Negative Chemical Ionization and Accurate Mass – A Novel Approach to the Analysis of Pesticides by GC/Q-TOF

Moritz Hebestreit; Jörg Riener; Bernhard Rothweiler; Agilent Technologies, Waldbronn, Germany

Agilent Technologies

Introduction

Abstract

Analysis of pesticide residues in feed and food is an ongoing challenge. Especially in "QuEChERS-times", highly selective methods are obligatory to eliminate matrix interferences. GC/MS with high mass accuracy and full scan acquisition opens up the possibility of highly selective determination of a theoretically unlimited number of compounds. Negative chemical ionization is adding additional selectivity and increases the molecular ion response for lower detection limits than electron impact or positive chemical ionization for dedicated pesticides like halogenated pyrethroides.

We present preliminary data for the analysis of γ-BHC, γ-chlordane, α-chlordane and trans-nonachlor in various food matrices.

Experimental

Standards

Calibration solutions of γ-BHC, γ-chlordane, α-chlordane and trans-nonachlor were prepared in ethyl acetate at 20 fg/µL (ppt), 50 fg/µL, 100 fg/µL, 200 fg/µL, 500 fg/µL, 1000 fg/µL, 2000 fg/µL and 5000 fg/µL. Calibration curves were generated from 20 fg/µL to 1000 fg/µL.

Samples

Food samples were prepared by Eurofins Food Testing UK Limited using a QuEChERS-like method to yield 1 g/mL matrix in acetonitrile. The following matrices were provided: a) Parsley b) Mint c) Tomato d) Grapes e) Brussel Sprouts f) Kale g) Swede h) Orange i) Cucumber j) Sage
Aliquots of each 90 µL of the extracts were spiked with 10 µL of calibration solutions to yield concentrations of 50 fg/µL, 100 fg/µL, 200 fg/µL and 500 fg/µL.

GC/MS System

The GC and MS configurations and conditions were as shown in Table 1. To ensure mass accuracy, recalibration of the TOF was performed automatically within the sequence. No further mass correction was applied.

Data Analysis

Agilent MassHunter Qualitative and Quantitative Analysis were used. γ-Chlordane, α-chlordane and trans-nonachlor showed molecular ions. For γ-BHC, the most abundant ion is the chlorine fragment. Quantifier ions are listed in table 2. At least two further ions served as qualifiers (not shown). Quantitative Analysis was performed with extraction windows of ± 50 ppm.

Experimental

Gas chromatograph	Agilent 7890A
Inlet	Air cooled multimode inlet (MMI), equipped with an ultrainert splitless liner with glass wool
Columns	Two 15.0 m x 0.25 mm ID x 0.25 µm HP-5MS Ultra Inert were connected to the MS via a pressure controlled tee.
Carrier gas	Helium
Carrier gas mode	Constant flow
Column flows	1.25 mL/min (col. 1) and 1.45 mL/min (col. 2) (retention time locked to chlorpyriphos methyl at 18.111 min)
Autosampler	Agilent 7693A
Injection mode	Cold splitless, purge flow 50.0 mL/min at 2.0 min
MMI Temperature program	70 °C (0.02 min), 600 °C/min to 300 °C (1 min), 100 °C/min to 280 °C Backflush: 280 °C
Injection volume	1.0 µL
Oven program	60 °C (1 min), 40 °C/min to 120 °C, 5 °C/min to 265 °C
Backflush conditions	Post run, 2.4 min, oven 280 °C, 40 psi at pressure controlled tee, inlet 1 psi
Transfer line	280 °C
Mass spectrometer	Agilent 7200 Q-TOF
Ionization	Negative chemical ionization (NCI)
Reactant gas	Methane at 40% (2 mL/min)
Source temperature	150 °C
Quadrupole temperature	150 °C
Quadrupole mode	Total ion transmission, cutoff at m/z 50
Collision gas	Nitrogen @ 1.5 mL/min
Scan range	m/z 65 to 600
Acquisition rate	5 Hz
Acquisition mode	2 GHz dual gain

