Better Pesticide Analysis with Agilent J&W Ultimate Plus Tubing in an Inert Flow

Application Note

Food Testing and Agriculture

Author

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Abstract

Fast, sensitive, and reproducible analysis of pesticides in food and drink using GC/MS remains a great challenge for food testing laboratories. The susceptibility of highly sensitive compounds to active sites in the instrument flow path can result in poor peak shape, poor reproducibility, and significant loss of sensitivity. Agilent J&W Ultimate Plus deactivated fused silica tubing has great potential in contributing to an inert flow path for reliable analysis of pesticides at trace levels. This application note provides a detailed evaluation of Ultimate Plus versus another supplier's tubing, promoted as having superior performance. Tubing was used as a GC restrictor for MS in the analysis of a pesticide checkout mixture. Ultimate Plus tubing delivered good peak shapes and significant response improvements for most analytes, especially challenging compounds susceptible to active sites on the surface of deactivated fused silica tubing.

Introduction

Modern GC/MS instruments have been widely used for monitoring many pesticides in food applications [1,2]. The presence of reactive functional groups in pesticides, for example hydroxyl (–OH), amino (R–NH–), carbamate (–O–CO–NH–), or organophosphate (–P=O), are prone to interact with silanol groups on the surface of fused silica columns and tubing. These sensitive compounds are susceptible to adsorption or degradation onto active surfaces in the sample flow path from injector to detector, resulting in poor peak shape and significant loss of sensitivity and reproducibility [3,4]. Trace analysis of these compounds, therefore, remains a great challenge for food analysts.

Agilent Technologies

Agilent introduced GC/MS coupled with inertness-verified consumables in the flow path to provide considerable advantages for reliable analysis of these challenging active substances at very low levels. The inertness performance of the flow path components that directly contact analytes has been improved to provide excellent peak shape, high sensitivity, and reproducible, reliable results.

Previous work focused on inertness improvements of liners, Ultimate Union, GC columns, and ferrules [3,4,5,6]. This application note focuses on deactivated fused silica tubing used as a GC restrictor for MS in the analysis of a pesticide checkout mixture. The use of restrictor tubing provides a fast and convenient analysis because it allows users to quickly change the analytical columns without turning off the high vacuum of the MS. The tubing is in direct contact with the analytes and, therefore, is a key component of the inert flow path, which requires high inertness performance to avoid adsorption or degradation of susceptible compounds. We evaluated the performance of Ultimate Plus tubing by comparing it with tubing from another supplier, using the same instrumental conditions to provide a fair comparison.

Experimental

The pesticide checkout standard at nominal concentration of 10 ng/µL was supplied by Agilent Technologies, Inc. (Santa Clara, CA) and contained 20 compounds in acetone (p/n 5190-0468) (Table 1). Acetone used as blank or dilution of standards was purchased from Sigma Aldrich, Corp. (Zwijndrecht, The Netherlands) at analytical grade. The 10 ng/µL of the original standard was directly used for injection. In addition, this standard was diluted two times and five times with solvent to concentrations of 5 and 2 ng/µL, respectively, for GC/MS analysis.

Instrumentation

The experiments were performed on an Agilent 7890A GC system equipped with an Agilent 5975C MSD with triple-axis detector, and an Agilent G4513A autosampler. The experimental setup is shown in Figure 1. The analytical column was connected to deactivated fused silica tubing provided by Agilent or another supplier using an Agilent Purged Ultimate Union.

Table 1. Pesticide checkout standard (peak no. on chromatogram).

Peak no.	Pesticide	Retention time (min)
1	Dichlorvos	5.144
2	Mevinphos	6.304
3	Ethalfluralin	8.131
4	Trifluralin	8.244
5	Atrazine	9.157
6	Lindane	9.501
7	Chlorpyrifos methyl	10.47
8	Heptachlor	10.884
9	Malathion	11.113
10	Chlorpyrifos	11.317
11	p,p'-DDE	13.281
12	Dieldrin	13.516
13	Hexazinone	14.833
14A	Propargite (isomer A)	14.972
14B	Propargite (isomer B)	15.003
15	Leptophos	16.351
16	Fenarimol	16.897
17	Mirex	16.966
18	Coumaphos	17.548
19	Etofenprox	18.633
20	Deltamethrin	20.428

