

Determination of pesticide residues in tea with QuEChERS and HPLC-MS/MS

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Introduction

The determination of pesticides in food and feed is part of routine food control. Therefore, the QuEChERS methodology is used for many sample matrices as part of sample preparation. It provides many advantages allowing rapid and cheap clean-up of strongly matrix-contaminated samples like black tea. It consists of an extraction and a clean-up step. Each compound of QuEChERS clean-up-mix shows different effects on matrices reduction. The Diamino phase removes, e.g., sugars and organic acids. Magnesium sulfate removes water, C₁₈ ec removes nonpolar interferences such as fats and so on [1–3].

Subsequently, a sensitive QuEChERS method with an efficient clean-up for pigmented sample matrices like tea was developed. The sample raw extract was purified with a clean-up-mix with customized composition. In this work, the recovery rates of pesticides and the effects on matrix-reduction for different clean-up-mix composition are shown and are discussed.

Dispersive solid phase extraction (dSPE)

Extraction

- Weigh 2 g homogenized black tea into a 50 mL centrifuge tube
- Add 10 mL water
- Add internal Standard mixture or pesticide standard mixture to determine recovery rates and agitate and wait 10 min
- Add 10 mL acetonitrile and agitate
- Add CHROMABOND® QuEChERS Mix I, shake vigorously for 1 min and cool the mixture down in an ice bath
- Centrifuge at 4500 rpm for 10 min at 4 °C
- Take organic phase for clean-up procedure

Clean-up

- Add 6 mL of organic phase into centrifuge tube with CHROMABOND® QuEChERS Mix III or special mix with high/middle/low CHROMABOND® NH₂ content
- Shake vigorously for 1 min
- Centrifuge at 4500 rpm for 10 min at 4 °C
- Dilute extract from dSPE with water (content of water 80 %)

Subsequent analysis HPLC-MS/MS

Chromatographic Conditions

Column: EC 50/4.6 NUCLEOSHELL® Bluebird RP 18, 2.7 µm, (REF 763432.46)
Eluent A: 0.1 % formic acid in water
Eluent B: 0.1 % formic acid in methanol
Gradient: in 5 min from 5 % to 100 % B, hold for 1.0 min, in 0.1 min to 5 % B, hold 5 % B for 3.9 min
Flow rate: 0.7 mL/min
Temperature: 30 °C
Injection volume: 20 µL
MS conditions: API 5500, ion source ESI, positive ionization mode, scan type MRM
Curtain gas 35 psig, ion spray voltage 5000 V, temperature 450 °C, nebulizer gas 45 psig, turbo gas 45 psig, CAD medium
For MRM transitions look at application number 128870 in our application database.



