Polychlorinated Biphenyls (PCB's) Analysis using Miniaturized High-resolution Time-of-Flight Mass Spectrometer "MULTUM-S II"

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Overview

[Purpose] To evaluate the performance of a miniaturized high-resolution time-of-flight (TOF) mass spectrometer "MULTUM-S II" for PCB's analysis.

[Experimental methods] Mass resolution, limit of detection (LOD), linearity and other experimental conditions were evaluated using hepta-CB (2,2',3,4,4',5,5'-heptachlorobiphenyl). Under optimized conditions, comprehensive native PCB mixture (66 PCBs mix) was used for establishing Fast-GC method.

[Results] At 20 cycles, **mass resolution of 8,000~10,000** was achieved, and **LOD was 1ppb**, and **linearity was 2.5 orders of magnitude**. In the high-resolution Fast-GC method, PCB mixture was able to measure **within 5 minutes**. Furthermore, background interference peaks were clearly separated even in the miniaturized mass spectrometer (MS).

Introduction

In our laboratory, a miniature multi-turn TOFMS was constructed and named "MULTUM-S II (INFITOF)". This instrument basically consists of four electric sectors and two additional electric sectors for the purpose of ion injection/ejection. Accelerated ions traverse the figure of eight flight orbit many times. As a result of **infinite flight length**, higher mass resolution is available in the miniaturized MS. **The size and weight of the system is 234 mm x 456 mm x 640 mm and 36 kg (including vacuum pump and electric circuits)**.

High-resolution selected ion monitoring (HRSIM) provides sensitivity and selective detection for compounds of environmental interest such as PCB's. The analysis as traditionally carried out by using magnetic sector mass spectrometers is highly effective. However, setup and method development can be complicated, requiring careful programming of SIM target masses, lock masses, and retention time groups. **Magnetic sector mass spectrometers** with a resolving power of 10,000 or greater tend to be **large and expensive**.

TOFMS is an attractive alternative because there is little or no tradeoff between high resolution and high sensitivity. However, previous commercially available GC/TOFMS systems are not offered with a resolving power of 10,000 or greater. The MULTUM-S II is well suited for PCB analysis. The system is compact, portable, and capable of achieving a resolving power of > 30,000 [1]. By acquiring high-resolution mass spectra in segments, method development is made easier.

MULTUM-S II

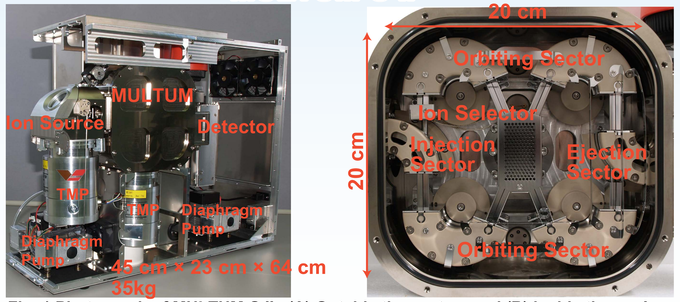
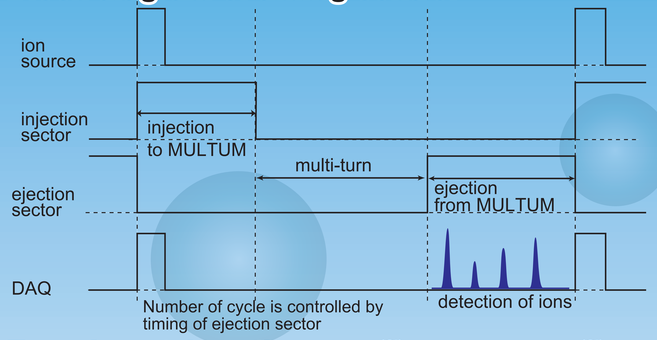


Fig. 1 Photograph of MULTUM-S II. (A) Outside the system and (B) inside the analyzer.

Block diagram of timing control



Experimental section

Fig. 2 Photograph of GC-MULTUM system.

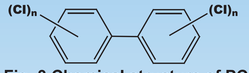


Fig. 3 Chemical structure of PCBs.

[Material and methods]

Analyte C-180S-TP (Hepta-CB, Accu standard inc.)
Comprehensive 66 PCBs mixture (EC-5433, CIL)
Dielectric fluids in coolant diluted by n-hexane.
PCB mixture was spiked into 1000-fold diluted fluids.

GC condition GC: Agilent 6890N
Column: FORTE HT8 (SGE)
12 m x 0.22 mm I.D. x 0.25 um film
Oven: 100°C (0.5 s) -> 40°C/min->320°C
Inlet : 320°C Splitless (purge time 0.5 sec)
Sample injection : 1 uL (1 ppb to 1 ppm)

MS condition Instrument: GC-MULTUM system (Fig. 2)
Ionization: EI (18 ~ 20 eV, see below)
Measurement mode: multi-segment
(*m/z* 180~505 in 10 segments)
DAQ: 0.1 sec (10 spectra/sec)

Results and Discussion

Performance evaluation

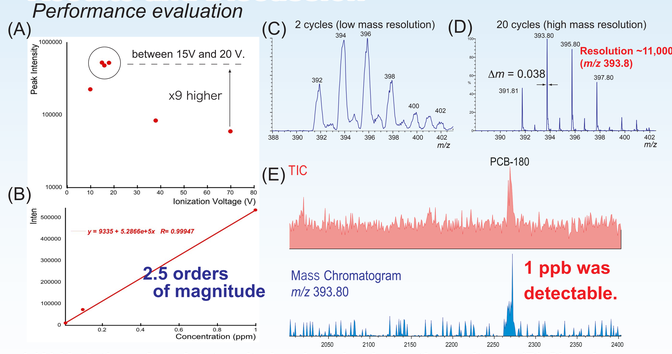


Fig. 4 (A) Variation of peak intensity by changing ionization voltage. (B) Signal response curve from 0.01 ppm and 1 ppm. Comparison of mass spectra of PCB-180-TP. (C) 2cycles (low mass resolution < 400) and (D) 20 cycles (high mass resolution ~11,000). (E) TIC and mass chromatogram of *m/z* 393.8 in 1 ppb.

