European Commission

EURL-SRM

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

$H_3C—Br$

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Anne Benkenstein
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Diana Kolberg
Ellen Scherbaum
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11th European Pesticide Residue Workshop
24th-27th May 2016, Limassol, Cyprus

1. Why putting the analytical focus on Bromide?

[1] Heywood, B. J., Pesticide residoues in total diet samples: bromine content, Science, 152 (5727): 1406, 1966
[2] Food and Agricultural Organisation, Evaluation of some Pesticide Residues in Food: Methyl Bromide, Report of a Joint Meeting of the FAO Working Party and the WHO Expert Committee on Pesticide Residues, Wld HLth Org. techn. Rep. Ser., 1967

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  - 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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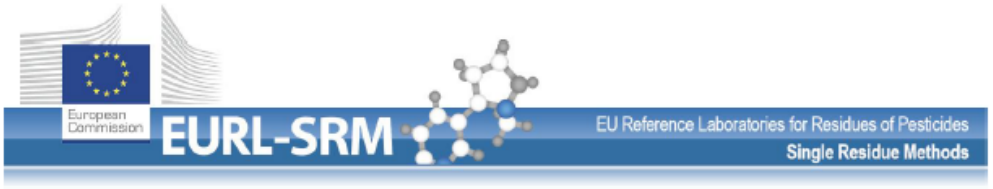
2. Extraction of Bromide: QuPPe method



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 dehydradet dry fruit 13.5 g ± 0.1 g (containing 5 g sample),
Cereals and dried pulses (dried commoditites): 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

S. Walse, W. Hall, M. Bruggeman, B. Beckham, J. Muhareb & T. Jones; Quantifying residues of phosphonic acid for tree nut export to European Union; submitted as reporting requirement for USDA-Foreign Agricultural Service Technical Assistance for Specialty Crops grant; 2015

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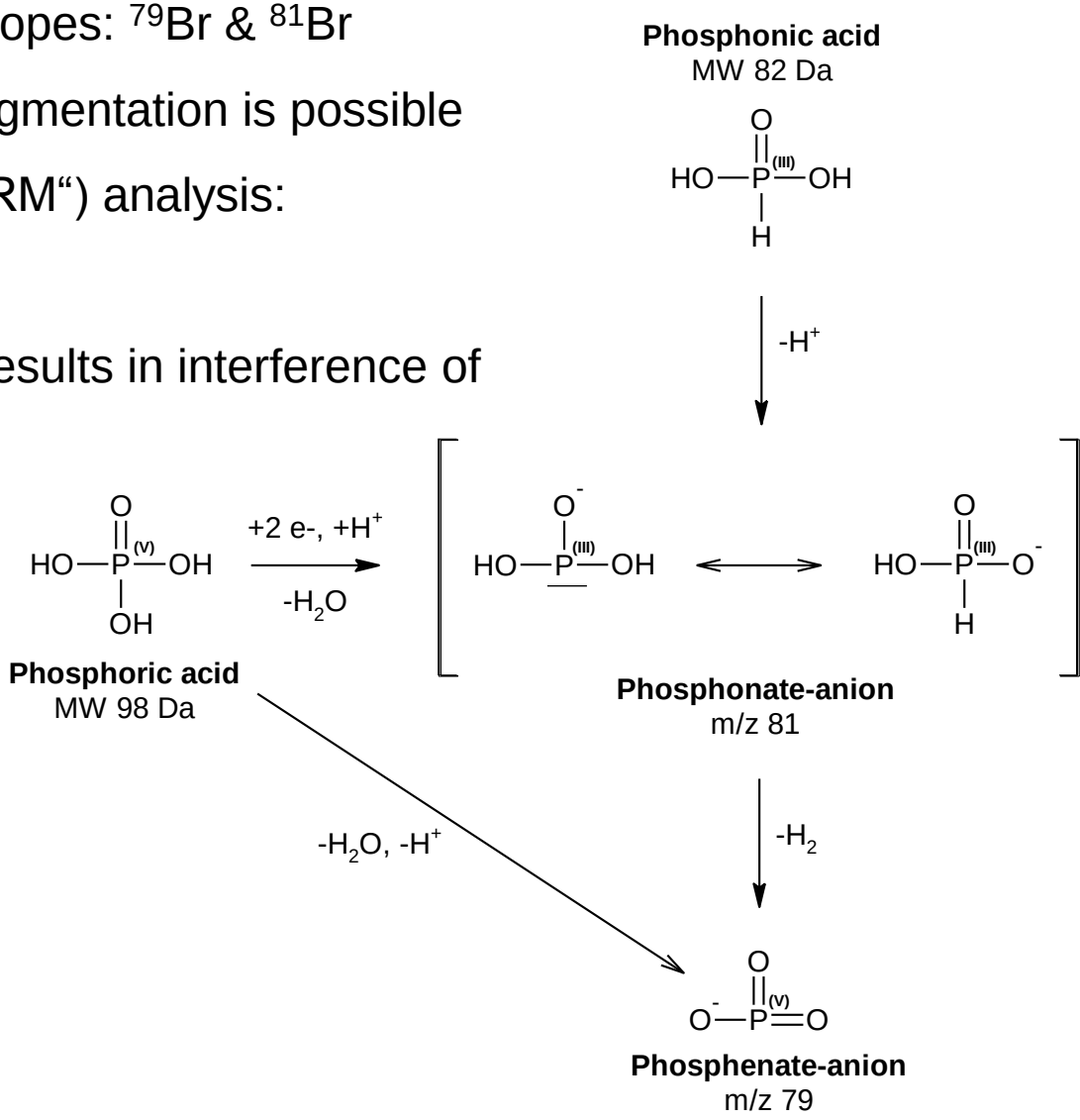
- non-selective MS/MS analysis results in interference of both mass traces:



