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# Elimination of Non-Volatile Sample Matrix Components After GC Injection using a Thermal Desorber and Microvial Inserts

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## Abstract
GC analysis of complex sample types containing non-volatile materials normally requires extensive sample preparation and cleanup prior to injection to eliminate the interference from non-volatile components. Accumulation of non-volatile matrix components in the inlet and at the head of the GC column can lead to generation of active sites, analyte degradation, poor quantitation due to suppressed or enhanced analyte response and deterioration of chromatographic performance.

In this study we describe direct liquid injection techniques compatible with “dirty” samples containing non-volatile components. Using a glass liner that can be removed and replaced after the injection can eliminate interference from accumulated sample matrix components. Liners are designed to accommodate larger than normal liquid injection volumes to provide improved detection limits. Furthermore, the entire process including the liner exchange can be automated.

To illustrate the utility of the technique, challenging liquid sample types such as samples prepared by the QuEChERS method for pesticide analysis and contaminated motor oils were repeatedly introduced into the GC. Chromatographic performance using the new sample introduction technique is compared to conventional injections into a hot inlet.

## Introduction

Direct sample introduction after minimal cleanup has been demonstrated for determination of pesticides in a number of challenging matrices [1, 2] . This approach offers the possibility to minimize or eliminate much of the labor and cost associated with routine analyses without sacrificing detection limits or data quality.

Up to now this technique has been performed by injecting liquid samples or extracts directly into the inlet liner or into a glass microvial inserted into the inlet liner under conditions that allow removal of solvents without loss of analytes. After solvent elimination, the analytes are transferred to the column by heating the inlet under conditions that hopefully minimize matrix decomposition and leave most low volatility matrix components behind. The inlet liner containing the matrix contaminants can then be removed and replaced with a new liner prior to the next sample. This process offers limited control of conditions for solvent elimination and analyte transfer, and may not offer a solution for low volatility viscous liquids containing volatiles of interest such as petroleum products or vegetable oils.

We describe here a technique that allows automated liquid injection into a glass microvial that can be heated in a compact thermal desorber coupled to a cooled GC inlet where analyte refocusing occurs. This configuration allows optimization of inlet conditions for solvent venting, analyte refocusing and transfer to the column independent of the presence of matrix components.

## Experimental

*Instrumentation.* Analyses were performed on a 6890 GC equipped with a 5975 mass selective detector (Agilent Technologies), PTV inlet (CIS 4, GERSTEL) and MPS 2 robotic sampler with TDU option (GERSTEL).

*Analysis conditions pesticides.*

| | |
|---|---|
| TDU: | splitless<br>20°C; 300°C/min; 100°C (3 min);<br>720°/min; 325°C (4 min) |
| PTV: | 0.2 min solvent vent (50 mL/min)<br>splitless<br>-10°C; 12°C/s; 280°C (0.5 min);<br>12°C/s; 325°C (5 min) |
| Column: | 30 m HP-5MS (Agilent)<br>$d_i$ = 0.25 mm $d_f$ = 0.25 µm |
| Pneumatics: | He; $P_i$ =10.6 psi;<br>constant flow = 1.2 mL |
| Oven: | 65°C (2 min); 20°C/min;<br>300°C (10 min) |

*Analysis conditions motor oil.*

| | |
|---|---|
| TDU: | splitless<br>40°C; 100°C/min; 100°C (5 min) |
| PTV: | 0.2 min solvent vent (50 mL/min)<br>split 50:1<br>-125°C; 12°C/s; 280°C (3 min) |
| Column: | 30 m HP-5MS (Agilent)<br>$d_i$ = 0.25 mm $d_f$ = 0.25 µm |
| Pneumatics: | He; $P_i$ = 9.05 psi;<br>constant flow = 1.2 mL |
| Oven: | 40°C (2.5 min); 15°C/min;<br>300°C (5 min) |

*Sample Preparation Pesticides.* Analyte protectant solution: A stock solution of 40 mg/mL 3-ethoxy-1,2-propanediol (Aldrich, Part# 260428), 4 mg/mL L-gulonic acid γ-lactone (Aldrich, Part# 310301) and 4 mg/mL D-sorbitol (Aldrich, Part# 240850) was prepared in 7/3 $H_2O$/MeCN.

Vegetable extracts and a composite standard of 44 pesticides prepared at a concentration of 2 ug/mL in MeCN and 0.1% HOAc were provided by Kate Maštovská, USDA. The samples were prepared following the buffered QuEChERS method [3].

The pesticide standard was diluted to obtain a concentration of 10 ppb in 1000 uL of the vegetable extracts. 25 uL of the analyte protectant solution was added to the working pesticide standard and extracts. 10 uL of sample was then added to the TDU microvial either manually or using the MPS 2 autosampler.

*Sample Preparation Motor oil.* Motor oil and used motor oil were analyzed directly. Gasoline was spiked into unused motor oil at a level of 0.5% by volume. Motor oil was introduced into the TDU microvial either manually (5-7 mg) or using the MPS 2 autosampler (1µL).

