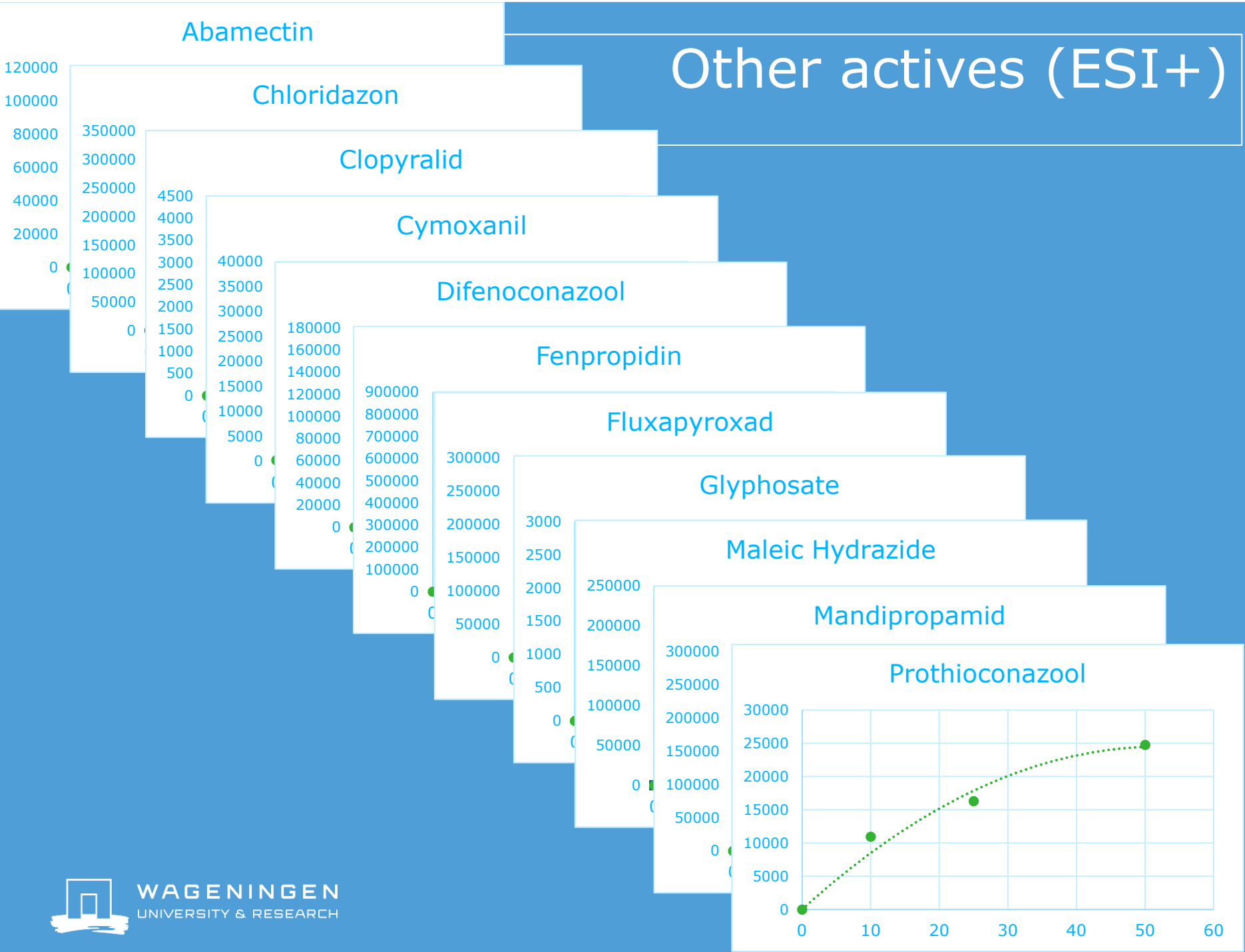


Calculated 257 g/l  $\pm$  1.0%

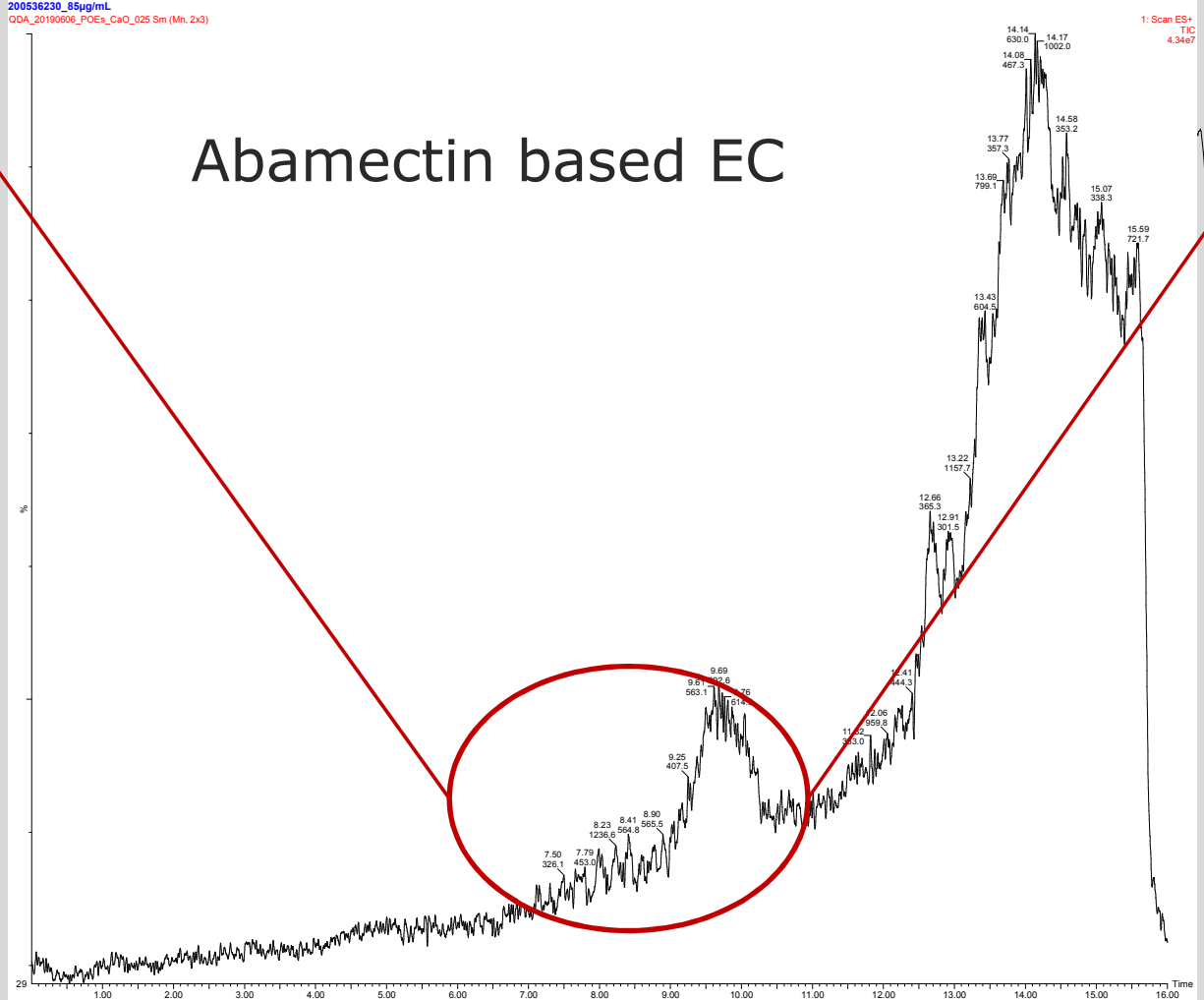
