

EVALUATION OF QUECHERS METHOD WITH ZIRCONIUM DIOXIDE-BASED SORBENT AS DSPE CLEAN-UP FOR PESTICIDES DETERMINATION IN AVOCADO AND ALMOND

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INTRODUCTION

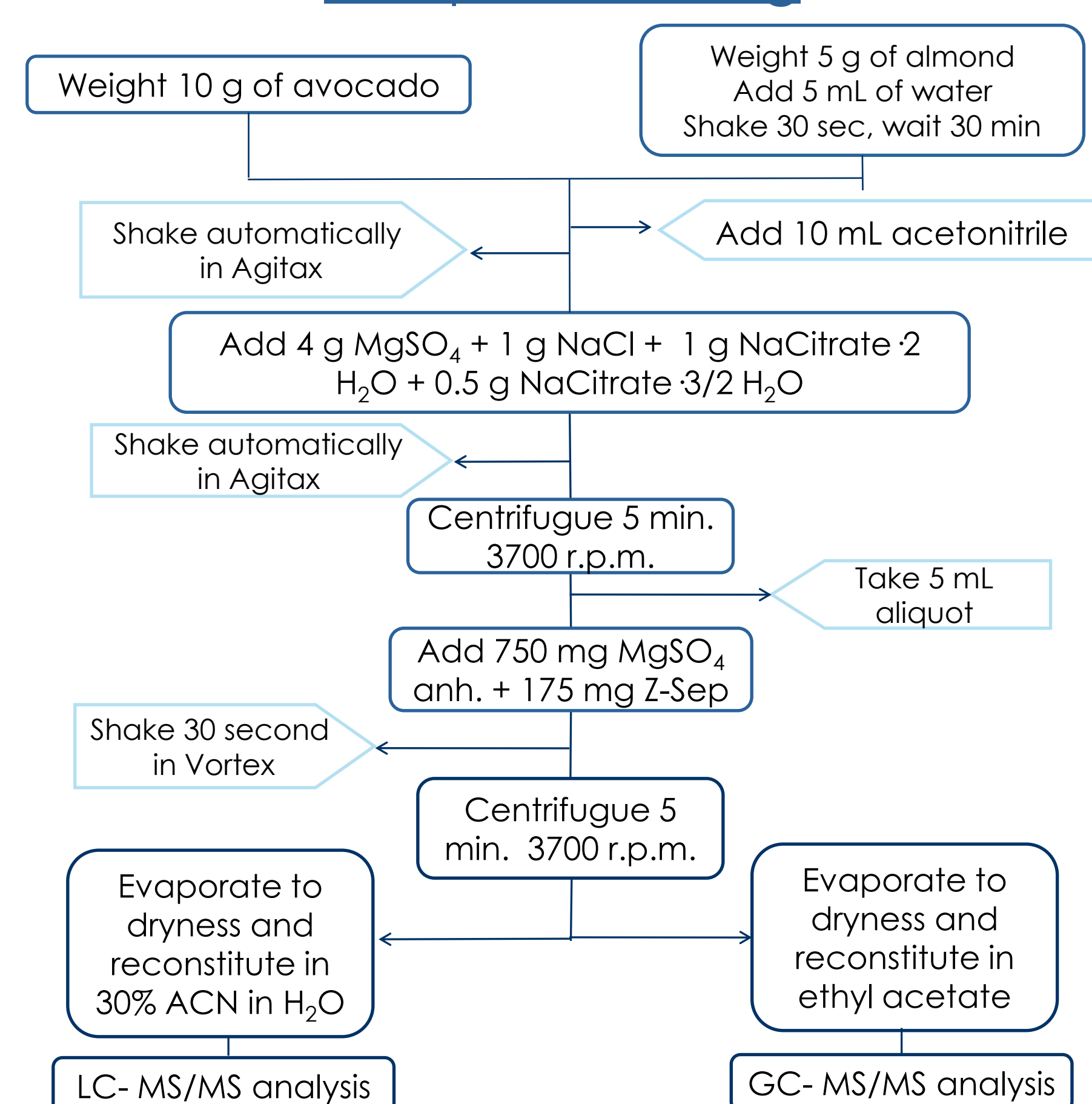
Because of high fat content avocado and almond are considered as “difficult” matrices. The main challenge is in obtaining an extract which contains the target analytes but possibly low amount of fat. The most common methods for fat removal from extract are low temperature precipitation (freezing-out), gel permeation chromatography (GPC) and adsorption (dispersive solid-phase extraction, solid-phase extraction). The aim of the work was to validate Z-Sep® sorbent as dSPE clean-up material for QuEChERS extraction of pesticide from avocado and almond. Z-Sep® is commercial name of mixture of two sorbents, C18 and silica coated with zirconium dioxide, proportion of ZrO₂/C18 is 2/5. Samples were analysed by gas chromatography and liquid chromatography coupled with triple quadrupole mass spectrometers working in multi-reaction monitoring mode. For experiments 241 pesticides were selected, 123 were analysed by LC-MS/MS and 183 by GC-MS/MS. Validation was carried out according to DG Sanco guideline. In the validation recoveries, limit of quantitation, linearity, matrix effects, as well as the inter- and intraday precision were studied. For recovery studies samples were spiked with the standard solution of pesticides in methanol. Selected spiking levels were 10 µg/kg and 50 µg/kg. Linearity of LC and GC systems were evaluated by assessing the signal responses of the target analytes from matrix-matched calibration solutions prepared by spiking blank extracts at seven concentration levels corresponding to 1–500 µg/kg in the sample. Matrix effects were calculated from slopes of calibration curves in solvent and in matrix. In case of each pesticide the lowest fully validated level was considered as limit of quantitation. Among LC analysed pesticides, 118 (96% of total number) were successfully validated in avocado and 104 (84% of total number) in almond. In case of GC analysed pesticides 166 (91% of total number) were successfully validated in avocado and 129 (70% of total number) in almond. European Commission DG-SANCO (2012) Method validation and quality control procedures for pesticide residues analysis in food and feed. No. SANCO/12495/2011.

