# QUANTITATIVE EVALUATION OF GAS CHROMATOGRAPHY COLUMN BLEED

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## INTRODUCTION

All gas chromatography capillary column manufacturers provide information on high temperature evolution or column "bleed". Each manufacturer's information is subjective, comparing proportional background signal at differing temperatures or times that are are not absolute and may be dependent on the state of the testing gas chromatograph. This information is normally not supplied with the individual column but available only as advertising.

### There is no available standard!

A direct mass rate method of a real column bleed component of the most common column polymer type, polydimethylsiloxane(PDMS) is outlined in this poster. Predominant breakdown products of this polymer are the permethylated linear or cyclosiloxanes, the latter containing 3, 4 or 5 monomer groups. A universal test of bleed would be to use the GC detector rate response to one of these as the chosen reference compound. The four membered ring compound octamethylcyclotetrasiloxane ***(Figure 1)*** was the chosen compound, as it had a sufficiently low vapor pressure to ensure separation from the pentane solvent peak tail.

For the total delivery of a known quantity of the reference material to the detector, a number of methods were evaluated.

The method chosen, the most universal of those we have evaluated, was to use conventional split/splitless injectors with the septum vent off and the split stream in continuous bypass.

## EXPERIMENTAL

### *Equipment*

Five instruments, three Hewlett-Packard 5890's, an Agilent 6890 and a Varian 3800 were used; all were fitted with the manufacturers flame ionization detector and a standard split/splitless injector. Data collection and manipulation used either the Agilent's Chemstation, a standalone Agilent 3396A integrator or the Varian Star system. A tapered FocusLiner™ was fitted to all standard injectors to ensure maximum transfer of calibrant into the column. An SGE 1µL plunger-in-needle syringe with a repeating adaptor was used to manually inject solution.

### *Columns*

SGE BPX5 columns or equivalent, of different diameters, lengths and stationary phase film thickness.

### *Material*

Octamethylcyclotetrasiloxane (D4) (Aldrich) was made into a 1000ppm solution in pentane.

### *Operating Conditions*

Injector temperature = 120°C

Detector temperature = 360°C

Oven program = 50°C (5min) ->360°C @15°C/min to 360°C (5min)

Gas flow, permanent splitless (bypass)>20mL/min

Helium column flow, unless otherwise stated 2mL/min

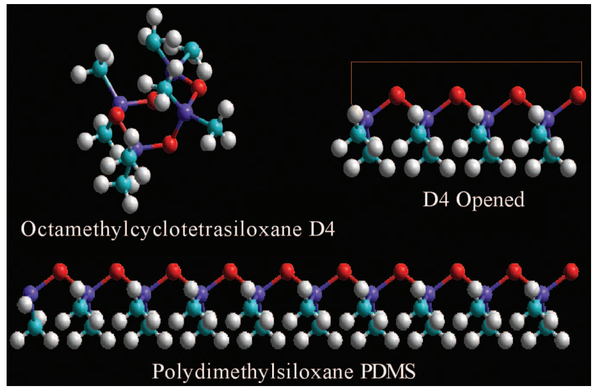


***Figure 1.*** *D4 and section of PDMS backbone (BP1, BP5 etc.) Silicon - violet, oxygen- red, carbon- cyan , hydrogen- white.*

### *Calibration*

The response of individual instruments was calibrated against a known quantity of calibrant. Response factors were calculated after injection of 1µL of a 1µg/µL solution of D4. For an instrument response of ***X*** counts:

Agilent 6890: 1pA.S = 1/(***X***µg of calibrant)

Agilent 5890 and 3396A Integrator:
1mV.S = 1/(***X***µg of calibrant)

Varian Star: 1mV.S = 0.125/(***X***µg of calibrant)

