Determination of Polar Organophosphorus Pesticides in Vegetables Using Automated SPE Clean-up and GC-FPD Detection

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Introduction

Size Exclusion Chromatography (SEC) has been used at SASA as a single, universal clean-up procedure for pesticides in fruit and vegetable extracts prior to multi-residue analysis by GCMS and GC-FPD. However, the extent of clean-up achieved for certain vegetables such as leek, cauliflower and cabbage is unsatisfactory for the determination of polar organophosphorus insecticides. Co-extracted materials cause adverse effects when deposited on the retention gap interfering with chromatographic transmission, and co-elution with analytes interferes with the detection process. Inconsistent chromatography and variability in responses occur, leading to difficulties in the analyte identification and quantification processes, and achievement of required reporting levels. Here we report an alternative automated solid phase extraction (SPE) clean-up that, combined with capillary GC-FPD determination, facilitates the screening of polar OP pesticides.

Experimental

Target Analytes

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>(n=3)</th>
<th>Mean (%), RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methamidophos</td>
<td>68</td>
<td>64</td>
</tr>
<tr>
<td>acephate</td>
<td>77</td>
<td>77</td>
</tr>
<tr>
<td>monocrotophos</td>
<td>69</td>
<td>76</td>
</tr>
<tr>
<td>dimethoate</td>
<td>78</td>
<td>76</td>
</tr>
</tbody>
</table>

Extraction:

Solvent extraction using ethyl acetate with anhydrous sodium sulphate and sodium hydrogen carbonate.

Clean-up:

a) SPE  Gilson ASPEC automated SPE system, with Sep-Pak Vac 3cc (500mg) silica cartridges (Waters).

b) SEC  Gilson 232-XL/402 automated system, with Environsep-ABC column and ethyl acetate/cyclohexane (1:1 v/v mobile phase).

Chromatographic Parameters:

Instrument:  Agilent 5890GC System with Flame Photometric Detector (P mode).

Column:  DB1301 30m x 0.32mm I.D., 1 µm film.

Retention Gap:  deactivated fused silica 1m x 0.53mm I.D.

Carrier Gas:  Helium, 40cm/sec, constant linear velocity.

Injection Mode:  Cool On-column, injection volume 1µl.

Injector Temp. Prog:  50ºC(1min) increasing @ 140ºC to 275ºC(16min).

Oven Temp. Prog:  50ºC(0.2min) increasing @ 30ºC/min to 205ºC, increasing @ 50ºC/min to 275ºC(10min).

Detector Temp:  275ºC.

Results and Discussion

A manual SPE procedure using a silica cartridge that had been applied to OPs in peppers was found to provide a reasonable clean-up for leek and cauliflower extracts. Migration of this procedure to the ASPEC system necessitated use of a Sep Pak Vac 3cc (500 mg) cartridge in place of the original Sep Pak Classic (650 mg) cartridge. Initial tests produced low recovery values for all analytes, especially dimethoate (~5%). Further investigation demonstrated that target compounds were not fully retained on the Sep Pak Vac cartridge when the wash solvents were passed through prior to intended elution. The composition of solvents for cartridge conditioning and for the washes were varied experimentally to control retention. Optimised conditions for automated operation were established (Table 1). Chromatograms comparing the effectiveness of SEC and automated SPE clean-ups on an extract from a fortified leek sample are shown in Figure 1.

The procedure was validated by testing fortified organic vegetables. Recovery data for leek and cauliflower (Table 2) were comparable with those generated using the manual SPE method. With the exception of acephate in leek (at 0.01 mg/kg), acceptable recoveries (≥ 60%) were obtained for all target analytes.

Automation allowed the clean-up step to be conducted unattended and released about 4.5 hours of Analyst time per analytical batch (~38% of the total input for the assay).

Conclusions

- Automated SPE provides simple and effective clean-up for 'difficult' matrices.
- Peak assignment and quantification improved in all cases.
- Recoveries acceptable for screening purposes.
- Analyst inputs significantly reduced.
- Overall process more cost efficient.

References:

1. Lindsay, D.A., and Blackie, C., Personal communication