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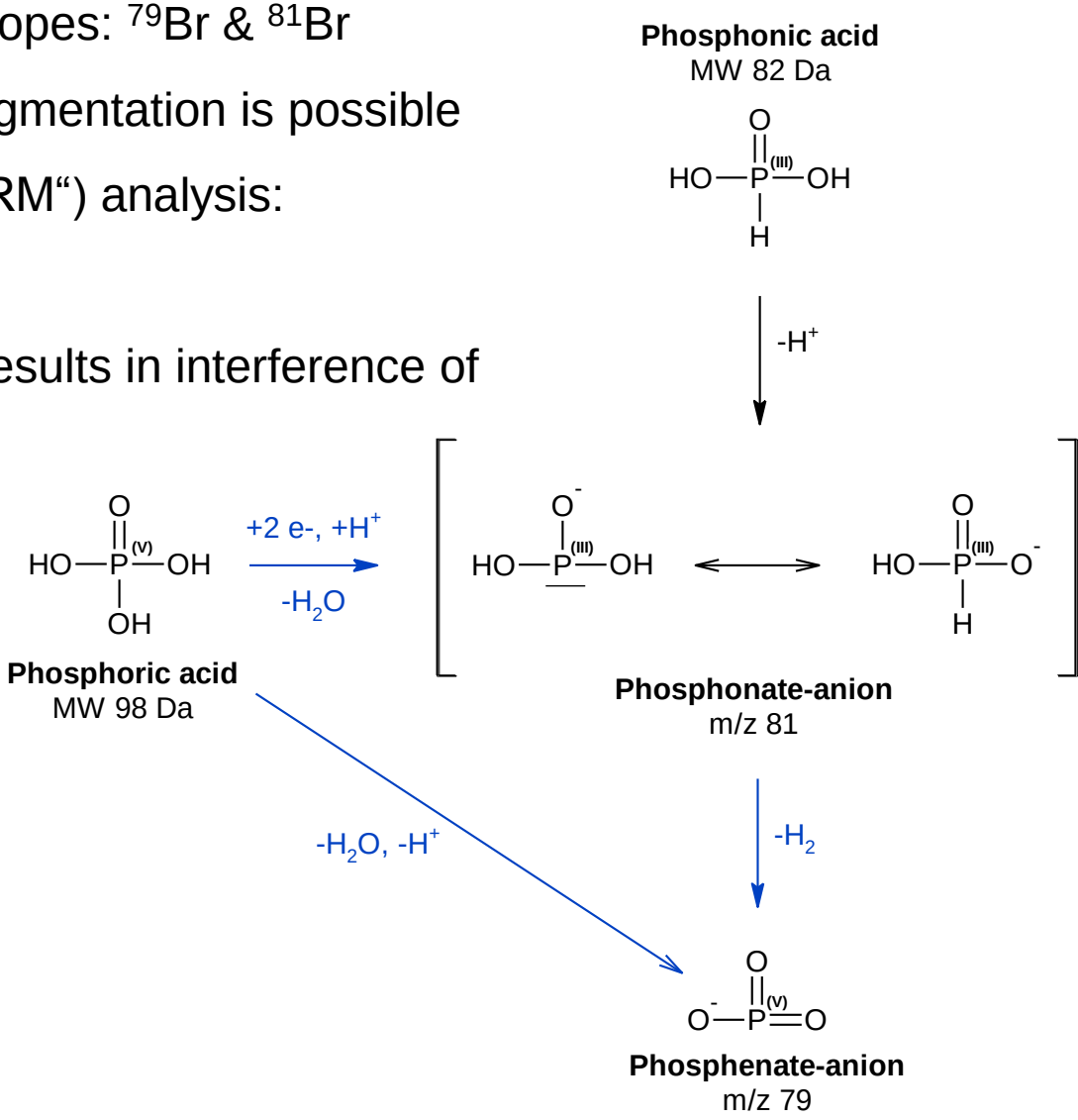

