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Influence of sample acidification in the presence of humic substances for determination of pesticides by LC-MS/MS

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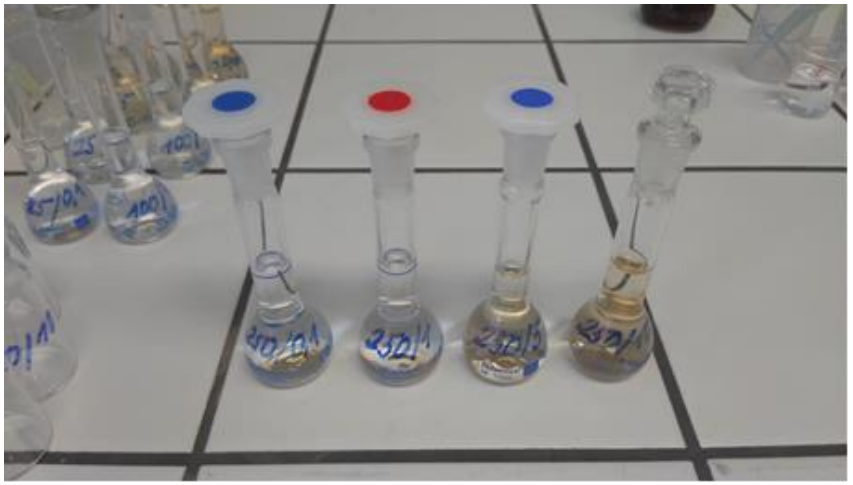
Introduction

- The influence of the organic matrix (HA) in the sample is a major problem in quantifying pesticides with LC-MS.
- The content of substances, other than the one to be detected, leads to a different ionization.
- The acidification of the sample should improve the signal for the measured pesticides.

Design of experiments

conc. pest (ng/L)	conc. HA (mg/L)	conc. FA/AA (%)
25	0.1	0.1
100	0.1	0.1
250	0.1	0.1
25	1	0.1
100	1	0.1
250	1	0.1
25	5	0.1
100	5	0.1
250	5	0.1
25	10	0.1
100	10	0.1
250	10	0.1

HA - Humic acid
FA – Formic acid
AA – Acetic acid



- Pesticides – Organophosphates, Ureas, 1,3,5-triazines, Chloroacetamides, Phenoxycarboxylic acids, Triazoles