Calculated >1000 g/l  $\pm$  16%

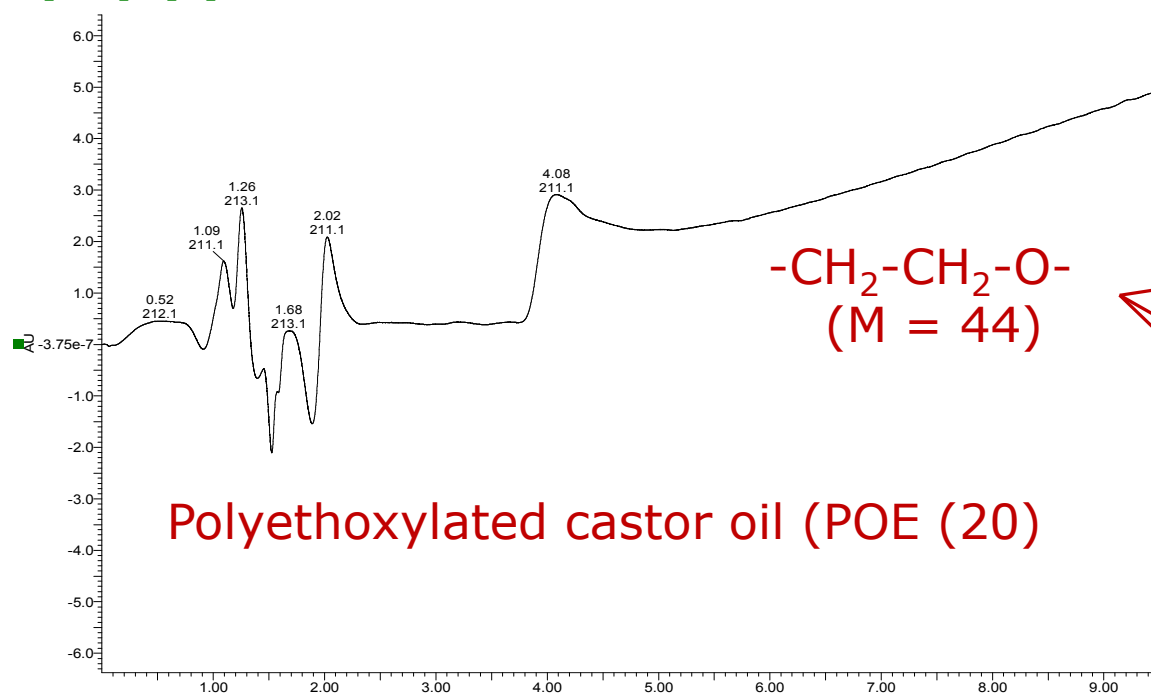
Target 250 g/l (235-265 g/l)