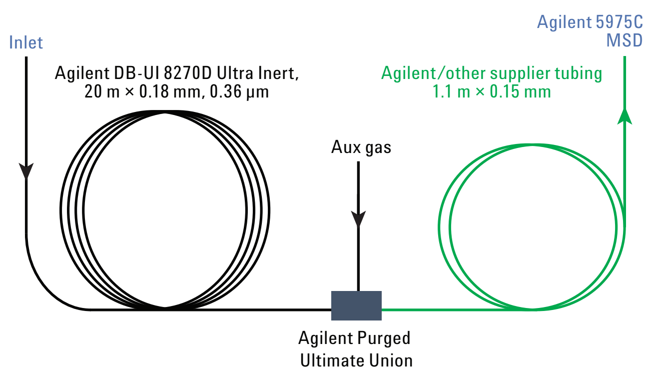

Figure 1. Experimental setup of an Agilent 7890A GC with an Agilent 5975C MSD for testing deactivated fused silica tubing.

Instrumental conditions

GC conditions

Column:	Agilent J&W DB-UI 8270D Ultra Inert, 20 m × 0.18 mm, 0.36 µm (p/n 121-9723)
Carrier:	He, constant flow, 1.0 mL/min
Inlet:	Splitless, 250 °C
Purge flow:	50 mL/min at 1.3 min
Oven:	60 °C for 1 min, to 170 °C at 40 °C/min, no hold, to 310 °C at 10 °C/min, hold 8.25 min
Aux EPC:	He plumbed to Agilent Purged Ultimate Union
Aux flow:	1.6 mL/min during run
Restrictor:	Inert fused silica tubing (1.1 m × 0.15 mm), Agilent J&W Ultimate Plus (p/n CP801505) or SilcoNert 2000
Pre- and post-injection solvent A (dichloromethane) washes: 3	
Pre- and post-injection solvent B (ethanol) washes: 3	
Sample washes:	2; sample pump, 3
Injection:	10 µL syringe (p/n 5181-1267), 1 µL injection volume

MSD conditions

Tune file:	Atune.u
EMV mode:	Gain factor 1 corresponds to voltage value of 1,282 V
Transfer line temperature:	310 °C
Source temperature:	250 °C
Quad temperature:	150 °C
Solvent delay:	3.4 min
Acquisition mode:	Full scan
Scan mass range:	50 to 550 amu

Flow path supplies

Vials:	Amber, screw cap (p/n 5182-0716)
Vial caps:	Blue, screw cap (p/n 5182-0717)
Vial inserts:	Glass, 150 µL, with polymer feet (p/n 5183-2088)
Septa:	Advanced Green non-stick, 11 mm (p/n 5190-3158)
Flow technology:	Self-Tightening column nut for Agilent inlet (p/n 5190-6194), for Agilent mass spec interface transfer line (p/n 5190-5233)
Ferrule:	Agilent Flexible Metal ferrule, 0.1 to 0.25 mm id (p/n G3188-27501)
Ferrule for inlet and mass spec interface:	0.4 mm id, 85/15 Vespel/graphite (p/n 5181-3323)
Union:	Agilent Ultimate Union kit, deactivated (p/n G3182-61580)
Inlet liners:	Agilent Ultra Inert deactivated single taper splitless liner with wool including O-ring (p/n 5190-2293)

Results and Discussion

Figure 2 shows the total ion current (TIC) chromatogram of the pesticide checkout mixture containing 20 components at a nominal concentration of 10 ng on-column for each substance. Ultimate Plus deactivated fused silica tubing was the GC restrictor for the MS interface. All 20 analytes were well identified and quantified with excellent peak shapes and responses within an analysis time of less than 21 minutes. In addition, all 20 target analytes exhibited good resolution with sharp symmetrical peaks. Propargite was found in two isomers. Organophosphorus and organochlorine compounds such as mevinphos, atrazine, and dieldrin are good indicators for the inertness performance of deactivated fused silica tubing due to their strong adsorption or degradation onto active sites on the surface of the tubing, resulting in tailing peaks and poor sensitivity. Figure 2 shows excellent peak shapes and strong responses for all target compounds, including these sensitive compounds. This indicates the improved inertness performance of Ultimate Plus deactivated fused silica tubing.