Table 1. GC/MS Conditions

Compound	Chemical Formulae of Ions used for Quantification	Exact Mass (Da)
γ-BHC	$[^{35}Cl_2]^{-\bullet} = [M\text{-}C_6H_6Cl_4]^{-\bullet}$	69.93825
γ-Chlordane	$[C_{10}H_6{}^{35}Cl_6{}^{37}Cl_2]^{-\bullet} = [M+4]^{-\bullet}$	409.79242
α-Chlordane	$[C_{10}H_6{}^{35}Cl_6{}^{37}Cl_2]^{-\bullet} = [M+4]^{-\bullet}$	409.79242
trans-Nonachlor	$[C_{10}H_5{}^{35}Cl_6{}^{37}Cl_3]^{-\bullet} = [M+2]^{-\bullet}$	441.75640

Table 2. Chemical formulae and exact masses of quantifier ions; chlorine isotopes are indicated

Results and Discussion

Calibration Solutions

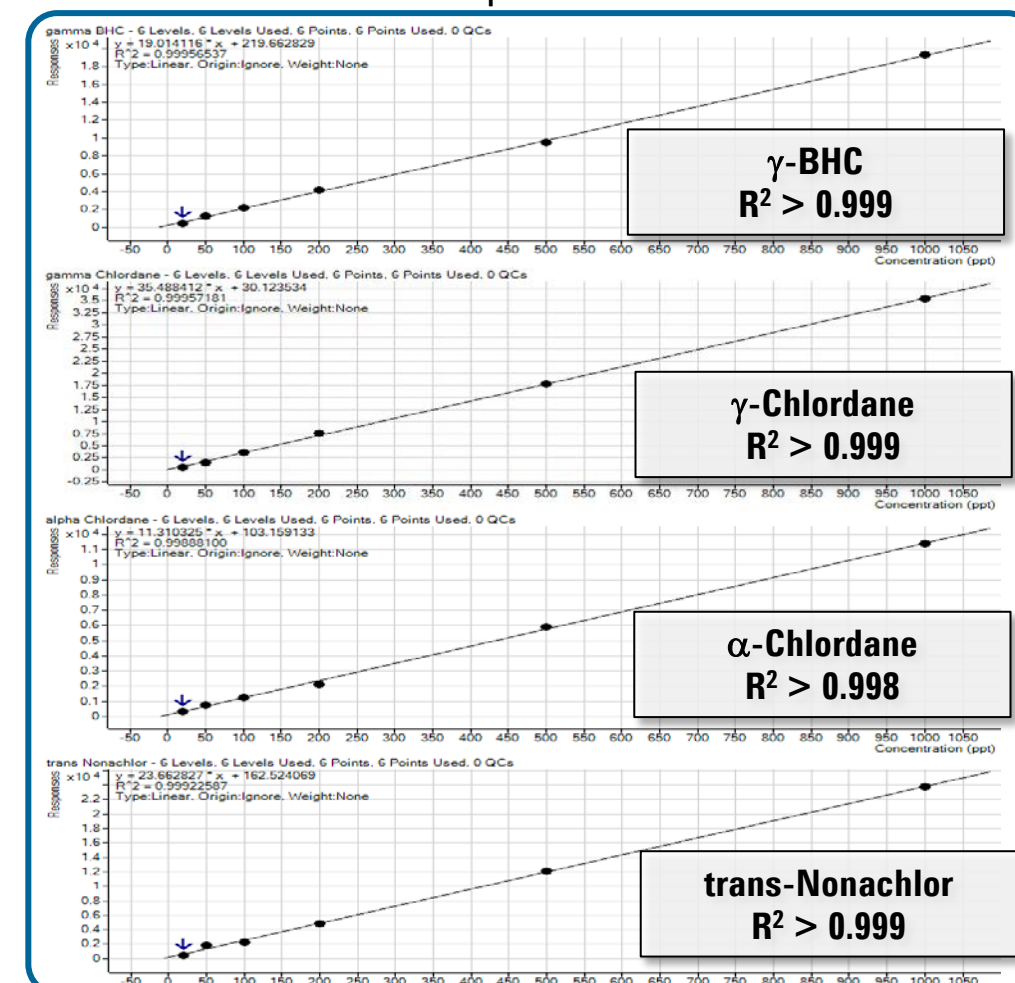All compounds were detectable at the lowest calibration level and showed linear responses.

