Addressing Concerns in QC Tests for GC Columns

Application Note

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Abstract

The stringency of QC tests have failed to keep pace with the advances achieved in column deactivation procedures. When pass rates rise and failure rates drop, it is time to design a more critical QC test. This application note describes a rigorous QC column testing approach that employs active tests probes to verify the inertness performance of modern GC capillary columns.

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Introduction

Batch testing is the practice of testing a single column and assuming the test results are representative of an entire production batch. It appeals to some manufacturers because it is much less expensive, requiring a fraction of the labor, equipment, and resources that must be committed to the more exacting process of testing each column individually.

Results obtained by individual testing have more veracity due to the established truth that within each production batch, every column quality measure, including bleed, inertness, and efficiency, follows a Gaussian distribution. With batch-tested columns, some customers are predestined to receive columns that should have been, and in individual testing, would have been rejected as scrap.

First, tests should be run at lower isothermal temperatures where sorptive forces are stronger. Secondly, probes should be small and sterically unhindered to facilitate their access to the column surface, and thirdly, the use of large amounts of low-boiling solvents that might drench (and thus shield) active sites during the passage of the probes should be avoided, or at least minimized.

We describe a new test procedure, using a more demanding test mixture that exposes column deficiencies that had been undetected by a typical "standard" QC test.

Proposed QC test parameters

The test temperature was 65 °C, isothermal, well below that normally used in conventional tests, and the probes included propionic acid, octane, nitrobutane, 4-methylpyridine, trimethyl phosphate, 1,2-pentanediol, propylbenzene, 1-heptanol, 3-octanone, and decane. Even on a poor column, the hydrocarbons (octane and decane) should generate well-formed peaks that serve as standards for comparison. When hydrocarbons tail it is rarely the fault of the column. Tailing hydrocarbons indicate vagaries in the flow path of the carrier gas, such as faulty column installation, inadequate split ratio, or insufficient or misdirected make-up gas. These problems should be corrected before proceeding further. The solvent used in this test was diisopropylbenzene, which eluted last and required a final temperature sweep.

When the test was reported in a plenary lecture at the 2004 International Symposium for Capillary Chromatography and Electrophoretic Separations, the response from manufacturers in the audience was muted. However, several sophisticated users that were experiencing column activity problems in their more demanding analyses expressed interest. Most notably, this group included Jim Luong [1] of Dow Chemical in Canada, who began using the test, and soon faulted the use of diisopropylbenzene because it often contains impurities, some of which elute long after the solvent. Consequently, its use can prolong test times to an hour or more.

Dow was also interested in detecting column activity at nanogram levels. Luong's test eliminated the need for solvent by using a plunger-in-needle microsyringe, and using the gas saver feature of an Agilent GC as a dynamic splitter. The latter was accomplished by employing a high split ratio (1:900) during the injection, followed by activation of the gas saver feature. This resulted in reproducible injections of nanoliter amounts of neat probes.

More rigorous testing leads to breakthroughs in coating and deactivation

The Agilent initial purpose in exploring these new test procedures was directed toward differentiating between good and excellent columns, none of which exhibited any flaws using our conventional QC test. For example, peaks were symmetrical, with no tailing, and at full intensity. On the new, more rigorous test, the pass rate on these same columns (all of which had passed the conventional test) dropped to approximately 70%.