# Other actives (ESI+)

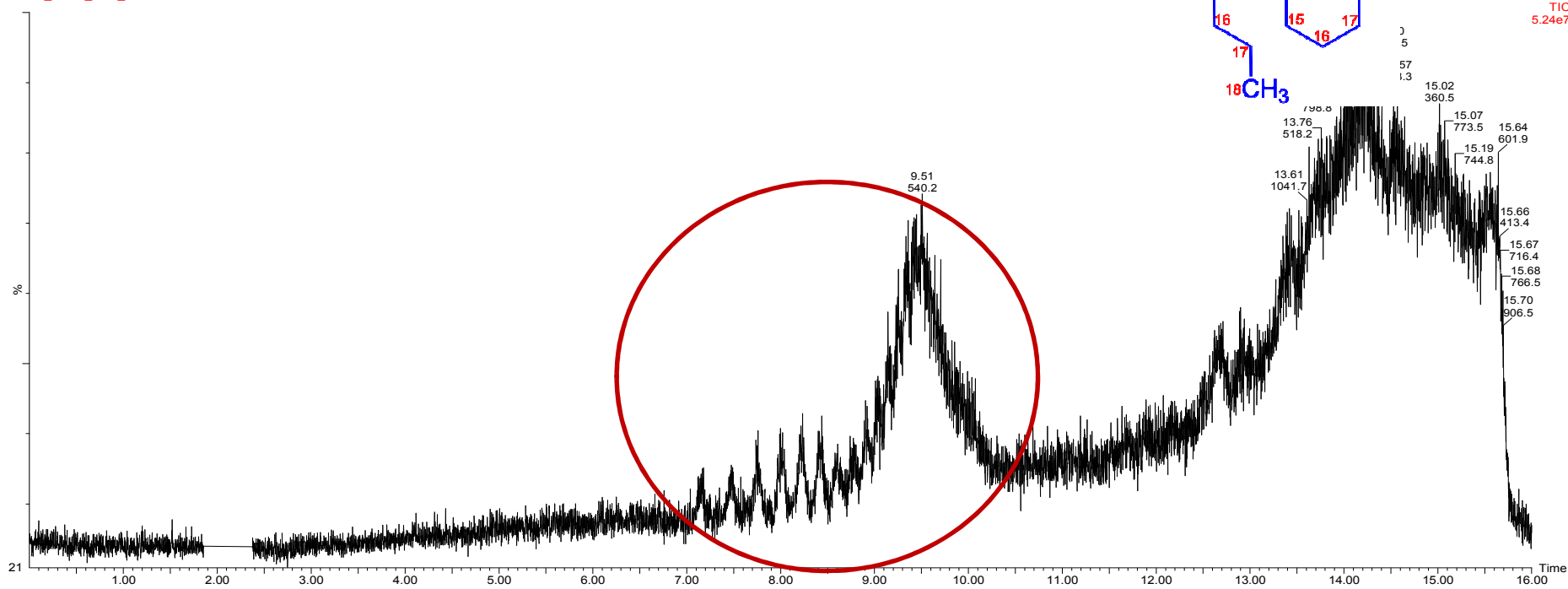
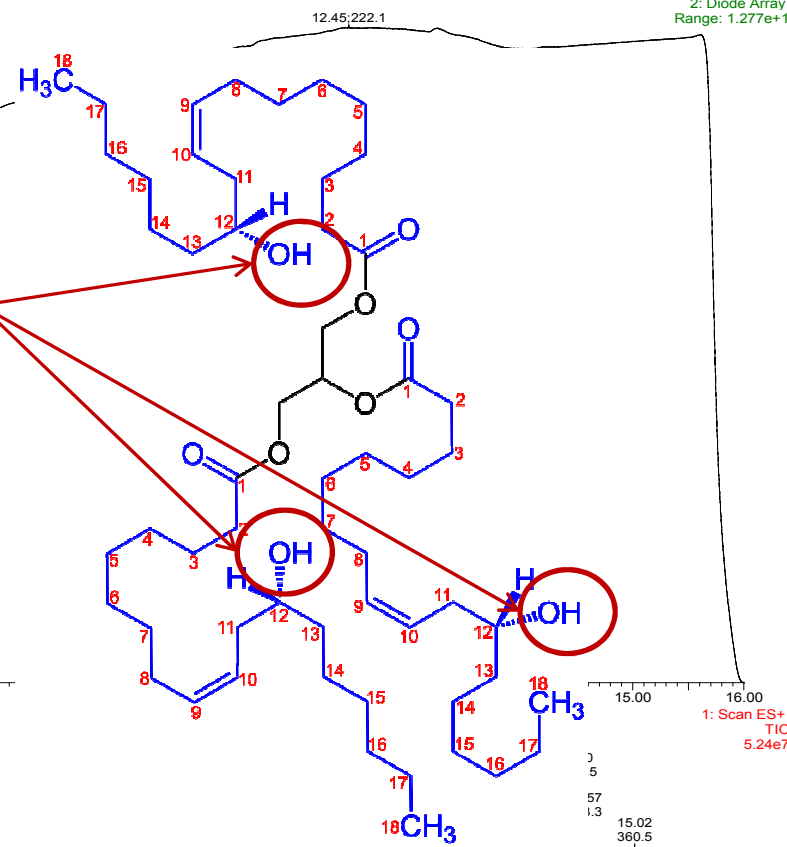


