

# Multi-residue Analysis of Pesticides in Green Tea with Headspace SPME and the Thermo Scientific TSQ Quantum XLS GC-MS/MS

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## Key Words

- TSQ Quantum XLS GC-MS/MS
- Food Safety
- GC/MS<sup>n</sup>
- Pesticide
- SPME
- Tea
- Triple Quadrupole

## Introduction

Food laboratories are being asked to meet lower detections over a wider range of compounds and matrices. Governmental regulating agencies are adding more compounds and lowering the MRLs for those already in existence. A key factor in improving sample throughput and providing a robust analysis begins with the sample extraction and concentration. The application of SPME uses a conventional Thermo Scientific TriPlus autosampler as an in-line sample extraction and concentration technique for multi-residue pesticide analysis. This method can be used for screening and confirming on the TSQ Quantum XLS<sup>™</sup> triple quadrupole mass spectrometer using selected reaction monitoring (SRM), or multireaction monitoring (MRM), while minimizing solvent consumption and extraction time.

## Experimental Conditions

The analysis took place using a Thermo Scientific TRACE GC Ultra gas chromatograph with a PTV inlet, a TriPlus<sup>™</sup> autosampler configured for solid phase micro extraction (SPME), sold under license from Supelco<sup>®</sup>, and a TSQ Quantum XLS GC-MS/MS. Chromatographic separation was achieved with a Thermo Scientific TR-Pesticide II 30 m × 0.25 mm × 0.25 μm column with 5 m guard column. The guard column was placed through the transfer line

and into the source of the MS. The green tea, purchased from a local grocery store, was used in this experiment to demonstrate the utility of this application with a matrix that has a large number of interfering compounds.

All GC and MS parameters, including SRM transitions, were taken from the Thermo Scientific Pesticide Analyzer Reference.<sup>1</sup>

## Sample Preparation

Dry tea leaves were homogenized with a blender. One gram of sample was weighed into 20 mL VOA vials. Stock standard solutions were diluted to construct calibration curves. Standards were prepared in methanol and 10 μL of each standard was spiked into the dry tea to keep the amount of methanol consistent. A 10 μL aliquot of the internal standard solution was also added. After the addition of the standards to the dry tea, 3 mL of a 1% methanol solution saturated with NaCl was added. The vial was capped, gently swirled, and placed in the autosampler rack.

## SPME Conditions

A 100 μ Polydimethylsiloxane (PDMS) fiber was employed for this experiment. The fiber was exposed to the headspace of the vial, while the sample was agitated and heated to 90 °C. After 30 minutes the fiber was placed into the inlet and desorbed for 6 minutes (Figure 1).



Figure 1: SPME drawing

## Injection

The injection was performed on the PTV inlet. The liner was a straight liner and provided with the SPME upgrade kit, Thermo Scientific part number 19050563. The initial injection temperature was 75 °C and was ramped to 250 °C at a rate of 2.5 °C/second, held for 3 minutes then increased to 280 °C at 14.5 °C/second and held for 20 minutes. A complete list of the inlet parameters can be found in Figure 2.

