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Study of co-extracted matrix compounds as interfering components for the analysis of pesticides in fruit and vegetables

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INTRODUCTION

The complexity of certain matrices can cause problems with the ionization efficiency of the analytical instruments. These problems in some cases lead to signal suppression effects and false negative occurrences. Furthermore, the presence of matrix compounds with very similar masses to target analytes could be a major drawback for an unequivocal identification and therefore false positive detections. The higher the complexity of the sample, the more false negatives and/or false positives will appear. The aim of this work is the study and chemical evaluation of co-extracted compounds as interfering components for the analysis of pesticides in relevant fruit and vegetables matrices

EXPERIMENTAL SECTION: SAMPLE TREATMENT AND LC-TOF-MS ANALYSIS

SAMPLE TREATMENT

Extraction of blank matrices
Citrate buffered **QuEChERS**

Blank extract

Spiked with 100 pesticides
100 µg/L

LC-QTOF-MS

Operational conditions
Full-scan ESI (+) mode
Nebulizer: 40psi
Gas Temp : 400ºC
Cap. Voltage: 4000 V.
Frag. Voltage: 90 V

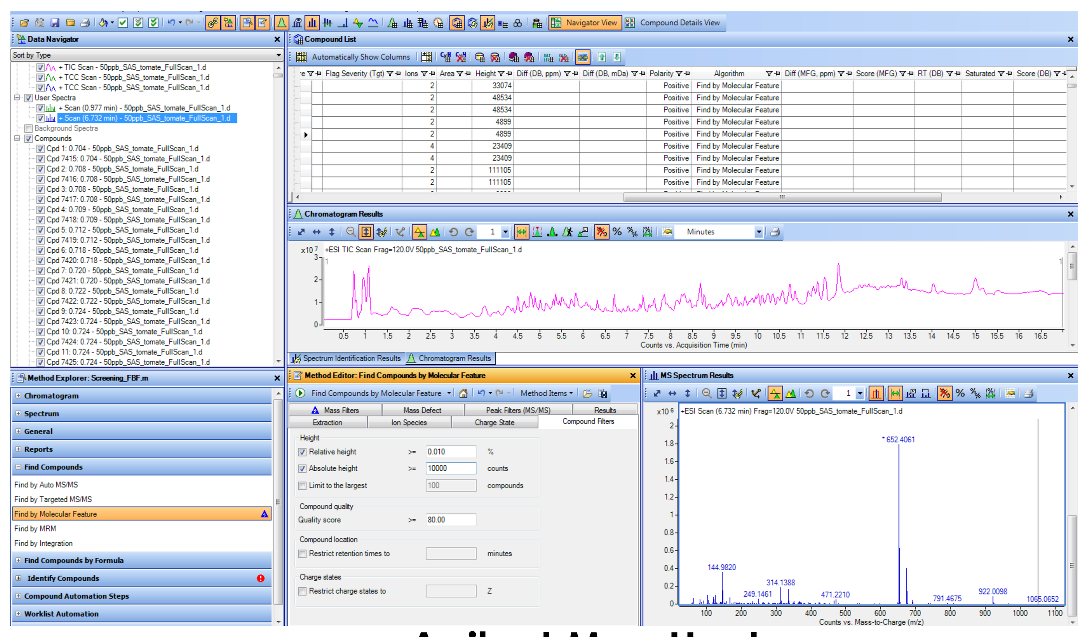
Chromatography Agilent 1200 HPLC system

Column: XDB-C18 Agilent. 50mm x 4.6 mm (1.8 µm)

Mobile phase:

AcN (A) (5% water, 0.1% formic acid) and MiliQ Water (B) (0.1 % formic acid)
10% (A) isocratic t=1 min, then to 100 % (A) in 10 min and maintained for 6 min, Flow rate of 0.6 mL/min.