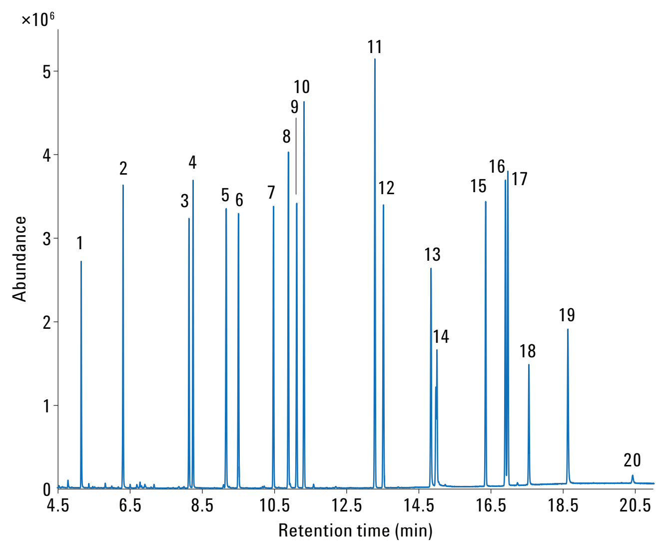

Figure 2. Total ion current chromatograms of 20 components in a pesticide checkout mixture at 10 ng on-column for each compound using Agilent J&W Ultimate Plus deactivated fused silica tubing (see Table 1 for peak IDs).

Figure 3 is an overlay of total ion current chromatograms of pesticides at 10 ng/component on-column when Ultimate Plus deactivated fused silica tubing (blue chromatogram) or another supplier's deactivated fused silica tubing (red chromatogram) was alternately installed as the GC restrictor. The experimental setup was the same for both tubing types to allow a fair comparison of their inertness performance. Figure 3 indicates that Ultimate Plus tubing improved inertness performance compared to tubing from another supplier. Good peak shapes and significant improvement in responses of all target compounds were found.

Figure 4 shows normalized peak areas of the pesticide checkout mixture at 5 ng/component and 2 ng/component on-column. Peak areas of all analytes were normalized to compound 6 (lindane) as a stable and inert component. The use of normalized peak areas instead of absolute values is advantageous in that it enables compensation for errors due to imperfect injection or dilution of the standard. Ultimate Plus tubing provided better compound responses for most analytes at the two different amounts. Figure 5 shows the percentage difference in responses of each compound from the two types of tubing, when responses from another supplier's tubing were set to 100%. This result clearly shows the improved inertness of Ultimate Plus tubing.

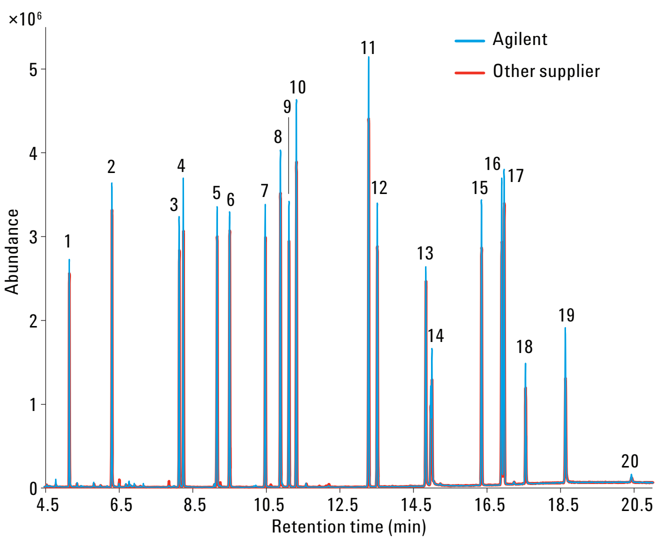

Figure 3. An overlay of total ion current chromatograms of a pesticide checkout mixture at 10 ng/component on-column when Agilent J&W Ultimate Plus and another supplier's tubing was alternately used as the GC restrictor for the MS interface (see Table 1 for peak IDs).