EXPERIMENTAL

Matrices



Sample handling

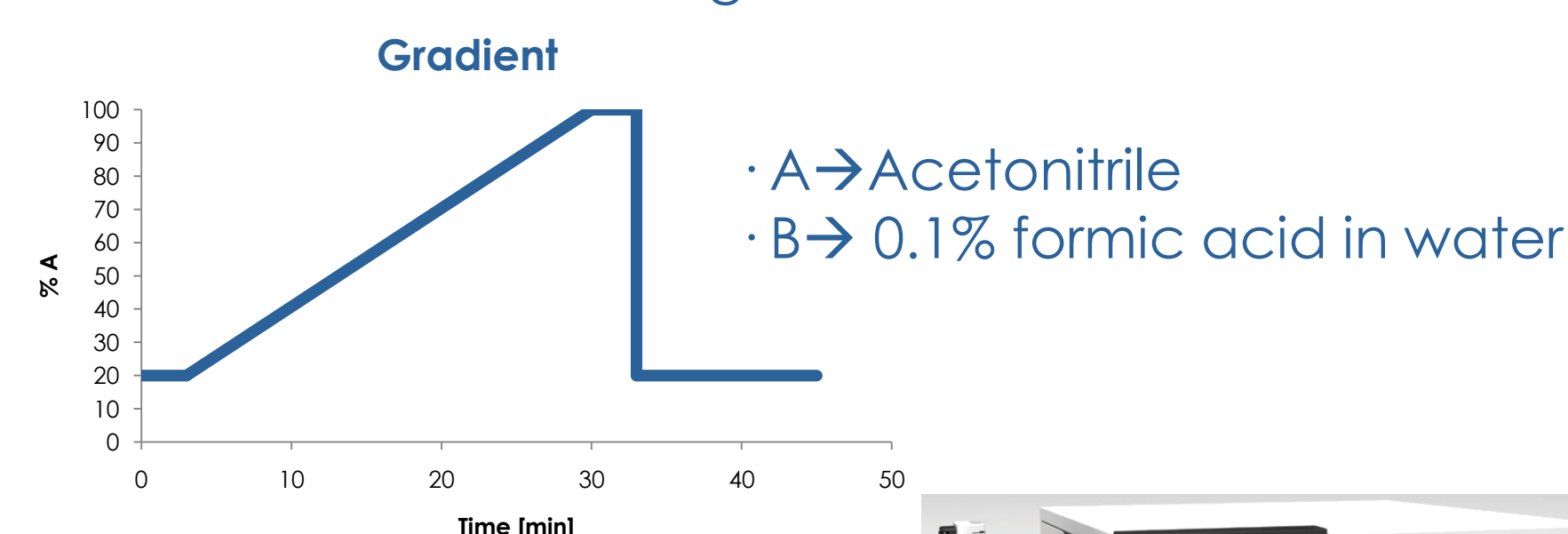


LC-MS/MS

System:
6490 QQQ MS/MS Agilent Technologies

HPLC parameters:

- Injection volume: 10 µL
- Flow rate: 0.6 mL/min
- Column: SB-C8; 4.6 × 150 mm, i.d. 5 µm (Agilent)
- Mobile Phases and gradient :



MS parameters:

- Ion source: ESI
- Polarity: positive
- dynamic MRM software feature

GC-MS/MS

System:
7000 QQQ MS/MS Agilent Technologies

GC parameters:

- Injection volume : 2 µL
- Injection mode: splitless
- PTV Temperature program: 80 °C for 0.1 min then 600 °C/ min to 300 °C.
- Column: HP-5MS UI 15 m × 0.25 mm i.d. × 0.25 µm (Agilent)
- Oven program :

	°C/ min	FINAL (°C)	HOLD (min)
Initial		70	1
Ramp1	50	150	0
Ramp2	6	200	0
Ramp 3	16	280	4.07