Screening Software

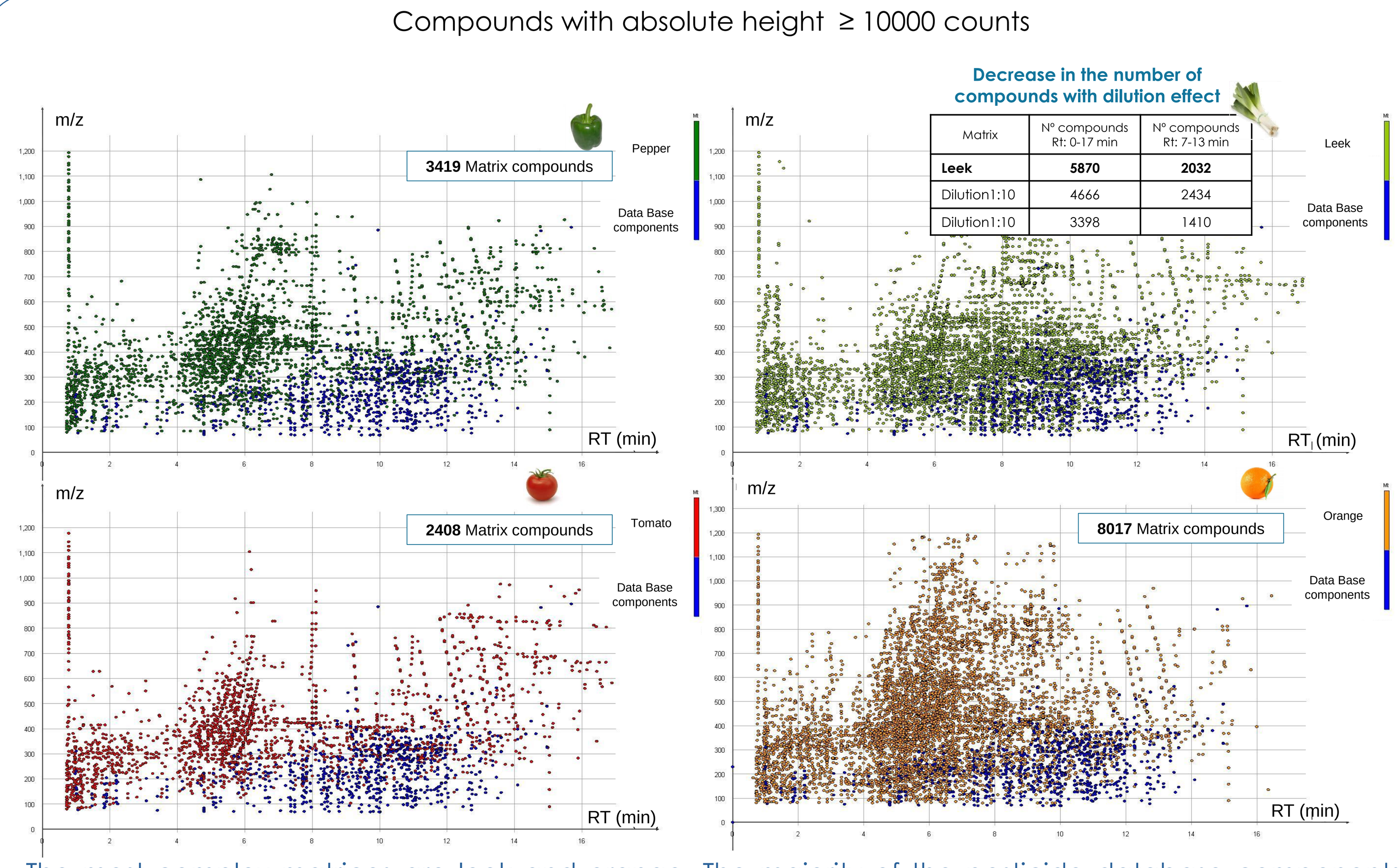


Agilent MassHunter
"Molecular Feature Extraction"

