



# Automated Solid Phase Extraction (SPE) Method for the Determination of Pesticides in Tea using GC/MS-MS

Application Note ENV0112

*A Solid Phase Extraction (SPE) method for the extraction of pesticides from tea samples was automated using the Gilson GX-271 ASPEC™ System. The method is rapid, sensitive and straightforward. The automated extraction and clean-up procedure is combined with the strength of GC/MS-MS tandem mass spectrometry and is thus suitable for development of food monitoring procedures that comply with EU legal requirements.*

## Introduction

Tea crops have both worldwide economic impact and widespread consumption due to their specific aroma as well as the promised health benefits, especially for green tea. During cultivation and storage, 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, indicating the need for adequate analytical methods to allow for routine monitoring of this commodity.

The method of choice so far for monitoring purposes in Austria is the multi residue method S19 by the Deutsche Forschungsgemeinschaft, German Research Foundation (DFG-S19); however drawbacks include laborious sample preparation and

strong matrix interferences.<sup>1</sup> Sample tea clean-up using Solid Phase Extraction (SPE) prior to the use of tandem mass spectrometry offers various advantages in selectivity and sensitivity at low quantities and especially in such complex matrices, where these techniques largely reduce these intrinsic matrix effects.

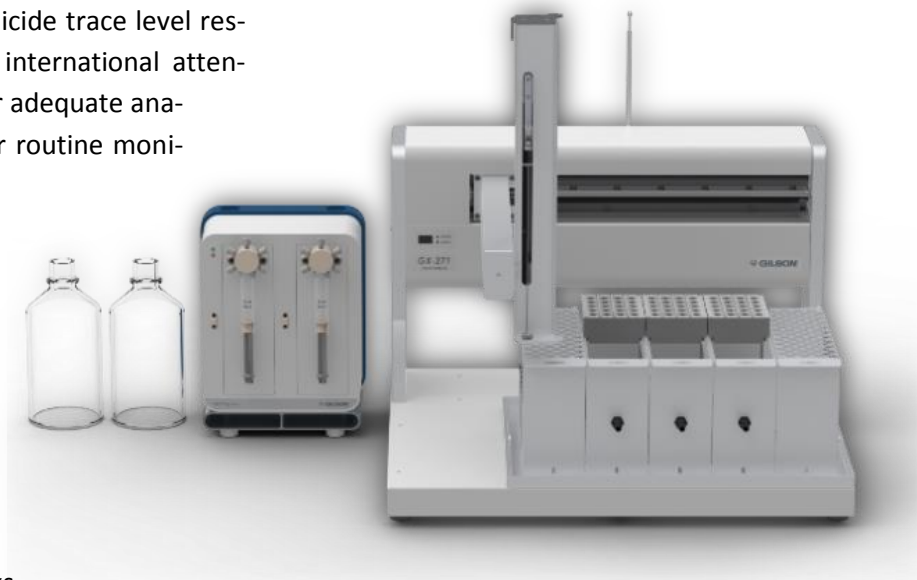


Figure 1. Gilson GX-271 ASPEC™ System



## Materials & Methods

The Gilson GX-271 ASPEC™ System was used to automate a Solid Phase Extraction (SPE) method for the extraction of pesticides from tea samples. The extracted pesticide samples were then analyzed by GC/MS-MS (Figure 2). The scope of the investigation included roughly 80 relevant pesticides (organophosphorous, organochlorine, pyrethroids, etc.), and the method has been tested using several tea varieties (green tea, mate tea, herbal tea, black tea and chamomile).

### Materials

SPE System: GX-271 ASPEC™ System

SPE Cartridges:

Phenomenex Strata™ SI-1 Silica (55 µM, 70 Å) 1 g/6 mL

SPE Solutions:

Toluene

Acetonitrile:Acetone (4:1)

GC/MS-MS System: Waters Quattro micro GC™

### Method

1. Weigh 1 g of tea sample spiked with pesticide standard
  - a. Add 10 mL of toluene
  - b. Shake for 1 hour
2. Spin at 5000 rpm for 5 minutes
3. Filter the extract
4. Reduce filtrate to 1.5 mL in Turbovap®
5. Automated SPE (using Gilson)
  - a. Load: 1.5 mL sample extract (Figure 3)
  - b. Elution 1: Toluene
  - c. Elution 2: Acetonitrile:Acetone (4:1)
6. Reduce to dryness with Turbovap
7. Reconstitute in Acetonitrile
8. Filter the extract
9. Transfer into ALS vial
10. Analyze by GC/MS-MS

