GC COLUMNS FOR THE DETERMINATION OF SPECIFIC POLYCHLORINATED BIPHENYL (PCB) CONGENERS IN ENVIRONMENTAL SAMPLES USING U.S. EPA METHOD 1668

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Introduction

U.S. EPA Method 1668 was originally developed for the congener-specific determination of the twelve PCB congeners designated as toxic by the World Health Organization (IUPAC Nos. 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189). In December 1999, this method was revised to include congener-specific determination of approximately 150 additional PCB congeners.[1] This method utilizes High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) and the "suggested" GC column is a 30m x 0.25mm ID, 0.25µm film SPB-octyl column (Supelco 2-4218 or equivalent). However, Method 1668 allows the use of any GC column or column system as long as it achieves unique resolution of the toxic PCB congeners. These congeners may be unresolved from each other provided that the overlapping congeners have the same Toxic Equivalency Factor (TEF) and the same response factor and that the unresolved toxic congeners are uniquely resolved from all other congeners. In addition, if the SPB-octyl column is used, the retention time for PCB 209 (decachlorobiphenyl) must exceed 55 minutes, and the column must resolve congeners 34 from 23 and 187 from 182 with a valley height less than 40 percent of the smaller of the two peaks. Also congeners 156 and 157 must coelute within 2 seconds at the peak maximum.

The SPB-octyl column is a high bleed column which exhibits extreme sensitivity to temperature, oxygen and water. Over the past year, our laboratory has attempted to implement Method 1668, using four different SPB-octyl columns. Two of these columns as received met the resolution requirements specified in U.S. EPA Method 1668, while two of the columns as received failed to meet the resolution specifications. After two to three days of use, all of these columns failed to meet the Method 1668 resolution requirements. These columns were used for some 600 PCB analysis runs, (even though the resolution requirements by Method 1668 could not be met), in the course of which we attempted to evaluate the stability and resolution of the columns for somewhat different temperature programs. Great care was taken to eliminate oxygen from the carrier gas (using the scrubber recommended by Supelco), and we adhered rigorously to the temperature limitations cited by the manufacturer. The conclusions drawn from these studies with respect to the use of the SPB-octyl column are described herein.

Methods and Materials

The instrumentation used for the studies described here consists of a Hewlett-Packard Model 5890 Gas Chromatograph coupled directly to a Kratos Model 1H Concept High Resolution Mass spectrometer. The mass spectrometer was operated in the selected-ion-monitoring (SIM) mode at a resolution of 10,000. SPB-octyl columns used here were obtained from Supelco and Rtx-5 sil MS columns were obtained from Restek. Environmental samples were

prepared for GC-MS analysis using the methods described in U.S. EPA Method 1668. PCB congener standards were obtained from AccuStandard, Inc.

Results and Discussion

The results of these studies indicated that the retention times for PCB congeners on the SPB-octyl column change continuously with column usage, and adjustments are required about every 12 hours in the GC operating parameters (head pressure, temperature program, and starting and ending times for the GC windows during which the PCB congener groups elute) in order to achieve some semblance of consistency in the chromatography from run to run. The SPB-octyl column performance degrades continuously with use and the column never achieves a plateau of stability. Table 1 shows the shifts which were observed for one SPB-octyl column, over a five-day period, in the times at which switching of the mass spectrometer between ion mass descriptors was required in order to monitor the various PCB congener groups. These continuous changes in column performance resulted in increased uncertainties with respect to PCB congener identification. The shifts in PCB congener profiles, which are typically observed with increasing use of the SPB-octyl column, are well illustrated by the mass chromatograms shown in Figure 1 and 2, which were obtained for a standard mixture injection. These analyses were conducted six days apart, initially with a new column and later after other sample analyses. Similar shifts in PCB congener patterns were also observed for the tetrachlorinated and pentachlorinated PCBs.