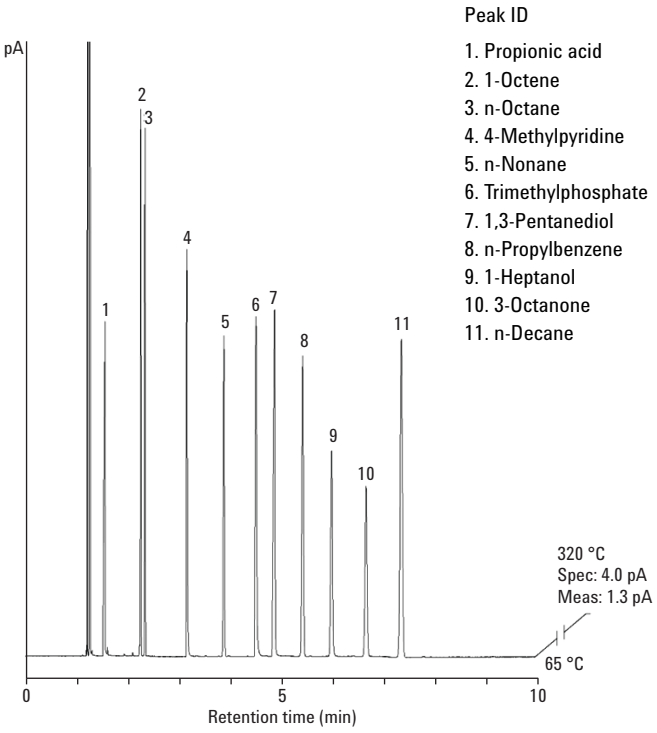
This precipitated serious discussions. Could Agilent afford to begin using the test while competing manufacturers continued to publish their test results using a far less demanding conventional test? Should the company institute an educational program so that less sophisticated users would recognize that columns showing defects on the new test could actually be better than columns showing no flaws on conventional tests? While this argument continued, Agilent also re-examined surface pretreatment and deactivation procedures. Breakthroughs in these latter areas yielded gains in column inertness and overall quality that increased pass rates (with the new test) to acceptable levels, rendering both of these questions moot.

Agilent adjusts parameters for high-volume testing

While the procedural changes employed by Luong *et al* greatly improved the test as originally proposed, the dynamic dilution step in particular would be considered somewhat risky in a high-volume manufacturing facility using hydrogen carrier gas. Agilent deemed it undesirable to use such high split ratios (approximately 1:900) on 25+ test chromatographs simultaneously. It was decided to use a minimal amount of solvent to dilute the injection, followed by autoinjection under normal conditions. To avoid interferences between solutes, the test mixture was also altered. For Agilent J&W DB-5ms Ultra Inert columns, the mixture (DB-5ms Ultra Inert mixture) was propionic acid, 1-octene, n-octane, 4-methylpyridine, n-nonane, trimethyl phosphate, 1,2-pentane diol, n-propylbenzene, 1-heptanol, 3-octanone, and n-decane. Figure 1 and Table 1 illustrate typical results using the newly designed test report, specific to this individual column.

Table 1. Typical Results Using the Newly Designed Test Report, Specific to this Agilent J&W DB-5ms Ultra Inert 30 m × 0.25 mm, 0.25 µm Column

Performance parameter	Result
Theoretical plates/meter	
n-Decane	4366
Retention index	
n-Propylbenzene	952.320
1-Heptanol	967.910
Resolution	
1-Octene, n-octane	3.60



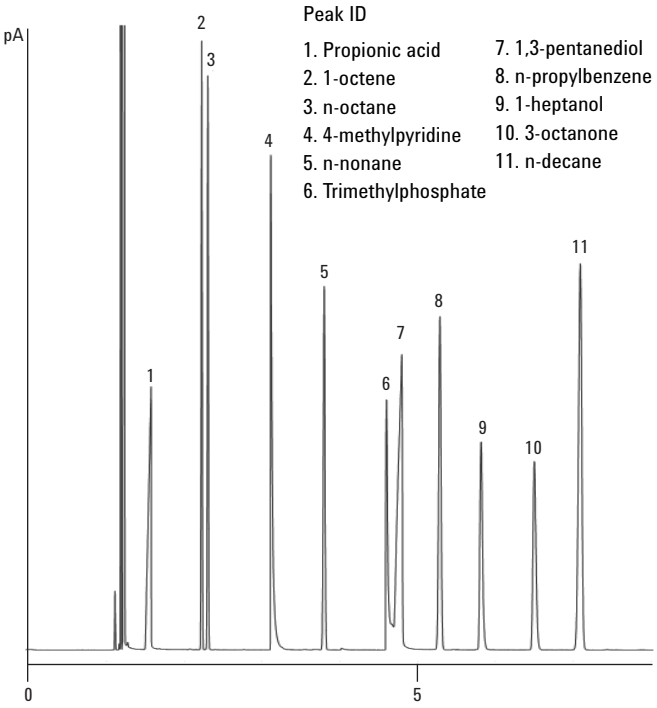
Column	Agilent J&W DB-5ms Ultra Inert 30 m × 0.25 mm, 0.25 µm (p/n 122-5532UI)
Inlet	Split, 250 °C
Carrier gas	Hydrogen
Holdup compound	Pentane, 1.207 min
Detector	FID, 325 °C
Flow rate	41.4 cm/s (1.2 mL/min)
Temperature program	Isothermal at 65 °C

