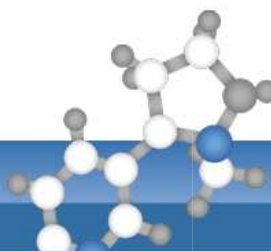




European
Commission

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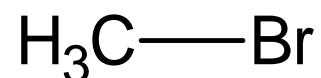
EU Reference Laboratories for Residues of Pesticides

Single Residue Methods

Selective analysis of Bromide via LC-MS/MS and comparison with a traditional GC- based method



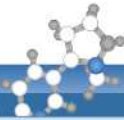
<http://www.forstercontainer.ch/>



https://www.containerhandbuch.de/chb_e/stra/index.html?/chb_e/stra/stra_03_08_00.html

**Eric Eichhorn
Anne Benkenstein
Cristin Wildgrube
Andrea Karst
Diana Kolberg
Ellen Scherbaum
Michelangelo Anastassiades**

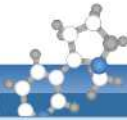
**11th European Pesticide Residue Workshop
24th-27th May 2016, Limassol, Cyprus**



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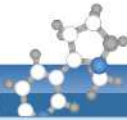


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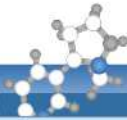


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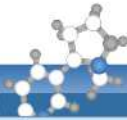


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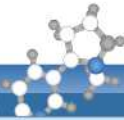


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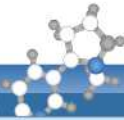
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Slide 7

E1

Kommt eventuell raus aufgrund Zeitmangel

Elladan; 18/05/2016



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 - high toxicity towards a wide-range of organisms (nervous system)
 - damages ozone layer & enhances the Greenhouse Effect
 - 2008/753/EC: non-approval of Methyl bromide
 - Maximum Residue Levels (**MRL's**) as **Bromide**, Reg. (EC) No. 149/2008 and Reg. (EC) No. 839/2008:
5 ppm (berries) – **400 ppm** (spices)

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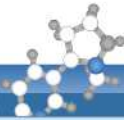
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Slide 8

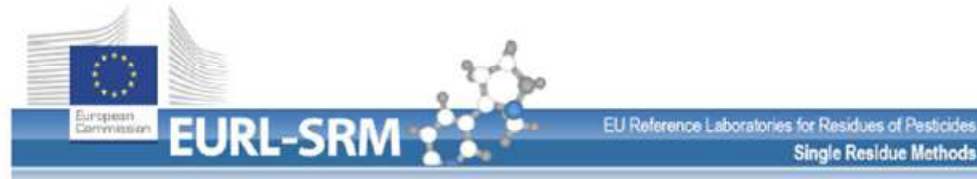
E1

Kommt eventuell raus aufgrund Zeitmangel

Elladan; 18/05/2016



2. Extraction of Bromide: QuPPe method



Quick Method for the Analysis of numerous Highly Polar Pesticides in Foods of Plant Origin via LC-MS/MS involving Simultaneous Extraction with Methanol (QuPPe-Method)

- **Version 9.1** (May 2016, Document History, see page 65)
Authors: M. Anastassiades; D. I. Kolberg; A. Benkenstein; E. Eichhorn; S. Zechmann;
D. Mack; C. Wildgrube; I. Sigalov; D. Dörk; A. Barth

Weigh sample homogenate in 50 mL centrifuge tube

Fresh fruits and vegetables (with high content of water): 10 g ± 0.1 g,
Previously dehydrated dry fruit 13.5 g ± 0.1 g (containing 5 g sample),
Cereals and dried pulses (dried commodities): 5 g ± 0.05 g



Adjust water content of sample to 10 mL

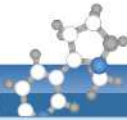
e.g. Rye Flour: add 10 g water; Potato: add 2 g of water



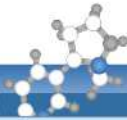
Add 10 mL MeOH containing 1 % formic acid



