Optimization of Gas Chromatographic Parameters for Reduced Analysis Times of Chlorinated Organic Compounds

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Abstract

Considerable reductions in analysis times and corresponding increases in sample throughput can be achieved for chlorinated organics (Dioxins, PCBs, OC Pesticides) by switching to shorter, narrow gas chromatographic columns. Converting methods from 60M to 40M columns can reduce analysis times by 25 to 50%. Switching to 20M columns can reduce analysis times by 50 to 80%. All parts of the system including the injection, injector, temperature and pressure program and detector must be optimized in order to obtain accurate and reproducible results.

Introduction

Complete chromatographic separation is required for an accurate determination of analyte concentrations prior to detection when non specific detectors (e.g. ECD, FID) are used. Complete chromatographic separation is also a prerequisite for isomer or congener specific analysis even with specific detection like mass spectrometry. Optimizing chromatographic separation of analytes for speed reduces analytical run times and increases sample throughput and instrument / analytical capacity. In order for chromatographic separation to occur, analytes passing through the GC column must spend a significant portion of the time in the stationary phase. The degree to which a peak (analyte) is retained on the column is dependent upon internal column diameter (id), stationary phase, film thickness, temperature, carrier gas and carrier gas flow rate. If the phase ratio (Ξ - ratio of gas-phase to liquid-phase volumes) which is proportional to the ratio of the id to film thickness is kept constant, column temperature and carrier gas flow rates can be programmed so that chromatography throughout the analysis remains relatively constant with a reduction in column length [1]. Therefore, analyte retention times can be shortened considerably by using narrower columns with thinner films. Retention times can be reduced even further by changing stationary phase formulations. The combination of analyte specific phases and Fast GC allows for the ultimate enhancement in chromatographic speed [2].

Gas chromatographs capable of doing Fast GC (Column head pressures of >60psi and temperature ramp rates of >75^{o}C) have only been available for the past few years. Analytical run times can be reduced by a factor of 5 or more using Fast GC. Significant reductions in analysis times (25 to 50%) can also be achieved with conventional GCs by using higher column head pressures and shorter narrower columns.

Experimental

Original gas chromatographic methods were translated to the corresponding shorter columns (40M, 20M, 10M) using Hewlett Packard Method Translation Software 1997. (Hewlett Packard - Palo Alto CA). Chromatograpy was also optimized using Pro EZ-GC (Restek Corporation - Bellefonte PA).

GC Conditions: Dioxins: Hewlett Packard 6890 with Mircromass Ultima HRMS @10,000RP.

Injector:280°C. Carrier gas:He
20M, DB-5, 0.1mm id, 0.1µm film thickness, column head pressure: 100psi. Initial temp:100°C, held 1 min, ramp to 200°C at 100°C/min, ramp to 235°C at 13°C/min, ramp to 300°C at 27°C/min and held 4 min. Injection volume:0.2µL.
40M, DB-5, 0.18mm id, 0.18mm film thickness, column head pressure: 61psi. Initial temp:100°C, held 0.62 min, ramp to 200°C at 64.5°C/min, ramp to 235°C at 4.8°C/min, held 6.2 min, ramp to 300°C at 9.7°C/min and held 5.6 min. Injection volume:1.0µL.
PCBs: Hewlett Packard 6890 with Micro ECD. 20M, DB-5 and DB1701, 0.1mm id, 0.1µm film thickness. Injector:280°C, Dectors:300°C. Carrier gas:He, at 0.4mL/min - column head pressure: 67psi. Initial temp:90°C, ramp to 160°C at 35.5°C/min, held 0.28 min, ramp to 200°C at 71°C/min, held 0.28min, ramp to 275°C at 5.3°C/min and held 6.7 min. Injection volume:0.2µL.
OC Pesticides: Hewlett Packard 6890 with Micro ECD. 20M, Restek CLPesticides-1 and CLPesticides-2 0.18mm id, 0.18µm film thickness. Injector:250°C, Dectors:300°C. Carrier gas:He, at 1.5mL/min - column head pressure: 34psi. Initial temp:90°C, ramp to 180°C at 45°C/min, ramp to 280°C at 12°C/min, held 1 min. Injection volume:1.0µL

Results and Discussion

Data summarized in Table 1 shows excellent agreement between predicted vs actual retention times of OCDD on 20M, 40M columns as calculated from the 60M 5% DB-5 column temperature program. For most cases, chromatography was equivalent to that of the longer column.

Table 1: Method Conversion Data	40M DB-5	20M DB-5
Predicted	27.9 min	13.2 min
Actual	27.8 min	13.9 min

In some instances, especially for compounds that are similar, peak shifting or reversal can occur when temperature ramps are modified. Chromatography was optimized to achieve separation of 2378 substituted congeners similar to the 60M DB-5 column. It is important that all components are checked separately to confirm retention times on the new chromatographic system. Figure 1 shows the Dioxin/Furan column performance mix on a 20M column. 2378-TCDD is separated from its nearest neighbours. Quantitative comparison data for dioxins/furans are summarized in Table 2.