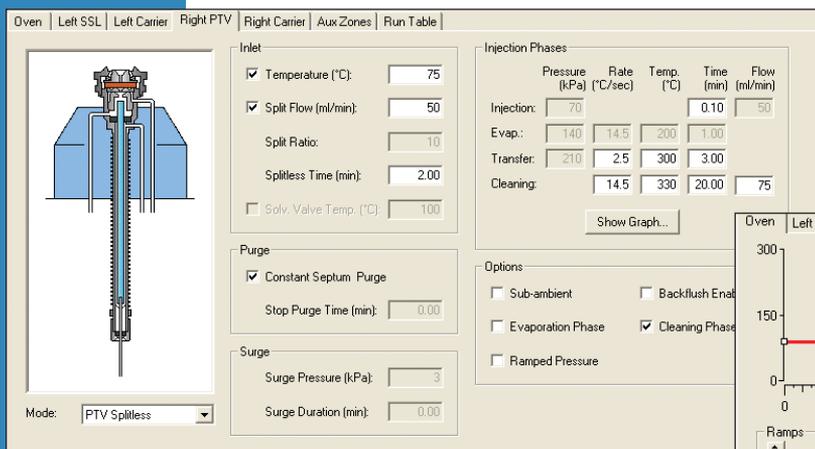


Figure 2: PTV parameters

## Separation

Chromatographic separation was achieved by using the TR-Pesticide II, a 5 % diphenyl/95 % dimethyl polysiloxane column (0.25 mm × 30 meter, and a film thickness of 0.25 µm with a 5 m guard column). The guard column was inserted through the transfer line and into the source of the MS. Placing the guard column through the transferline reduces the column bleed caused by the constant high temperature at the end of a normal column. The oven was programmed as follows: Initial Temp: 90 °C, 5.0 min., 25 °C/min. to 180 °C, 0.0 min., 5 °C/min. to 280 °C, 0.0 min., 10 °C/min. to 300 °C with a final hold time of 2 min. and a constant column flow rate of 1.2 mL/min. The entire set of oven parameters is listed in Figure 3.

