Analyze Semivolatiles with Agilent J&W Ultimate Plus Tubing in an Inert Flow Path

Application Note

Environmental

Author

Ngoc A Dang
Agilent Technologies, Inc.

Abstract

A fast and reliable analysis of semivolatile contaminants in environmental samples at trace levels remains a great challenge due to the broad variety of compounds and matrix complexity. Highly sensitive analytes often show poor peak shape, poor reproducibility, and significant loss of sensitivity because of their adsorption or degradation onto active sites anywhere in the instrument flow path. The reproducible and sensitive analysis of these compounds, therefore, requires an inert flow path from injector to detector. Agilent J&W Ultimate Plus deactivated fused silica tubing has great potential in contributing to an inert flow path. This application note provides a detailed evaluation of Ultimate Plus deactivated fused silica tubing versus tubing promoted as having superior performance from another supplier, as GC restrictors for MS in the analysis of a semivolatile checkout mixture. 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, provide evidence of better inertness performance from the Agilent tubing.

Agilent Technologies

Introduction

Trace analysis of a wide range of semivolatile (S-VOA) contaminants is of great interest in environmental samples. Modern GC/MS instruments have been widely used for monitoring many of these compounds in matrixes of different complexity [1]. The sensitive analytes of interest contain reactive functional groups, for example hydroxyl (-OH), amino (R-NH-), carbamate (-O-CO-NH-), or organophosphate (-P=O). These often show poor peak shape and reproducibility as well as low sensitivity. This is caused by their adsorption or degradation onto active surfaces in the sample flow path from injector to detector. Agilent successfully combined GC/MS with inertness-verified consumable components in the flow path. The system offers considerable advantages for reliable analysis of these challenging active substances at very low levels because it minimizes active sites. Previous work has focused on inertness improvements of GC columns, liners, Ultimate Union, and ferrules [2,3,4,5,6].

In this application note, we focus on deactivated fused silica tubing used as GC restrictors for MS for analysis of an S-VOA checkout standard. The use of restrictor tubing provides fast and convenient operation in which analysts can quickly change columns without turning off the high vacuum of the MS. However, high inertness of the restrictor tubing is required to minimize adsorption or degradation of susceptible compounds onto active sites on the surface of the tubing, because it comes into direct contact with analytes.

We compared Agilent deactivated fused silica tubing with tubing from another supplier using the same instrument conditions to provide a fair comparison.

Experimental

The S-VOA checkout standard at nominal concentration of 10 ng/µL was supplied by Agilent Technologies, Inc. (Santa Clara, CA). It consisted of 29 components in dichloromethane solvent (p/n 5190-0473) (Table 1). Dichloromethane used as blank or diluent of original standards was purchased from Sigma Aldrich, Corp. (Zwijndrecht, The Netherlands) at analytical grade. The 10 ng/µL of each original standard was directly used for injection. In addition, this standard was diluted two and five times with solvent to concentrations of 5 and 2 ng/µL, respectively, for GC/MS analysis.

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

Peak no.	Semivolatile	Retention time (min)
1	*n*-Nitrosodimethylamine	4.316
2	Aniline	6.959
3	1,4-Dichlorobenzene-d4	7.35
4	Isophorone	8.31
5	1,3-Dimethyl-2-nitrobenzene	8.822
6	Naphthalene-d8	8.889
7	Hexachlorocyclopentadiene	9.961
8	Mevinphos	10.467
9	Acenaphthene-d10	11.066
10	2,4-Dinitrophenol	11.106
11	4-Nitrophenol	11.154
12	2,4-Dinitrotoluene	11.272
13	Fluorene	11.751
14	4,6-Dinitro-2-methylphenol	11.782
15	Trifluralin	11.949
16	Simazine	12.488
17	Atrazine	12.526
18	Pentachlorophenol	12.677
19	Terbufos	12.716
20	Chlorothalonil	12.901
21	Phenanthrene-d10	12.93
22	Aldrin	13.959
23	Heptachlor epoxide-isomer B	14.335
24	Endrin	15.222
25	4,4'-DDT	15.634
26	3,3'-Dichlorobenzidine	16.172
27	Chrysene-d12	16.243
28	Benzo[b]fluoranthene	17.641
29	Perylene-d12	18.244

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.