## Results and Discussion

The instrumentation used for this analysis includes a GERSTEL TDU thermal desorption unit designed for sample introduction in combination with Stir Bar Sorptive Extraction (SBSE) and for short-bed adsorbent tubes. Glass microvials (approximately 200 uL capacity) were inserted into clean thermal desorption tubes to allow introduction of liquid samples into the vertical thermal desorption system (Figure 1).

**Figure 1.** TDU empty tube with microvial.

***QuEChERS pesticide samples.***

Initial studies were conducted by introducing 10 uL of sample into the TDU microvial manually with a 10 uL syringe.

Figures 2A and B show the chromatographic profiles of a spinach extract spiked with a pesticide mix collected using the synchronous SIM/Scan mode on the Agilent 5975MSD. The SIM method was created to allow identification of the pesticides in the spinach matrix.

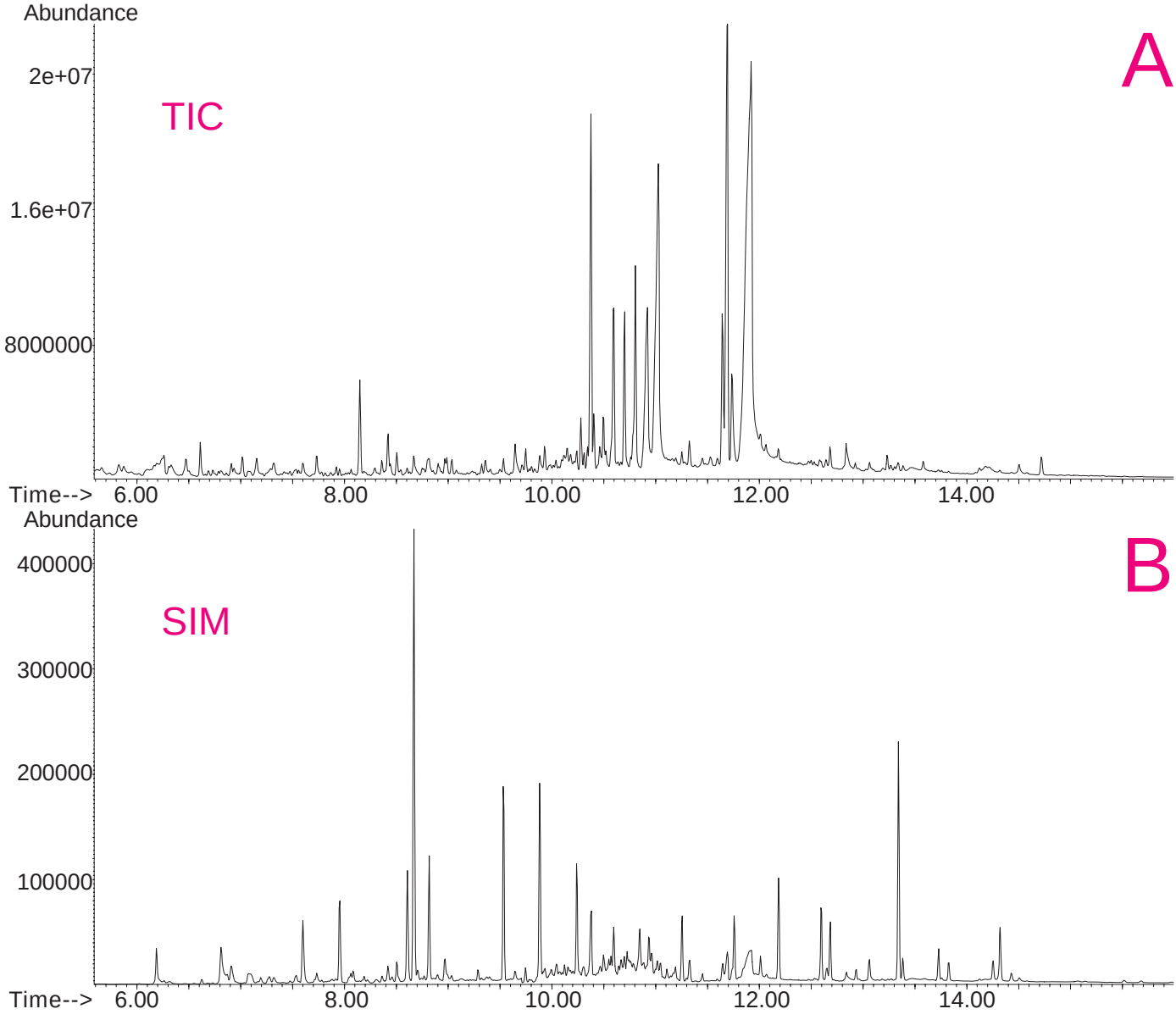


**Figure 2.** TIC (A) and SIM (B) of spiked spinach extract.

Figures 3A and B show overlays of replicate pesticide -spiked carrot extracts analyzed in synchronous SIM/Scan mode. Excellent reproducibility was obtained using this technique. In Figure 3B the compounds of interest are numbered and these are identified in Table 1. Twenty of the 44 pesticides present in the sample were profiled for the purposes of this study.

