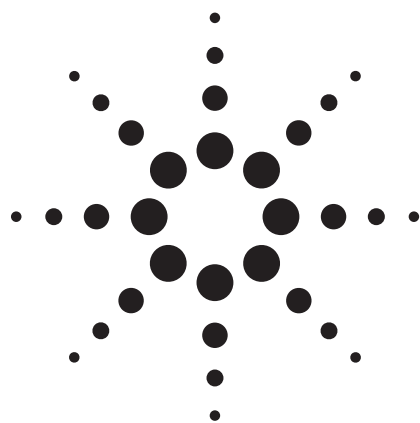


Semivolatile Analysis Using an Inertness Performance Tested Agilent J&W DB-5ms Ultra Inert Column



Application

Environmental

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Abstract

Agilent Technologies Inc. has implemented new testing procedures to more effectively evaluate GC column inertness performance. The new testing procedure uses deliberately aggressive probes to thoroughly investigate column inertness quality. The value of using probes such as 1-propionic acid, 4-picoline, and trimethyl phosphate to establish a column inertness baseline is discussed. This baseline inertness profile is then extended to a real-world application example with challenging analytes in the semivolatile sample set. Inertness performance with analytes such as 2,4-dinitrophenol, benzoic acid, and benzidine clearly shows the advantage of using the Agilent J&W DB-5ms Ultra Inert columns for semivolatile analysis.

Introduction

Semivolatile analyses using methods similar to USEPA method 8270 [1] are important in environmental laboratories worldwide. A number of very

active analytes presents significant challenges for analysts, equipment providers, and column manufacturers in terms of inertness. Acidic compounds such as benzoic acid or 2,4-dinitrophenol and strong bases such as pyridine or benzidine are examples of active species found in the semivolatile sample set. These chemically charged species are particularly susceptible to adsorption onto active surfaces in the sample flow path, including the column itself. Both system and column inertness are critical for effective analysis of these active chemical species.

For many years Grob's mix [2] has been the standard mix to evaluate capillary GCs and columns. This mix consists of a series of alkanes, a substituted phenol (acidic component), an amine (basic component), an alcohol, and a diol. Virtually all capillary column manufacturers have used Grob's or a very similar test mix to evaluate column performance historically. These mixtures work well to evaluate column efficiency, system suitability against solute discrimination during injection, and potential solute absorption in the chromatographic flow path. Inertness evaluation based on single acidic and basic species in these mixes, though valuable, falls short of the rigorous requirements for inertness that applications on modern capillary GC columns require [3-4]. Modern GC applications demand a more comprehensive approach to properly investigate column inertness performance.



Agilent Technologies

Experimental

Baseline inertness testing of columns was on an Agilent 6890N GC equipped with a 7683B autosampler and an FID. Semivolatiles application-specific chromatograms were generated using an Agilent 6890N GC/5975B MSD equipped with a 7683B autosampler.

Tables 1 and 2 list the chromatographic conditions used on each of the chromatographic systems. Table 3 lists flow path consumable supplies used in these experiments.

Table 1. Chromatographic Conditions 6890N/FID System

GC:	Agilent 6890N
Sampler :	Agilent 7683B, 0.5- μ L syringe (Agilent p/n 5188-5246), 0.02- μ L split injection, 1 ng each component on column
Carrier:	Hydrogen constant pressure 38 cm/s
Inlet:	Split/splitless; 250 °C, 1.4 mL/min column flow, split flow 900 mL/min, gas-saver flow 75 mL/min. on at 2.0 min
Inlet liner:	Deactivated single taper w/glass wool (Agilent p/n 5183-4647)
Column:	Agilent J&W DB-5ms Ultra Inert, 30 m \times 0.25 mm \times 0.25 μ m (Agilent p/n 122-5532UI)
Oven:	65 °C isothermal
Detection:	FID at 325 °C, 450 mL/min air, 40 mL/min hydrogen, 45 mL/min nitrogen makeup

Table 2. Chromatographic Conditions 6890N/5975B MSD System

GC:	Agilent 6890N/5975B MSD
Sampler :	Agilent 7683B, 5.0- μ L syringe (Agilent p/n 5181-5246), 1.0- μ L splitless injection, 5 ng each component on column
Carrier:	Helium constant flow 30 cm/s
Inlet:	Split/splitless; 260 °C, 53.7 mL/min total flow, purge flow 50 mL/min on at 0.5 min, gas-saver flow 80 mL/min on at 3.0 min
Inlet liner:	Deactivated single taper w/glass wool (Agilent p/n 5183-4647)
Column:	Agilent J&W DB-5 ms Ultra Inert, 30 m \times 0.25 mm \times 0.25 μ m (Agilent p/n 122-5532UI)
Oven:	40 °C (1 min) to 100 °C (15 °C/min), 10 °C to 210 °C (1 min), 5 °C/min. to 310 °C (8 min)
Detection:	MSD source at 300 °C, quadrupole at 180 °C, transfer line at 290 °C, scan range 50–550 AMU

The flow path supplies used in these experiments are listed in Table 3.