γ-BHC R² > 0.999
γ-Chlordane R² > 0.999
α-Chlordane R² > 0.998
trans-Nonachlor R² > 0.999

Figure 1. Calibration curves of target compounds

γ-BHC, 20 ppt
γ-Chlordane, 20 ppt

Figure 2. Quantifier response of γ-BHC and γ-chlordane at 20 fg/µL (i.e. lowest calibration level)
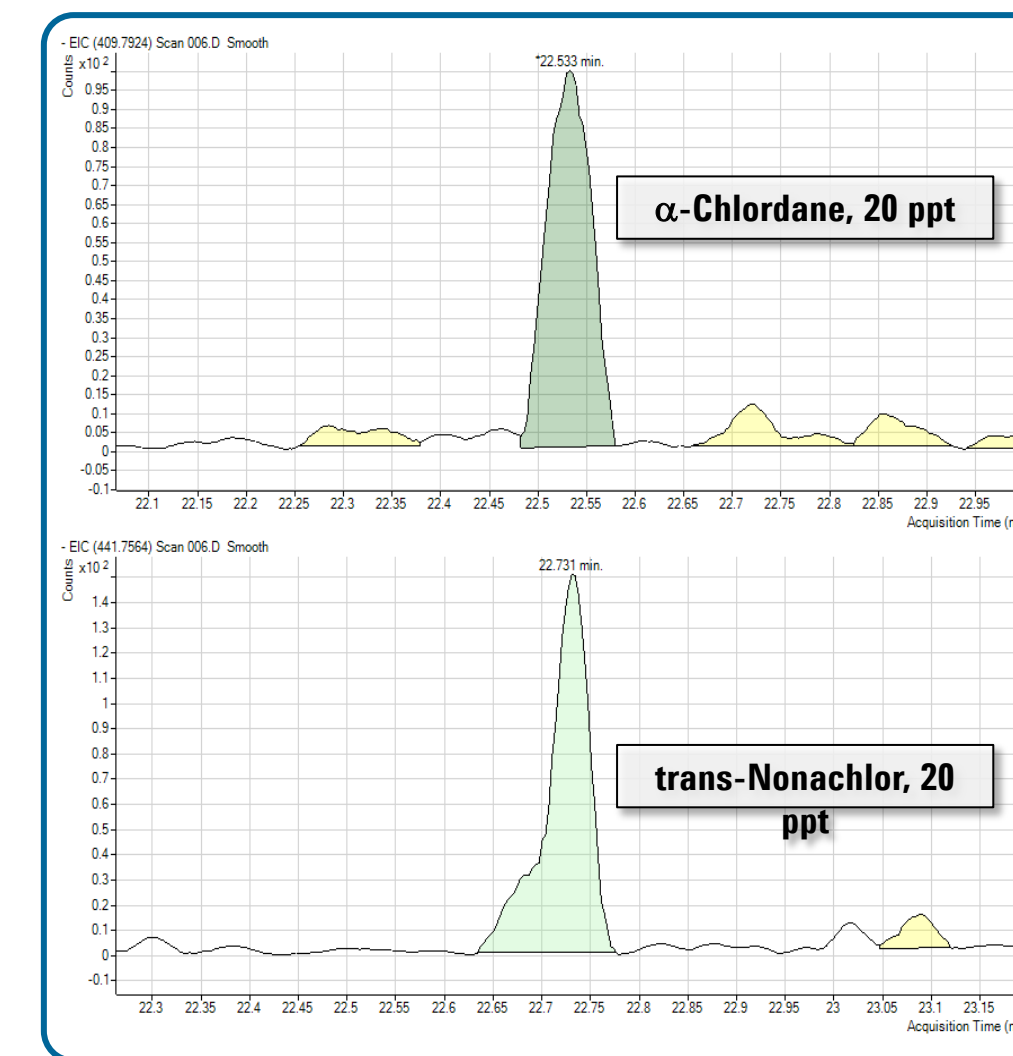

α-Chlordane, 20 ppt
trans-Nonachlor, 20 ppt

Figure 3. Quantifier response of α-chlordane and trans-nonachlor at 20 fg/µL

Samples

The quantifier ions with extraction windows of ± 50 ppm were sufficiently selective in all matrices. All targets could be detected at the lowest spiked level (50 ppt) and higher, except of γ-chlordane and α-chlordane in parsley as well as γ-BHC in mint. γ-Chlordane and α-chlordane in parsley as well as γ-BHC in mint were detectable at 100 ppt or higher. S/N ratios (peak to peak) at the lowest detectable levels are shown in table 3.