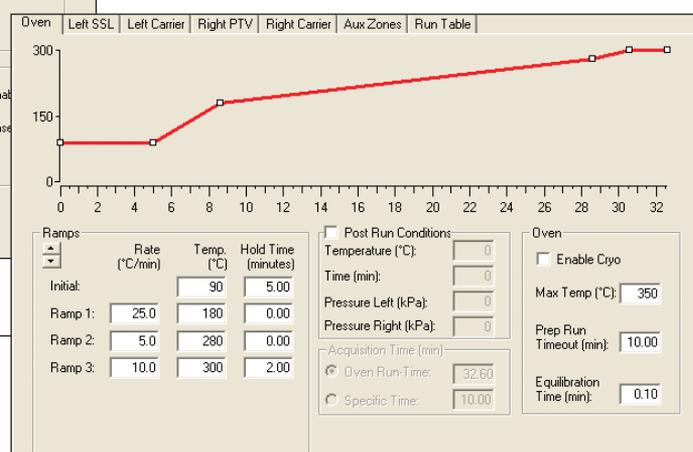


Figure 3: GC oven parameters

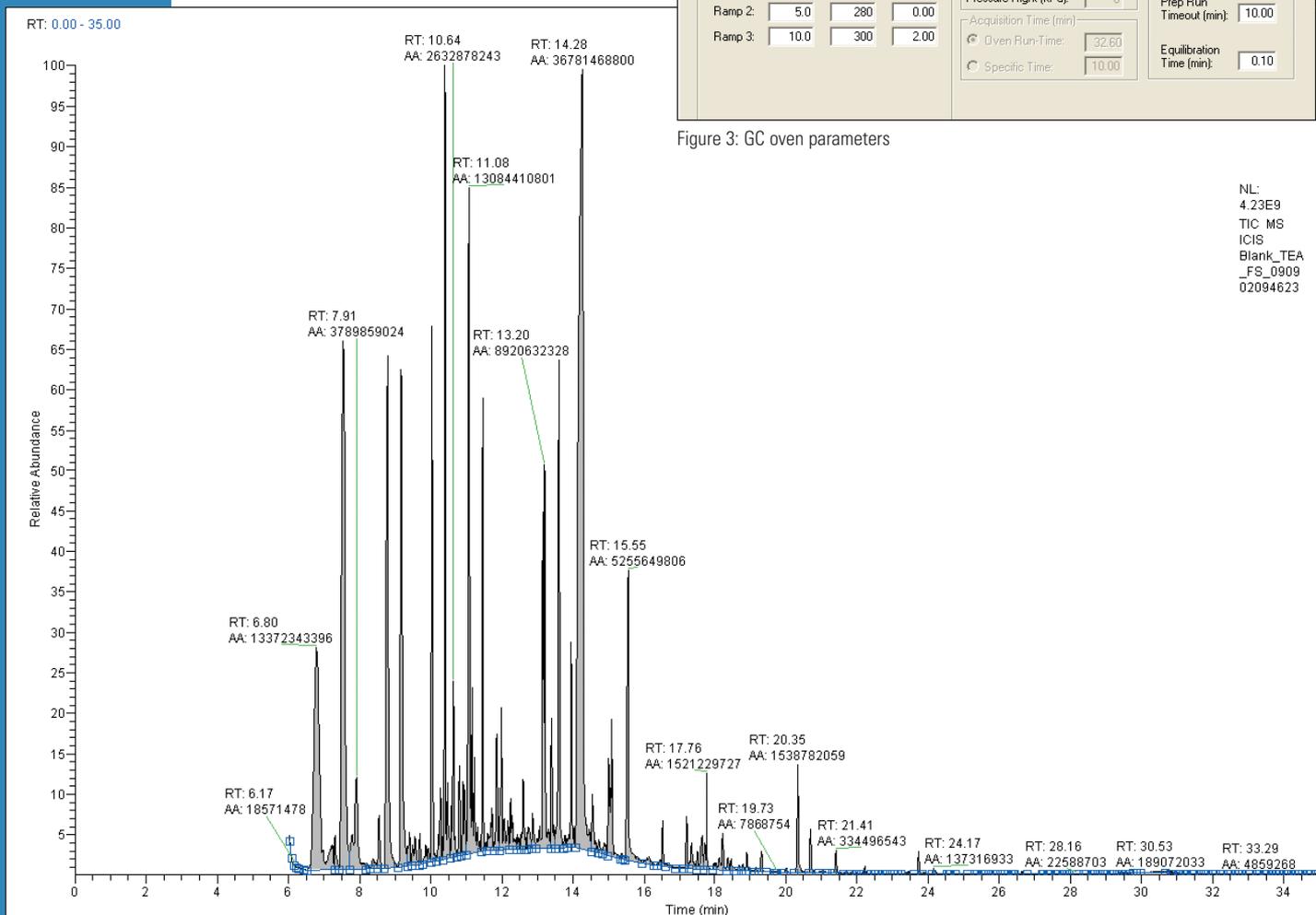


Figure 4: Full scan analysis of green tea

NL:  
4.23E9  
TIC MS  
ICIS  
Blank\_TEA  
\_FS\_0909  
02094623

## Detection

The detection of the pesticides was performed using the TSQ Quantum XLS triple quadrupole mass spectrometer. After retention times were determined in full scan, a timed-SRM method was constructed to analyze the compounds in different standard vials. Calibration curves were analyzed by each individual vial to prevent the SPME fiber from becoming saturated.

One or two confirming ions were utilized for each compound. (Figure 5) Tea contains large amounts of aromas, flavors, polyphenols, and caffeine which can interfere with the detection and identification of the pesticide residues. Figure 4 shows a full scan analysis of a blank green tea sample.

## Results and Discussion

### Linearity

The calibration curve was spiked into the green tea matrix. Levels ranged from 1 to 2000 ng/g (ppb). The linearity for most of the compounds was  $r^2 > 0.995$ . Curves were generated in the green tea matrix using Thermo Scientific QuanLab Forms (Figure 6). Quantification of the standards using the curves demonstrated excellent results at levels at or below those required by international regulators for most compounds (Table 1).