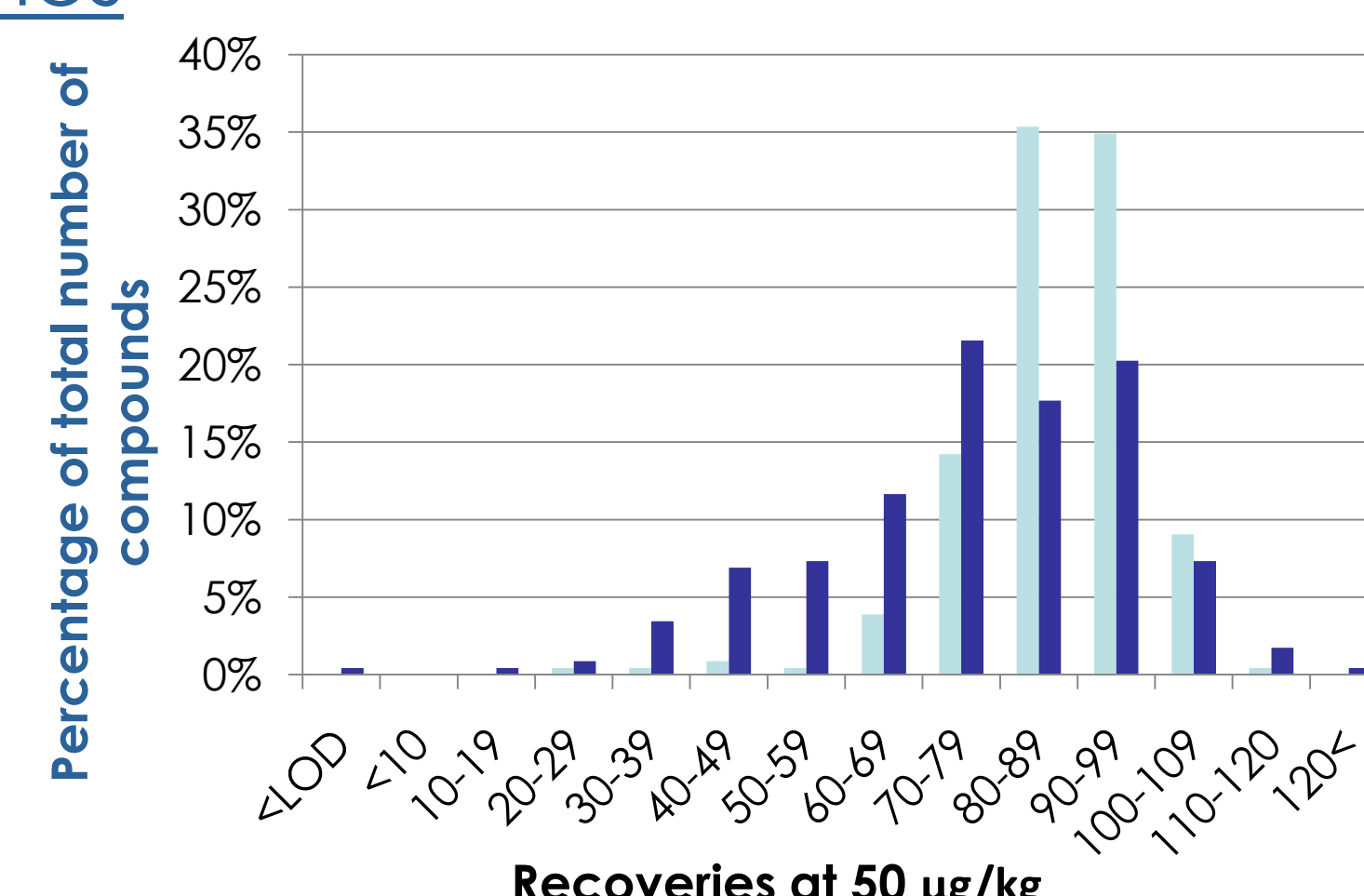
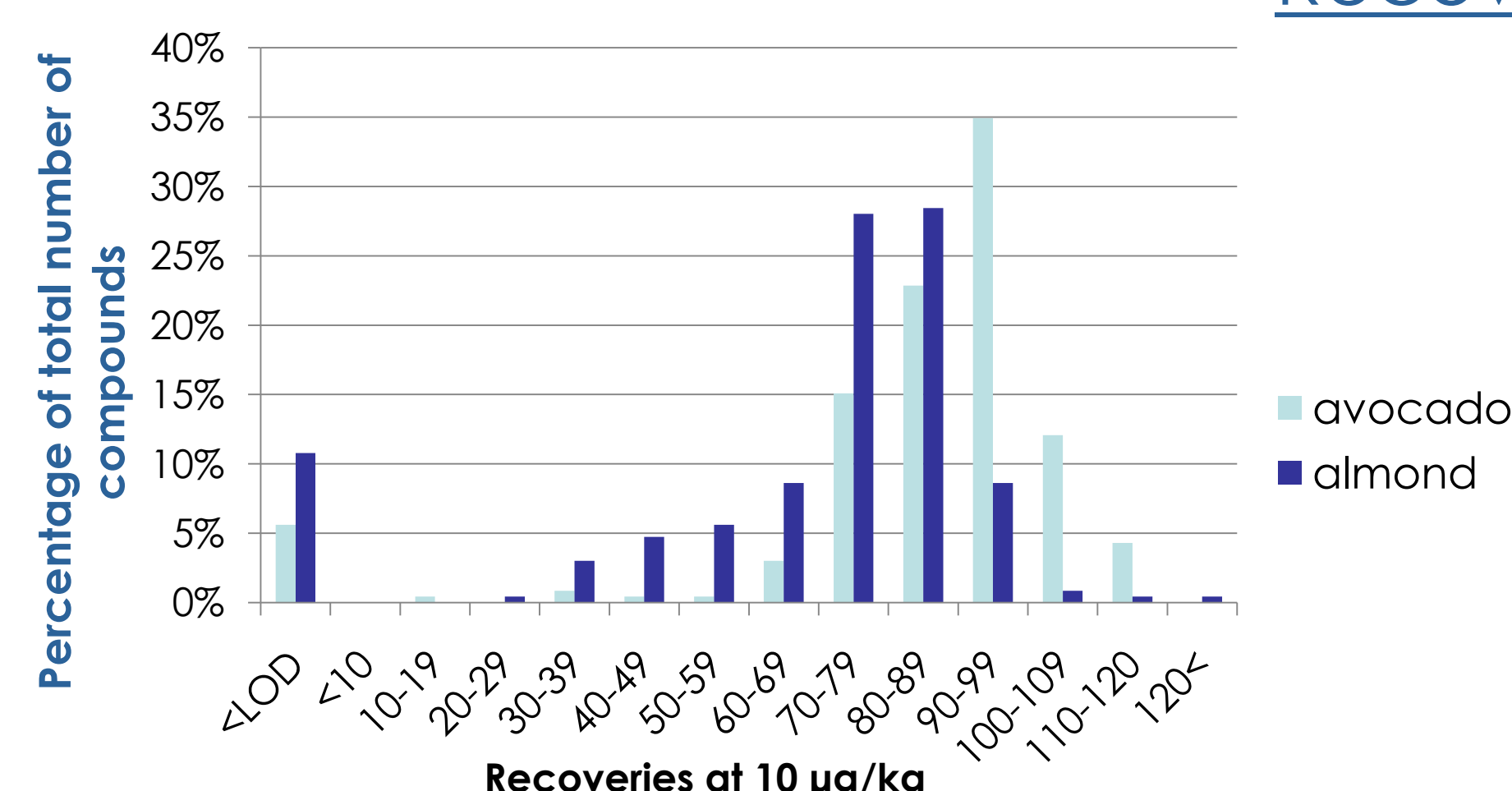
MS parameters:

- Ionisation mode: EI
- Retention Time Locking (RTL)
- Backflush at 280°C
- 39 segment SRM method
- 20 min run time

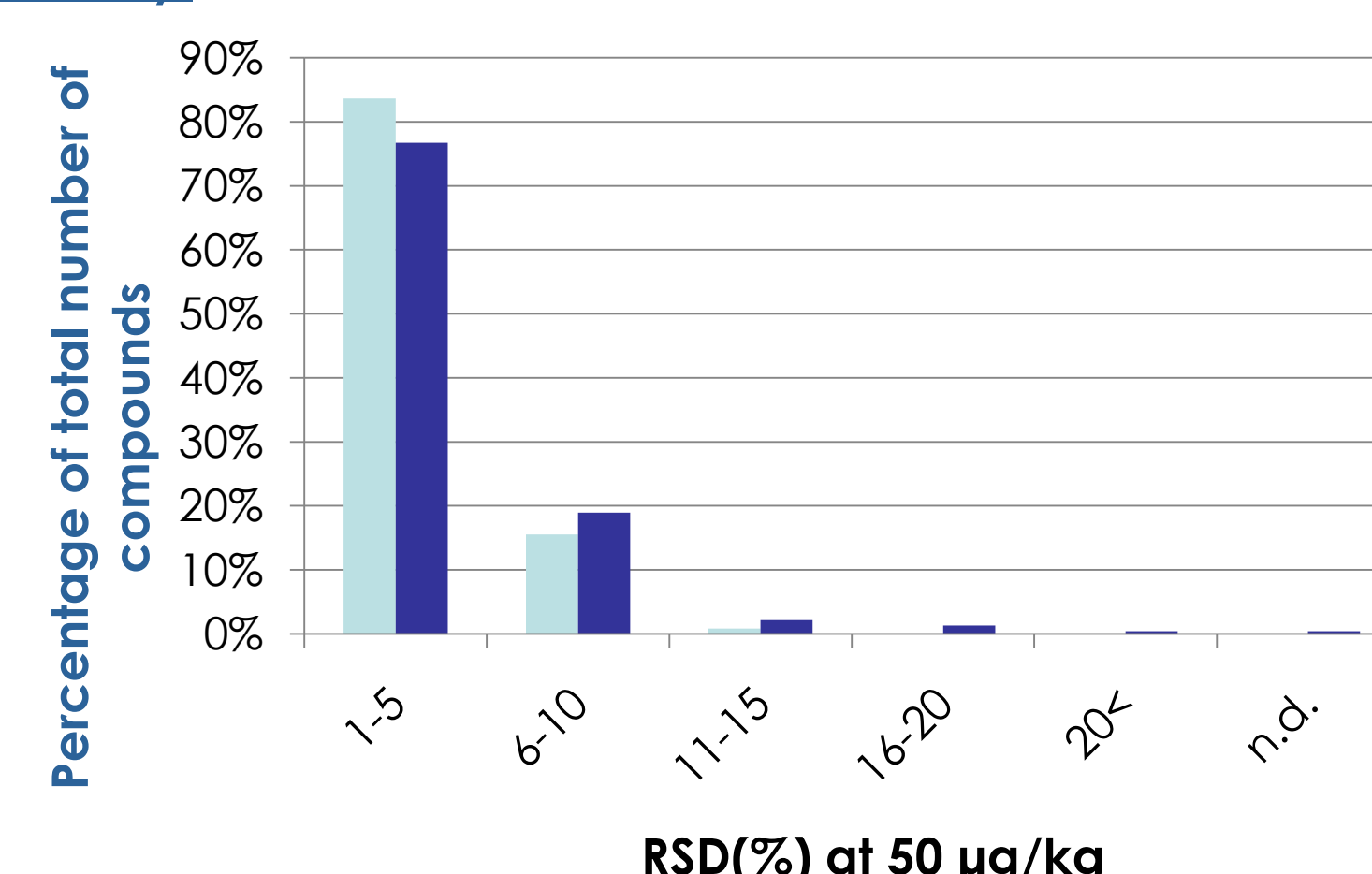
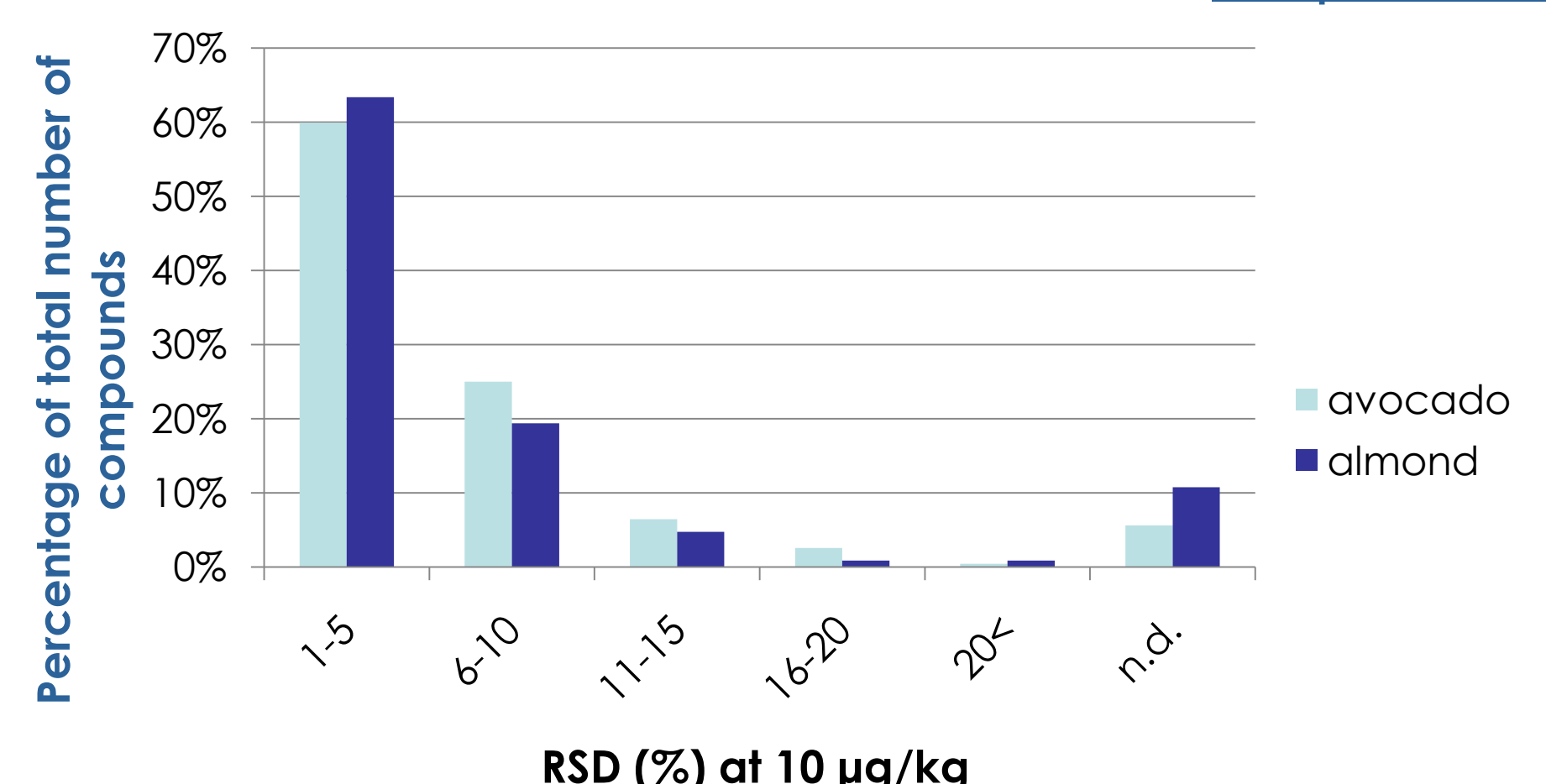