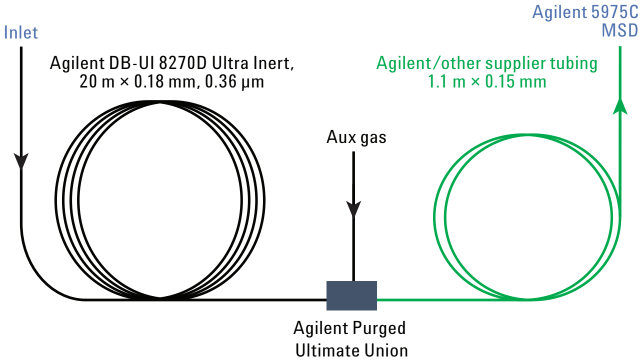

Figure 1. Experimental setup of GC/MSD for testing deactivated fused silica tubing.

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 1.3 mL/min
Inlet:	Splitless mode, 300 °C
Purge flow:	50 mL/min at 1.3 min
Oven:	40 °C for 2.5 min, to 320 °C at 20 °C/min, hold 3.5 min
Aux EPC:	He plumbed to Agilent Purge Ultimate Union
Aux flow:	1.7 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
Postinjection solvent A (dichloromethane) washes:	3
Postinjection 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:	Relative mode
Transfer line temperature:	320 °C
Source temperature:	250 °C
Quad temperature:	150 °C
Solvent delay:	3 min
Acquisition mode:	Full scan
Scan mass range:	35 to 400 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, nonstick, 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:	Flexible Metal ferrule, 0.1 to 0.25 mm (p/n G3188-27501)
Ferrule for inlet and mass spec interface:	0.4 mm id, 85/15 Vespel/graphite (p/n 5181-3323)
Union:	Ultimate union kit, deactivated (p/n G3182-61580)
Inlet liners:	Ultra Inert deactivated single taper splitless liner with wool including O-ring (p/n 5190-2293)

Results and Discussion

The 29 representative components in the S-VOA checkout mixture consist of a wide range of chemically active compounds including acidic phenols, organic bases, and organophosphorus and organochlorine pesticides. This checkout mixture, therefore, allows us to sufficiently access the inertness performances of two different tubing types.

Figure 2 shows the total ion current (TIC) chromatogram of the S-VOA checkout mixture containing 29 components at a nominal concentration of 10 ng on-column for each analyte using Ultimate Plus deactivated fused silica tubing as a GC restrictor for the MS interface. At 10 ng/component on-column, all 29 analytes were well identified and quantified with symmetrical peak shapes and good responses, and an analysis time of less than 19 minutes (Figure 2).

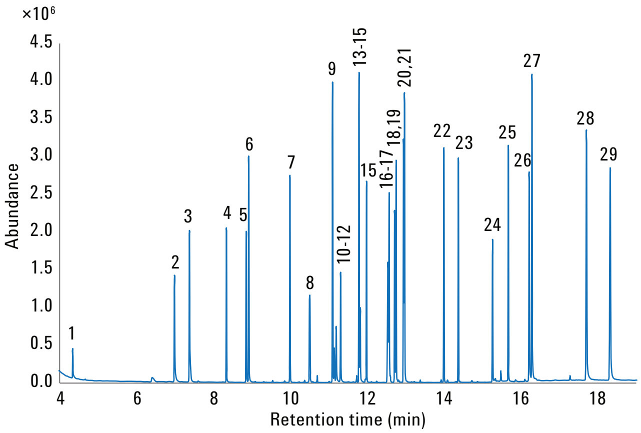

Figure 2. Total ion current chromatogram of 29 components in a semivolatile checkout mixture at 10 ng/component on-column when the Agilent J&W Ultimate Plus deactivated fused silica tubing was used as the GC restrictor for the MS interface (see Table 1 for peak IDs).