Chromatograms

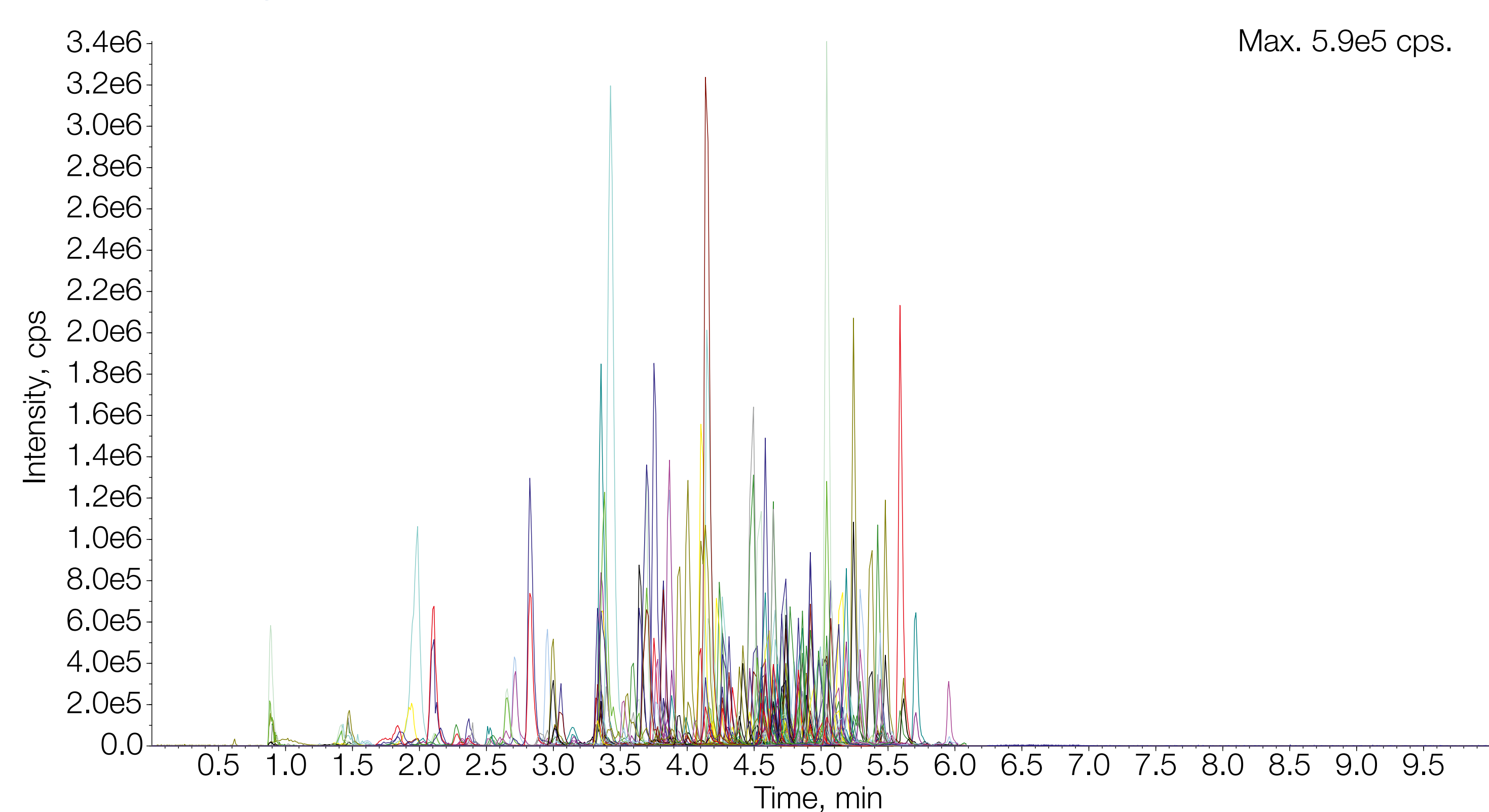


Fig. 1: Chromatogram of a green tea extract cleaned with CHROMABOND® QuEChERS Mix with middle CHROMABOND® NH₂ content