Matrix	γ-BHC	γ-Chlordane	α-Chlordane	trans-Nonachlor
Parsley	6*	7 (100 ppt)	48 (100 ppt)	4
Mint	63 (100 ppt)	61	69	7
Tomato	64	133	46	73
Grapes	6	130	49	85
Brussel Sprouts	37*	133	27	92
Kale	82*	124	45	76
Swede	62*	188	63	149
Orange	23	47	70	28
Cucumber	38	207*	60	73
Sage	4	72	46	7

* Very low residues already detectable in unspiked sample

Table 3. S/N ratios (peak to peak) in matrix at 50 ppt if not indicated differently

Results and Discussion

Mass Accuracy

The following figures illustrate obtained mass accuracy of the quantifier ions at different concentrations in the calibration solutions and in the matrices.
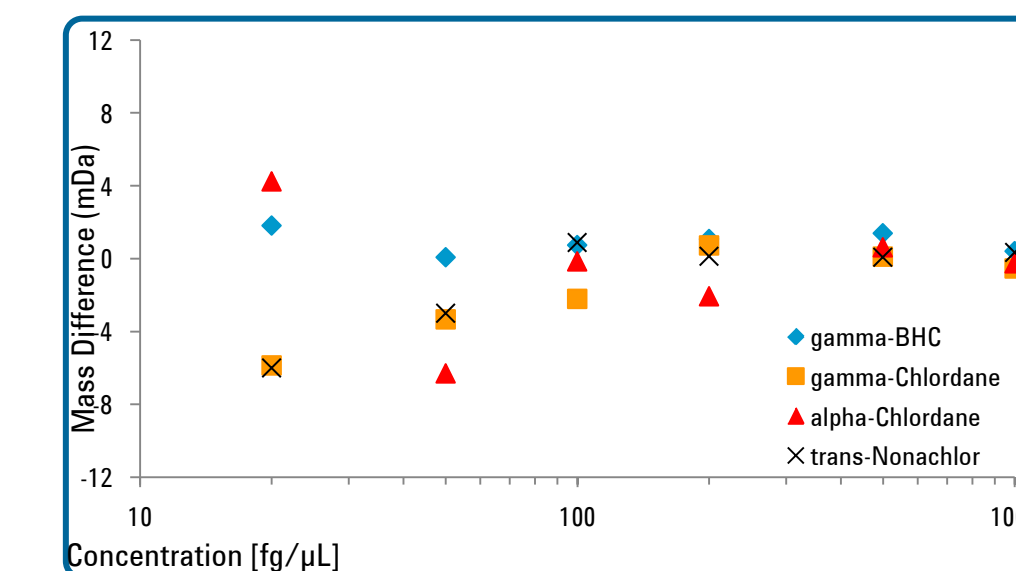No post-acquisitional recalibration was applied.

Legend: gamma-BHC, gamma-Chlordane, alpha-Chlordane, trans-Nonachlor

Figure 4. Mass difference of measured mass minus exact mass vs. concentration in calibration solutions