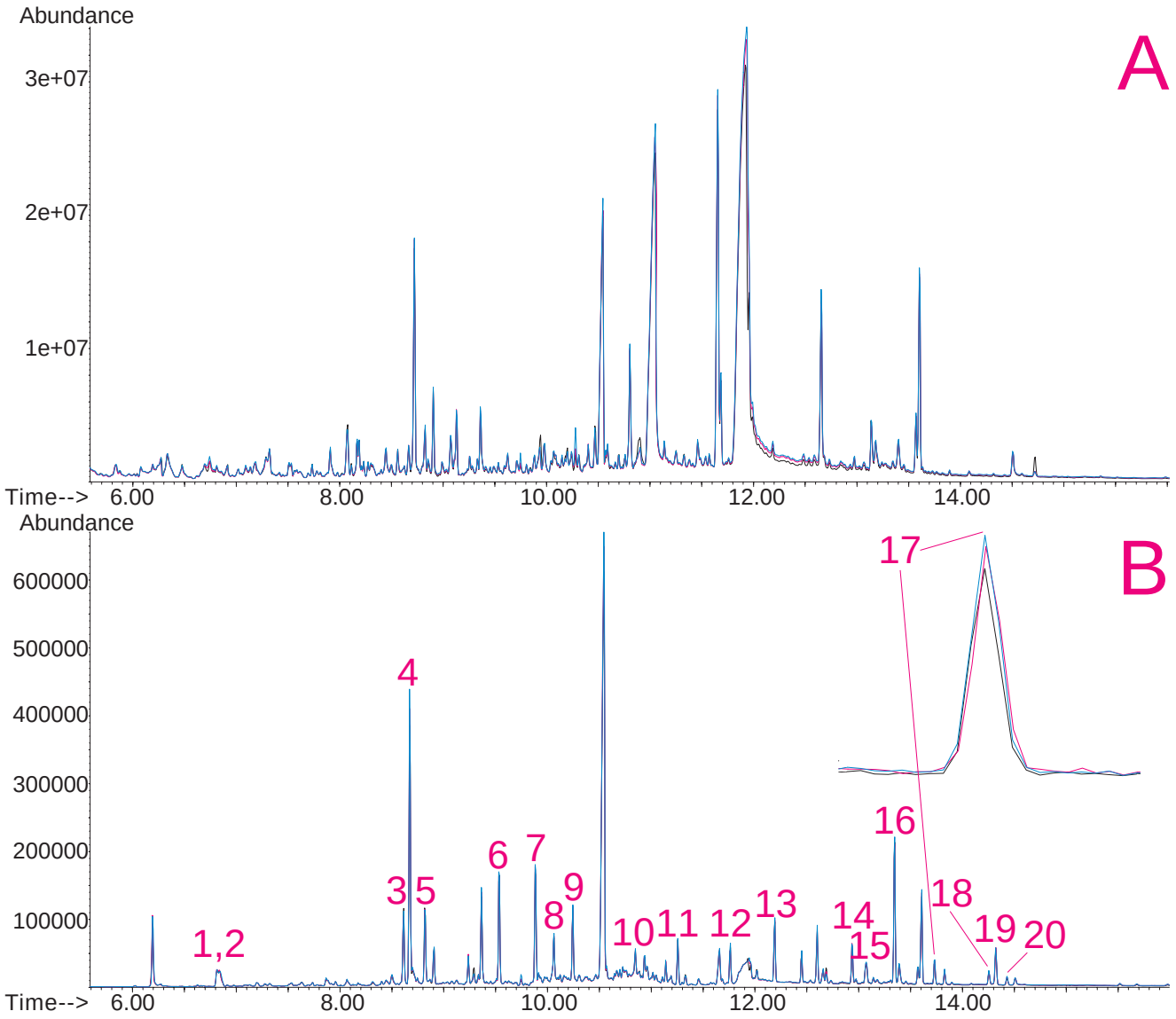


**Figure 3.** TIC (A) and SIM (B) overlay of replicate spiked carrot extracts with enhanced view of Phosalone (B).

**Table 1.** List of pesticides

| No. | Compound | R.T. [min] | Quant Ion | Area RSD[1] [%] |
|---|---|---|---|---|
| 1 | Dichlorvos | 6.814 | 109 | 3.75 |
| 2 | Methamidophos | 6.840 | 94 | 4.51 |
| 3 | Carbaryl | 8.614 | 144 | 3.30 |
| 4 | o-Phenylphenol | 8.674 | 170 | 3.27 |
| 5 | Methiocarb | 8.822 | 168 | 3.95 |
| 6 | Trifluoralin | 9.536 | 306 | 3.94 |
| 7 | Hexachlorobenzene | 9.886 | 284 | 4.64 |
| 8 | Lindane | 10.150 | 219 | 2.46 |
| 9 | Diazinon | 10.245 | 179 | 2.15 |
| 10 | Heptachlor | 10.909 | 272 | 2.46 |

| No. | Compound | R.T. [min] | Quant Ion | Area RSD[1] [%] |
|---|---|---|---|---|
| 11 | Chlorpyrifos | 11.257 | 197 | 3.40 |
| 12 | Procymidone | 11.761 | 96 | 3.30 |
| 13 | p,p-DDE | 12.191 | 246 | 2.69 |
| 14 | o,p-DDT | 12.938 | 235 | 6.30 |
| 15 | Tebuconazole | 13.067 | 125 | 4.15 |
| 16 | Bifenthrin | 13.348 | 181 | 3.76 |
| 17 | Phosalone | 13.734 | 182 | 7.83 |
| 18 | Permethrin I | 14.256 | 183 | 5.07 |
| 19 | Permethrin II | 14.232 | 183 | 2.42 |
| 20 | Coumaphos | 14.432 | 362 | 11.5 |