RESULTS

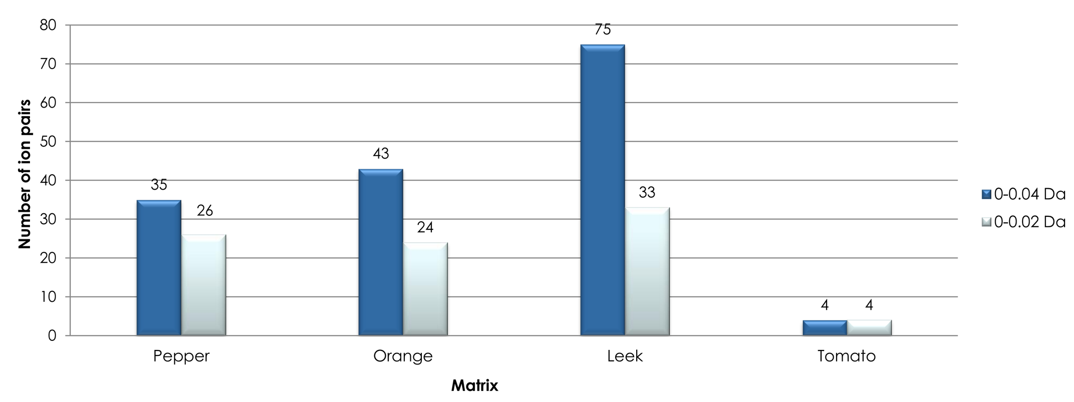
Number and distribution of Co-extracted matrix compounds- Pesticide database components

Compounds with absolute height ≥ 10000 counts

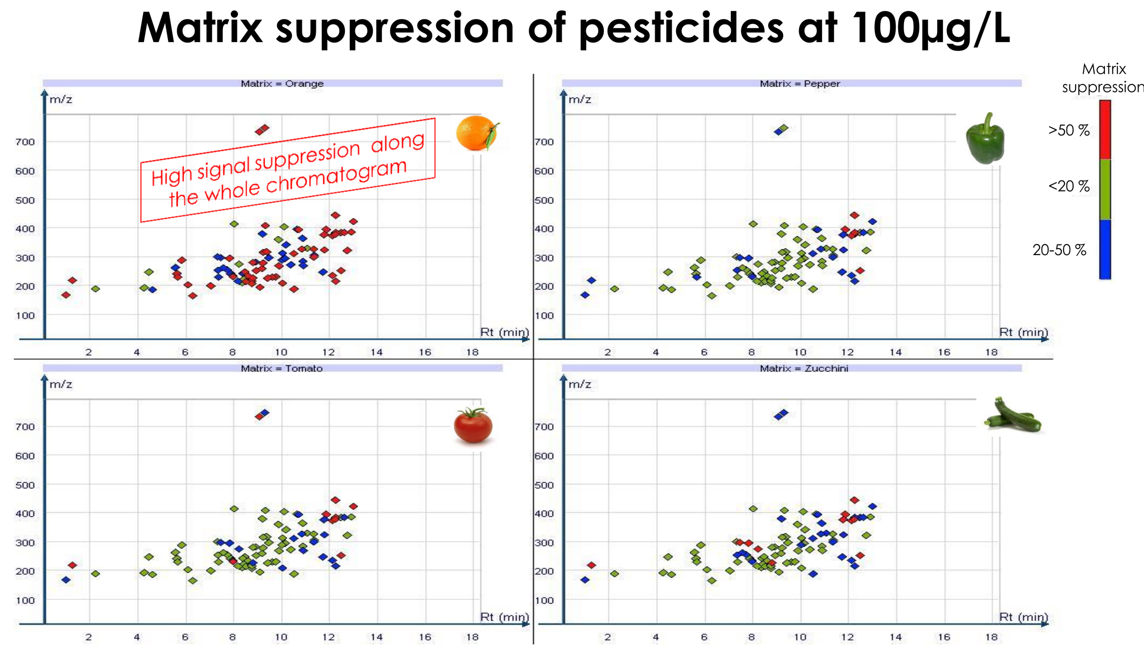


The most complex matrices are leek and orange. The majority of the pesticide database components including fragments and Cl isotopes eluted in the 7–13 min range. Co-extracted matrix compounds in orange are distributed in the first part of the chromatogram whilst they are more homogeneously distributed along all the chromatogram for leek. Consequently, despite orange contain more interfering compounds, in the time range of greatest interest, 7–13 min, the number of co-extracted compounds in orange (2743) is similar to the compounds extracted in leek (3032).