Figure 1. Recently designed DB-5ms Ultra Inert mixture QC test on an Agilent J&W DB-5ms Ultra Inert Column provides more information, even during high-volume testing.

Figure 2 and Table 2 show the results of early tests on an HP-5ms Ultra Inert column using this same test mixture. HP-5ms and DB-5ms columns have always exhibited slightly different selectivities because of the subtle differences between their manufacturing processes. With the 2000 merger of J&W Scientific and Agilent Technologies, the Agilent column production was moved and assimilated into the J&W operation. There were discussions about discontinuing one of these products because of their close similarity; after all, they use the same stationary phase. However, the slight differences in their manufacture do cause slight differences in their selectivities, and different customers have established methods on one or the other. Agilent feels an obligation to continue to offer both columns.

Table 2. Typical Results Using the Newly Designed Test Report, Specific to This Agilent J&W HP-5ms Ultra Inert 30 m × 0.25 mm, 0.25 µm Column

Performance parameter	Result
Theoretical plates/meter	
n-Decane	4183.6
Retention index	
n-Propylbenzene	954.806
1-Heptanol	969.765
Resolution	
1-Octene, n-octane	3.229



Column	Agilent J&W HP-5ms Ultra Inert 30 m × 0.25 mm, 0.25 µm (p/n 19091S-433UI)
Inlet	Split, 250 °C
Carrier gas	Hydrogen
Holdup compound	Pentane, 1.204 min
Detector	FID, 325 °C
Flow rate	54 cm/s (2 mL/min)
Temperature program	Isothermal at 65 °C

Figure 2. Agilent J&W DB-5ms Ultra Inert mixture analyzed on an Agilent J&W HP-5ms Ultra Inert column. Subtle differences in these two phases can be seen.

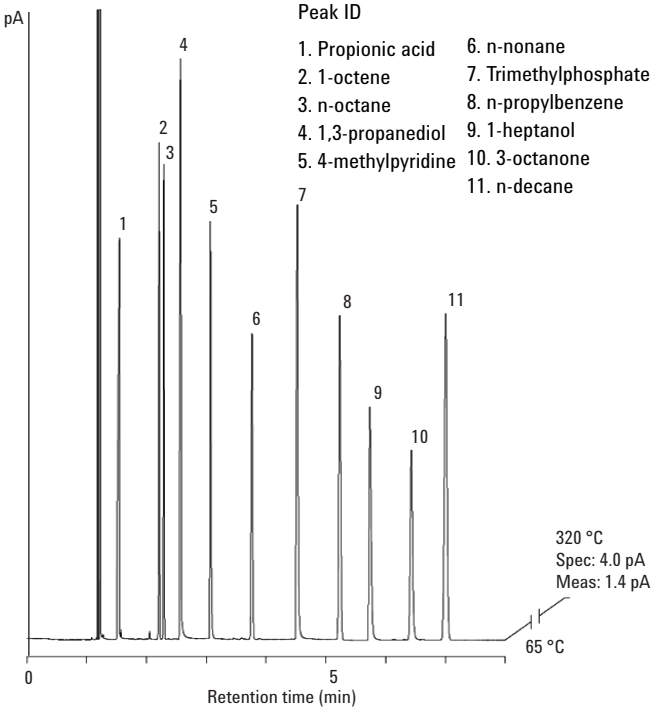
Figure 2 shows the resolution for trimethyl phosphate and 1,2-pentanediol was minimal. These are both important probes. Is the tailing entirely attributable to the phosphate, or is the diol also tailing? Because of the close proximity of these two solutes and the desirability of unmasking any defects in the shape of the trimethylphosphate peak (one of the most stringent probes), it was decided to substitute 1,3-propanediol for 1,2-pentanediol in Agilent QC tests for Agilent HP-5ms Ultra Inert columns. A typical chromatogram with this altered mixture is shown in Figure 3. Table 3 lists the performance characteristics.

