

Taking the Solvent out of Extractions for Multi-Residue Pesticide Methods

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Overview

Purpose: This work is designed to demonstrate the proof of concept for the analysis of pesticides in heavy matrix without the need for typical laboratory extractions. It justifies further method development. It is designed to give analysis of these pesticides by MS/MS and save a significant amount of time and money for the laboratory.

Methods: Solid phase micro extraction (SPME) is the technique that is used. The sample is homogenized and weighed into a headspace vial. The sample is then placed onto the Thermo Scientific TriPlus SPME (SPME sold under license from Supelco®) autosampler. The sample is incubated and the SPME fiber is inserted and exposed only to the headspace of the sample. The fiber is then inserted into the injector to begin the analysis. The Thermo Scientific TSQ Quantum GC is then used to analyze the sample.

Results: Calibration curves showed correlation coefficients (r^2) of 0.99 or higher in matrices tested. Vernolate was detected in one tea sample in duplicate at just over 6 ppb. However, this was lower than the maximum residue limit (MRL). Initial calculations show that the cost savings for the lab using this technique are approximately \$158,000/year.

FIGURE 1. Demonstrates potential cost savings. Calculation is based on 10,000 samples/year in the lab, number of hours for extraction, consumables required, and the number of instruments that are needed to analyze the samples.

	TSQ GC with SPME	Single Quad
MS cost/yr – 5 year depreciation	120000.00	176000.00
Columns cost/year	3600.00	13200.00
Liner cost/year	720.00	2640.00
Gas cost/year	7200.00	26400.00
Resource cost/yr	0.00	32000.00
Extraction cost	0.00	40000.00
Samples/inst	4800	960
Total samples	10000	10000
Cost/sample	13.15	29.02
Savings/year	US\$ 158720.00	

Introduction

Multi-residue pesticide methods are pushed to greater and greater complexity as the number of pesticides required by law for measurement by the EU and Japan continues to expand. Most analytical methodologies focus on improving the analytical method for improved analysis. This is significant, as the need for robust analytical methods for multi-residue analysis is great. However, the bottleneck in such methods is the sample preparation. In addition to the sample through-put issue, sample

preparation consumes solvent, increasing costs for analysis and disposal. We note a key factor in improving sample throughput and robust analysis begins with sample extraction and concentration. We discuss the application of SPME using a conventional TriPlus™ autosampler as an in-line sample extraction and concentration technique for multi-residue analysis methods for screening and confirming on the TSQ Quantum GC™ triple quadrupole GC-MS/MS system, while minimizing solvent consumption and extraction time.

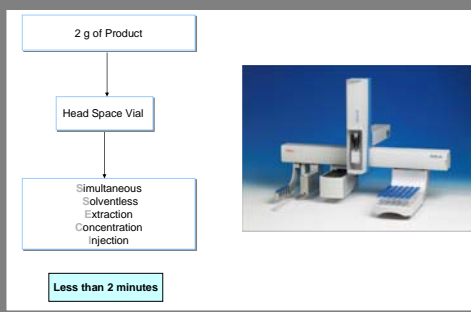
Methods

Several matrices were run through this evaluation, however, tea matrix was used for a more in-depth evaluation. This allowed the comparison of samples from one of the experimenters. The sample is homogenized and 2 g each was weighed into headspace vials. The vials were then placed into the tray of the TriPlus autosampler, configured for SPME injections. This information is demonstrated in figure 2. The time that was taken was approximately 2 minutes to weigh the sample and load the autosampler.

The TriPlus autosampler was programmed to incubate the sample and expose the SPME fiber to the headspace. This eliminates the need for traditional extractions. However, it is required the detection system be able to deal with the volatile matrix.

Using the multiple reaction monitoring (MRM) the TSQ Quantum GC was able to deal with the volatile compounds that were in the headspace and provide the sensitivity required to meet the MRLs for any of the pesticides that were evaluated. Method parameters are seen in figure 3.