This includes both early eluting *n*-nitrosodimethylamine and late eluting perylene-d12. In this work, the difference in inertness performance was attributed to the deactivated tubing used as the GC restrictor because the rest of the system was unchanged. Compound 10 (2,4-dinitrophenol) is considered challenging, often appearing with a distorted peak shape and poor response due to its strong adsorption and degradation onto active sites throughout the flow path. This compound is, therefore, a good indicator of differences in the inertness of the system.

Figure 3 shows an expanded view of the chromatogram of 2,4-dinitrophenol with a sharp symmetrical peak and strong response that is evidence of good inertness performance with Agilent tubing. In addition, good peak shapes and strong responses were obtained for active organophosphorus and organochlorine pesticides such as mevinphos, terbufos, simazine, and atrazine. These often show tailing peaks and weak responses due to their interactions with active sites on the surface of deactivated fused silica tubing. The results provide excellent evidence of the good inertness performance of Ultimate Plus tubing.

Figure 4 is an overlay of total ion current chromatograms of 10 ng/component on-column of the S-VOA checkout standard when Ultimate Plus deactivated fused silica tubing (blue chromatogram) or a deactivated fused silica tubing from another supplier (red chromatogram) were alternately installed as the GC restrictor to the MS interface. The experimental setup was the same for both tubing samples, which allows a fair comparison of their performance. Figure 4 indicates that Agilent tubing had superior inertness performance with significant improvement in response of all target compounds.

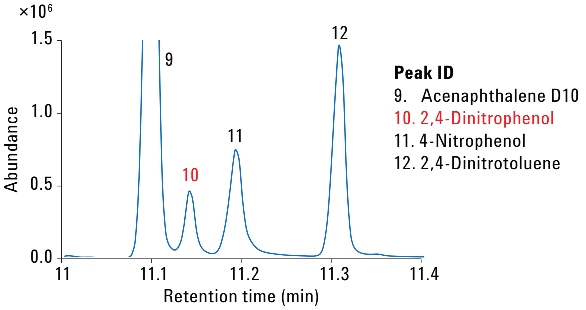

Figure 3. 2,4-Dinitrophenol expanded view at 10 ng on-column when the Agilent J&W Ultimate Plus deactivated fused silica tubing was used as the GC restrictor for the MS interface (see Table 1 for peak IDs).

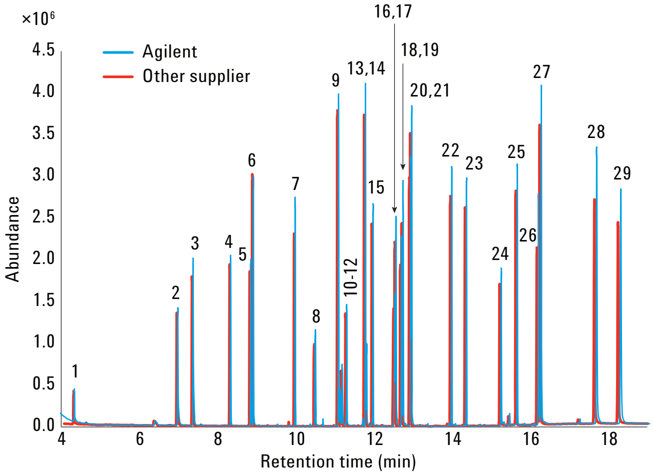

Figure 4. An overlay of total ion current chromatograms of 10 ng/component on-column of the semivolatile checkout mixture with Agilent J&W Ultimate Plus deactivated fused silica tubing (blue chromatogram) or deactivated fused silica tubing from another supplier (red chromatogram) used as the GC restrictor for MSD (see Table 1 for peak IDs).