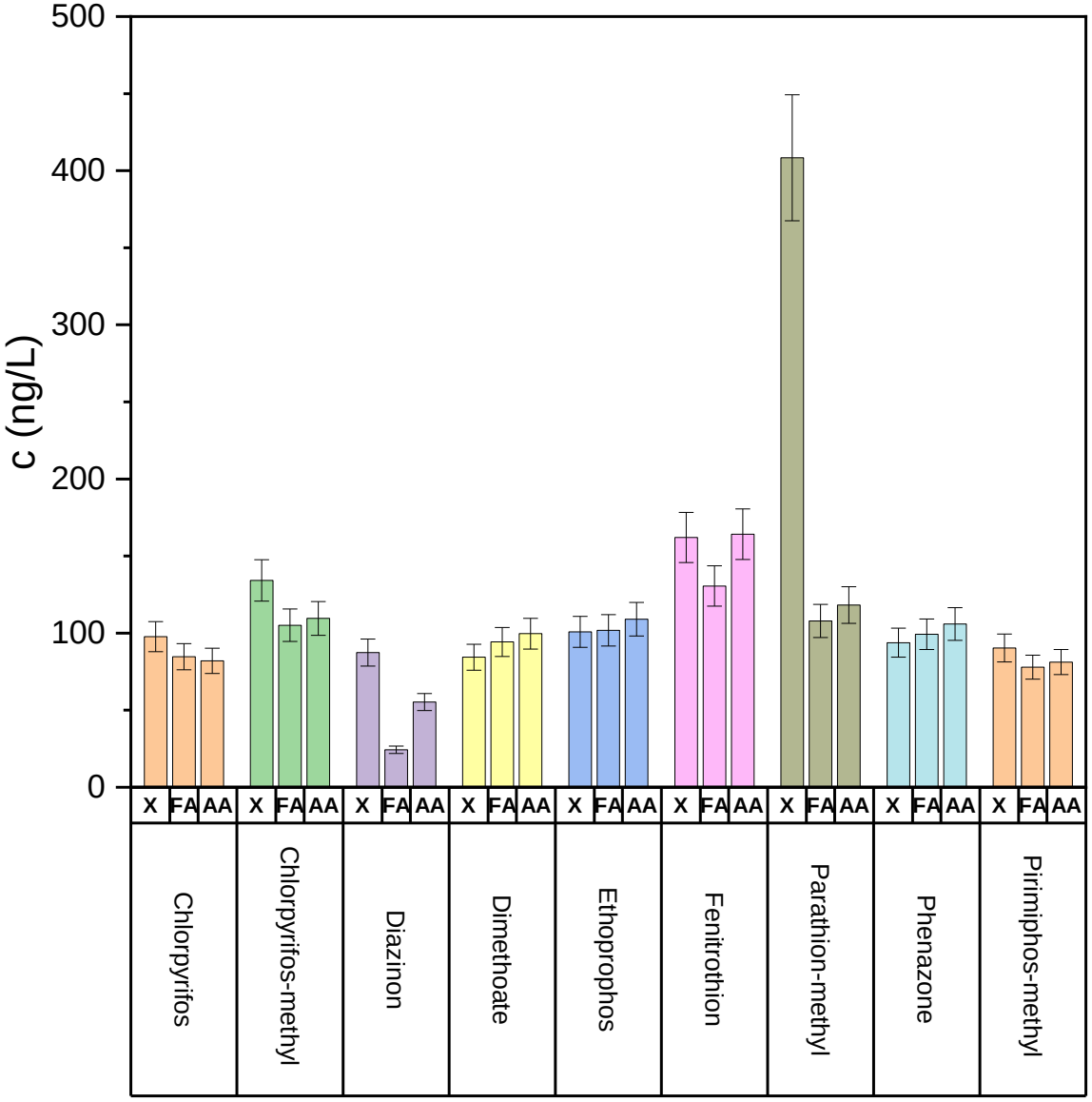
HPLC-MS/MS

- HPLC 1290 Infinity II, Agilent Technologies
- Column - Zorbax SB-Aq 150 x 2.1 mm, 3.5 µm
- Mobil phases:
  - A1 – 0.25 mM NH_4F + 0.01% FA
    B1 – 0.1 mM NH_4F in CH_3OH
    A2 – 0.1 mM CH_3COONH_4
    B2 – CH3CN