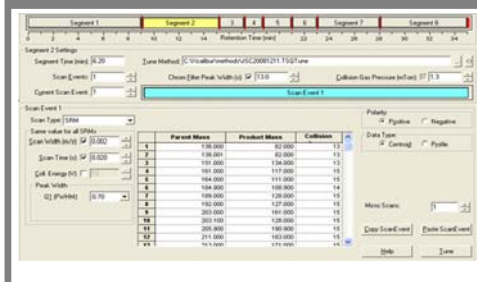
FIGURE 2. These are the steps that are part of the SPME sample preparation. In this experiment 2 g of homogenized sample is weighed into a vial and placed on the autosampler.



Results

Calibration curves were developed for those compounds listed in figure 5. Matrices tested were tea, coffee, and cabbage. The calibration curves showed a 0.99 and better r^2 correlation

FIGURE 3. TSQ Quantum GC method parameters for MRM analysis.



coefficient for all of the compounds tested. Samples of tea purchased at the local store were tested. Vernolate was found in two of the samples at greater than 6 ppb. This is lower than the MRL, however, it does demonstrate the capability of this technique.

Conclusions

It was found during this experiment that the use of SPME as an extraction method required MRM functionality of the TSQ Quantum GC to detect low levels in this technique. This was due to both the sensitivity requirements and the matrix that is also

FIGURE 4. Calibration curve data for compounds studied. Curves were from 0.1 to 10 ppb with greater than 0.995 r^2 values.

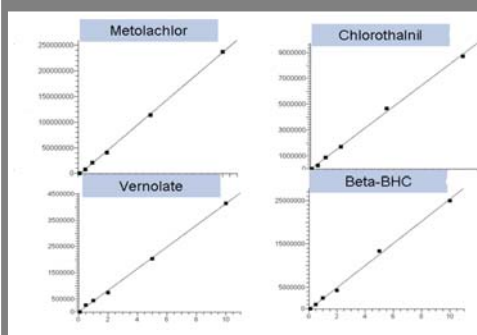
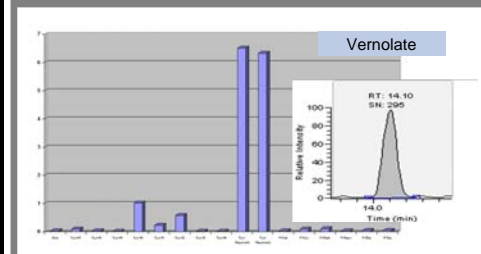


FIGURE 5. Samples of tea were analyzed and data showing vernolate found in tea, at concentrations just over 6 ppb.



forced into the headspace. The potential cost savings for the laboratory range to approximately 158,000/year depending on sample load.

The calibration curves showed at least 0.99 or greater r^2 correlation coefficient values. The tea samples that were tested showed vernolate at values of just over 6 ppb. This is below any MRL for this compound in this matrix but it does show the sensitivity of SPME sampling technique with the TSQ Quantum GC in this typically very challenging matrix.

Although this technique provided good calibration curves and interesting data in several types of sample there remains more work to do. Future work will entail reproducibility studies, efficiency in analyzing the pesticides, robustness studies, and different matrices.

FIGURE 6. Compound classes that were studied in coffee, tea, and vegetables.

Chemical Class	Pesticide
Explosive	2,4-Dinitrotoluene, 2,6-Dinitrotoluene
Organochlorine	alpha-BHC, beta-BHC, Aldrin, delta-BHC, Endosulfan-I, Endosulfan-II, Heptachlor, gamma-BHC, gamma-Chlordane
Chloroacetamide	Alachlor, Metolachlor
Triazine	Ametryn, Atraton, Cyanazine, Metribuzin, Prometon, Propazine, Simazine, Simetryn
Thiocarbamate	Butylate, Cycloate, EPTC, Molineate, Pebulate, Vernolate
Substituted benzene	Chloroneb
Carbamate	Chlorpropham
Pyrethroid	cis-Permethrin, trans-Permethrin
Organophosphate	Dichlorvos, Methyl-parathion, Mevinphos, Terbufos
Amide	Diphenamid, Proxamide
Thiazole	Etridiazole
Pyridazinone	Norflurazon
Uracil	Terbacil
2,6-Dinitroaniline	Trifluralin
Azole	Triadimefon
Unclassified herbicide	Fluridone

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