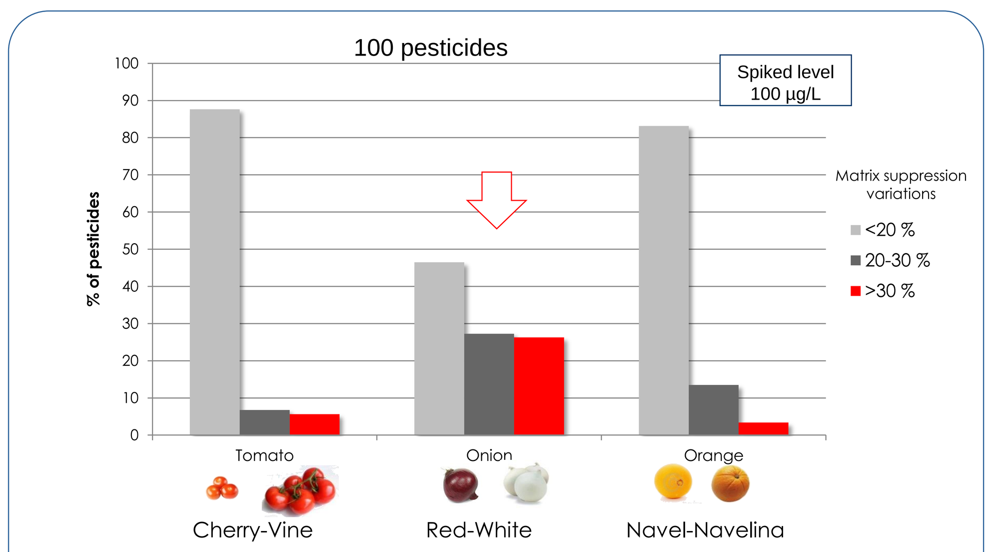
Number of pesticides and interferences with exact mass differences from 0 to 0.02 Da and from 0 to 0.04 Da with retention time differences lower than 0.5 min.



Matrix suppression of pesticides at 100µg/L

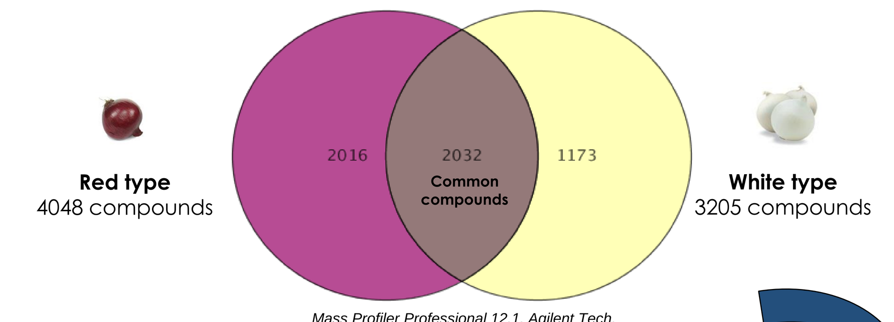


Variations in matrix suppression (%) between types of the same matrix.



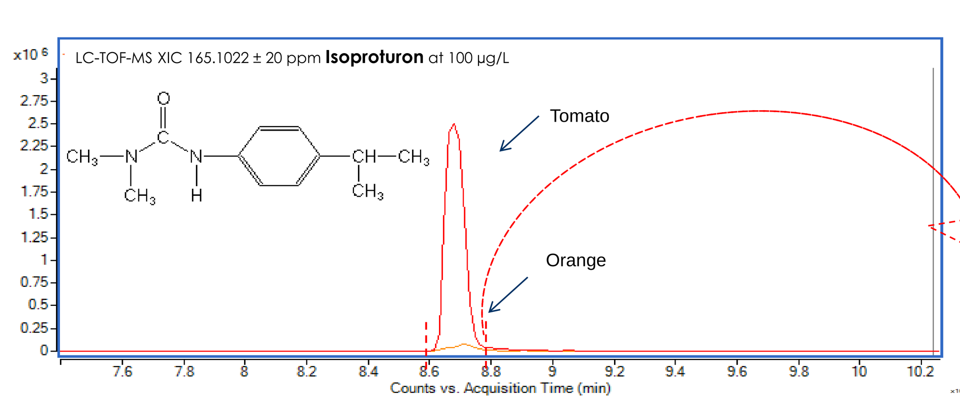
Variations in matrix suppression between types of the same matrix could represent a drawback for quantitation. Between the two onion types the 26 % of pesticides have a variation in matrix suppression over 30%.