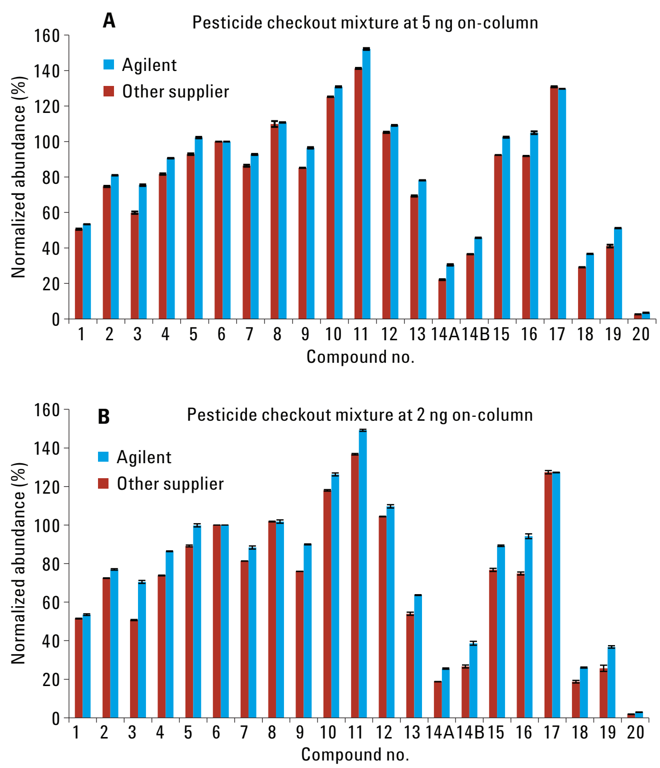

Figure 4. Normalized peak areas of duplicate injections of a pesticide checkout mixture at 5 ng/component on-column (A) or 2 ng/component on-column (B) with Agilent J&W Ultimate Plus deactivated fused silica tubing (blue bars) or deactivated fused silica tubing from another supplier (red bars) used as the GC restrictor. The peak areas of all compounds were normalized to compound 6, lindane. Full scan mode was selected for recording the MS signal. Compound 14 was present under two isomers, A and B (see Table 1 for peak IDs).

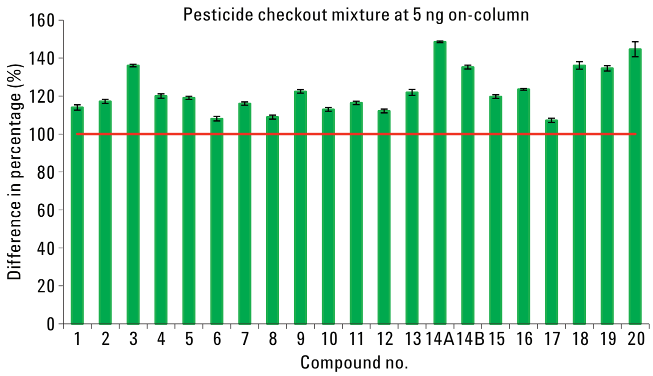

Figure 5. Analyte response comparison for Agilent J&W Ultimate Plus and another supplier's tubing. The results were based on the average response (duplicate injections) of 5 ng/component on-column of a pesticide checkout mixture using GC/MS in full scan mode. The response of each analyte for tubing from other supplier was set to 100%, and the response of each analyte was scaled for Ultimate Plus tubing (see Table 1 for peak IDs).

Conclusions

In an investigation of GC restrictors for MSD, we compared Agilent J&W Ultimate Plus deactivated fused silica tubing to premium-deactivated tubing from another supplier. Ultimate Plus tubing clearly delivered good symmetrical peak shapes and significant improvements in responses for most target compounds in a pesticide checkout mixture. Sensitive compounds such as organophosphorus and organochlorine pesticides were especially well resolved. These results are encouraging, and suggest that Agilent Ultimate Plus deactivated fused silica tubing plays a key role to delivering an inert flow path for fast, sensitive, and reproducible analysis of pesticides in food applications.

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