Organochlorine pesticides, such as DDT and endrin, are known to break down in response to surface activity. Improved responses of these two compounds with Agilent tubing are good differentiators to demonstrate improved inertness performance of the tubing. Figure 5 shows a comparison of normalized peak areas (to compound 9, acenaphthene-d10) of 29 semivolatile components at two different working levels (5 ng and 2 ng on-column for each component). Acenaphthene-d10 was chosen because it is considered as stable and inert. These results indicate significantly improved responses and excellent peak symmetry of many target compounds with the Agilent tubing,

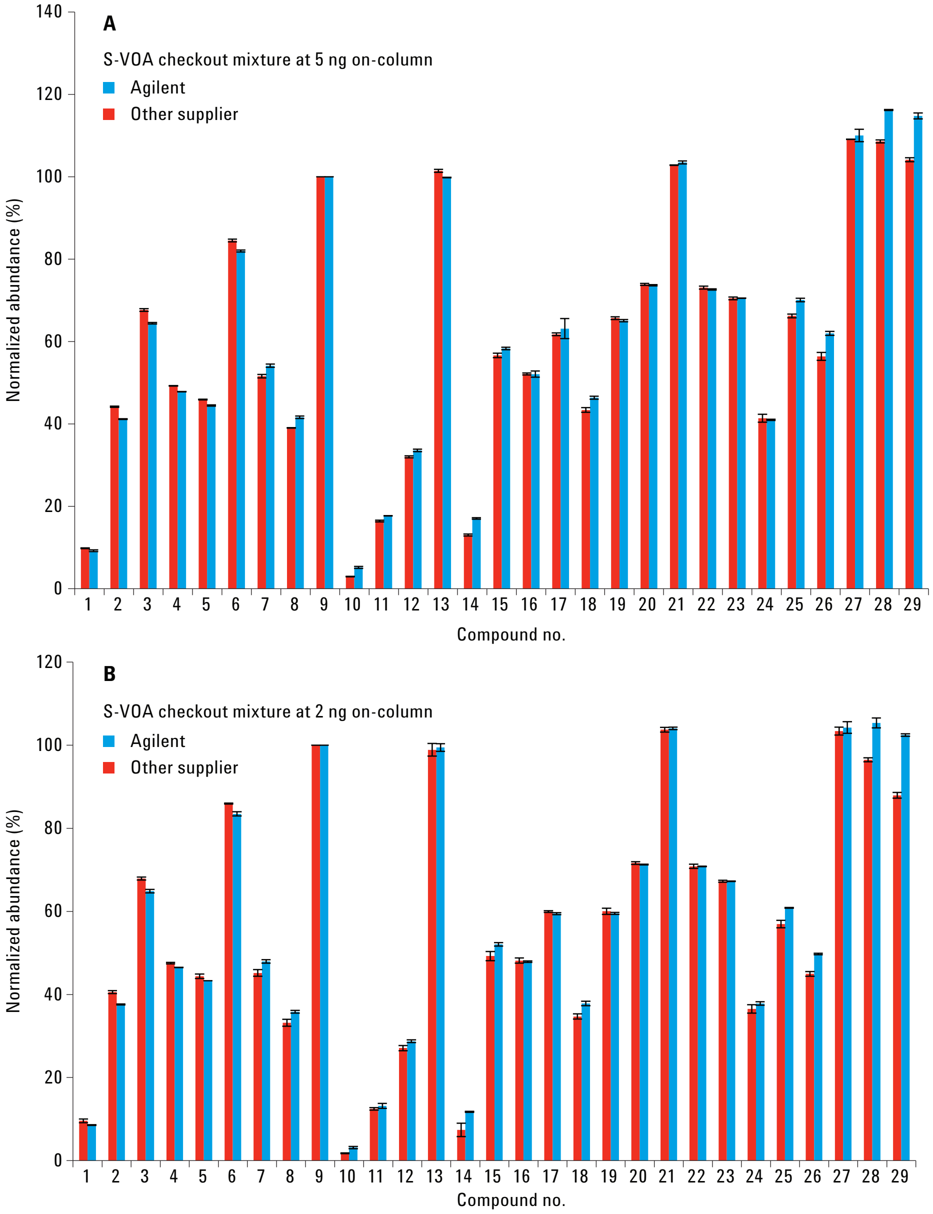

Figure 5. Normalized peak areas of duplicate injections of a semivolatile checkout mixture at 5 ng/component (A) or 2 ng/component on-column (B) with Agilent J&W Ultimate Plus deactivated fused silica tubing (blue bars) or deactivated fused silica tubing from another supplier (red bars) used as the GC restrictor for MSD (see Table 1 for peak IDs). The peak areas of all compounds were normalized to compound 9, acenaphthene-d10. Full scan mode was selected for recording the MS signal.

especially for challenging analytes that are sensitive to the inertness of deactivated fused silica tubing. The responses of components obtained with tubing from another supplier were set to 100%, and the compound responses with Agilent tubing were scaled. Figure 6 shows differences in percentage response of each compound in the checkout mixture. Improved responses of all target compounds were observed for Agilent tubing, most notably for 2,4-dinitrophenol.