[1]n=3

Figure 4 shows a TIC overlay of the initial desorption and redesorption of a pesticide spiked carrot extract from the TDU microvial illustrating absence of carryover from the sample. The minor peaks seen in the redesorption were present in the background and were not pesticides.

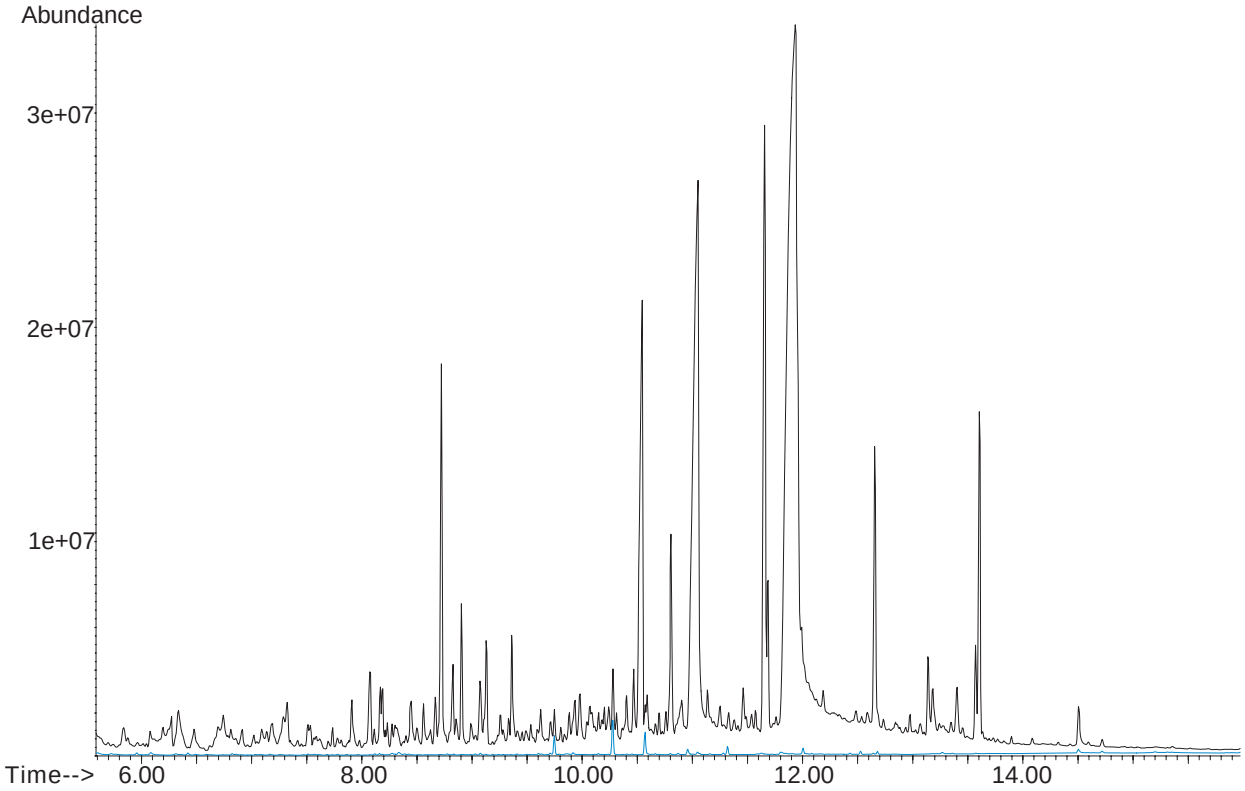


**Figure 4.** TIC overlay of initial desorption and redesorption of a spiked carrot extract sample.

Figure 5 shows an overlay (SIM) of automated injections of a 10 ppb pesticide standard and a carrot extract spiked at 10 ppb illustrating similar peak response for the components of interest when spiked into the carrot extract.