in-source fragmentation

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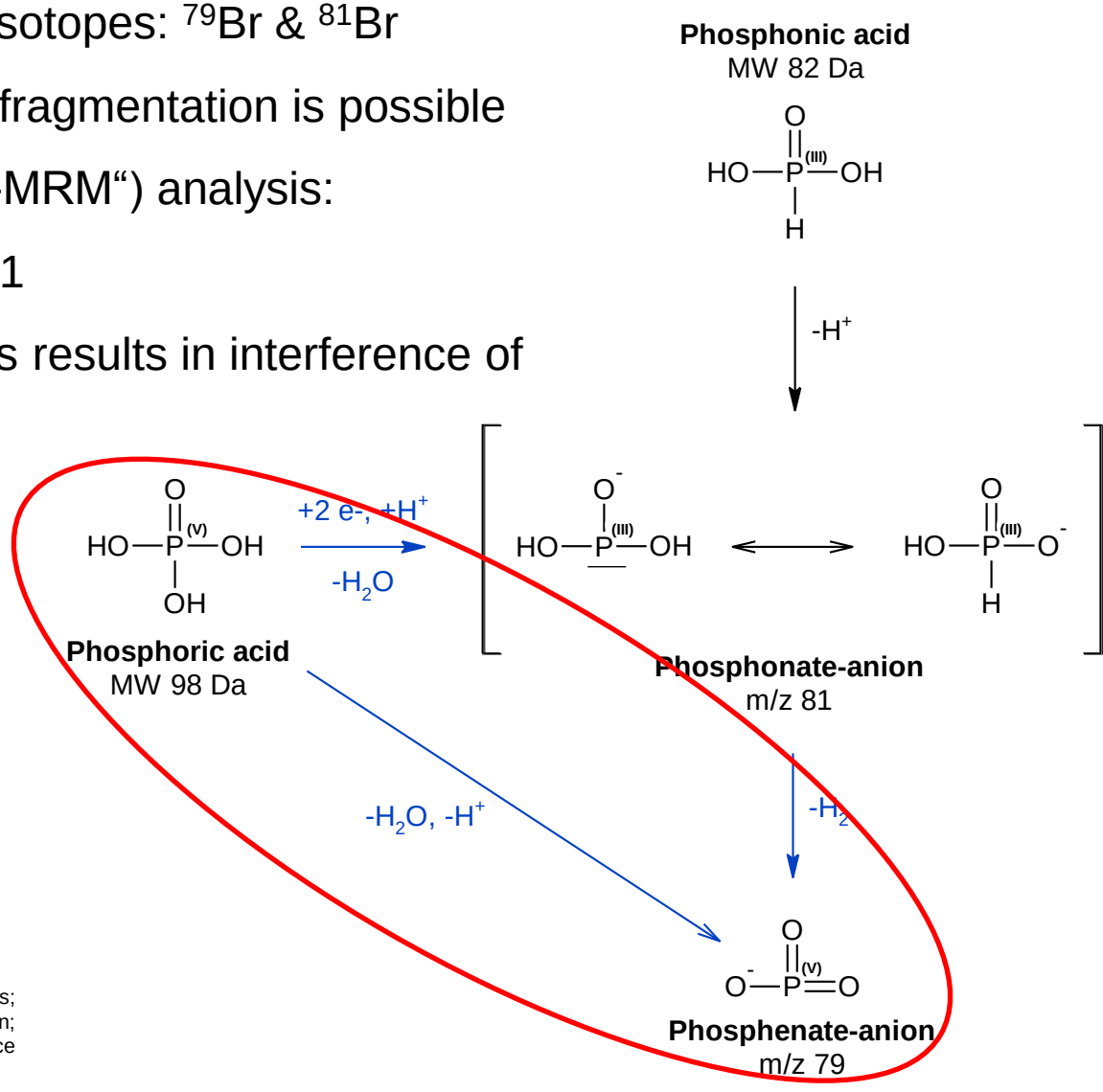