LC-MS/MS analysis

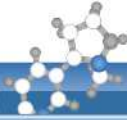


3. Facts regarding the MS/MS analysis of Bromide



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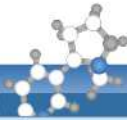
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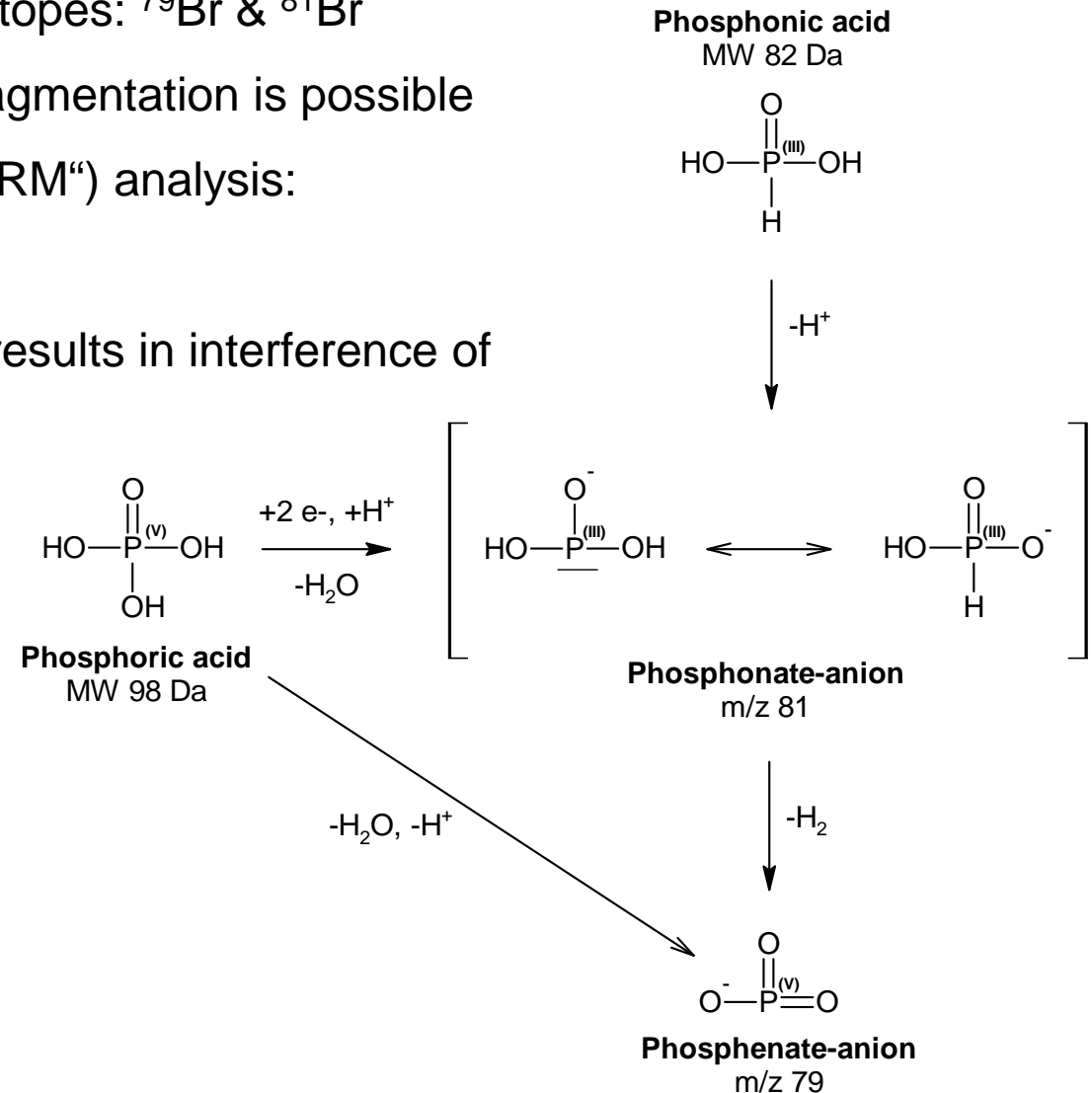
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- „parent/parent“ (= „pseudo-MRM“) analysis:

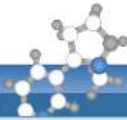
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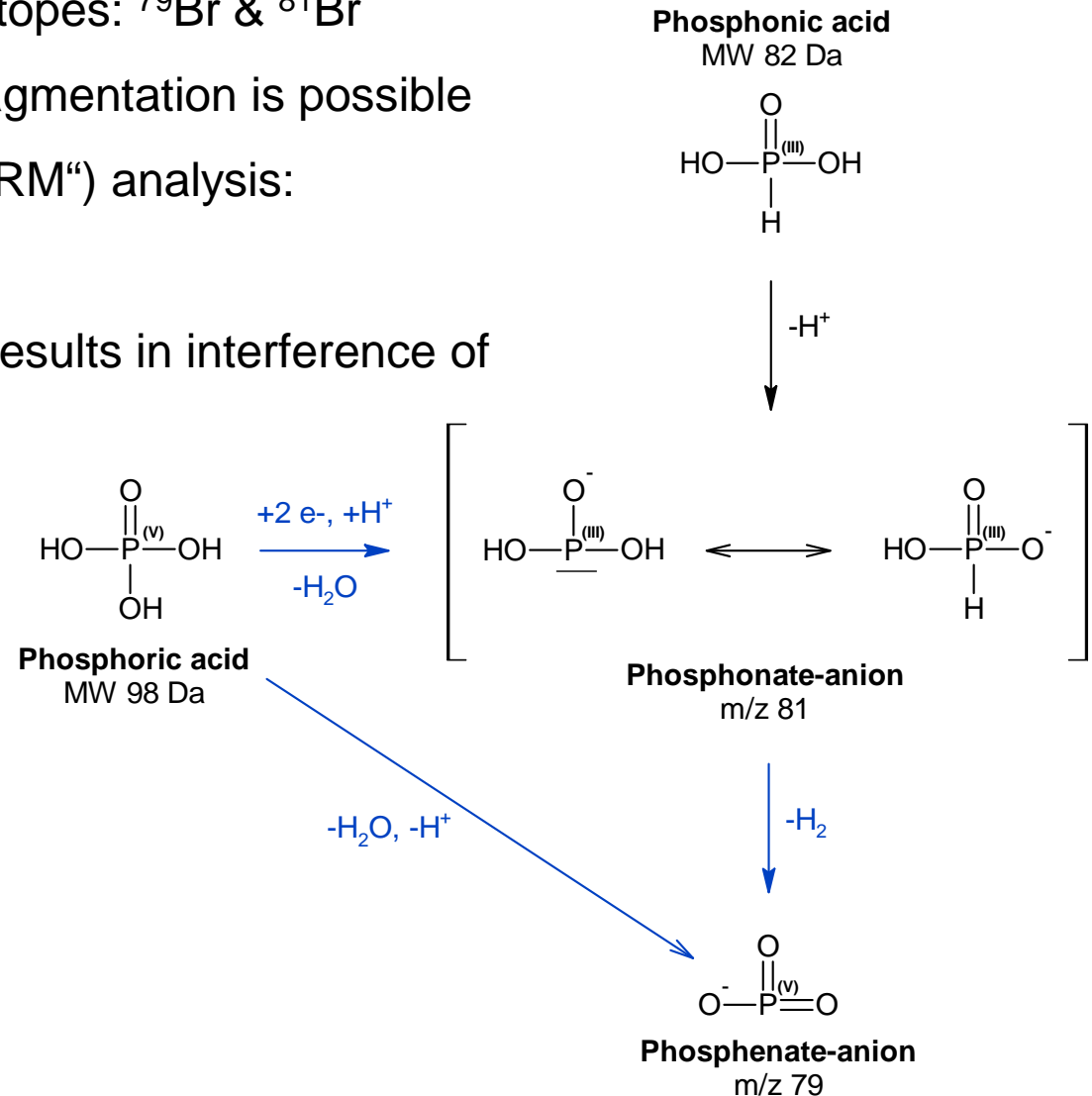


