Application Note No. 053

Multi-Residue Scanning for Pesticides in Fruit and Vegetables Using On-Line Clean-up GC-MS

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Introduction

Pesticides, insecticides, fungicides and herbicides are agrochemicals designed to combat the attacks of various pests on agricultural and horticultural crops. Due to the ever-lower detection levels required by regulatory bodies and the complex nature of the matrices in which the target compounds are entrained, efficient sample preparation, trace-level detection and identification are important aspects in analytical method development. In the case of pesticides in vegetables and fruit, the maximum residue levels that are set by government agencies and the European Union are in the range of 100-1000 µg/kg. Method development is focused on achieving the detection of 10-50 µg/kg, but 5-10 µg/kg is preferred.

The ATAS Vision for automated SPE was interfaced to the GC/MS using the OPTIC 2 programmable injector in large volume injection mode as shown in Figure 1.
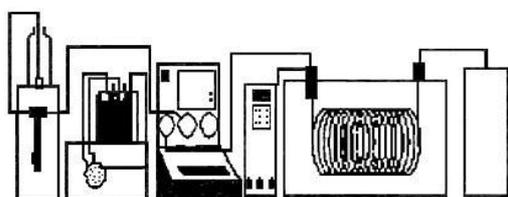
Figure 1: *System Diagram:*   *(1) HPLC pump*
(2) Solvent delivery unit
(3) PROSPEKT
(4) OPTIC 2 Programmable Injector
(5) HP6890 GC
(6) HP5973 MSD

Apples, cabbage and potatoes were used as representatives of the food classes to be examined by this technique. Samples were chopped, macerated and extracted with ethyl acetate. The extracts were then spiked with pesticide mixes to correspond to the Maximum Residue Levels and an order of magnitude above and below this level to represent gross contamination and the lower levels of interest respectively. The ethyl acetate extracts were presented to the Vision.

The mixed pesticide standards were analysed on the GC/MS to determine the optimum GC, Optic and Vision conditions for this application. Optimisation of the Optic included establishing the maximum volume to be injected, the solvent venting time and the temperature programming. The the washing steps of the cartridges of the Vision were optimised.

Instrumentation & Conditions

- Hewlett-Packard HP6890 & HP5973
- ATAS OPTIC2-200 programmable injector
- ATAS Vision system with: MIDAS auto-sampler, Prospekt, solvent delivery unit and HPLC pump

The column used was an HP5-MS 30m x 0.25mm i.d. x 0.25 µm film. An ATAS 'A' Type liner was used for a 50 µL injection volume. Large volume mode was used with autovent at 100 mL/min , purge pressure 25 kPa and a solvent threshold of 50. The initial temperature was 45 °C then ramped to a final temperature of 350 °C at a rate of 6 °C/s. The split open time was 3 minutes, with a split flow of 50 ml/min. The transfer pressure was 50 kPa for 3 minutes then ramped to a final pressure of 170 kPa.

The GC oven was ramped from an initial temperature of 40 °C (hold time 3 minutes) to a final temperature of 350 °C (hold time 5.5 minutes) at a rate of 20 °C/min. The MSD was in scan mode with a solvent delay of 6.5 minutes.

The Vision used SPARK disposable cartridge 10 mm x 2 mm cyanopropyl.

Clean-up Method Principles

- Cut vegetable or fruit into small pieces without any pretreatment such as washing or removing their skin.
- Ground the sample in a blender.
- Extract the sample with ethyl acetate and spike accordingly with the pesticide mix.
- Solvate the cartridge with ethyl acetate
- Transfer 25µl of the ethyl acetate extract to the Optic packed liner via the cartridge then through a fused capillary transfer line at a rate of 100 µl/min
- Vent the solvent in large volume mode
- Transfer the analytes on to the GC column by temperature programming the injector

Interfacing the Clean-up with GC

On combining the clean-up with the GC the most important parameters were found to be:
- The internal volume of the Vision-GC line
- The internal volume of tubing at the valves
- The rate of transfer of the eluent to the cartridge and into the GC

It was established that carryover was dependent on the length of time the line was purged for. Increasing the purge time or purge flow eliminated this problem. The Vision valve connections to carry out on-line coupling are shown in Figure 2.