Table 3. Flow Path Supplies

Vials:	Amber screw cap (Agilent p/n 5182-0716)
Vial caps:	Blue screw cap (Agilent p/n 5282-0723)
Vial inserts:	100- μ L glass/polymer feet (Agilent p/n 5181-1270)
Syringe:	5 μ L (Agilent p/n 5181-1273)
Septum:	Advanced Green (Agilent p/n 5183-4759)
Inlet liners:	Deactivated single taper w/glass wool (Agilent p/n 5183-4647) for FID Deactivated single taper direct connect (Agilent p/n G1544-80730) for MSD
Ferrules:	0.4 mm id short; 85/15 Vespel/graphite (Agilent p/n 5181-3323)
20x magnifier:	20x magnifier loupe (Agilent p/n 430-1020)

Sample Preparation

Test probes for baseline inertness evaluation were purchased from Sigma Alrich (Milwaukee, WI 53201, USA). Dichloroethane used was Burdick and Jackson spectral grade purchased thorough VWR International (West Chester, PA 19380, USA). semivolatiles standard (USEPA 8270) solutions were obtained either from Ultra Scientific (North Kingstown, RI 02852, USA) or AccuStandard (New Haven, CT 06513, USA).

Solutions were prepared using dichloroethane solvent and class A volumetric pipettes and flasks.

Results and Discussion

Baseline Inertness Profile for the Ultra Inert Columns

One means of quickly evaluating the suitability of a chromatographic system and the column component of that system is the deliberate injection of challenging analyte mixes on the system. Good sample recoveries and peak shapes quickly show that the injection system is functioning properly and establish a baseline inertness profile for the column. The baseline inertness profile then serves as a predictor for successful analysis of chemically active species like those in the semivolatiles sample set. The use of more demanding test mixes to certify column inertness performance is the approach taken for every column offered in the Ultra Inert series of capillary GC columns.

This application illustrates the implementation of more rigorous testing procedures to certify GC capillary column inertness. The baseline test mix selected for inertness contains 1-propionic acid, 4-picoline, trimethyl phosphate, and 1-heptanol. Key column evaluation criteria include efficiency of n-decane elution at a k' of 5, probe peak shapes, and peak height ratios of 4-picoline and trimethyl phosphate relative to closely eluting alkanes. The peak height ratio of active analytes, such as 4-picoline and trimethyl phosphate, relative to less active alkanes indicate the degree of surface activity for the reactive analyte. A higher ratio indicates better inertness. Testing with these aggressive probes provides more probative tools for evaluating inertness with problematic acidic and basic species. This testing procedure raises the bar for column inertness QC testing and sets a new industry standard for consistent column performance.

Figure 1 shows a baseline inertness chromatogram for an Ultra Inert DB-5ms column. Please note the peak shapes for trimethyl phosphate. This compound exhibits minor peak tailing in this example chromatogram and, for this analyte, represents

very good peak shape. The observable peak tailing for this analyte is what makes it an excellent tool for evaluating column inertness. On a lesser column this peak may not be seen at all.

Semivolatile Challenging Analytes

The evaluation of column performance went beyond the new baseline testing for inertness and looked at an abbreviated list of compounds specific to the USEPA Method 8270 sample set. The semivolatiles mix [5] contained N-nitrosodimethylamine, aniline, benzoic acid, 2,4-dinitrophenol, 4-nitrophenol, 2-methyl-4,6-dinitrophenol, pentachlorophenol, 4-aminobiphenyl, benzidine, 3,3'-dichlorobenzidine, benzo [b] fluoroanthene, benzo [k] fluoroanthene as well as recommended internal standards. These species were selected to range in polarity from basic to acidic species and from very early eluting nitrosamine to late eluting polynuclear aromatic hydrocarbons (PAHs). Figure 2 is a total ion chromatogram of the challenging analyte mix with a 5-ng on-column loading of each component.