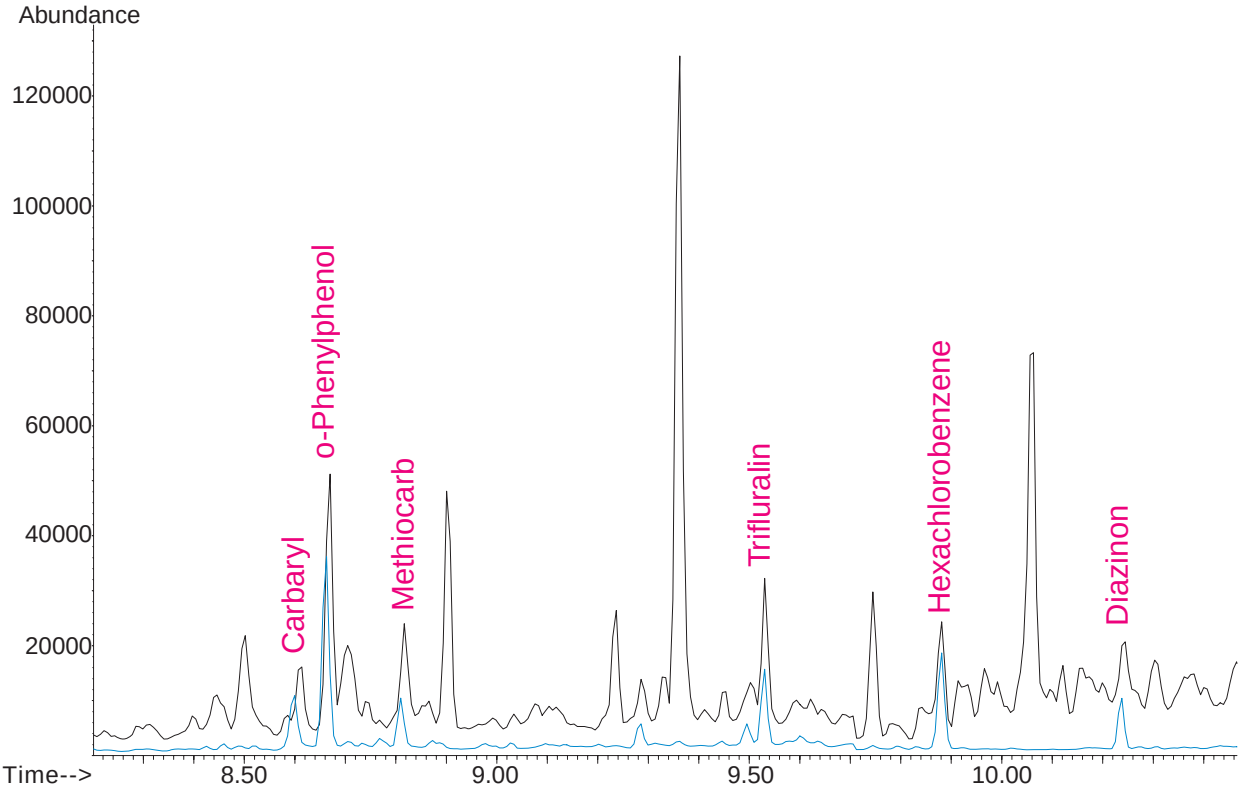


**Figure 5.** Overlay of 10 ppb pesticide standard and 10 ppb spiked carrot extract chromatograms – SIM mode.

***Motor oil***

Figure 6 shows an FID trace of a direct injection into the GC inlet of 1 uL of unused motor oil spiked with gasoline. The figure shows poor resolution of the gasoline range organic (GRO) peaks early in the chromatogram and a large peak from the motor oil eluting late in the chromatogram. The gasoline range peaks are not sufficiently resolved for good quantitation.

