Automated SPE-method for the determination of pesticides in tea using GC-MS/MS

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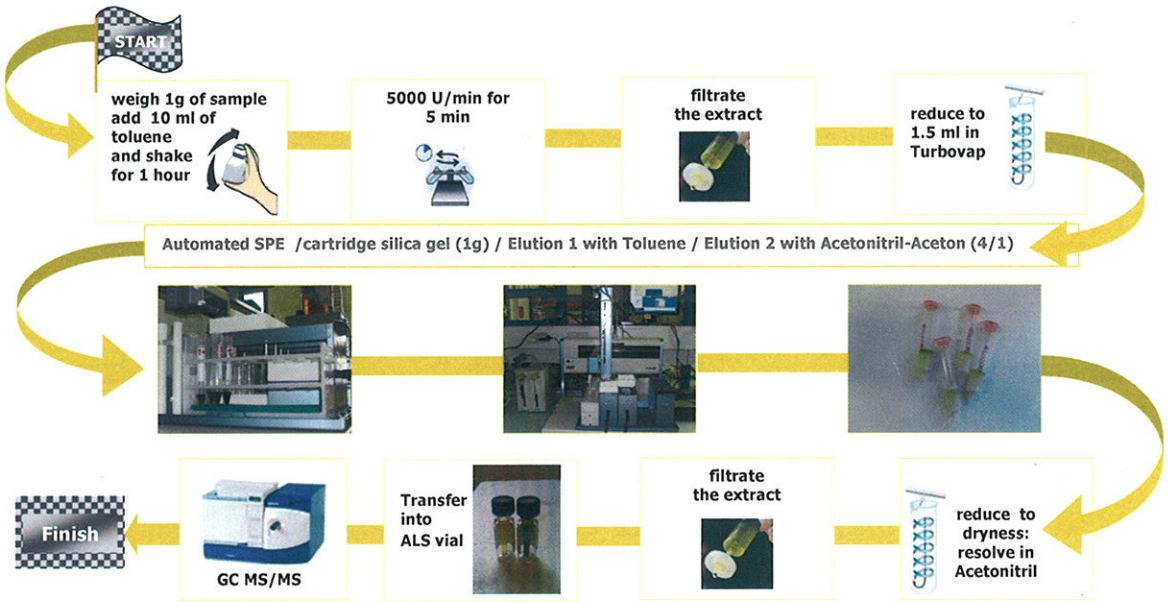
Introduction

Tea crops have a worldwide economic impact and a widespread consumption due to its specific aroma as well as the promised health benefits, especially green tea. During cultivation and storage, however, various pesticides are widely used. Over the past years several reported cases of fungicide and herbicide trace level residues in green tea gained international attention and indicate the need for adequate analytical methods for routine monitoring of this commodity. The method of choice so far for monitoring purposes is the DFG-S19 multi-residue method, however with the drawback of very laborious sample preparation and strong matrix interferences. The use of tandem mass spectrometry offers various advantages in selectivity and sensitivity at low quantities and especially in such complex matrices, as it largely reduces these intrinsic matrix effects.

The proposed alternative multi-residue method presented here involves extraction with Toluene following a clean up step via silicagel cartridges using an automatable SPE device (Liquid Handler, Gilson) coupled to GC-MS/MS analysis to provide the necessary selectivity. The scope of investigation included roughly 80 relevant pesticides (organophophorous, organochlorine, pyrethroids, ...) and the method has been tested in several tea varieties (Green Tea, Mate Tea, Herbal tea, Black tea and in Chamomile).

Method



Results

Method validation calculations were performed on five matrix samples spiked at two concentration levels each (near the LOD of 10 µg/kg and 100 µg/kg). The results clearly demonstrate good linearity, recoveries between 70-140% for the majority of analytes and adequate precision (average RSD of 10.6%), meeting the criteria of EU guidelines (SANCO/10684/2009) (see Tab.1.).

organochlorine	RSD [%]	recovery [%]
Hexachlorbenzol	8	114
Dieldrin	19	123
Heptachlorepoxid	7	109
4,4'-DDD	3	109
2,4'-DDE	3	121
Endosulfan -alpha	6	115

pyrethroid	RSD [%]	recovery [%]
Bifenthrin	6	157
Cypermethrin techn.	9	104
Deltamethrin	4	114
lambda-Cyhalothrin	14	96
Permethrin	12	101
Fenvalerate	7	121

organophosphorous	RSD [%]	recovery [%]
Chlorpyriphos	6	111
Ethion	5	111
Fenitrothion	11	106
Malathion	10	106
Pirimiphos-methyl	23	77
Triazophos	8	118

Table 1: Validation data for representative Analytes in tea matrix

FAPAS (PT 2006) - tea matrix	assigned value (mg/kg)	analysed value (mg/kg)
p,p-DDD	0.204	0.176
Ethion	0.332	0.386
Quintozene	0.094	0.082

Table 2: Validation of the method using reference material

In addition, the presented method was successfully validated using a FAPAS tea sample from 2006 (Tab.2).

The method was also tested for a couple of real tea samples (Tab.3) In every sample batch two spiked blank matrices (10 µg/kg /100 µg/kg) were analysed and used for calibration purposes. Only in case of MRL violations the alternative approach of standard addition for quantification has been performed.

Compounds	analysed value (mg/kg)	MRL (mg/kg)
Bifenthrin	0.197	5.00
Chlorpyriphos	0.009	0.10
Cypermethrin	0.048	0.50
Fenvalerate	0.093	0.05
l-Cyhalothrin	0.07	1.00
Endosulfane	0.092	30.00

Table 3: Analysis of chinese green tea

Conclusion

The method presented demonstrates a rapid, sensitive and straightforward multi-residue approach for pesticide residue analysis in tea samples combining an automated extraction and clean-up procedure with the strength of GC-MS/MS tandem mass spectrometry and is thus suitable for food monitoring according to EU legal requirements. As a next step the method has to be validated for its suitability in daily routine analysis – with the possibility to broaden the scope of investigation.