

Fast Gas Chromatography/Time of Flight Mass Spectrometry for the Determination of Polychlorinated Biphenyls (PCBs)

INTRODUCTION

Polychlorinated biphenyls (PCBs) were extensively used in the past, especially as coolants and dielectric fluids, stabilizing additives in PVC and plastic products, flame retardants, sealants etc. These substances are a class of man-made organic compounds with notable and useful characteristics, such as non-flammability, heat resistance, insulation, and chemical stability. Nevertheless, PCBs are very dangerous chemicals and exposure to them can cause acute and chronic effects (e.g. chlorine acne, irritation of mucous membranes, cancer, and immunological disturbances) [1].

The analysis of PCBs is routinely carried out by Gas Chromatography (GC) using 30 m capillary columns with 0.25-0.32 mm I.D. and taking 20 to 60 min per run [1]. Taking in consideration that extended analysis times correspond directly to increased costs, Fast GC has resulted in a very powerful approach to address complete PCB analysis within a few minutes, while increasing productivity and reducing costs per sample.

Moreover, Fast GC requires the use of adequate instrumentation and analytical columns in combination with optimized method parameters to maintain the proper resolving power in shorter analysis run times. As it is well-known, the use of narrow bore columns combined with faster GC oven temperature programming generate sharper peaks (typical peak widths ≤ 0.5 seconds). However, when complex samples are analyzed the high quantity of very narrow peaks results in crowded chromatograms and mass spectrometric detection is needed. Nevertheless, conventional quadrupoles or ion trap mass spectrometers do not provide enough information for the reliable reconstruction of these very narrow peaks over the entire mass range [2].

The time of flight mass spectrometer (TOF-MS) is the only system capable of providing high speed acquisition rate to collect sufficient information (15-20 points/peak) for trustworthy peak reconstruction, enabling an accurate recognition and quantification of unknown and co-eluting peaks typically present in complex samples [3].

The present application note investigates the suitability of an innovative Fast GC/TOF-MS system, supported by an original software, to determine PCBs.



FIGURE 1. The MASTER TOF GC/MS equipped with MASTER AS Liquid Autosampler.

EXPERIMENTAL

Sample

A standard mixture containing 19 PCB congeners, each at 100 ppm, was diluted in *n*-hexane to different concentrations ranging from 2.5 pg to 500 pg. The standard mix was purchased from Restek (Part No. 32416).

System configuration and control

Fast GC/TOF-MS conditions are summarized in *Table 1*.

The MASTER Lab software provides the complete control of the MASTER AS Liquid Autosampler, the MASTER GC Fast Gas Chromatograph and the MASTER TOF-MS, from autotuning procedures to GC and sample sequence management. The system is also equipped with the *NIST 08 Mass Spectral Library* and the *NIST MS Search Program*, version 2.0, 2002 (Gaithersburg, U.S.A.).

Calibration

A six-concentration-level calibration curve covering the entire analytical range was plotted for each one of the 19 PCB congeners.

TABLE 1. FAST GC/TOF-MS EXPERIMENTAL CONDITIONS

MASTER GC

| | |
|------------------------------|---|
| Column | SLB 5ms 5 m x 0.1 mm, 0.1 μm |
| Oven Temp. Program | 120 °C at 35 °C/min to 200 °C, at 30 °C/min to 300 °C (2 min) |
| Injector | SL/IN (320 °C) |
| Split Ratio | 1:20 |
| Carrier Gas Flow (He) | 0.5 mL/min (constant flow) |
| Injected Volume | 0.5 μL |

MASTER TOF-MS

| | |
|----------------------------|----------------------|
| Transfer Line Temp. | 250 °C |
| Ion Source Temp. | 240 °C |
| Sampling Rate | 50 Hz (50 spectra/s) |
| Mass Range | 50 - 500 amu |
| Solvent Delay | 30 s |
| Acquisition Time | 5 min |