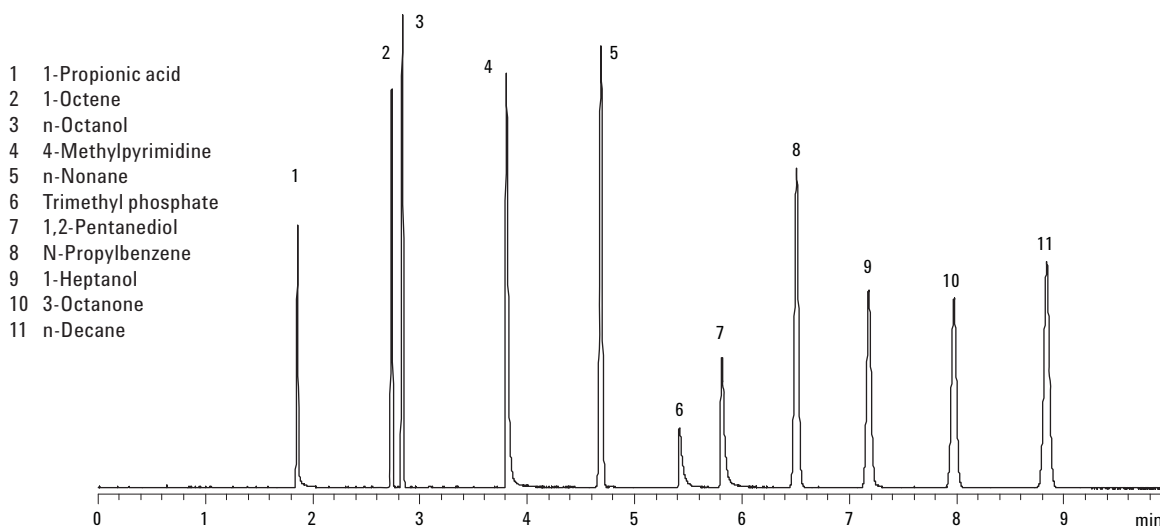


Figure 1. Baseline inertness test chromatogram, 1 ng/component load on the Agilent J&W DB-5ms Ultra Inert column (Agilent p/n 122-5532U), chromatographic conditions as in Table 1, flow path supplies as in Table 3.

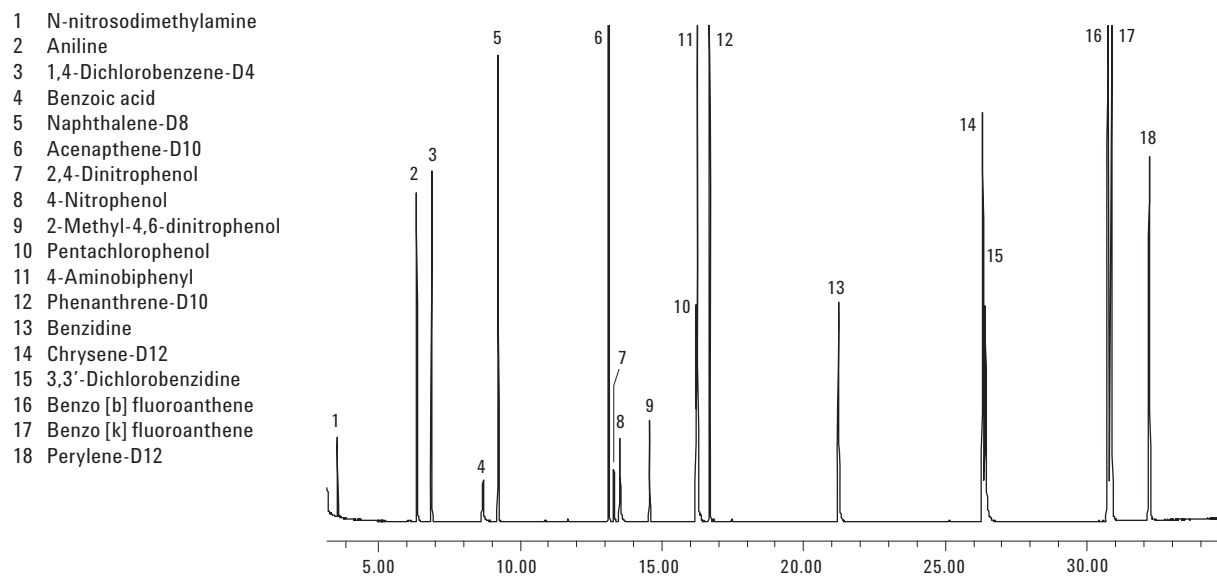


Figure 2. Abbreviated semivolatile test chromatogram, 5 ng/component load on the Agilent J&W DB-5ms Ultra Inert column (Agilent p/n 122-5532UI), chromatographic conditions as in Table 2, flow path supplies as in Table 3.

One key assessment criterion for USEPA 8270 system suitability is the response factor for 2,4-dinitrophenol and its most closely eluting internal standard acenaphthene-d10. The minimum acceptable average response factor (over the entire concentration range) is 0.050 and the typical range is between 0.1 to 0.2. This response tends to decrease at lower concentrations and as the chromatographic system or the standard starts to deteriorate. In Figure 2, response factors for 2,4-dinitrophenol were greater than 0.1, and for 4-nitrophenol, they were greater than 0.2, each at a concentration of 5 µg/mL. These values are indicative of excellent column performance even at low standard concentration.