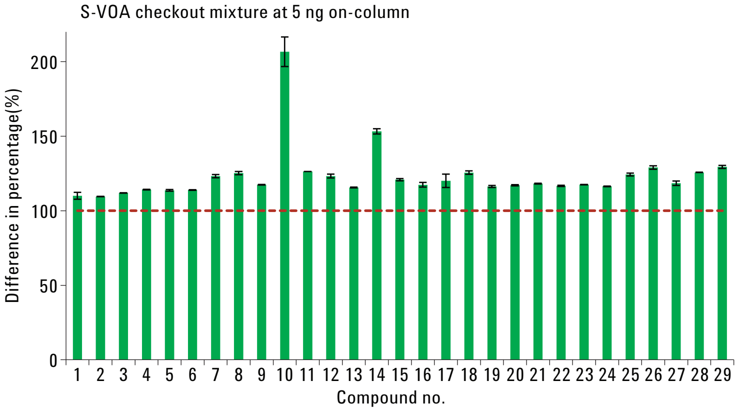

Figure 6. Analyte response comparison for Agilent J&W Ultimate Plus and other supplier tubing. The results were based on the average response (duplicate injections) of 5 ng/component on-column of a semivolatile checkout mixture using GC/MS in full scan mode. The response of each analyte for tubing from another supplier was set to 100% and the response of each analyte was scaled for Ultimate Plus tubing (see Table 1 for peak IDs).

Conclusions

We compared Agilent J&W Ultimate Plus deactivated fused silica tubing to deactivated premium tubing from another supplier when used as GC restrictors for MSD. The Agilent tubing clearly showed better inertness performance with good symmetrical peak shapes and significant improvements in responses for most target compounds in a semivolatile checkout mixture. Highly active compounds such as 2,4-dinitrophenol, and organochlorine and organophosphorus pesticides were especially well resolved and quantified at low levels. These results are encouraging, and suggest that Ultimate Plus fused silica tubing plays a key role to an inert flow path for fast, sensitive, and reproducible analysis of semivolatile contaminants in environmental applications.

References

1. Szelewski, M. *Semivolatiles Retention Time Locked (RTL) Deconvolution Databases for Agilent GC/MSD Systems*; Agilent Technologies, Inc. Application Note, publication number 5989-5875EN, **2008**.
2. Lynam, K. *Semivolatile Analysis Using an Inertness performance Tested Agilent J&W DB-5ms Ultra Inert Column*; Agilent Technologies, Inc. Application Note, publication number 5989-8616EN, **2008**.
3. Lynam, K. *Semivolatile Analysis with Specially Designed Agilent J&W DB-UI 827OD Columns*; Agilent Technologies, Inc. Application Note, publication number 5991-0250EN, **2012**.
4. Zhao, L., Broske, A. D., Mao, D., Vickers, A. *Evaluation of the Ultra Inert Liner Deactivation for Active Compounds by GC*; Agilent Technologies, Inc. Technical Overview, publication number 5990-7380EN, **2011**.
5. Anon. *Purged Ultimate Union*; Agilent Technologies, Inc. Technical Overview, publication number 5991-1114EN, **2013**.
6. Lynam, K. *Agilent Inert Flow Path Enhancements: Impact on Semivolatile Analysis*; Agilent Technologies, Inc. Application Note, publication number 5991-2745EN, **2013**.

Acknowledgements

The author would like to acknowledge Eric De-Witte and Norbert Reuter for the use of the GC/MSD instrument. Thanks also to John Oostdijk and Jan Peene for their assistance during the work.

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc., 2014

Printed in the USA
December 17, 2014
5991-5441EN

Agilent Technologies