γ-BHC
γ-Chlordane

Legend: 50 ppt, 100 ppt, 200 ppt, 500 ppt

1 = Cucumber, 2 = Swede, 3 = Kale, 4 = Tomato, 5 = Grapes
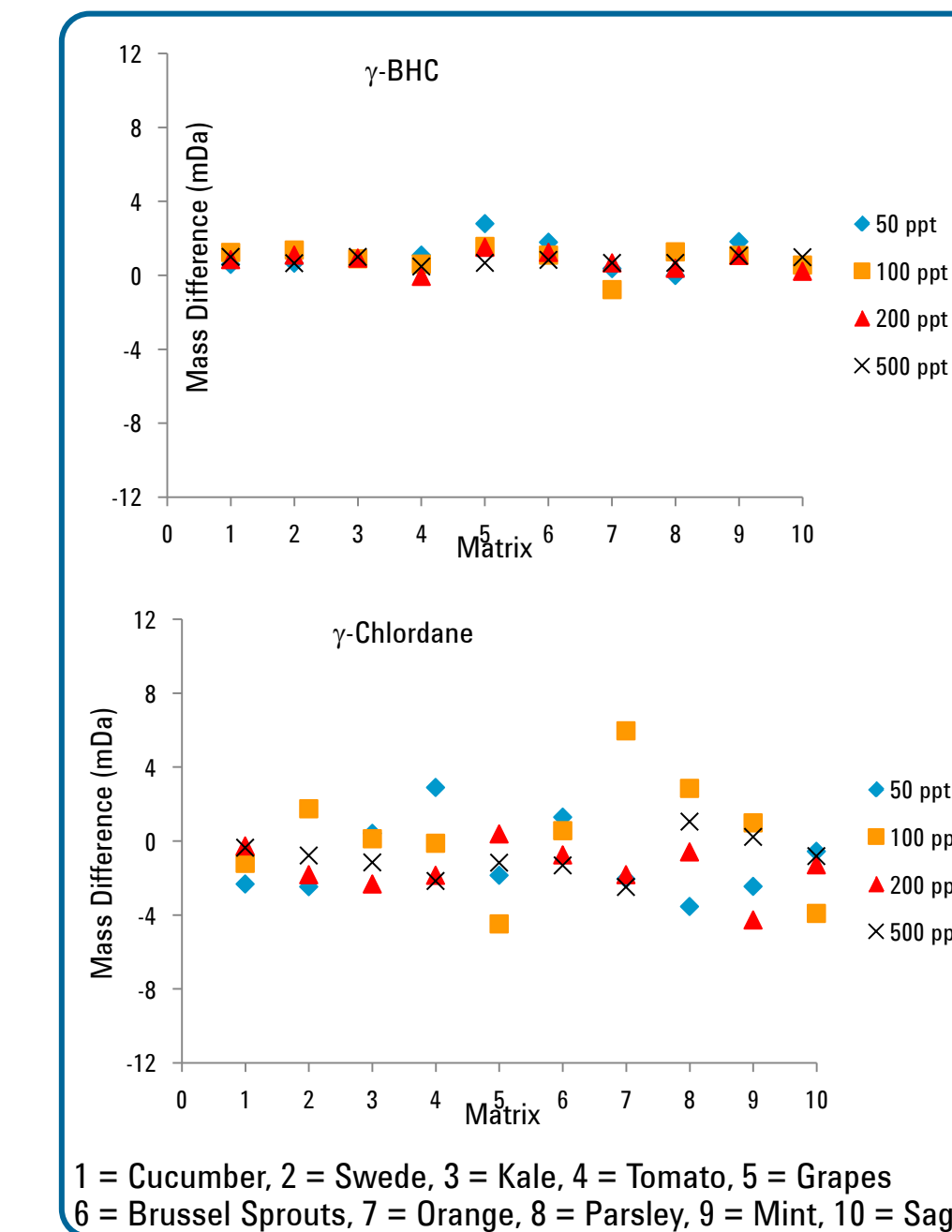6 = Brussel Sprouts, 7 = Orange, 8 = Parsley, 9 = Mint, 10 = Sage

Figure 5a. Mass difference of measured mass minus exact mass of γ-BHC (top) and γ-chlordane (bottom) in the ten different matrices