RESULTS

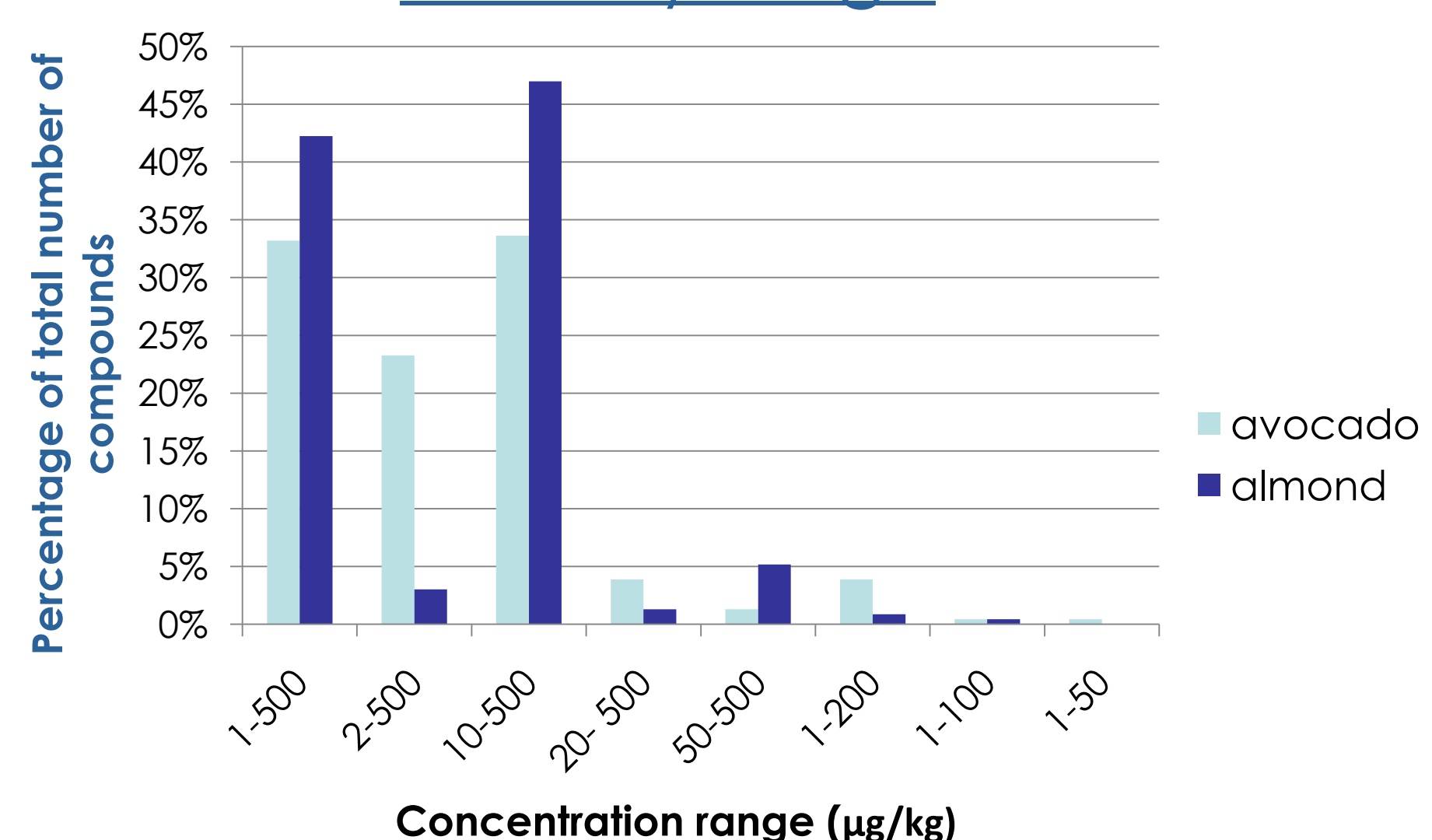
Recoveries



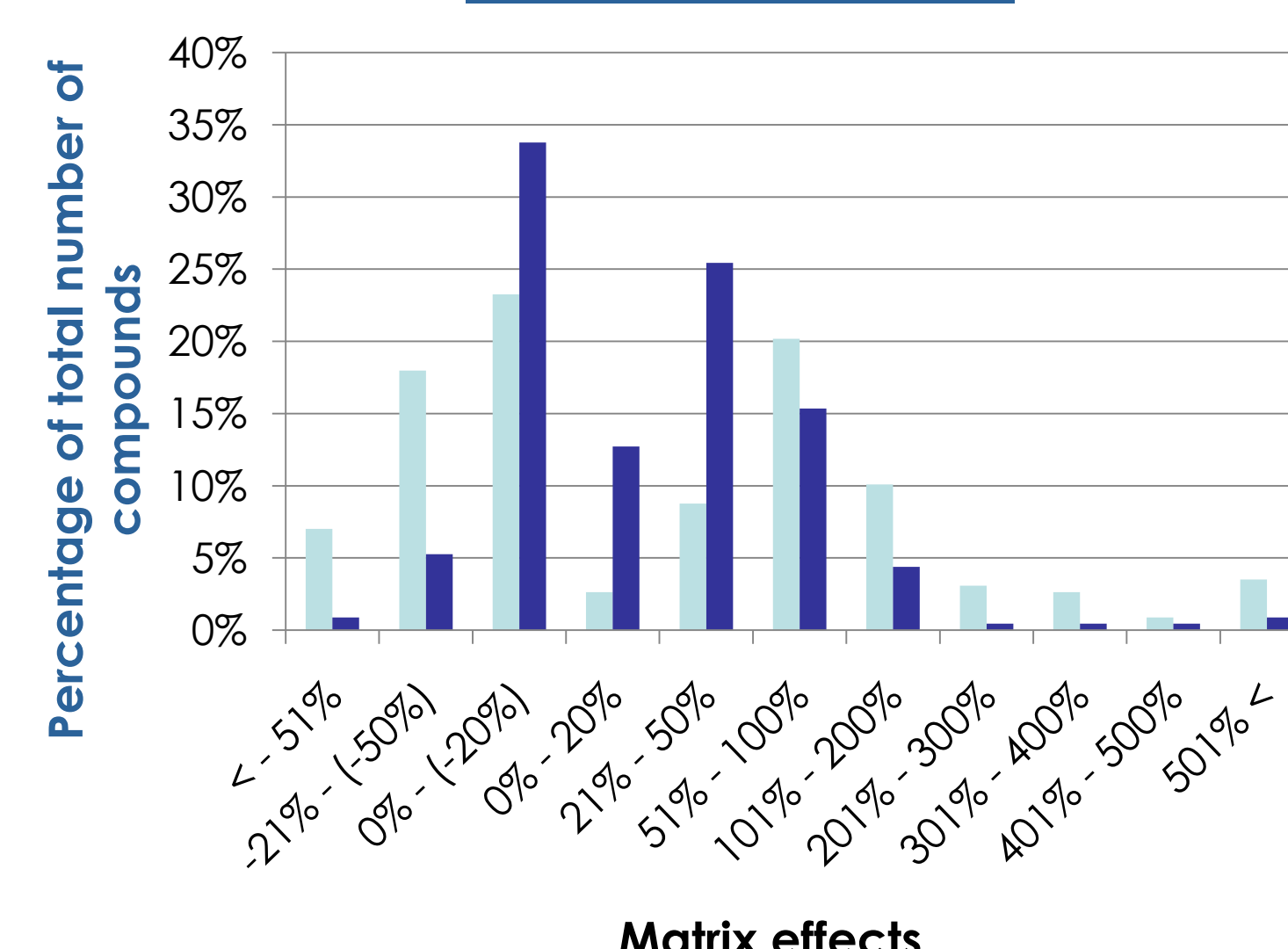