Comprehensive 66 PCBs mixture Analysis by Fast-GC

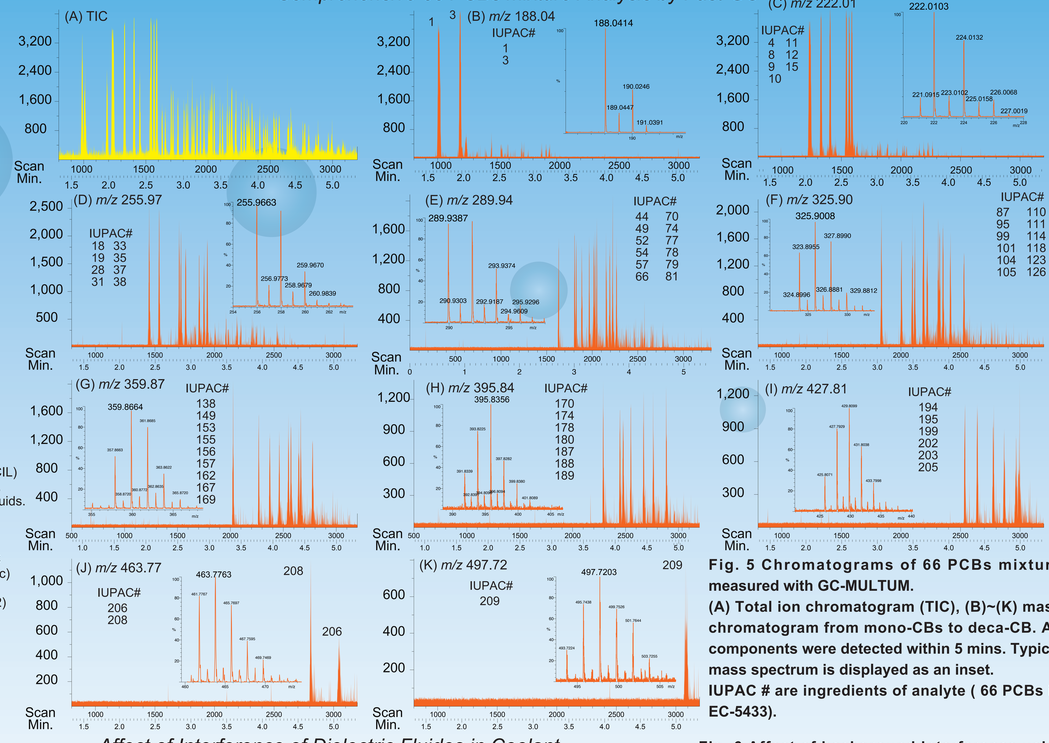


Fig. 5 Chromatograms of 66 PCBs mixture measured with GC-MULTUM.
(A) Total ion chromatogram (TIC), (B)~(K) mass chromatogram from mono-CBs to deca-CB. All components were detected within 5 mins. Typical mass spectrum is displayed as an inset.
IUPAC # are ingredients of analyte (66 PCBs in EC-5433).

Affect of Interference of Dielectric Fluides in Coolant

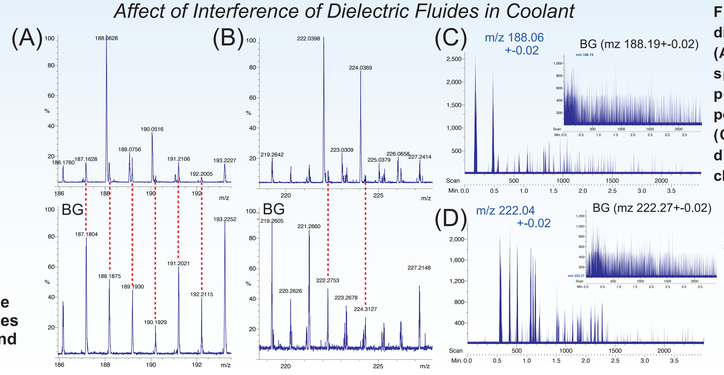


Fig. 6 Affect of background interference using diluted dielectric fluids (PCB mix was spiked).
(A) mono-CBs and (B) di-CBs. Comparing signal spectra and background spectra, target signal peaks were clearly separated from interference peak.
(C) Mass chromatogram of mono-CBs and (D) di-CBs. HRSIMS (+-0.02 Da) could provide correct chromatogram w/o interference.

Conclusion

1. MULTUM-S II can provide HRSIMS data.
2. In 20 cycles, mass resolution was 10,000 and LOD was 1 ppb.
3. High-resolution mass spectra were beneficial for mixture analysis with brief preparation.

Reference

1. Shimma S et al. *Anal. Chem.*, 82, 8456 (2010)