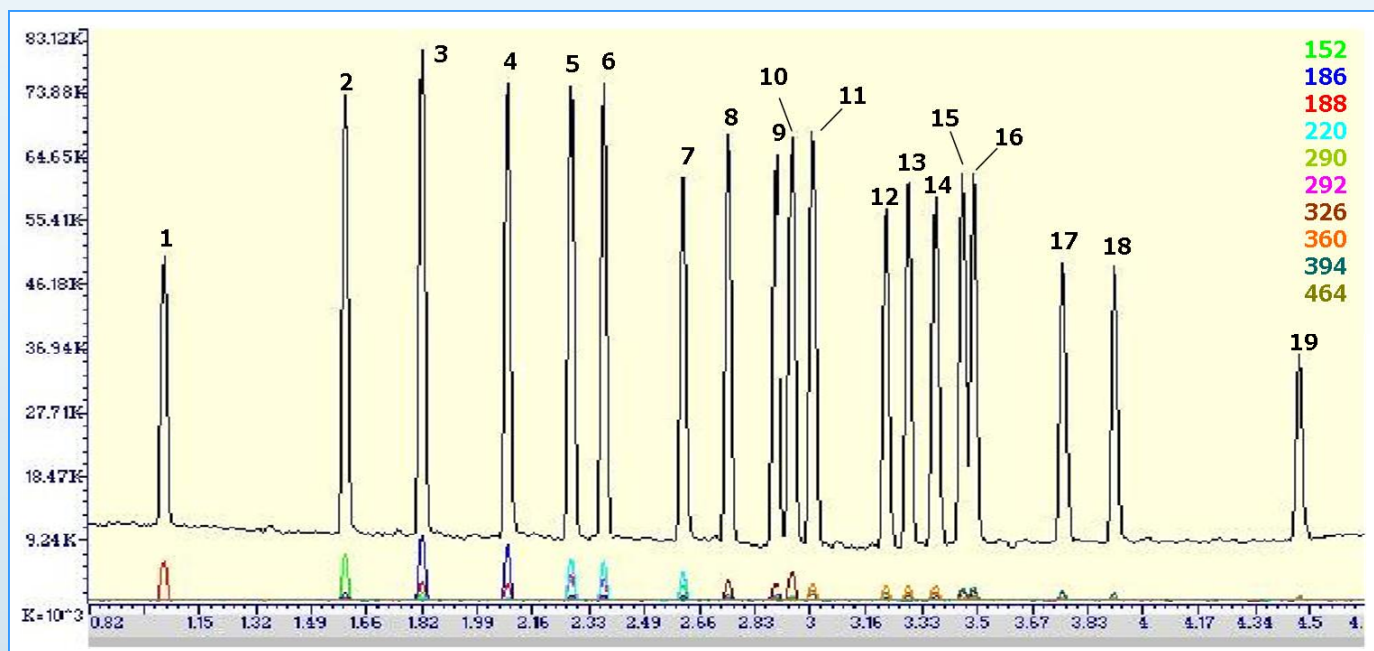


FIGURE 2. Fast GC/TOF-MS chromatogram of the standard mixture of 19 PCB congeners (500 pg). The numbers refer to those in *Table 2*.

RESULTS

The standard mixture of PCB congeners was analyzed by Fast GC/TOF-MS; *Figure 2* shows the chromatogram acquired using a 5 meter narrow-bore column. Although the analysis time is very short (5 minutes), the separation of the 19 compounds is maintained throughout analysis, demonstrating the outstanding capabilities of Fast GC.

Table 2 reports retention times, library search matching (using NIST® MS Search Program) and coefficients of determination (r^2) for each PCB standard compound. Limits of Detection (LOD) and Limits of Quantification (LOQ) determined for each PCB congener are also reported.

Calibration responses were evaluated in a range of 2.5 pg to 500 pg in column. The calibration curve plotted for 2,4',5'-Trichlorobiphenyl (refer to *Figure 2*), demonstrates the linear response within the abovementioned concentration range.

It is worth noting that the drastic reduction in analytical run times (to less than 5 min) may be accompanied by a loss in chromatographic resolution, that may result in decreased number of baseline separated components or induce the overlapping of peaks. The MASTER Lab algorithms use automatic spectral deconvolution procedures to detect totally and partially overlapped peaks. The unresolved mass spectra are deconvoluted, pure mass spectra are generated and then submitted as unknowns to mass spectral library search.