The recovery of benzidine is another key indicator of inertness performance for semivolatile analysis. This particular base is subject to thermal breakdown in the inlet and to oxidation from standing in solution. Injection temperatures above 260 °C caused benzidine recoveries to drop dramatically. It was necessary to balance benzidine recoveries with the elution of heavier PAHs when setting

injection port temperatures. An injection port temperature setting of 260 °C gave good recoveries for benzidine and was still hot enough for higher molecular weight PAHs to volatilize.

Semivolatile Large Mix

Figure 3 shows a 5-ng on-column loading of a broader range of semivolatile analytes. This large mixture was prepared by combining AccuStandard® semivolatile mixes 1, 2, 3, 4a, 4b, 5, and 6 all at a nominal concentration of 5 µg/mL. In total, 93 semivolatile compounds were included in this mix, ranging in boiling points from very low-boiling N-nitrosodimethylamine to high-boiling benzo (g,h,i) perylene. In addition, a wide diversity of analyte polarities was represented in this mix. The highlighted area in Figure 3 shows the elution and peak shape of highly basic benzidine and its response relative to the nearest eluting peak, flouranthene. Even in this large mix, benzidine gave good relative response and peak shape.

- 1 N-nitrosodimethylamine
- 2 2- Methyl pyridine
- 3 Benzidine
- 4 Fluoranthene
- 5 Benzo (g,h,i) perylene

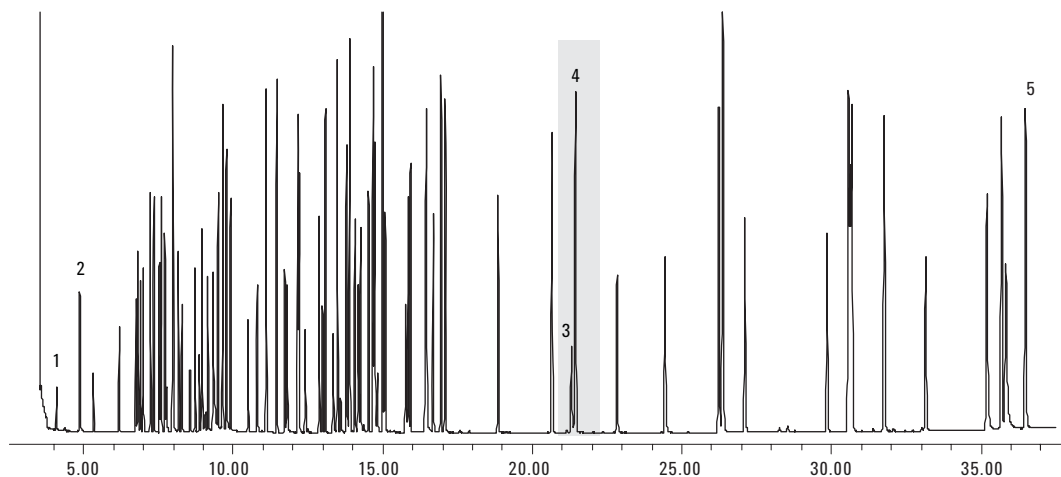


Figure 3. Semivolatile (large mix) test chromatogram, 5 ng/component load on the Agilent J&W Ultra Inert DB-5ms column (Agilent p/n 122-5532UI), chromatographic conditions as in Table 2, flow path supplies as in Table 3. Several peaks of interest are labeled to indicate early- and late-eluting species. Benzidine (peak 3) and fluoranthene (peak 4) peaks are shown in the highlighted section.

Conclusions

Rigorous column inertness testing with aggressive probes ensures consistent and reliable column inertness performance for active analytes. Challenging probes such as 1-propionic acid, 4-picoline, and trimethyl phosphate are better predictive indicators of column behavior toward active analytes than traditional Grob style mixes used by many column manufacturers. Inertness testing with these aggressive probes produces columns with well-defined baselines for inertness performance.

Columns with well-defined inertness baselines provide a reliable platform for the analyst to begin analysis of semivolatiles. The Ultra Inert DB-5ms column used in this series of experiments demonstrates excellent inertness performance for some of the most difficult analytes in the semivolatile sample set, including N-nitrosodimethylamine, 2,4-dinitrophenol, 4-nitrophenol, and benzidine. The good recoveries and peak shapes observed for these difficult species, even with a 5-ng on-column loading, are indicative of successful semivolatile analyses on these new Ultra Inert DB-5ms columns.

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