Test sheets shipped with each column list the test conditions, test probes used, and the new test results obtained on each particular column, for example, theoretical plates per meter and retention indices of n-propylbenzene and 1-heptanol (a check of the column's selectivity).

Test probes used for DB-1ms UI and HP-1ms UI columns are propionic acid, 1-octene, n-octane, 1,2-butanediol, 4-methylpyrindine, trimethyl phosphate, n-propylbenzene, 1-hepatanol, 3-octanone, tert-butylbenzene, and n-decane. Using this mix, 1,2-butanediol and trimethyl phosphate are well resolved peaks whose peak shapes can be evaluated individually on both the DB and HP version of the 1ms UI columns. Example test results for a typical DB-1ms UI column appear in Figure 4, while typical results for a HP-1ms UI column are in Figure 5.

Table 3. Typical Results using the Newly Designed Test Report, Specific to this Agilent J&W HP-5ms Ultra Inert 30 m × 0.25 mm, 0.25 µm Column

Performance parameter	Result
Theoretical plates/meter	
n-Decane	2972
UTE	0.0%
Retention index	
n-Propylbenzene	953.080
1-Heptanol	968.050
Resolution	
1-Octene, n-octane	2.91

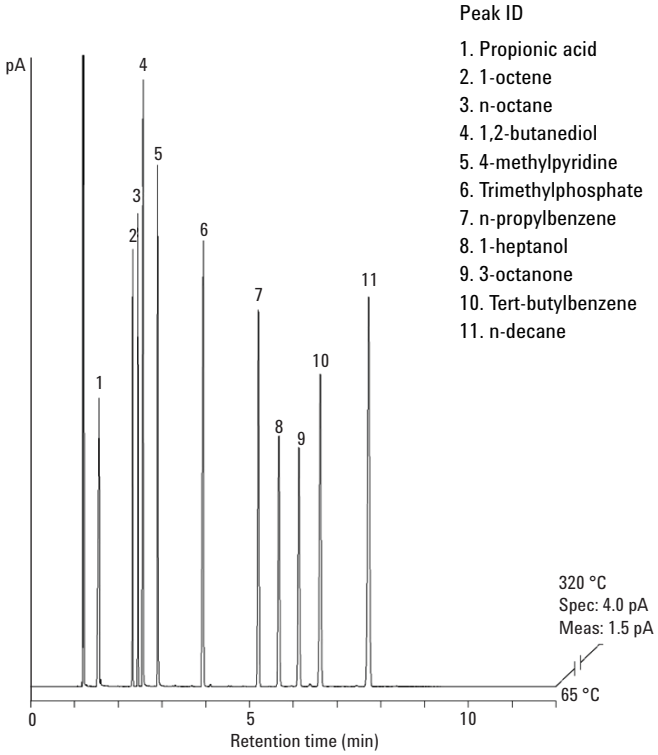


Column	Agilent J&W HP-5ms Ultra Inert 30 m × 0.25 mm, 0.25 µm (p/n 19091S-433UI)
Inlet	Split, 250 °C
Carrier gas	Hydrogen
Holdup compound	Pentane, 1.143 min
Detector	FID, 325 °C
Flow rate	43.8 cm/s (1.3 mL/min)
Temperature program	Isothermal at 65 °C

Figure 3. For the DB-5ms Ultra Inert mixture, substituting 1,3-propanediol unmasks defects in peak shape.