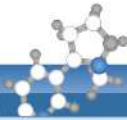


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in-source fragmentation



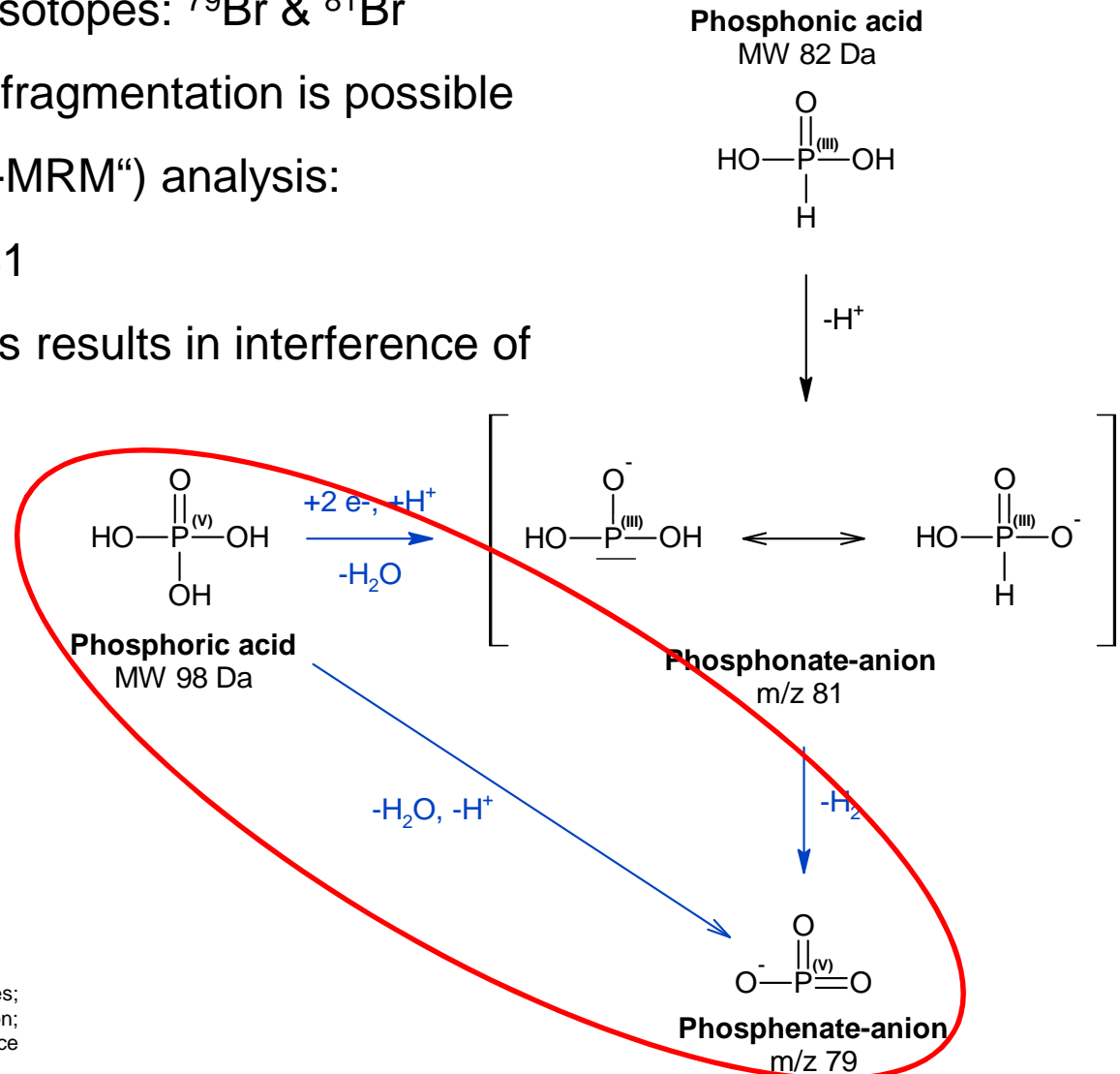


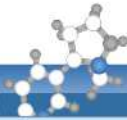
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most critical pathway