# Other MS findings



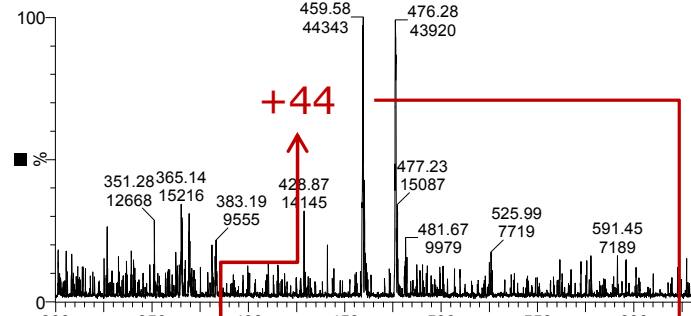


Polyethoxylated castor oil (POE (20))



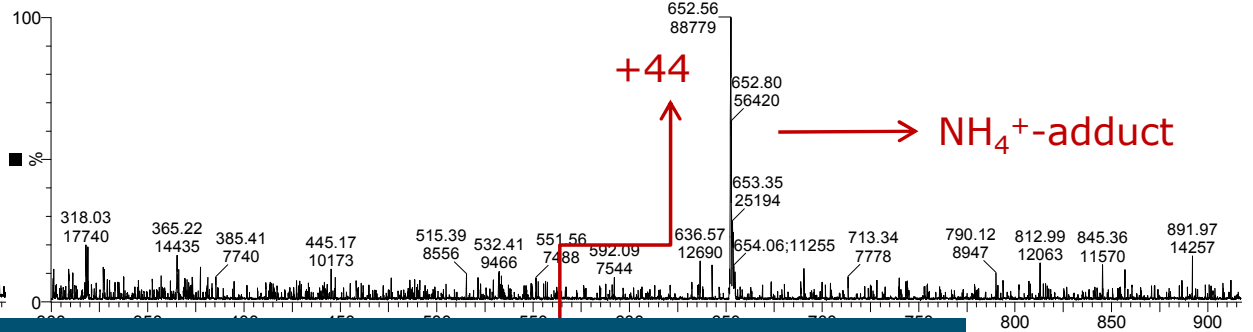
200536230\_85µg/mL

QDA\_20190606\_POEs\_CaO\_025 3829 (7.972) Cm (3828:3856)