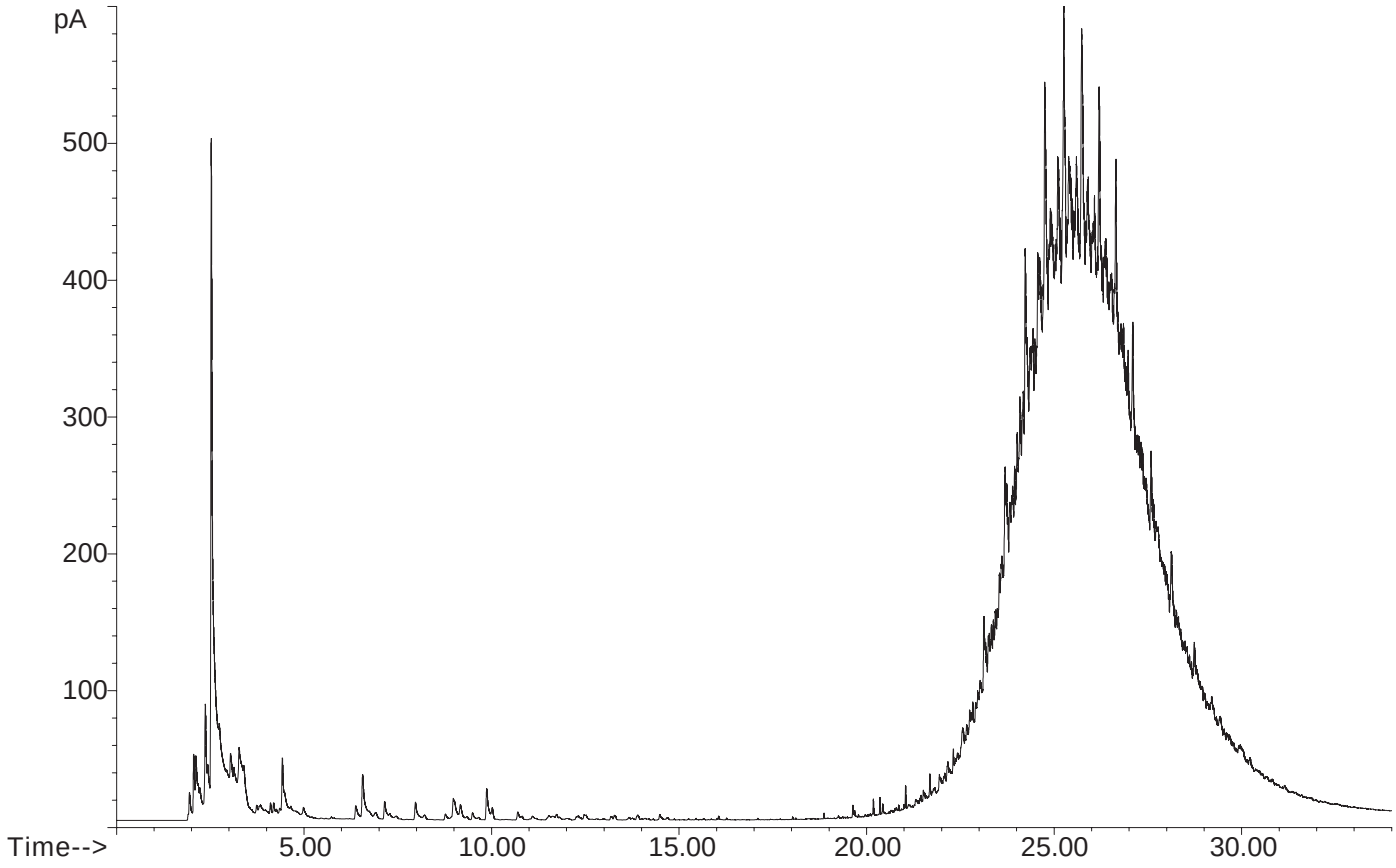


**Figure 6.** FID trace of direct liquid injection of motor oil spiked with 0.5% gasoline. 1uL direct injection, split 100:1.

Figures 7A and B show chromatograms of unused motor oil and unused motor oil spiked with 0.5% gasoline manually introduced into the TDU microvial. The GRO peaks evident in the 2-10 minute retention time range exhibit good response and peak shape. The amount of oil getting onto the column is minimized with this sample introduction technique. When sample introduction was automated the reproducibility for peaks in the gasoline range was less than 6% RSD for n=4. Figure 7C shows a blank TDU tube run immediately after the gasoline spiked motor oil on a 10x expanded scale. No carryover is seen in the resulting chromatogram.