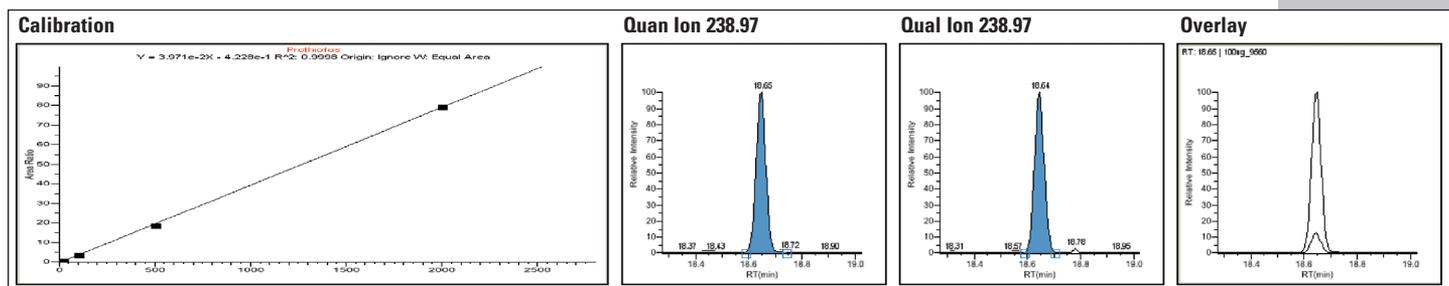


Figure 5a: Prothiofos at 100 ppb with the calibration curve from 20 to 2000 ppb

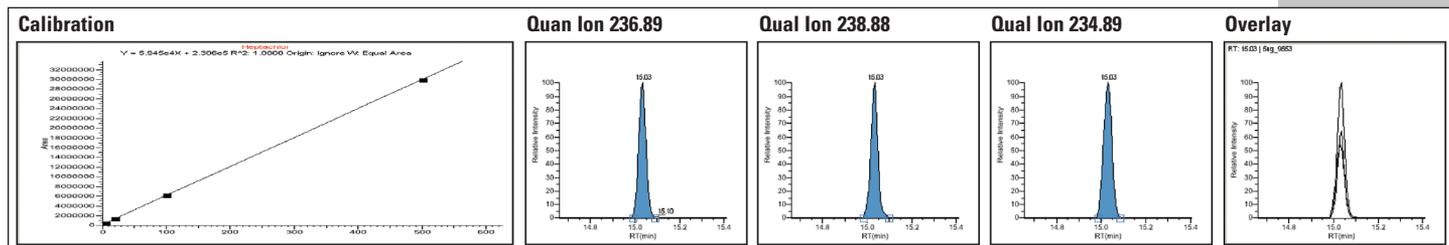


Figure 5b: Heptachlor at 5 ppb with the calibration curve from 5 to 500 ppb

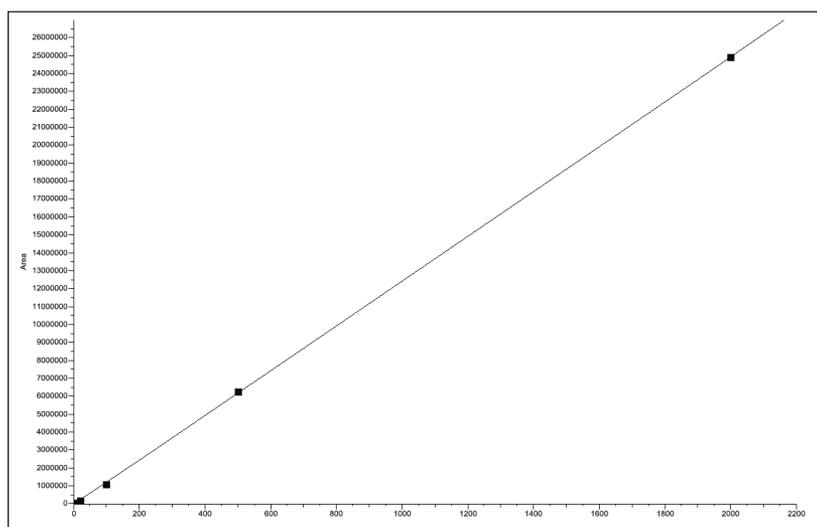


Figure 6: Calibration curve for Clomazone

| Compound             | Japanese MRL (ppb) <sup>2</sup> | Curve (ppb) | r <sup>2</sup> | Classification      | Type                    |
|----------------------|---------------------------------|-------------|----------------|---------------------|-------------------------|
| Aldrin               | ND                              | 20-2000     | 0.9999         | Organochlorine      | Insecticide             |
| Atrazine             | 100                             | 100-2000    | 0.9986         | Triazine            | Herbicide               |
| BHC-beta             | 200                             | 20-2000     | 1.0000         | Organochlorine      | Insecticide             |
| Buprofezin           | 20,000                          | 100-2000    | 0.9997         | Unclassified        | Insect Growth Regulator |
| Chlorfenapyr         | 40,000                          | 100-2000    | 0.9967         | Pyrazole            | Insecticide             |
| Chlorfenson          | 100                             | 20-2000     | 0.9986         | Unclassified        | Insect Growth Regulator |
| Chlorpyrifos, ethyl  | 10,000                          | 20-2000     | 0.9995         | Organophosphorus    | Insecticide             |
| Clomazone            | 20                              | 20-2000     | 1.0000         | Unclassified        | Herbicide               |
| DDT, o, p            | 200                             | 20-500      | 0.9998         | Organochlorine      | Insecticide             |
| Diallate             | 100                             | 100-2000    | 1.0000         | Thiocarbamate       | Herbicide               |
| Diazanone            | 100                             | 20-2000     | 0.9992         | Organophosphorus    | Insecticide             |
| Diadrin              | ND                              | 20-2000     | 0.9975         | Organochlorine      | Insecticide             |
| Endosulfan I (alpha) | 30,000                          | 5-100       | 0.9999         | Organochlorine      | Insecticide             |
| Endrin               | ND                              | 20-500      | 1.0000         | Organochlorine      | Insecticide             |
| Ethion               | 300                             | 20-500      | 0.9994         | Organophosphorus    | Insecticide             |
| Fenclorfos (Ronnel)  | 100                             | 5-500       | 0.9996         | Organophosphorus    | Insecticide             |