*(Units: milliVolt seconds = m V.S, picoAmp seconds = pA.S)*

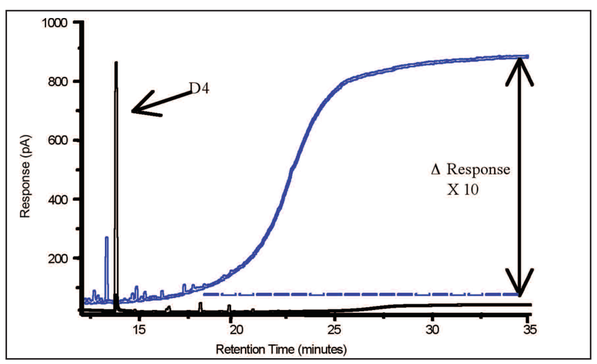


***Figure 2.*** *GC chromatogram of 1µg D4 injection. Superimposed (blue) column bleed chromatogram expanded 10 times.*

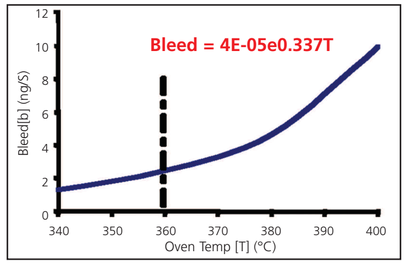


***Figure 3.*** *Plot of column bleed rate at different temperatures. Line indicates test temperature.*

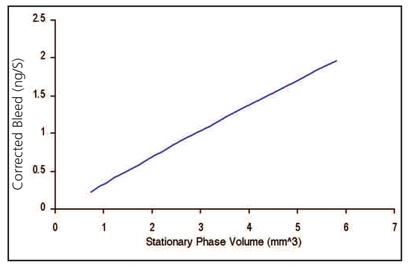


***Figure 4.*** *Plot of bleed rate at 360 0C for columns containing indicated volumes of stationary phase.*

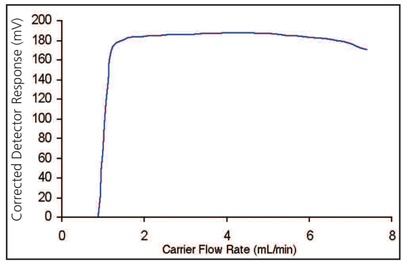


***Figure 5.*** *Plot of HP 5890 FID response to carrier gas flow rate. (Line indicates test temperature)*

### *Method*

Injection of the D4 in pentane under the conditions outlined gave a well defined peak clear of the majority of the solvent tail ***(Figure 2)***. The low injector temperature minimized D4 breakdown.

The actual bleed measurement was taken as the difference in base signal at the column recommended maximum operating temperature and that at 50°C. For BPX5 this was at 360°C.

Column bleed, is as expected, not an artifact which appears at a particular temperature but increases exponentially. ***Figure 3*** shows the increase in bleed rate of a column at different temperatures. The oven was held constant until a stable detector signal was attained. Detector calibration used the method outlined above for octamethylcyclotetrasiloxane.

Bleed rate is, for a given conditioned stationary phase, dependent only on the phase volume, not the column surface area. ***Figure 4*** shows absolute bleed measurements of a number of columns of different diameters, lengths and film thicknesses.

While the bleed rate is only dependent on column temperature, the evolved products must be transferred to the detector. Although it would be expected that any discernable flow rate would be sufficient to transport these vapors, there may be other determining factors. For the HP 5890 flow characteristics shown ***(Figure 5)***, there is a minimum value of 1.5mL/min. All measurements were carried out with a helium flow of 2mL/min.

### *Results*

A series of experiments were carried out on different manufacturers columns of the same type, length, internal diameter and film thickness, on an Agilent 6890/Chemstation system. The results are presented as bleed/second, a measure of the detection limit at the maximum operating temperature and the percentage loss rate. The first values are of most use to the analyst, as they allow the estimation of detection limit at the upper temperature limit of the column. The second set of values, the percentage rate of loss of the total stationary phase volume may be used as a predictor of column life.

| Column | ng / sec | % / sec |
|---|---|---|
| BPX | 2.668 | 4.52 E-05 |
| Brand Z | 4.48 | 7.59 E-5 |
| Brand D | 5.727 | 9.71 E-05 |

On the same Agilent 6890, three bleed measurements were carried out on a thick film (1.0µm) BPX5 column. As expected the bleed rate was proportionally higher than for the 0.25mm columns.

Repeatability ( BPX5 30m x 0.25mm **1.0µm**)

| | ng / sec |
|---|---|
| Mean | 8.965 |
| Coeff of Variance | 0.021 |

A single BPX5 (30m x 0.25mm x 0.25mm) was tested on a number of gas chromatographs and data collecting systems. Five measurements of D4 response and a single determination of signal were taken for each instrument.

| Instrument (BPX5 30m x 0.25mm x 0.25µm) | ng / sec |
|---|---|
| Varian 3800 (detector 1) | 2.6 |
| Varian 3800 (detector 2) | 2.58 |
| HP 5890 (1) Chemstation | 2.9 |
| HP 5890 (1) Integrator | 2.84 |
| HP 5890 (2) Integrator | 2.68 |
| Agilent 6890 Chemstation | 2.668 |

## CONCLUSION

A versatile, stable method of determining column bleed has been developed. It is independent of gas chromatographic or data collection system. While the octamethylcyclotetrasiloxane was chosen as indicative of breakdown products from polydimethylsiloxane phases, this material may be regarded as a bleed calibration standard for production quality and control parameters of new columns or sensitivity monitor for contamination level. Using this method, this, or a different reference compound, may be suitable for more polar capillary columns.

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