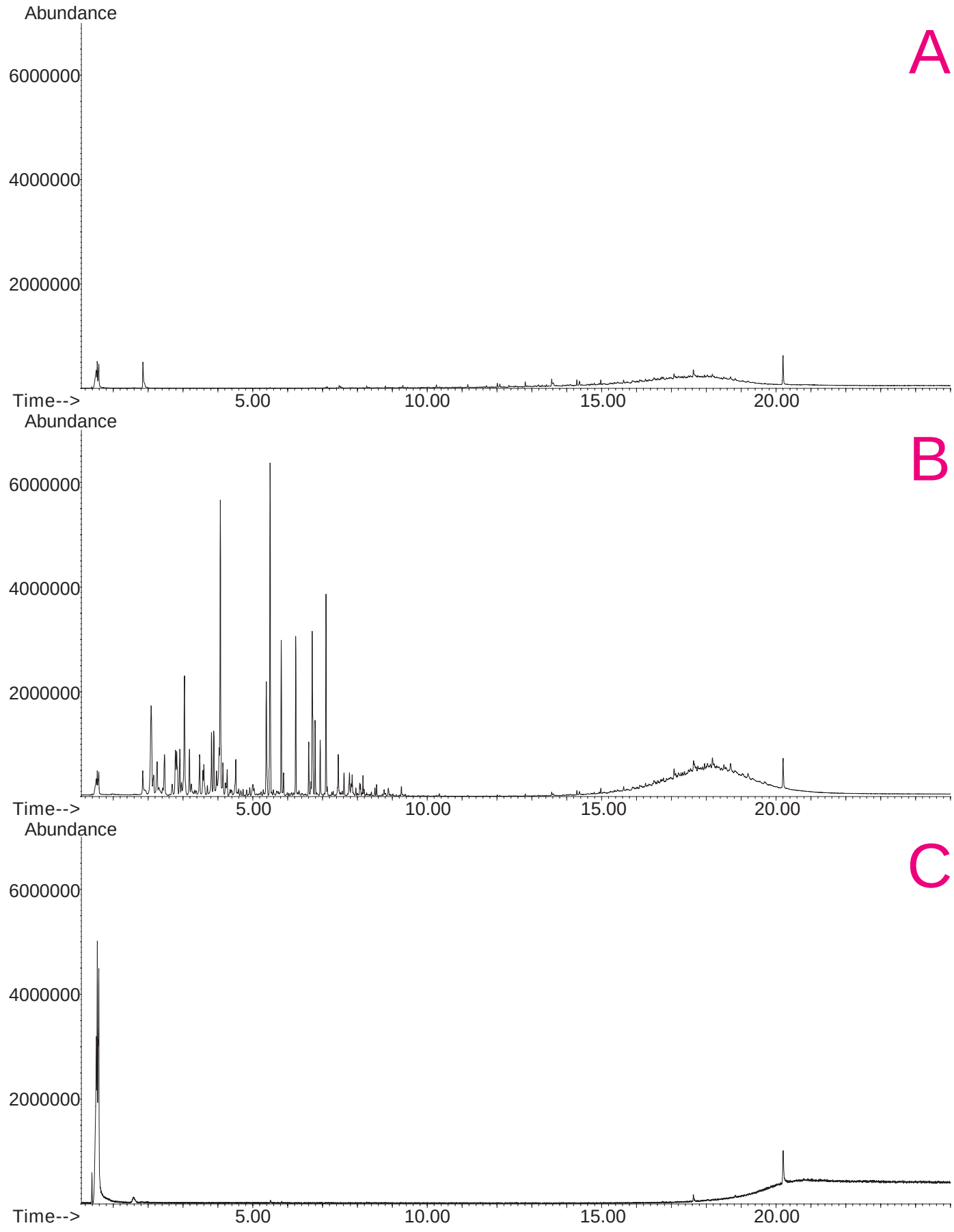


**Figure 7.** (A) TIC of unused motor oil, (B) TIC of unused motor oil spiked with 0.5% gasoline, (C) TIC of blank TDU tube analyzed immediately after spiked motor oil sample.

Figure 8 shows this sample introduction technique applied to the analysis of a used motor oil sample. It shows the presence of gasoline range compounds in this oil.

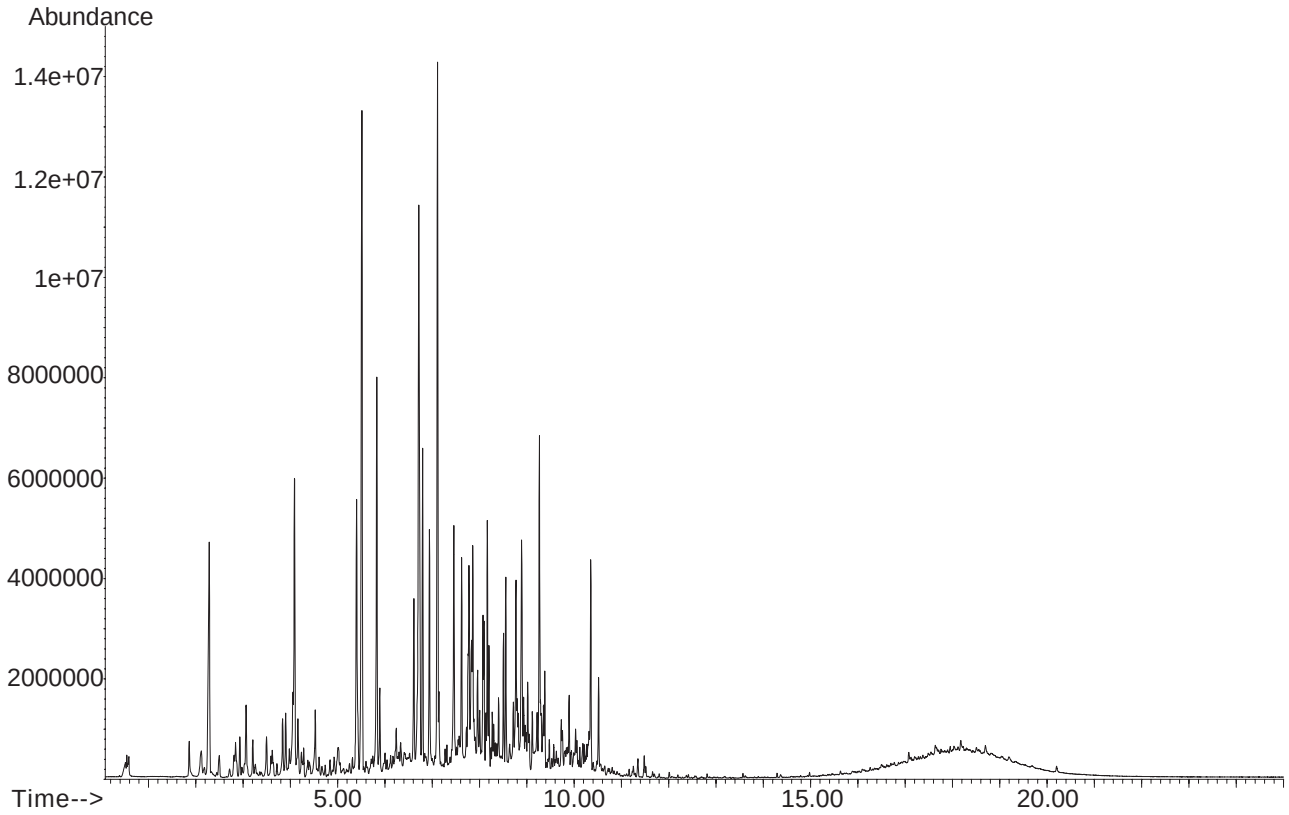


**Figure 8.** TIC of used motor oil.

Figure 9 shows a sample of olive oil manually introduced into the TDU microvial. Several components of interest were identified in the figure.