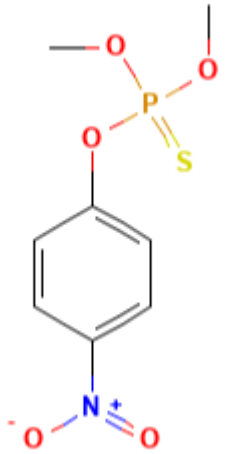
- MS/MS
- 6495A QQQ

Agilent Technologies

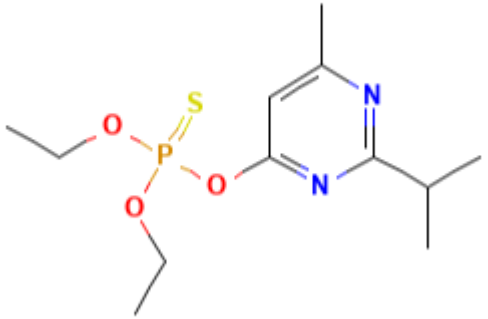
Results



Diazinon – ESI+

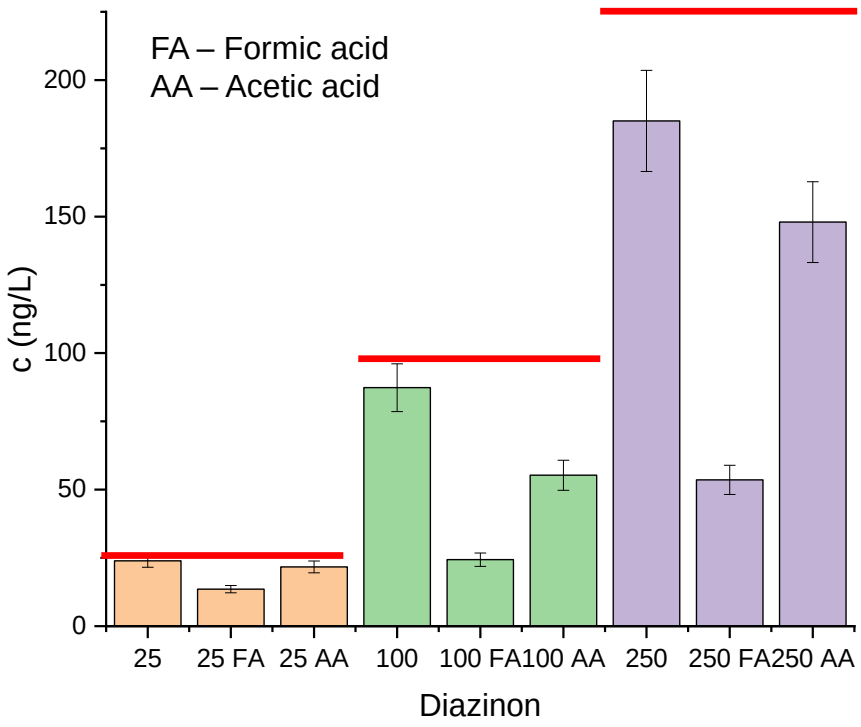


Parathion – methyl – ESI -

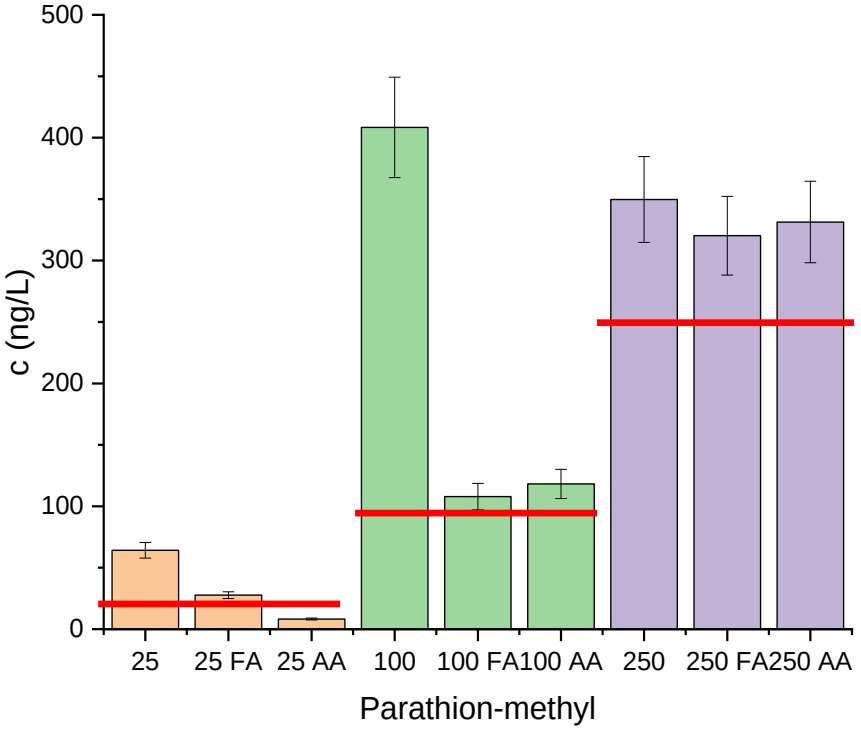


Concentration of all pesticide solutions – 100 ng/L

Results



Signal of samples is lower



Signal of samples is higher

Conclusion

- Ionization in the source (ESI) plays an important role – positive ionization or negative ionization.
- The ESI-MS HA spectra of positive ions exhibit the highest molecular mass distribution and Diazinon exhibit lower signal in this matrice.
- In presence HA negative ions are produces more easily from carboxylic acids therefore Parathion-methyl exhibit higher signal.
- The acidification of the sample does not always contribute to improving the signal of the pesticides.

Thank you for your attention

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Humic acid