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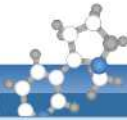




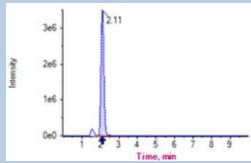
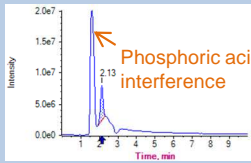
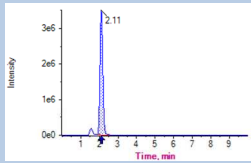
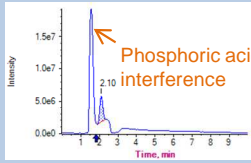
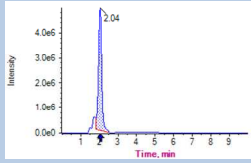
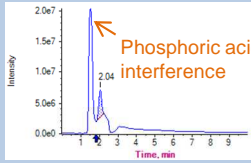
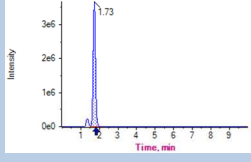
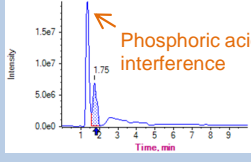
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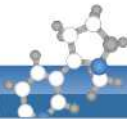
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 m/z 79/79 and m/z 81/81
- non-selective MS/MS analysis results in interference of both mass traces
- strategies to decrease these interferences:
 - improve chromatographic separation
 - reduce matrix effects
 - more selective measurement (e. g. Differential Mobility Mass Spectrometry)

} dilution (e. g. 50-fold)

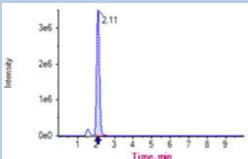
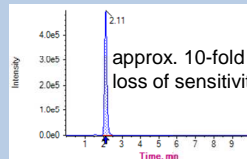
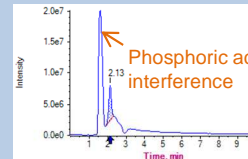
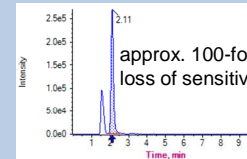
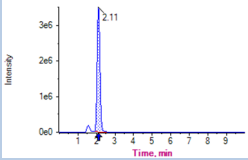
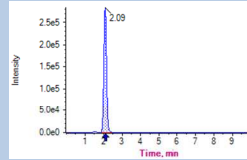
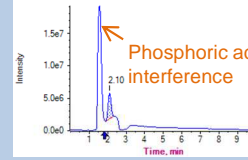
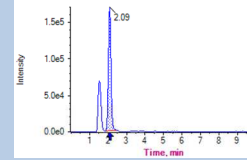
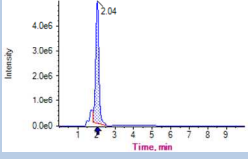
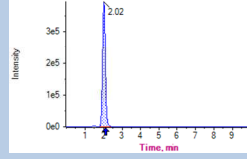
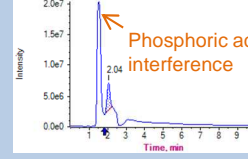
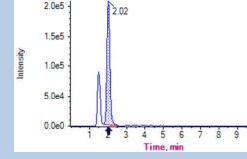
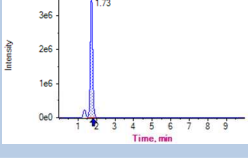
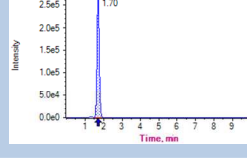
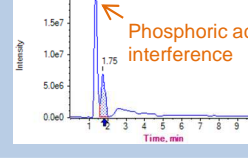
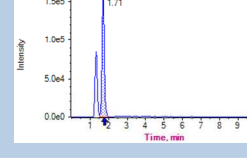