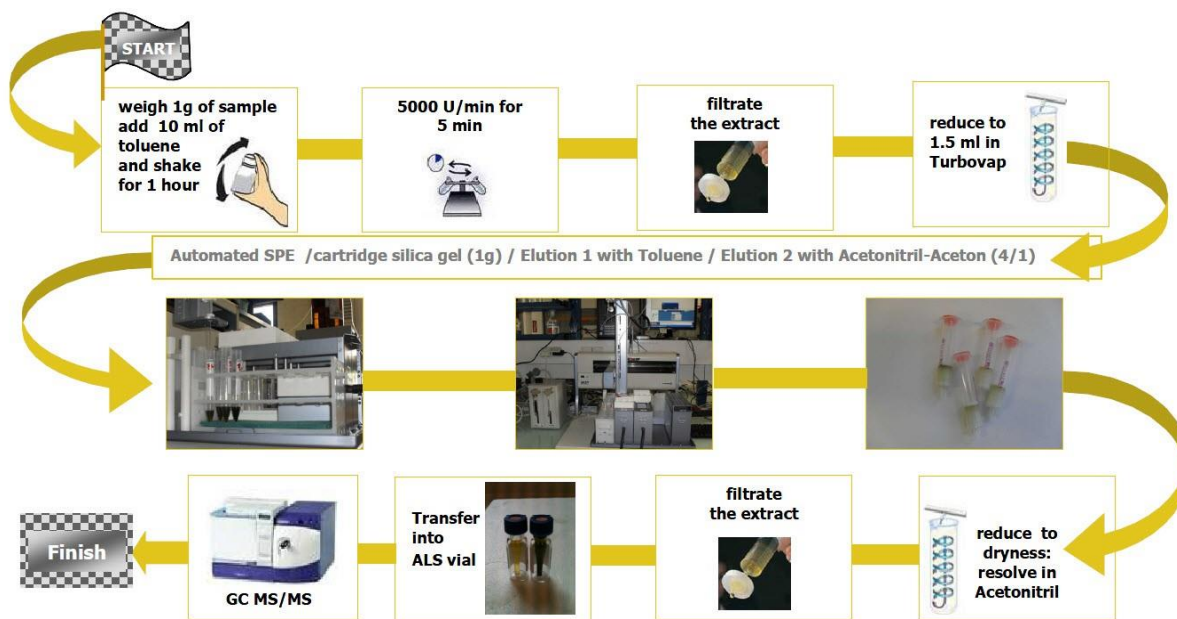


Figure 2. Extraction and analysis of Pesticides in Tea Samples



Figure 3. SPE Load Task Property Page

## Results and Discussion

Method validation calculations were performed on 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) (Table 1). In addition, the presented method was successfully validated using a Food Analysis Performance Assessment Scheme (FAPAS®) tea sample from 2006 (Table 2).



Organic Group	Pesticide	RSD (%)	Recovery (%)
Organochlorine	Hexachlorbenzol	8	114
	Dieldrin	19	123
	Heptachlorepoxyd	7	109
	4-4'-DDD	3	109
	2,4'-DDE	3	121
	Endosulfan-alpha	6	115
Pyrethroid	Bifenthrin	6	157
	Cypermethrin techn.	9	104
	Deltamethrin	4	114
	Lambda-Cyhalothrin	14	96
	Permethrin	12	101
	Fenvalerate	7	121
Organophosphorous	Chlorpyrifos	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)	Analyzed 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 FAPAS® (PT 2006) Reference Material



The method was also tested for several real tea samples. In every sample batch, two spiked blank matrices (10 µg/kg and 100 µg/kg) were analyzed and used for calibration purposes. Only in cases of Maximum Residue Limit (MRL) violations was the alternative approach of standard addition for quantification performed. In the Chinese green tea, Fenvalerate was found to be nearly twice the MRL (Table 3).

Compounds	Analyzed Value (mg/kg)	MRL (mg/kg)	% of MRL
Bifenthrin	0.197	5.00	3.9
Chlorpyrifos	0.009	0.10	9.0
Cypermethrin	0.048	0.50	9.6
<b>Fenvalerate</b>	<b>0.093</b>	<b>0.05</b>	<b>186</b>
1-Cyhatothrin	0.07	1.00	7.0
Endosulfane	0.092	30.00	0.3

Table 3. Analysis of Chinese Green Tea

## References

1. JMPR, 2004. Pesticide residues in Food 2004. Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group on Pesticide Residues, Rome, Italy, 20-29 September 2004. WHO and FAO, Rome 2004.

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*FAPAS® is a registered trademark of The Food and Environment Research Agency TurboVap® is a registered trademark of Caliper Life Sciences*

## Acknowledgements

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## Summary or Conclusions

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.