Figure 2: *VISION valve configuration for injection into a GC with Optic2 injector*
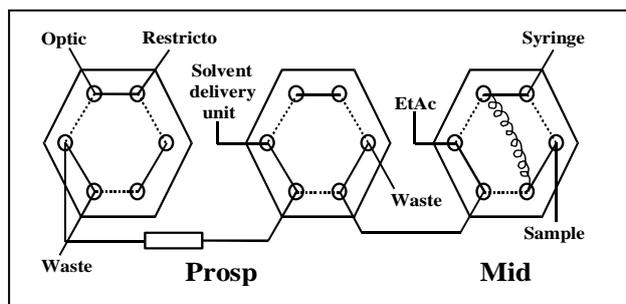
Compound list

The pesticide mixture present in the spiking solutions and analysed by this method.

Aldrin	Endosulphan A	p,p-DDE
α-HCH	Endosulphan B	p,p-DDT
Atrazine	Endrin	Parathion-ethyl
Azinphos-methyl	EPTC	Pendamethalin
β-HCH	Fenitrothion	Phosalone
Bifenox	Fenpropidin	Prometryn
Bromacil	Fenpropimorph	Propazine
Carbendazim	Fluaz-p-butyl	Propetamphos
Carbophenothion	Flutriafol	Propiconazole
Chlorfenvinphos	HCB	Propyzamide
Chloridazon	HCBD	Quintozene
Chlorpyriphos	Heptachlor	Simazine
Chlorthalonil	Heptachlor epoxide	Tecnazene
cis-Chlordane	Iprodione	Terbuthylazine
Cyanazine	Isodrin	Terbutryn
δ-HCH	Lindane	trans-Chlordane
Desmetryn	Malathion	Triademefon
Diazinon	Methoxychlor	Triallate
Dichlobenil	o,p-DDD	Triazophos
Dichlorvos	o,p-DDE	Trietazine
Dieldrin	o,p-DDT	Trifluralin
Dimethoate	Oxadixyl	

Chromatograms
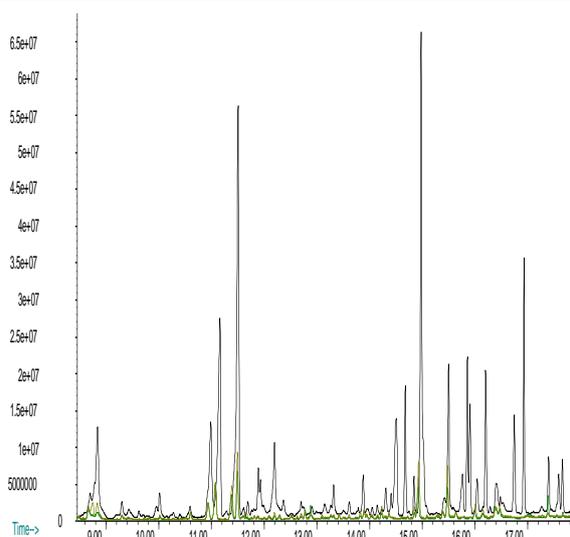
Figure 3: TICs of cabbage samples spiked at ~10 ppb individual OC and OP pesticides
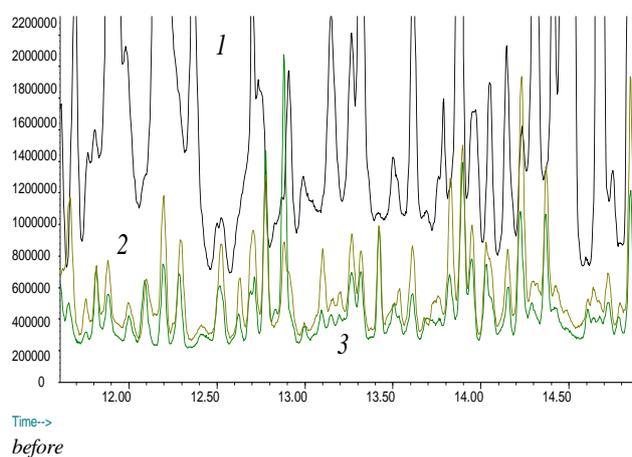
Figure 4: Cabbage TICs before and after online clean-up: (1) before online clean-up (2) after online clean-up + spiked at ~10 ppb OC/OP pesticides (3) after online clean-up

Conclusions

The Vision system has demonstrated to be a suitable instrument for the on-line clean-up of vegetable and fruit extracts in the detemination of pesticides using large volume injection gas chromatography mass spectrometry. The system is fully automated, resulting in cost saving, and gives better analytical data, due to far less manual sample handling.

Acknowlegements