TABLE 2. COMPOSITION OF THE PCB STANDARDS MIX.

| | Compounds | Retention Time (min) | MS Library Search | | r^2 | LOD (pg) | LOQ (pg) |
|----|--|----------------------|-------------------|------------------|--------|----------|----------|
| | | | Matching | Reverse Matching | | | |
| 1 | 2-Chlorobiphenyl | 1.05 | 915 | 964 | 0.9996 | 0.46 | 1.55 |
| 2 | 2,3-Dichlorobiphenyl | 1.59 | 911 | 961 | 0.9994 | 0.33 | 1.10 |
| 3 | 2,2',5-Trichlorobiphenyl | 1.82 | 928 | 980 | 0.9996 | 0.47 | 1.55 |
| 4 | 2,4',5-Trichlorobiphenyl | 2.08 | 887 | 955 | 0.9999 | 0.47 | 1.55 |
| 5 | 2,2',5,5'-Tetrachlorobiphenyl | 2.27 | 882 | 955 | 0.9999 | 0.21 | 0.69 |
| 6 | 2,2',3,5'-Tetrachlorobiphenyl | 2.37 | 878 | 940 | 0.9991 | 0.28 | 0.95 |
| 7 | 2,3',4,4'-Tetrachlorobiphenyl | 2.61 | 888 | 949 | 0.9993 | 0.58 | 1.94 |
| 8 | 2,2',4,5,5'-Pentachlorobiphenyl | 2.74 | 865 | 913 | 0.9998 | 0.26 | 0.88 |
| 9 | 2,2',3,4,5'-Pentachlorobiphenyl | 2.89 | 862 | 922 | 0.9996 | 0.47 | 1.55 |
| 10 | 2,3,3',4',6-Pentachlorobiphenyl | 2.94 | 874 | 936 | 0.9992 | 0.71 | 2.35 |
| 11 | 2,2',3,5,5',6-Hexachlorobiphenyl | 3.00 | 685 | 941 | 0.9982 | 0.57 | 1.89 |
| 12 | 2,2',4,4',5,5'-Hexachlorobiphenyl | 3.22 | 849 | 901 | 0.9999 | 0.31 | 1.04 |
| 13 | 2,2',3,4',5,5'-Hexachlorobiphenyl | 3.29 | 872 | 911 | 0.9993 | 0.65 | 2.17 |
| 14 | 2,2',3,4,4',5'-Hexachlorobiphenyl | 3.37 | 713 | 950 | 0.9995 | 0.74 | 2.47 |
| 15 | 2,2',3,4',5,5',6-Heptachlorobiphenyl | 3.45 | 586 | 954 | 0.9946 | 0.35 | 1.17 |
| 16 | 2,2',3,4,4',5',6-Heptachlorobiphenyl | 3.48 | 787 | 873 | 0.9999 | 0.60 | 1.98 |
| 17 | 2,2',3,4,4',5,5'-Heptachlorobiphenyl | 3.75 | 623 | 946 | 0.9984 | 0.75 | 2.50 |
| 18 | 2,2',3,3',4,4',5-Heptachlorobiphenyl | 3.91 | 547 | 926 | 0.9999 | 0.75 | 2.50 |
| 19 | 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl | 4.47 | 795 | 882 | 0.9999 | 0.55 | 1.84 |

The identification process of the PCB congeners was obviously supported by mass spectral library search functions. *Figure 3* presents the comparison between the acquired mass spectrum of 2,2',5-Trichlorobiphenyl (top) and the spectrum stored in the NIST® MS Library (bottom). A matching of 928 and a reverse matching of 979 were obtained. It is worth mentioning that the spectra acquired with the MASTER TOF-MS are fully comparable with spectra contained in the NIST® MS Library.

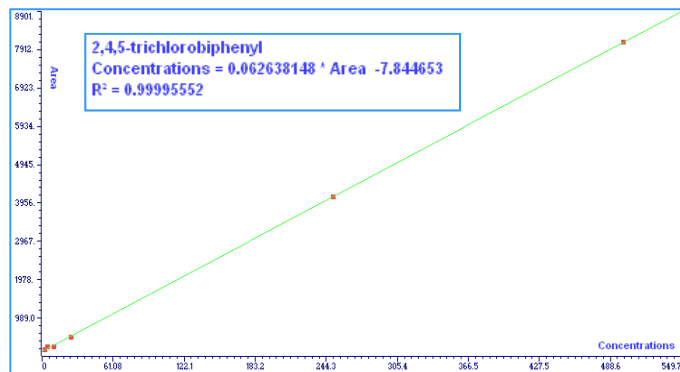


FIGURE 3. Calibration curve plotted for 2,4',5-Trichlorobiphenyl (range 2.5 pg - 500 pg).