most critical pathway

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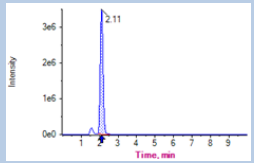
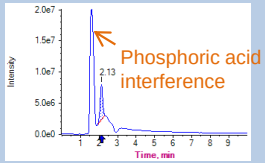
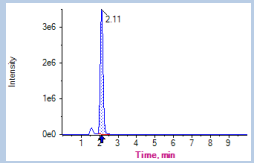
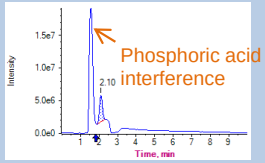
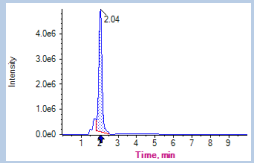
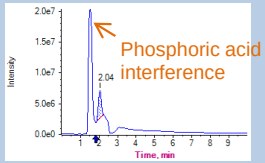
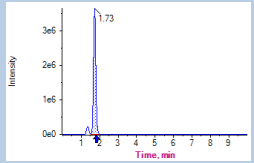
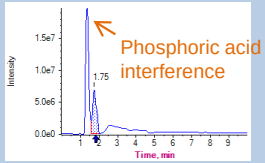
- non-selective MS/MS analysis results in interference of both mass traces
- strategies to decrease these interferences:
  - improve chromatographic separation
  - reduce matrix effects

  } dilution (e. g. 50-fold)

  - more selective measurement (e. g. Differential Mobility Mass Spectrometry)

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

QuPPe extract of	m/z 81/81		m/z 79/79	
	CE -5 V		CE -5 V	
cucumber				
	containing 1.7 ppm Bromide, approx. 300 ppm Phosphoric acid & 2.0 ppm Phosphonic acid			
mint leaves				
	containing 1.1 ppm Bromide, approx. 370 ppm Phosphoric acid; Phosphonic acid n. d.			
fennel				
	containing 2.2 ppm Bromide, approx. 400 ppm Phosphoric acid & 5.4 ppm Phosphonic acid			
sweet corn				
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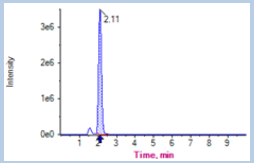
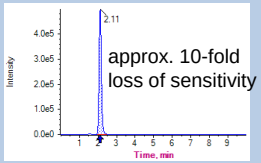
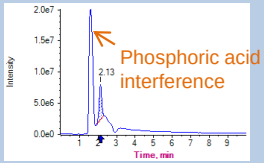
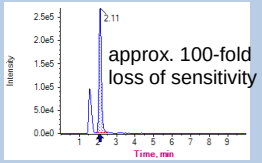
cucumber				
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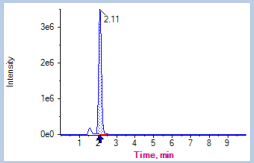
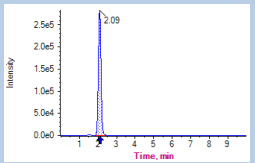
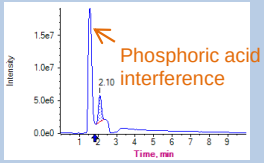
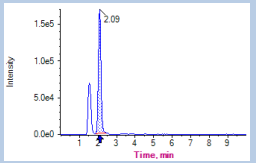
mint leaves				
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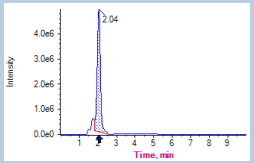
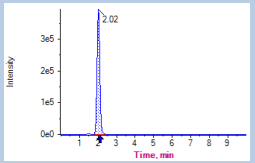
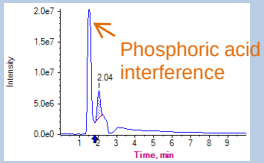
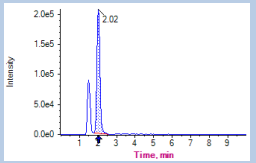
fennel				
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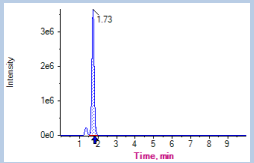
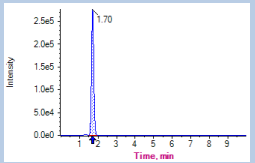
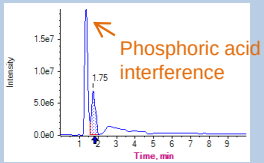
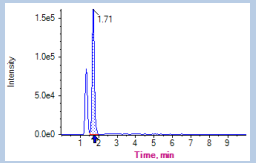
sweet corn				
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5. Comparison with a traditional GC-based method