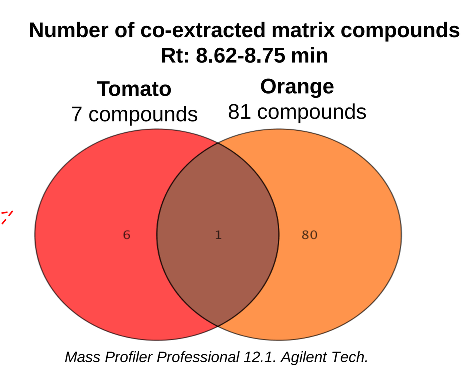
Onion matrix compounds

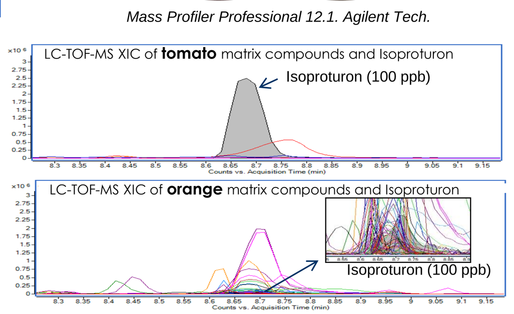


Specific cases

Differences of isoproturon matrix suppression between tomato and orange

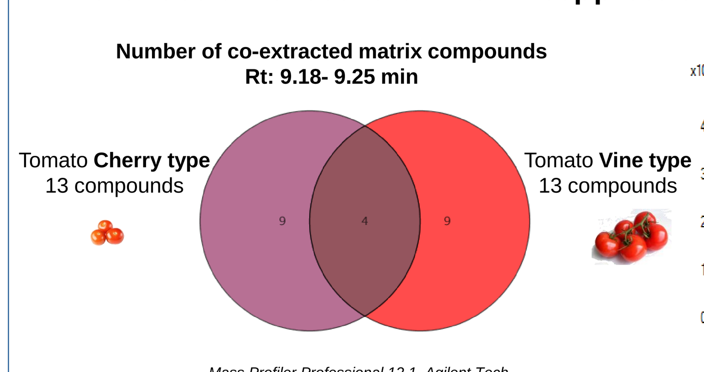


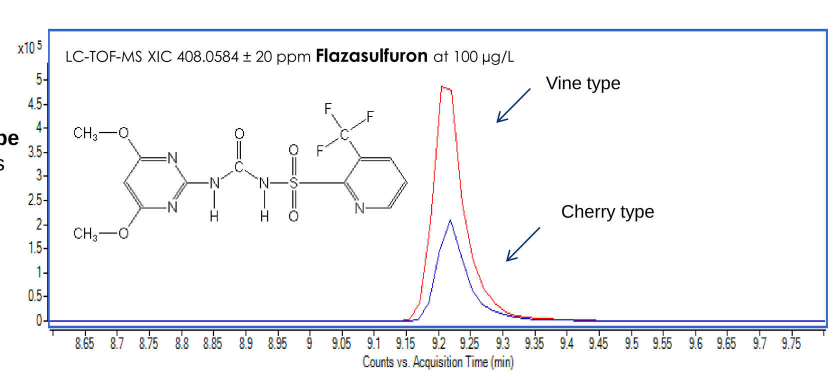




Isoproturon shows high matrix suppression on orange matrix. In this case matrix suppression is due to the high number of interfering components coeluting with the pesticide (Rt: 8.62-8.75 min).

Differences of flazasulfuron matrix suppression between tomato types (Cherry and Vine)