Reproducibility



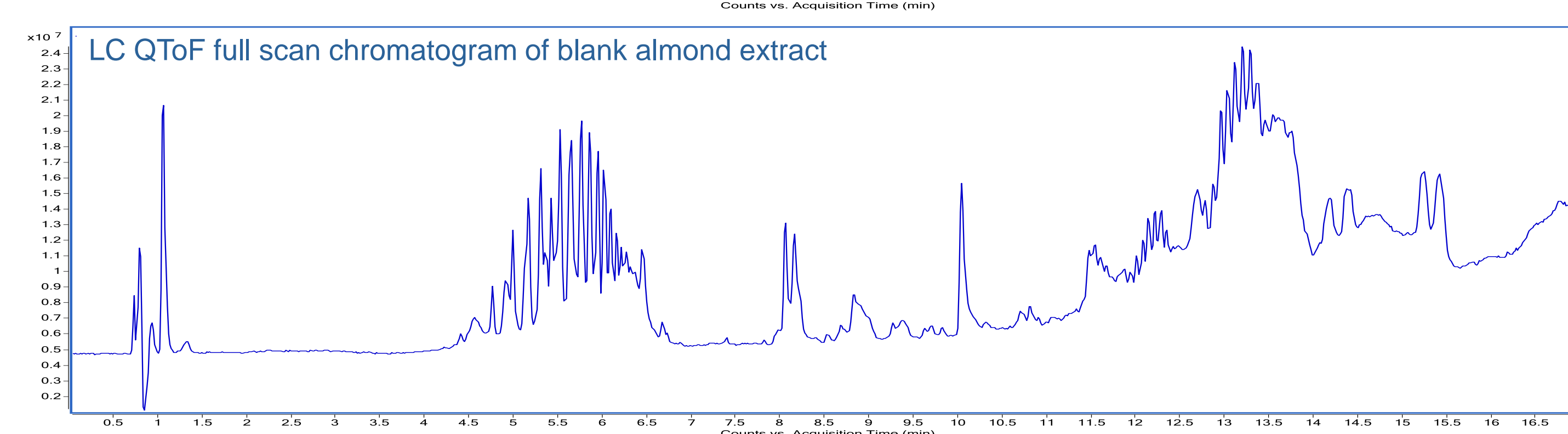
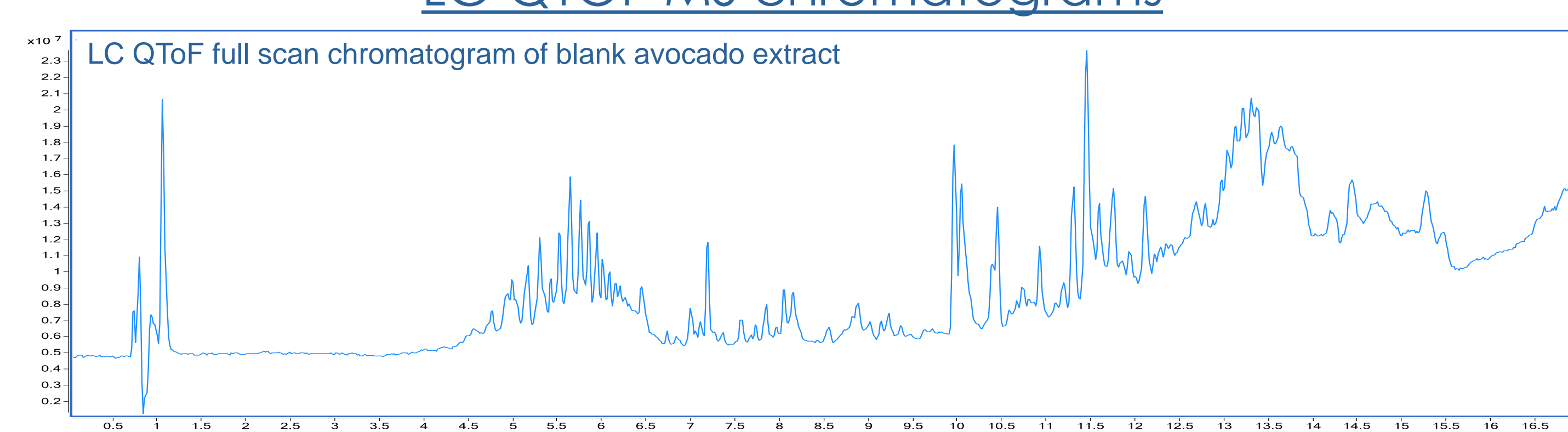
Linearity range