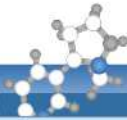
4. Improving the selectivity of the MS/MS measurement by modifying the Collision Energy (CE)

| QuPpe extract of | m/z 81/81 | | m/z 79/79 | |
|------------------|--|--|---|--|
| | CE -5 V | | CE -5 V | |
| cucumber |  | |  | |
| | <i>containing 1.7 ppm Bromide, approx. 300 ppm Phosphoric acid & 2.0 ppm Phosphonic acid</i> | | | |
| mint leaves |  | |  | |
| | <i>containing 1.1 ppm Bromide, approx. 370 ppm Phosphoric acid; Phosphonic acid n. d.</i> | | | |
| fennel |  | |  | |
| | <i>containing 2.2 ppm Bromide, approx. 400 ppm Phosphoric acid & 5.4 ppm Phosphonic acid</i> | | | |
| sweet corn |  | |  | |
| | <i>containing 1.1 ppm Bromide, approx. 350 ppm Phosphoric acid; Phosphonic acid n. d.</i> | | | |



4. Improving the selectivity of the MS/MS measurement by modifying the Collision Energy (CE)

| QuPpe extract of | m/z 81/81 | | m/z 79/79 | |
|------------------|--|--|---|---|
| | CE -5 V | CE -60 V | CE -5 V | CE -70 V |
| cucumber |  |  |  |  |
| | <i>containing 1.7 ppm Bromide, approx. 300 ppm Phosphoric acid & 2.0 ppm Phosphonic acid</i> | | | |
| mint leaves |  |  |  |  |
| | <i>containing 1.1 ppm Bromide, approx. 370 ppm Phosphoric acid; Phosphonic acid n. d.</i> | | | |
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| | <i>containing 1.1 ppm Bromide, approx. 350 ppm Phosphoric acid; Phosphonic acid n. d.</i> | | | |



5. Comparison with a traditional GC-based method

Community Reference Laboratories for Residues of Pesticides



Single Residue Methods

Bromine Containing Fumigants Determined as Total Inorganic Bromide

Weigh sample homogenate in 100 mL Erlenmeyer flask

Fresh fruits and vegetables (with high content of water): $5 \text{ g} \pm 0.05 \text{ g}$,
Cereals and dried pulses (dried commodities): $5 \text{ g} \pm 0.05 \text{ g}$



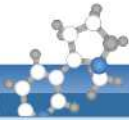
**Add 5 mL Propylene oxide solution (4 % in water, w/v) and
1 mL Sulphuric acid (3 mol/L) solution**