| Fenitrothion         | 200                             | 5-500       | 0.9984         | Organophosphorus    | Insecticide             |
| Fenpropimorph        | 100                             | 20-2000     | 0.9995         | Morpholine          | Fungicide               |
| Heptachlor           | 20                              | 5-500       | 1.0000         | Organochlorine      | Insecticide             |
| Parathion, ethyl     | 300                             | 20-2000     | 0.9992         | Organophosphorus    | Insecticide             |
| Phenthoate           | 100                             | 1-100       | 0.9990         | Organophosphorus    | Insecticide             |
| Pirimiphos, Methyl   | 10,000                          | 20-500      | 0.9999         | Organophosphorus    | Insecticide             |
| Procyimdone          | 100                             | 20-2000     | 0.9975         | Dicarboximide       | Fungicide               |
| Propyzamide          | 50                              | 20-500      | 0.9999         | Amide               | Herbicide               |
| Prothiofos           | 5,000                           | 20-2000     | 0.9998         | Organophosphorus    | Insecticide             |
| Quinalphos           | 100                             | 20-2000     | 0.9985         | Organophosphorus    | Insecticide             |
| Quintozene (PCNB)    | 50                              | 20-2000     | 0.9999         | Substituted Benzene | Fungicide               |
| Trifluralin          | 50                              | 5-500       | 0.9990         | 2,6-Dinitroaniline  | Herbicide               |

Table 1: Comparison of MRLs with the calibration curve linear range

## Conclusions

The TSQ Quantum XLS GC-MS/MS paired with the TRACE GC Ultra gas chromatograph showed excellent results at low concentrations for the pesticide residues analyzed in the green tea. Using the instrument's SRM functionality allows the user to identify, confirm, and quantify at a wide range of concentrations in one analytical run. Calibration curves for most of the pesticides studied met a linear least squares calibration with a correlation coefficient of  $r^2 > 0.995$ . One or two ion ratios were used to confirm each pesticide. These results demonstrate that the TSQ Quantum XLS GC-MS/MS is able to meet the international regulatory requirements for low level detection, confirmation, and quantitation for the analysis of pesticides in matrix without the need for manual extraction techniques.

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## References

1. *Pesticide Analyzer Reference*, Thermo Fisher Scientific, Austin 2009
2. The Japan Food Chemical Research Foundation  
<http://www.m5.us001.squarespace.com/jfcrf/foundation/search.html>

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