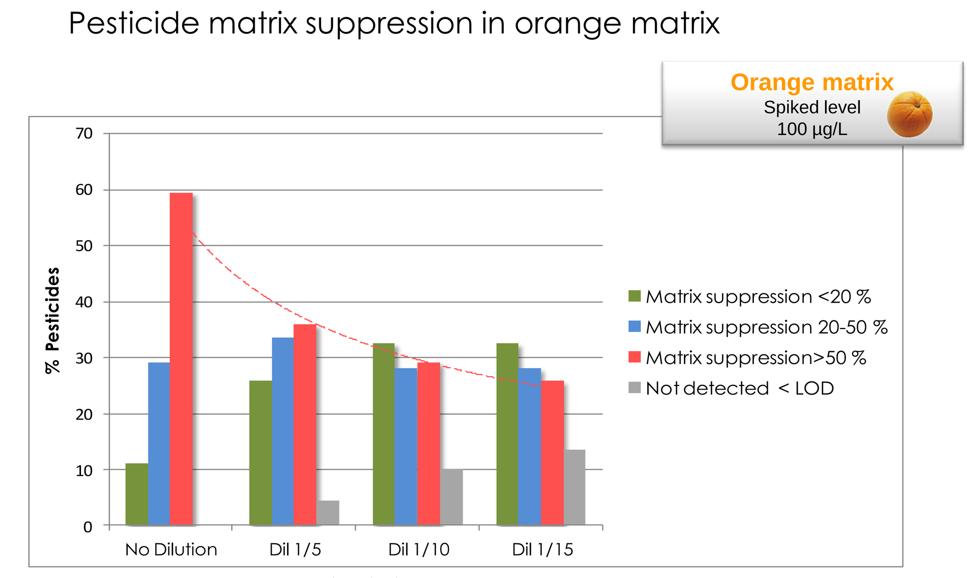




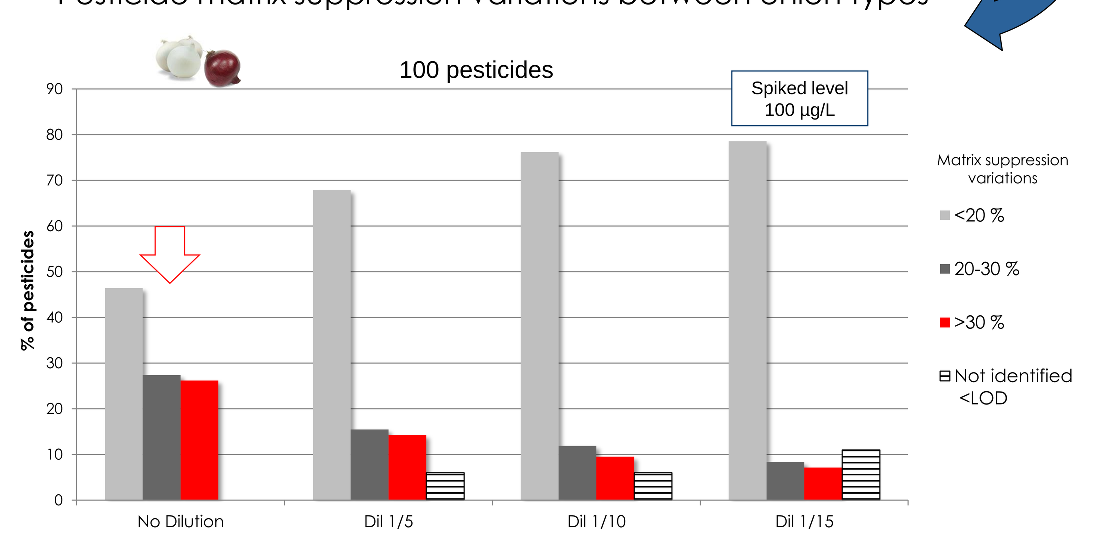
Flazasulfuron shows matrix suppression on Cherry tomato. At the pesticide retention time there are 4 common coeluting matrix compounds and 9 different interfering components. In this case matrix suppression is due to the chemical characteristic of co-eluting compounds.

Dilution effect on matrix suppression

Pesticide matrix suppression in orange matrix



Pesticide matrix suppression variations between onion types



A sample dilution decreases the number of competing molecules, the ionization efficiency increases and thus the analyte signal increases. A dilution factor of 10 diminish to around 30 % the pesticides with high suppression in orange matrix. In the case of matrix suppression variations between two onion types, a dilution factor of 10 diminish the percentage of pesticides from 26 % to less than 10%.

CONCLUSION

The number and distribution of interfering matrix components varies greatly depending on the particular vegetable matrix; even those included within the same commodity group according to EU guidelines[1]. In complex vegetables matrix such as orange, leek, onion, etc. the high signal suppression of pesticides along the whole chromatogram could be associated with the high number of interfering compounds co-eluting at the same retention time than the analytes. In other cases, matrix effects can be associated to chemical characteristics of the matrix compound or the analyte. Signal suppression due to co-eluting matrix compounds and matrix suppression variations would be partially solved through extract dilution. However this implies a reduction in the analyte amount and, consequently, very sensitive analytical systems must be used.

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