Table 1. Retention Time Changes for PCB Congeners
On an SPB-octyl GC Column Over a Five-Day Period

Mass Group	10/14/99	10/15/99	10/16/99	10/17/00	11/18/99
1 (mono-, di-, tri- CBs)	13:48	13:23	13:12	13:02	12:40
2 (tri-, tetra-, penta-CBs)	20:23	20:21	20:02	19:45	19:34
3 (tetra-, penta-, hexa-CBs)	28:30	28:00	27:38	27:20	26:54
4 (penta-, hexa-, hepta-CBs)	37:11	37:10	37:02	36:48	34:48
5 (hexa-, hepta-, octa-CBs	44:00	43:00	42:35	42:10	41:54
6 (deca-CB)	51:00	50:48	50:00	49:22	49:00

It is clear from these studies that use of the SPB-octyl column for routine analyses by Method 1668 would require substantially greater effort and cost for column replacement and extra data interpretation than would be required with a well-performing GC column. Moreover, the SPB-octyl column cannot consistently meet the resolution requirements of Method 1668. Even some new columns fail to satisfy these criteria.

In still further tests, we have evaluated a Restek Rtx-5 sil MS GC column (60m, 0.25mm ID, 0.25μm film) for use in Method 1668. It appears that this column will meet the resolution requirements of Method 1668 and the column is extraordinarily stable with respect to PCB-congener retention times. Figure 3 shows the resolution of PCB congeners 156 and 157 which was achieved on the Rtx-5 Sil MS column. The retention time of deca-CB, 84 minutes, was observed to vary by no more than ±5 seconds over a period of three weeks on this column. We are in the process of further evaluating the long-term stability and lifetime of this column for environmental sample analyses.

References

1. U.S. Environmental Protection Agency (EPA) (December, 1999), Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, U.S. EPA Office of Water, EPA-821-R-00-002

Figure 1. Chromatogram of Hexa-CBs on New SPB-Octyl Column - Day 1

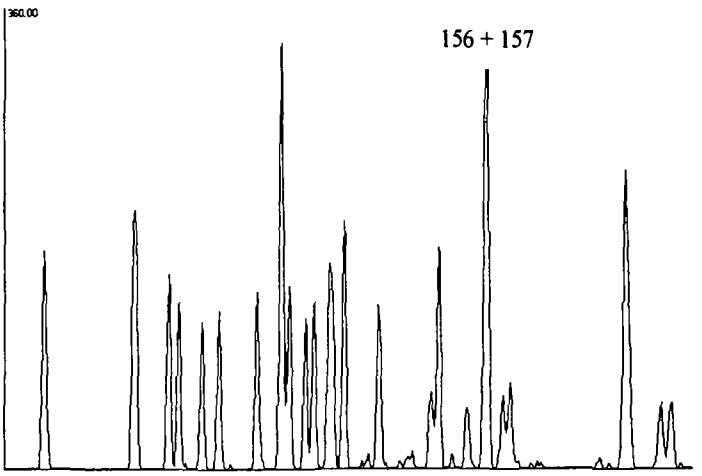

Figure 2. Chromatogram of Hexa-CBs on Used SPB-Octyl Column - Day 7

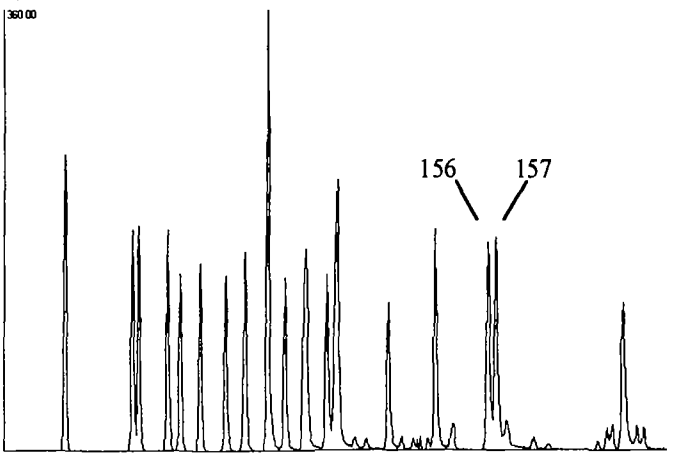

Figure 3. Chromatogram of Hexa-CBs on Rtx-5 sil MS Column