Table 3 contains results for the analysis of NRC Reference Fish for the certified PCB congeners.The complete list if congeners includes BZ#s:18,19,22,28,33,37,44,49,52,54,70,74,77, 81,87,95,99,101,104,105,110,114,118,119,123,126,128,138,149,151,153,155,156,157,158,167,16 8,169, 170, 171,177,178,180,183,187,188,189,191,194,199,201,202,205,206,208 and 209. The analytical run times were reduced from 80 minutes using 60M columns to 18 minutes on the 20M columns. Data reported for the certified congeners are in excellent agreement with the certified values.

Figure 1: Column Performance Mixture for 5% Phenyl Columns on a 20M DB-5 Column

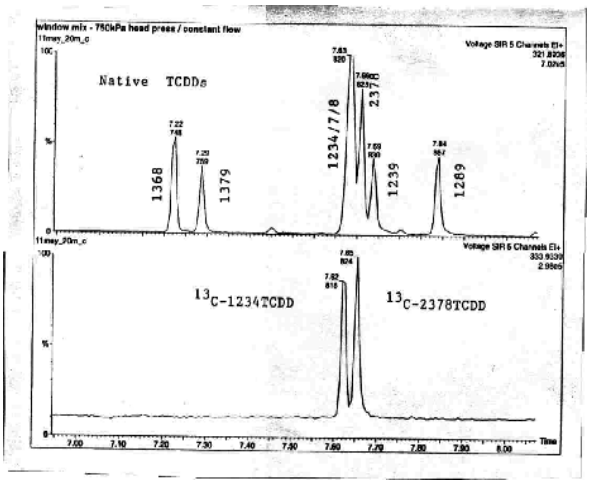

TABLE 2: Comparison of Dioxin Data		CONVENTIONAL GC/HRMS (60M)	FAST GC/HRMS (20M)
SOIL EXTRACT	2,3,7,8-T_4CDF	2.2 (PPT)	2.3 (PPT)
FISH EXTRACT	2,3,7,8-T_4CDF	14 (PPT)	13 (PPT)
AIR EXTRACT	1,2,3,7,8-P_5CDD	0.0093 (PG/M^3)	0.0093 (PG/M^3)

TABLE 3: PCB Congener Analysis of NRC CARP-1 Reference Fish

PCB CONGENER	CERTIFIED VALUE (ng/g)	N	AVERAGE
52	124 $\pm$ 32	3	141
101	124 $\pm$ 37	3	131
105	54 $\pm$ 24	3	51
118	132 $\pm$ 60	3	126
138	102 $\pm$ 23	3	102
153	83 $\pm$ 39	3	96
170	22 $\pm$ 8	3	22
180	46 $\pm$ 14	3	48
187	36 $\pm$ 16	3	39

Table 4 shows data for OC pesticides. Samples were analyzed using analyte specific CLPestcides-1 and CLPestcides-2 columns. Chromatographic resolution was enhanced over conventional 5% phenyl and cyanopropyl columns, even at shorter column lengths because the stationary phase formulation has been optimized for the separation of OC pesticides. Both columns have higher maximum column temperatures than the cyanopropyl column which allows the use of higher final oven temperatures. This results in further reductions in retention times as well as the ability to drive off high boiling contaminants. Analysis times were reduced from 55 minutes to just over 10 minutes.

TABLE 4: Comparison of OC Pesticide Data in a Fish Sample

Pesticide	CONVENTIONAL GC/ECD (30M)	FAST GC/ECD (20M)
∀ - Chlordane	22 ng/g	19 ng/g
(- Chlordane	8 ng/g	6 ng/g
op-DDT	14 ng/g	17 ng/g
pp-DDT	69 ng/g	65 ng/g
pp-DDD	83 ng/g	79 ng/g

Conclusions:

Fast GC can be used for the analysis of a number of chlorinated organic compounds to significantly reduce analysis times. Temperature programs are easily converted from conventional 60M and 30M columns to 20M and 10M columns. All areas/parameters of the chromatographic system must be optimized including the injection, injector and detector. Smaller injection volumes (0.2 - 0.5µL) and injection liners (1 - 2 mm) are typically required to obtain optimum (reproducible) chromatography on 0.1 and 0.05µm id columns. Analysis times can also be reduced on older gas chromatographs that do not have electronic pressure programming or the ability to produce the fast temperature ramp rates required with Fast GC by using 0.18 - 0.20 mm id columns. Increasing column head pressures to above 30psi and using a 40M, 0.18µm, 0.18mm column can reduce analysis times by 50% when compared to 60M columns. Some manufacturers have retrofit kits to allow column head pressures of up to 60psi on older instruments. Similar results can also be achieved by switching to 20M, 0.18µm, 0.18mm columns from 30M, 0.25µm, 0.25mm columns.

References

1. Hinshaw, J.V.; LC-GC, Volume 13, Number 12, December **1995,** 994.
2. Dorman, F; The Advantage - Restek, Winter **1998**, 1.