α-Chlordane
trans-Nonachlor

Legend: 50 ppt, 100 ppt, 200 ppt, 500 ppt

1 = Cucumber, 2 = Swede, 3 = Kale, 4 = Tomato, 5 = Grapes
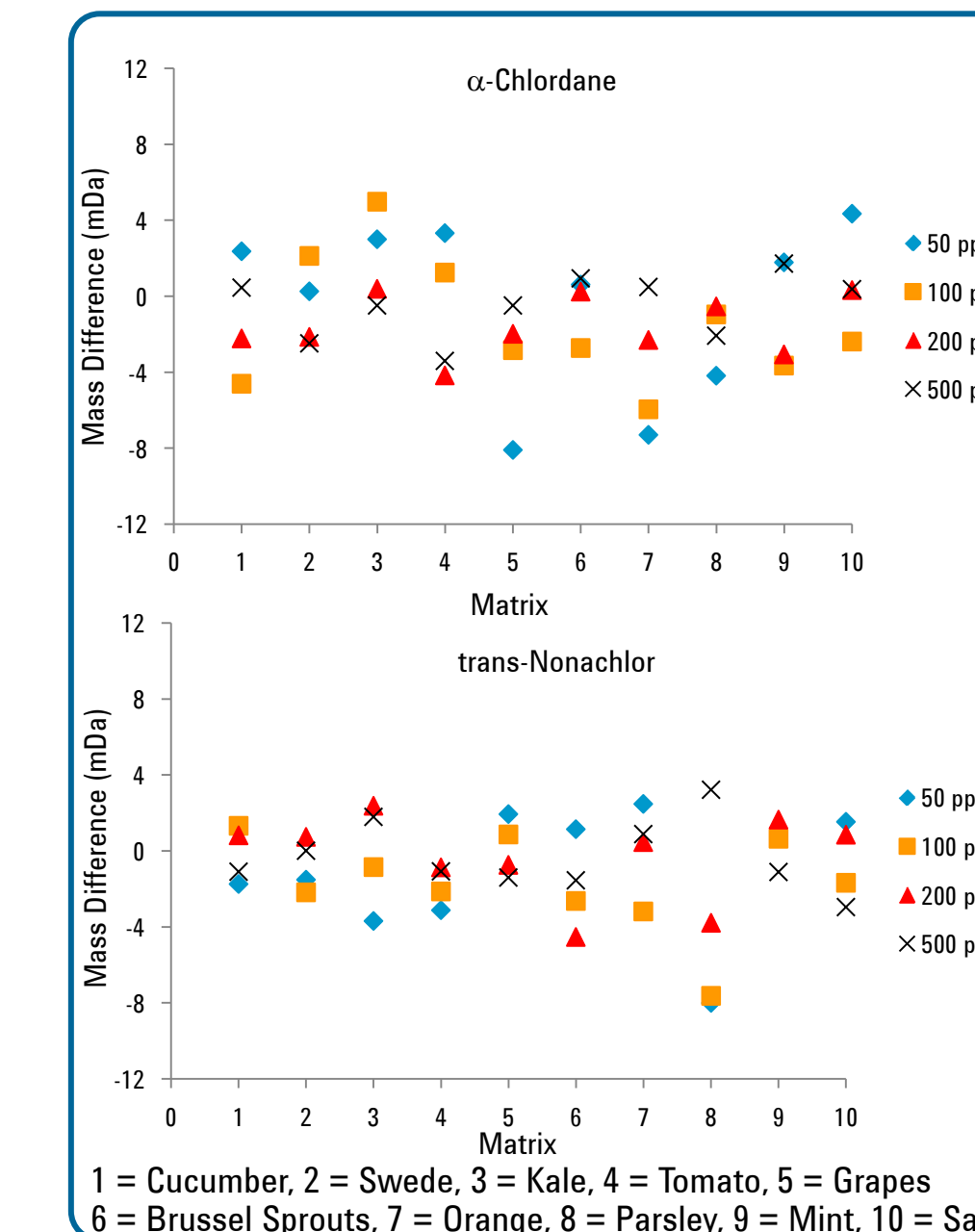6 = Brussel Sprouts, 7 = Orange, 8 = Parsley, 9 = Mint, 10 = Sage

Figure 5b. Mass difference of measured mass minus exact mass of α-chlordane (top) and trans-nonachlor (bottom) in the ten different matrices

Fig. 4 shows the influence of the concentration on mass accuracy. At low ion counts, higher errors are most probably due to the ion statistics. At higher concentrations, mass accuracy is stable for all ions (-0.03 mDa ± 0.46 mDa (n = 4) at 1 ppb for the four different quantifier ions).
Figures 5a and 5b illustrate mass accuracy depending on the matrix. Mass differences are within few mDa in all matrices at all spiked levels. As expected, mass accuracy in matrix is better at higher levels (-0.25 mDa ± 1.44 mDa (n = 40) at 500 ppt for all quantifiers in all matrices).

Conclusions

The results of this preliminary study let us confirm, that negative chemical ionization combined with high mass accuracy and sufficient resolving power can provide excellent selectivity and sensitivity for organochlorine pesticides regarding GC/MS analyses.

Acknowledgements