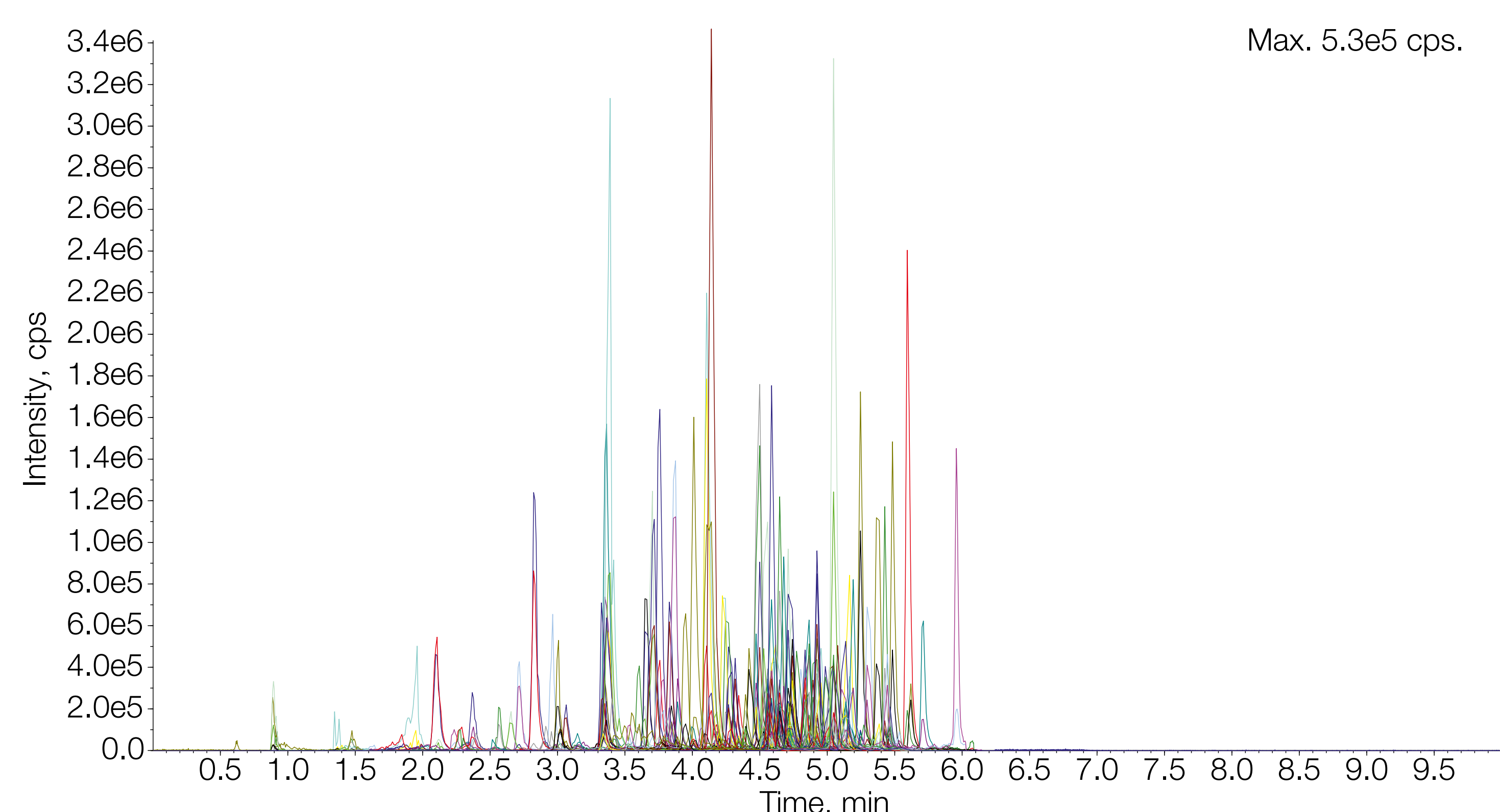


Fig. 3: Chromatogram of a black tea extract cleaned with CHROMABOND® QuEChERS Mix with middle CHROMABOND® NH₂ content

Recovery rates

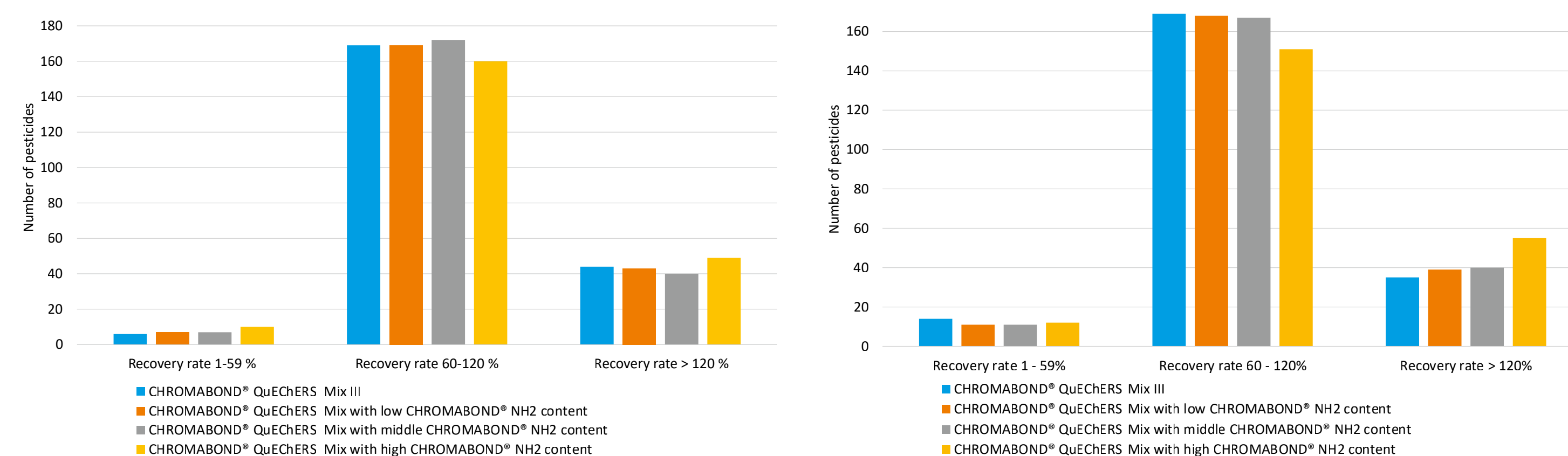


Fig. 3 (left): Number of pesticides in green tea in different value segments of recovery rates, sample spiked with 50 ng/g for each pesticide.

Fig. 4 (right): Number of pesticides in black tea in different value segments of recovery rates, sample spiked with 50 ng/g for each pesticide.