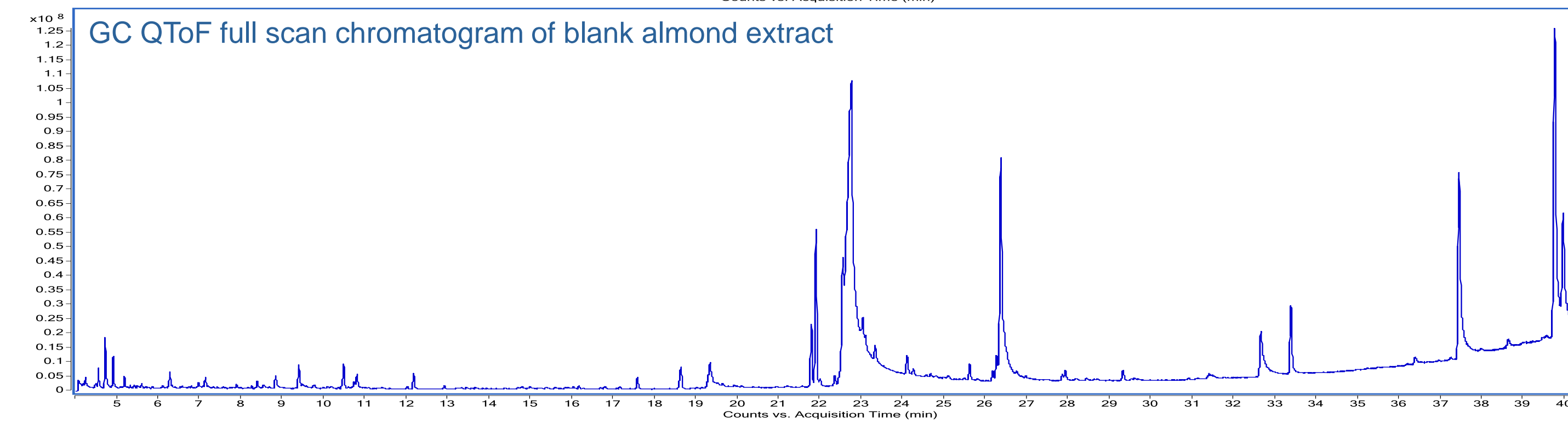
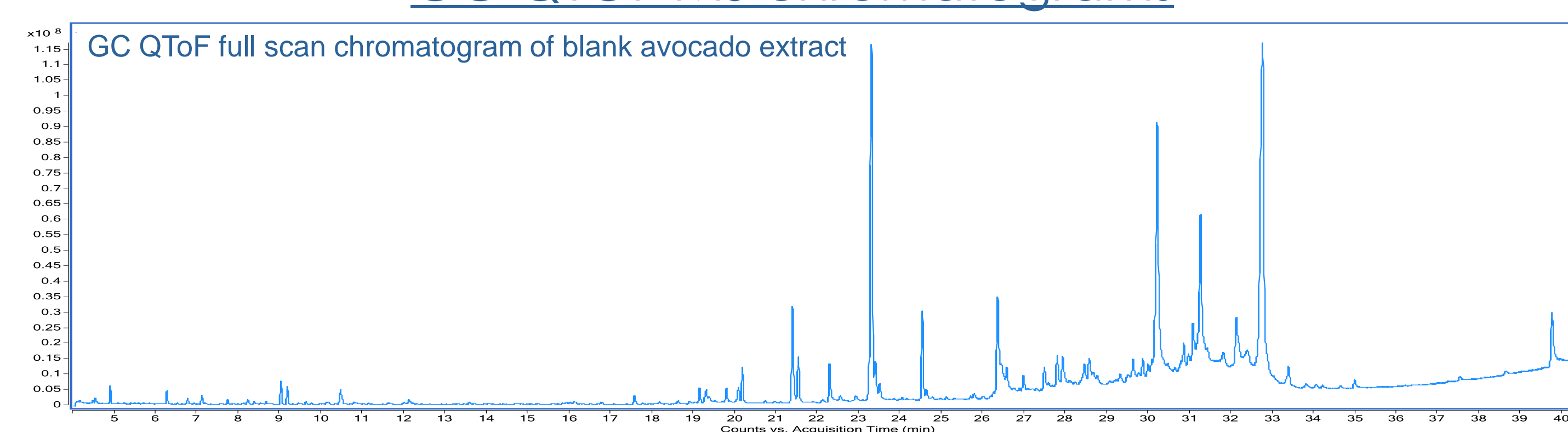
Matrix effects



LC-QTOF-MS chromatograms



GC-QTOF-MS chromatograms



CONCLUSIONS

- Criterion of recoveries in the range 70%-120% was fulfilled by: 207 (89% of total number) and 218 (94% of total number) of analysed pesticides in avocado at levels 10 µg/kg and 50 µg/kg respectively. In case of almond were 154 (66%) at 10 µg/kg and 159 (69%) at 50 µg/kg.
- The extraction of pesticides from almond was more “difficult” than from avocado. High fat matrices such as avocado and almond represent a challenge due to low fat solubility in acetonitrile. This situation is more pronounced in almond than in avocado. This point was especially problematic for highly lipophilic analytes.
- However, the presented method is characterised by very good precision, with RSD values below 10% in most cases.
- For the majority of pesticides in both extracts, the detector response was linear from at least 10 µg/kg (in many cases even from 1 or 2 µg/kg) up to 500 µg/kg.