Table 4. Typical Results using the Newly Designed Test Report, Specific to this Agilent J&W DB-1ms Ultra Inert 30 m × 0.25 mm, 0.25 µm Column

Performance parameter	Result
Theoretical plates/meter	
n-Decane	4130
Retention index	
n-Propylbenzene	931.180
1-Heptanol	946.270
Tert-butylbenzene	973.120
Resolution	
1-Octene, n-octane	5.08

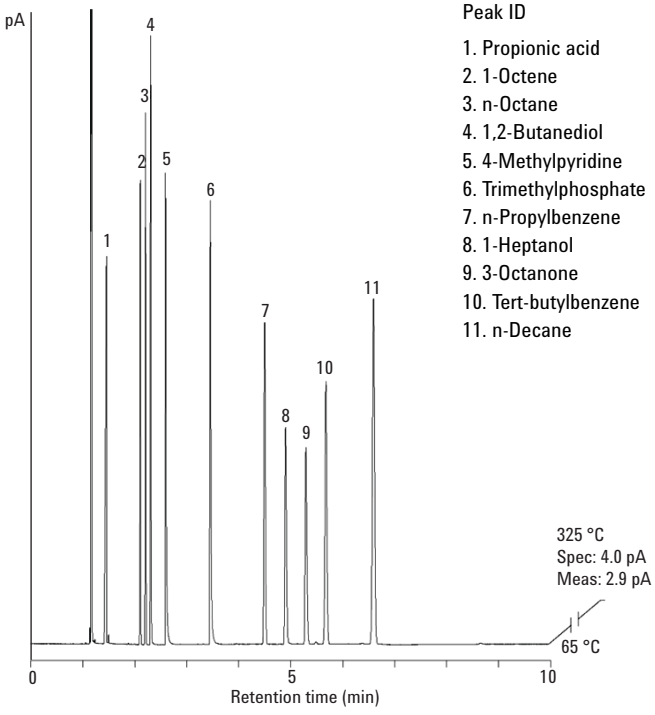


Column	Agilent J&W DB-1ms Ultra Inert 30 m × 0.25 mm, 0.25 µm (p/n 122-0132UI)
Inlet	Split, 250 °C
Carrier gas	Hydrogen
Holdup compound	Pentane, 1.189 min
Detector	FID, 325 °C
Flow rate	42 cm/s (1.2 mL/min)
Temperature program	Isothermal at 65 °C

Figure 4. 1,2-butanediol and trimethyl phosphate are well resolved peaks whose shapes can be evaluated individually on the Agilent J&W DB-1ms Ultra Inert 30 m × 0.25 mm, 0.25 µm column.

Table 5. Typical Results using the Newly Designed Test Report, Specific to this Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm, 0.25 µm Column.

Performance parameter	Result
Theoretical plates/meter	
n-Decane	3839
Retention index	
n-Propylbenzene	930.220
1-Heptanol	944.750
Tert-butylbenzene	972.690
Resolution	
1-Octene, n-octane	4.56