Matrix reduction

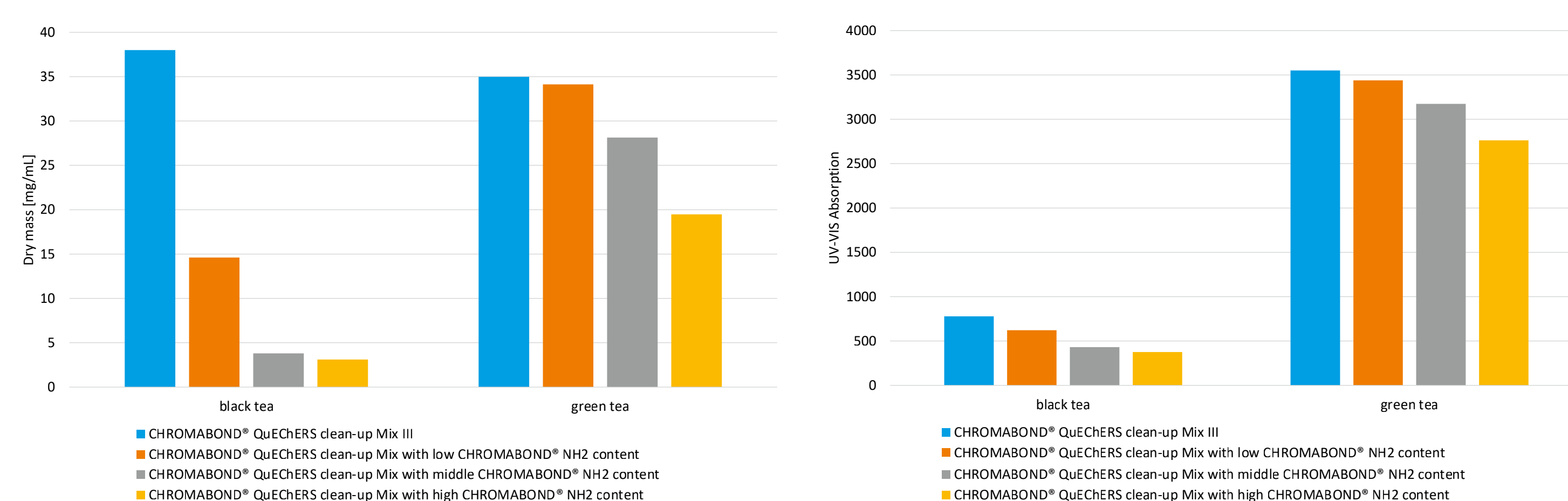


Fig. 5 (left): Reduction of dry mass for sample matrices black tea and green tea.

Fig. 6 (right): Reduction of UV-VIS absorption for sample matrices black tea and green tea



Conclusion

The recovery rates of pesticides and the effects on matrix-reduction for different clean-up-mix composition are shown in figure 3–6. Using CHROMABOND® QuEChERS clean-up Mixes with additional CHROMABOND® NH₂ sorbent leads to significant matrix reduction without decreased recovery rates for black tea and for green tea. It is assumed the phenolic compounds of the tea extracts have a high affinity to the sorbent. Therefore, matrix reduction in black tea is more efficient than in green tea. For achieving a better reduction of the chlorophyll content in green tea extracts the QuEChERS Mix composition must be adapted for instance with additional graphitized carbon black. For the determination of acidic pesticides, the use of CHROMABOND® NH₂ or CHROMABOND® diamino should still be avoided.

In summary, the presented application describes a quick and convenient method for the determination of pesticides in tea prior dSPE using CHROMABOND® QuEChERS Mix with additional content of CHROMABOND® NH₂.

References

- [1] M. Anastassiades, S. J. Lehotay, D. Stajnbaher, F. J. Schenck, J. AOAC Int. 86 (2003), 412–431.
- [2] L 00.00-115, Bestimmung von Pestizidrückständen in pflanzlichen Lebensmitteln mittels GC-MS und/oder LC-MS/MS nach Acetonitril-Extraktion/Verteilung und Reinigung mit dispersiver SPE (QuEChERS) (nach DIN EN 15662).
- [3] L 00.00-115/1, Neufassung der Multimethode zur Bestimmung von Pestizidrückständen in pflanzlichen Lebensmitteln mittels GC-MS und/oder LC-MS/MS nach Acetonitril-Extraktion/Verteilung und Reinigung mit dispersiver SPE (QuEChERS)

Product information

The following MACHEREY-NAGEL products have been used in this application:
REF 763432.30, EC 50/3 NUCLEOSHELL® Bluebird RP 18, 2.7 µm
REF 730970, CHROMABOND® QuEChERS Mix I
REF 730972, CHROMABOND® QuEChERS III
CHROMABOND® QuEChERS Mix with high/middle/low CHROMABOND® NH₂, order on request