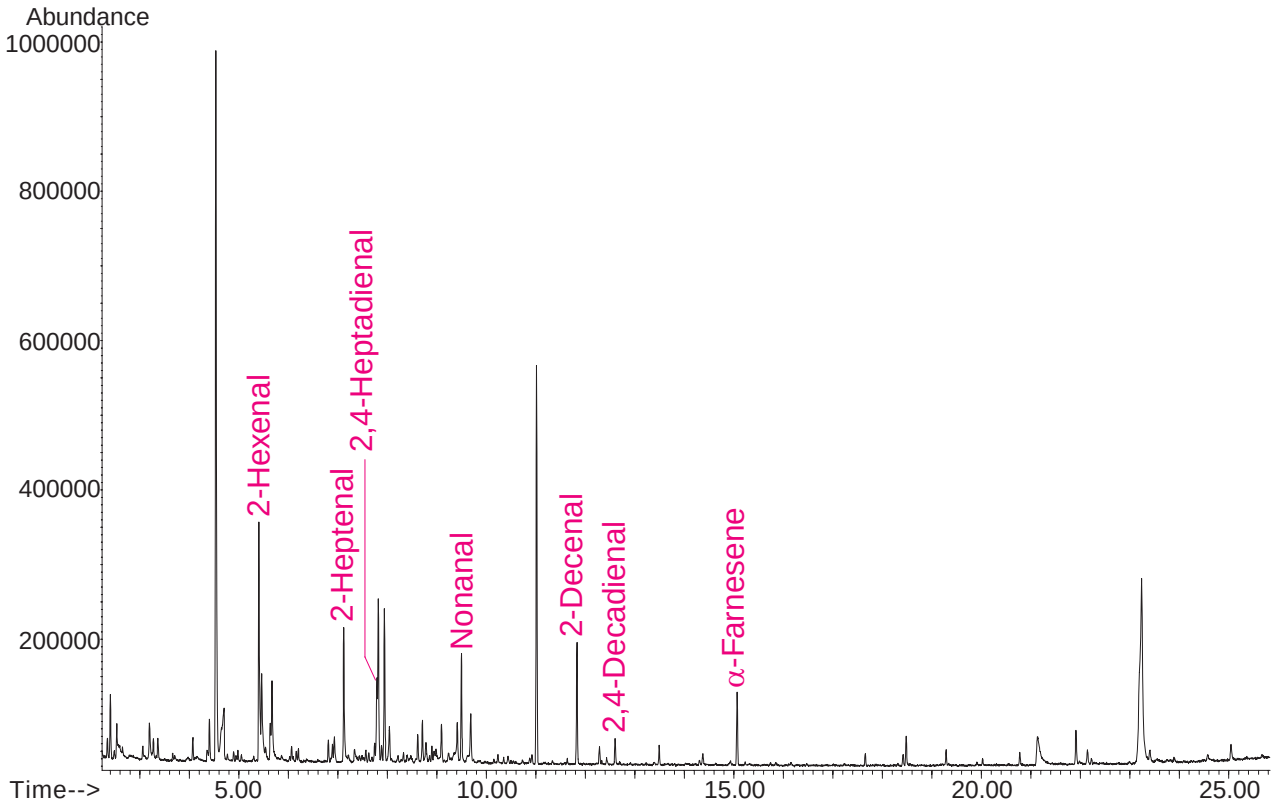


**Figure 9.** TIC of 9.3 mg of extra virgin olive oil.

## Conclusions

The compact GERSTEL TDU thermal desorber can be configured with a glass microvial to allow direct analysis of liquid samples. Furthermore, it is possible to use transport adapters with septum seals to automate liquid introduction into the microvials using the MPS 2 robotic autosampler.

Two types of liquid samples were used to demonstrate the viability of this technique: Vegetable extracts prepared using the buffered QuECHERS method and spiked with a pesticide mix were used to illustrate the removal of extraction solvent followed by thermal transfer and separation of the pesticides with good reproducibility. Non-volatile matrix components were left behind in the disposable microvial without contaminating the inlet or column.

Extra virgin olive oil, and motor oil containing gasoline range organics were used to illustrate the direct thermal extraction of volatiles from viscous, high boiling liquids with good reproducibility and no carryover or contamination of the inlet or column. The oil matrix was left behind in the disposable microvial.

## References


[1] K. Maštovská, S.J. Lehotay, M. Anastassides Anal. Chem. (2005) 77, 8129-8137

[2] S.J. Lehotay, A.R. Lightfield, J.A. Harmon-Fetcho, D.J. Donoghue J. Agric.Food Chem. (2001), 49, 4589-4596

[3] T. Cajka, K. Maštovská, S. J. Lehotay, and J. Hajslova, J. Sep. Sci. 2005, 28, 1048-1060.


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