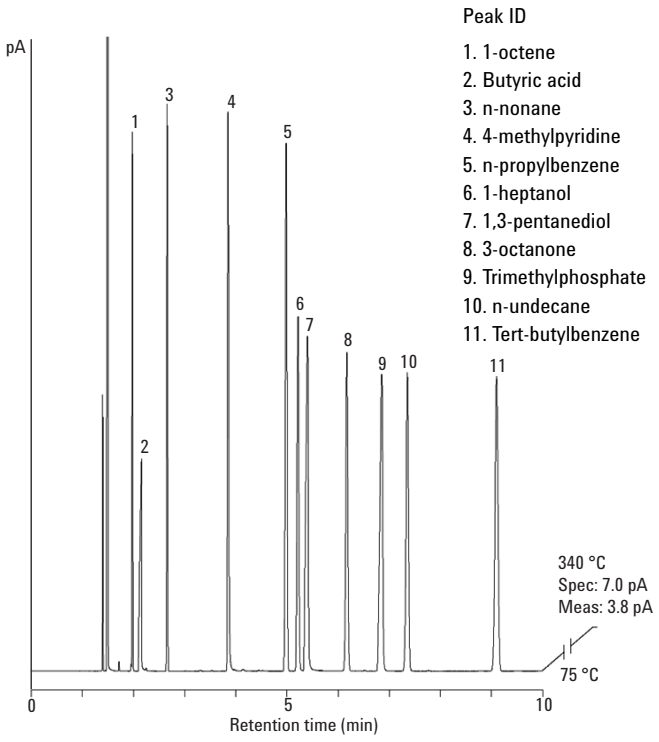
Column	Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm, 0.25 µm (p/n 19091S-933UI)
Inlet	Split, 250 °C
Carrier gas	Hydrogen
Holdup compound	Pentane, 1.154 min
Detector	FID, 325 °C
Flow rate	43.8 cm/s (1.3 mL/min)
Temperature program	Isothermal at 65 °C

Figure 5. 1,2-butanediol and trimethyl phosphate again show individually resolved peaks on the Agilent J&W HP-1ms Ultra Inert 30 m × 0.25 mm, 0.25 µm.

Ultra inert testing for the intermediate polarity DB-35ms phase required the use of probes that would be retained by the phase. A fully probative acid, butyric acid, a fully probative base, 4-methylpyrindine, trimethyl phosphate and 1,2-pentanediol were included in this test mix. Tert-butyl benzene was used as an efficiency probe. It was necessary to increase the isothermal temperature for this test to 75 °C to achieve elution times in line with the needs of a high throughput manufacturing facility. Example test results for a typical DB-35ms UI column are shown in Figure 6.

Table 6. Typical Results using the Newly Designed Test Report, Specific to this Agilent J&W DB-35ms Ultra Inert 30 m × 0.25 mm, 0.25 µm Column

Performance parameter	Result
Theoretical plates/meter	
Tert-butylbenzene	3853
Retention index	
n-Propylbenzene	1023.580
1-Heptanol	1032.510



Column	Agilent J&W DB-35ms Ultra Inert 30 m × 0.25 mm, 0.25 µm (p/n 122-3832UI)
Inlet	Split, 250 °C
Carrier gas	Hydrogen
Holdup compound	Pentane, 1.398 min
Detector	FID, 340 °C
Flow rate	35.8 cm/s (1.1 mL/min)
Temperature program	Isothermal at 75 °C

Figure 6. Assessing an Agilent J&W DB-35ms Ultra Inert 30 m × 0.25 mm, 0.25 µm column with a text mix containing probes retained on the phase.

Conclusions

In retrospect, when first broached at that 2004 meeting, it was thought it might eventually be possible for column manufacturers and column users to make a distinction between good and excellent columns. The history of GC column development led to the logical assumption that there would be renewed efforts in the areas of surface preparation and deactivation, which we felt would be painstakingly slow. However, the breakthroughs in surface pretreatments and improvements in surface deactivation came much more rapidly than had been anticipated. The quality of the Agilent Ultra Inert columns exceeds expectations. We are satisfied that customers with the most demanding analyses of active analytes can have confidence that the DB-5ms Ultra Inert (UI), HP-5ms UI, DB-1ms UI, HP-1ms UI and DB-35ms UI columns will provide the highest level of performance.

I want to express my gratitude to the Agilent team for acknowledging my efforts to continuously improve GC column quality by publishing this work. Walt Jennings.

Reference

1. J. Luong, R. Gras, and W. Jennings, "An Advanced Solventless Column Test for Capillary GC Columns," *J. Separation Sci.*, Vol 30, No 15, Oct 2007, pp 2480–2492.

For More Information

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