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 g ± 0.05 g,
Cereals and dried pulses (dried commoditites): 5 g ± 0.05 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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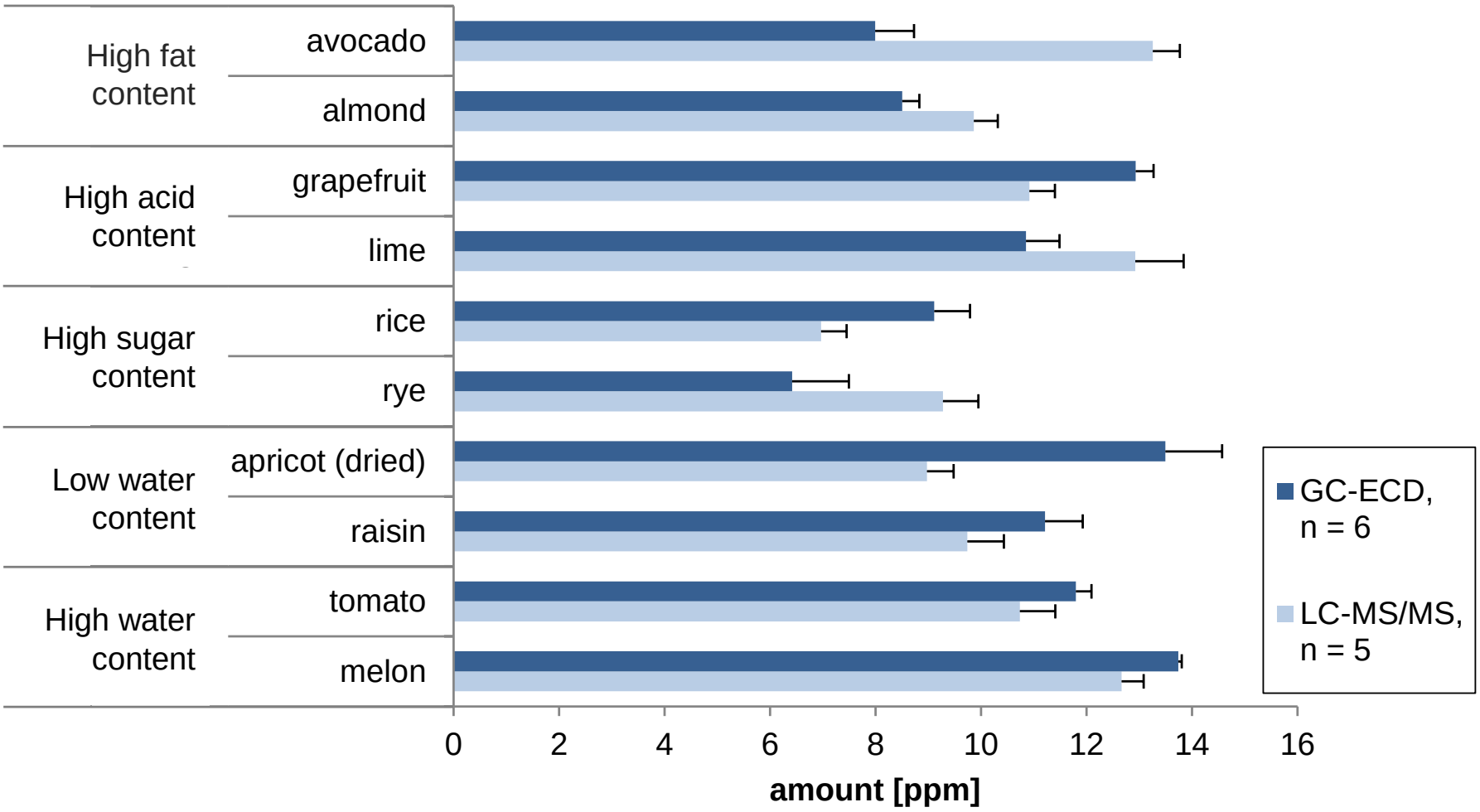

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Thank you for your attention!

Questions to EURL-SRM@CVUAS.BWL.de