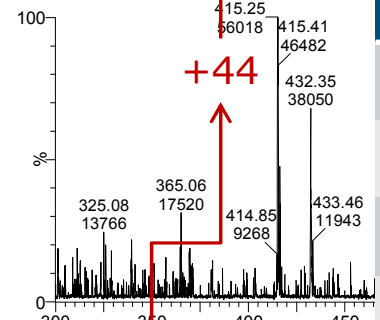


200536230\_85µg/mL

QDA\_20190606\_POEs\_CaO\_025 4205 (8.754) Cm (4198:4224)

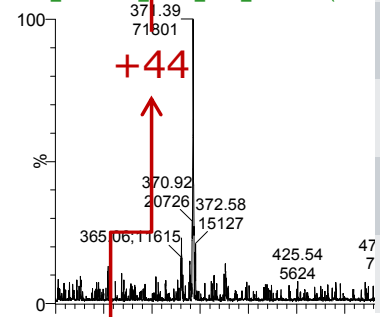


QDA\_20190606\_POEs\_CaO\_025 3730 (7.766)

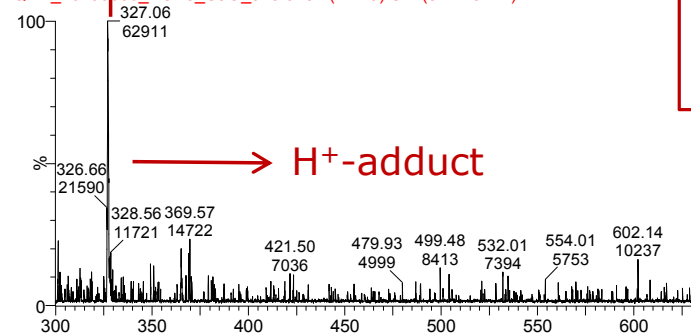


Ret. time	H <sup>+</sup> adduct	NH <sub>4</sub> <sup>+</sup> adduct
7.15	100%	0%
7.49	100%	15%
7.67	100%	70%
7.97	100%	100%
8.24	30%	100%
8.41	20%	100%
8.58	25%	100%
8.75	0%	100%

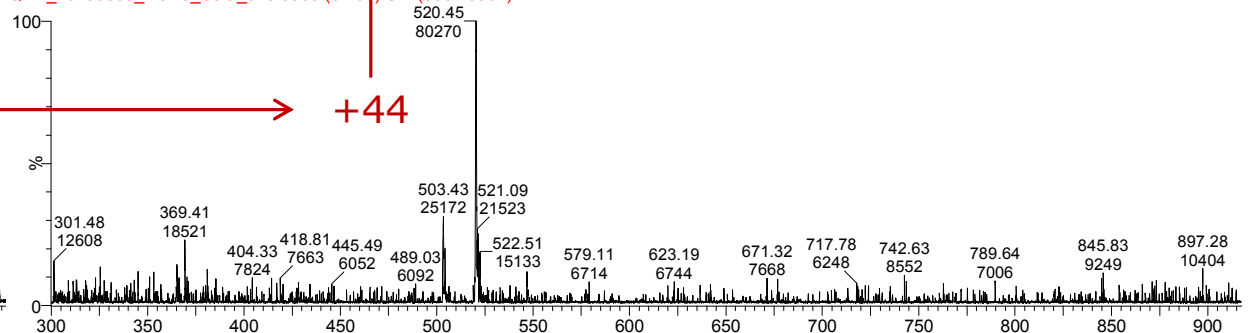
QDA\_20190606\_POEs\_CaO\_025 3599 (7.493)



QDA\_20190606\_POEs\_CaO\_025 3434 (7.149) Cm (3414:3442)



QDA\_20190606\_POEs\_CaO\_025 3956 (8.236) Cm (3934:3967)





# QDA summary

## ■ MS

- Active substance identification possible
- Other compounds when reference is available
- Quantitation more difficult
- Development continues

## ■ Diode-array

- Assists with identification, not very specific
- Good quantification parameters

# Summary & Conclusions

The Four Fingers approach gives the maximum amount of product information and would be suited for product control without the need of analysis of all individual compounds



**Thank you for your attention !**