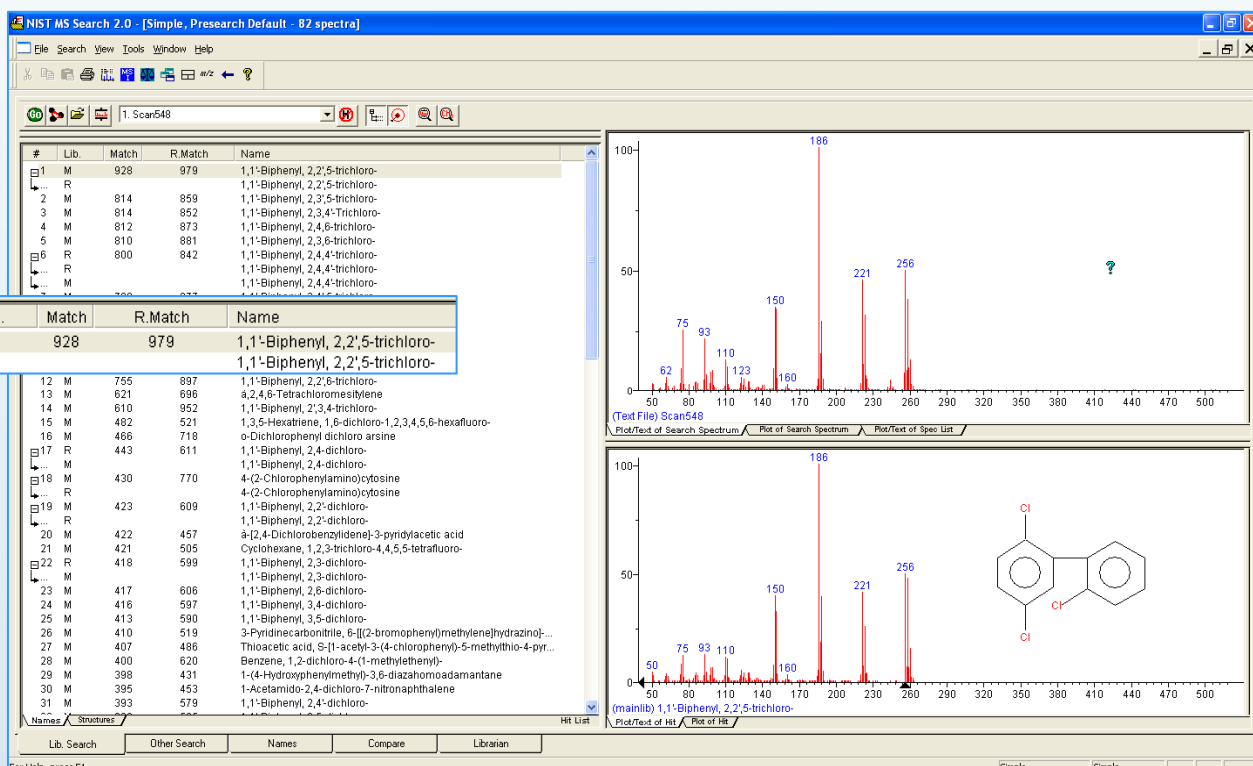


FIGURE 4. NIST® similarity search of 2, 2', 5- Trichlorobiphenyl. Acquired mass spectrum (top) and spectrum stored in the NIST® MS Library (bottom).

CONCLUSION

The application of Fast GC using 0.10 mm I.D. narrow-bore column has greatly shortened PCB analysis time, while the use of TOF-MS detection enabled to obtain distinguishable signals for the PCBs, providing their identification and quantification over several orders of magnitude.

In addition, the MASTER Lab provides a powerful data processing solution and an original deconvolution algorithm capable to handle the large amount of information in a smart and effective way resulting in reliable identification.

REFERENCES

- [1] Erickson, M. D., *Analytical Chemistry of PCBs*, CRC Press, Boca Raton, FL, U.S.A., 2nd ed., 1997.
- [2] Gross, J.H., *Mass Spectrometry. A Textbook*, Springer Verlag, Berlin, 2004.
- [3] Casilli, A. *TOF-MS for Fast GC and GCxGC*. G.I.T. Laboratory Journal Europe 14 (2010) 13-15.

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