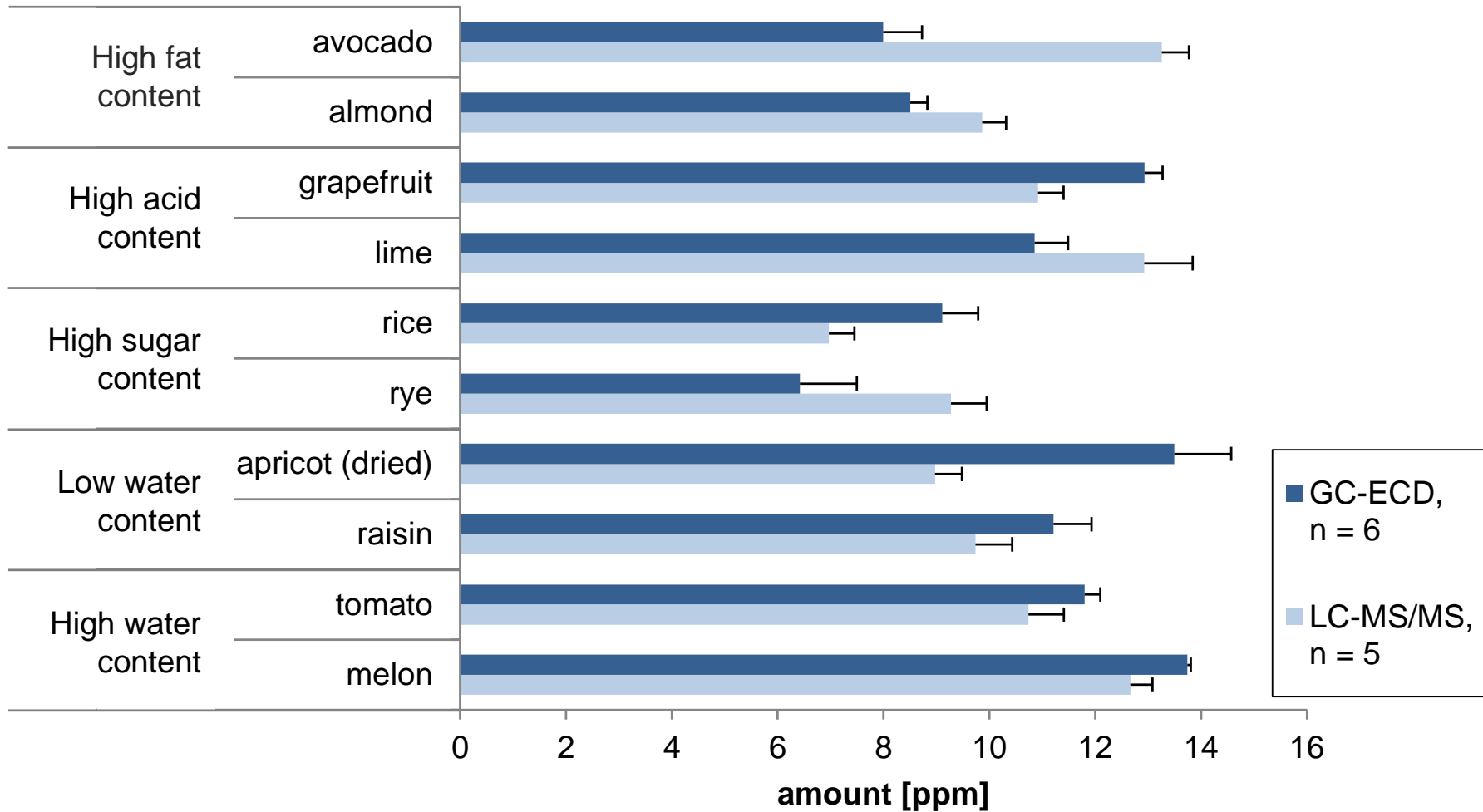
Add 50 mL Ethyl acetate and 4 g Ammonium sulfate



GC-ECD analysis

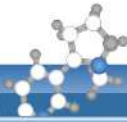


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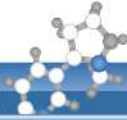


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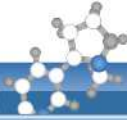
EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

6. Final Conclusion



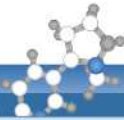
6. Final Conclusion

- **interferences** could be **largely decreased** using optimized collision energies



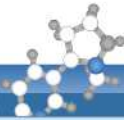
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6. Final Conclusion

- **interferences** could be **largely decreased** using optimized collision energies
- **quick and simple determination of Bromide** compared to the traditional GC-method
- determination can be **included in the QuPPE routine analysis** (M.1.4 PerChloPhos)



6. Final Conclusion

- **interferences** could be **largely decreased** using optimized collision energies
- **quick and simple determination of Bromide** compared to the traditional GC-method
- determination can be **included in the QuPPE routine analysis** (M.1.4 PerChloPhos)

Thank you for your attention!

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