

FAST GC ANALYSIS AND ACCURATE MASS MEASUREMENT OF POPs BY USING A GAS CHROMATOGRAPH – HIGH RESOLUTION TIME-OF-FLIGHT MASS SPECTROMETER

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Abstract

The fast GC techniques for persistent organic pollutants (POPs) analysis by using electron ionization (EI) and negative ion chemical ionization (NICI), have been investigated with a gas chromatograph – high resolution time-of-flight mass spectrometer (GC-HRTOFMS). As the result, POPs could be analyzed in only seven minutes under the fast GC conditions. To make effective use of a HRTOFMS, high-resolution mass chromatogram techniques were used. High sensitivity, repeatability and linearity on calibration curve were obtained under the fast GC and HRTOFMS conditions in EI mode and NICI mode. Especially in NICI mode, POPs standard sample of 0.03pg/ μ L could be detected clearly. By using a GC-HRTOFMS, high-sensitivity measurement and high-speed data acquisition could be compatible.

Introduction

In general, several types of equipments as mass spectrometer of GC-MS were applied¹⁻². There are magnetic sector type, quadruple type and TOF type and so on as available GC-MS equipments. In comparison with these types of mass spectrometers, a TOFMS has small systematic error due to relationship between mass and time of flight in entire mass range³. As indicated above, GC-HRTOFMS can easily perform the accurate mass measurement using one point mass calibration by an internal reference ion.

The fast GC techniques provide high-throughput samples analysis, however it requires high-speed data acquisition such as a flame ionization detector. In the case of fast GC with a narrow bore column, adequate sampling rate is e.g. ≥ 10 Hz.

The fast GC analysis of POPs upon EI mode and NICI mode, have been investigated by using a GC-HRTOFMS. In addition, accurate mass (m/z) measurements have been carried out in order to make a high-resolution mass chromatogram that made by within the narrow range of m/z .

Materials and Methods

POPs standard solutions were purchased from KANTO CHEMICAL CO., INC. They were applied for analysis without further purification. We have prepared a standard solution containing 12 target compounds (α -HCH, β -HCH, γ -HCH, δ -HCH, Heptachlor, Aldrin, 4,4'-DDE, Dieldrin, 2,4'-DDT, 4,4'-DDT, Methoxychlor, Mirex) and one internal standard compound (d_8 -Naphthalene for GC/EI, 9-Bromoanthracene for GC/NICI).

Mass spectrometer was calibrated by using PFK as standard calibrant before measurement. The m/z values of all data were compensated on the

Table 1 GC-HRTOFMS conditions for measurement of POPs.

Instrument	JMS-T100GCV "AccuTOF GCv" (JEOL Ltd.)
Quantitative software	Escribe (JEOL Ltd.)
Injection mode	Splitless
Inlet temp.	280 °C
Column	DB-5, 10m \times 0.18mm, 0.18 μ m
Oven temp. program	50 °C(1.5 min) \rightarrow 75 °C/min \rightarrow 80 °C \rightarrow 50 °C/min \rightarrow 280 °C(1.1 min), Total 7 min
Sample volume	2 μ L
Carrier gas	He (0.5 mL/min)
Ionization mode	EI(+), 70 eV, 300 μ A CI(-), 200 eV, 300 μ A, Methan gas (1.5 mL/min)
Chamber temp.	280 °C(EI(+)), 200 °C(CI(-))
Transfer line temp.	280°C
m/z range	35-600
Data acquisition speed	0.1 sec (10 Hz)

basis of background peak of capillary column (m/z 207.0329: $C_3H_{15}O_3Si_3$) for EI or peak of C_7F_{12} from PFK (m/z 311.98084) for NICI after the measurement.

The standard mixture solutions of POPs at 0.3, 1, 3, 10, 30, 100 $pg/\mu L$ were applied for EI measurement and the solution at 0.03, 0.1, 0.3, 1, 30, 10 $pg/\mu L$ were applied for NICI measurement. All standard solutions were measured by a JMS-T100GCV "AccuTOF GCv" (JEOL Ltd.), GC-HRTOFMS system combined with EI or NICI ion source. The JMS-T100GCV can acquire data of up to 25 spectra per second (25 Hz) with a high resolution of 6,000 full width at half maximum (FWHM). The conditions and parameters of the GC/HR-TOFMS for measurement of POPs are shown in Table 1.

Results and Discussion

The total ion current (TIC) chromatogram of the standard solution is shown in Figure 1. All target compounds of POPs could be detected within seven minutes under the fast GC condition.

In figure 2, peak shapes of β -HCH and γ -HCH measured at different data acquisition speed were shown. Peak separation between β -HCH and γ -HCH was not clear on the TIC chromatograms measured at 2 Hz data acquisition speed that is normally used for conventional GC condition. The number of data point within one peak was insufficient 2 Hz data acquisition speed. But that separation became more clear at faster data acquisition speed. The results in figure 2 suggested that at least 5 Hz data acquisition speed was necessary for fast GC condition. It means that the high-speed data acquiring capability such as TOFMS was required for the quantitative analysis under the condition on fast GC. Therefore, 10 Hz data acquisition speed was employed in this study.

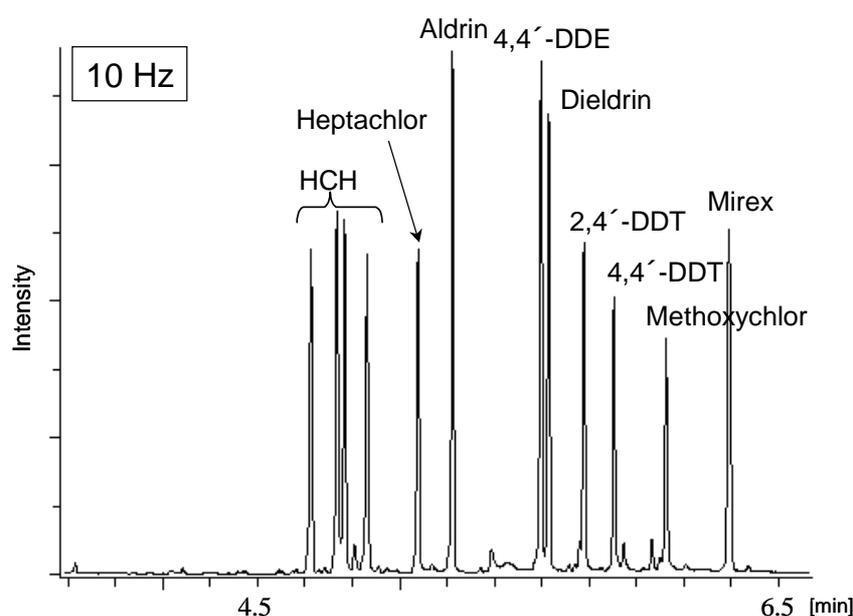


Figure 1 TIC chromatogram under the fast GC condition (1000 $pg/\mu L$)

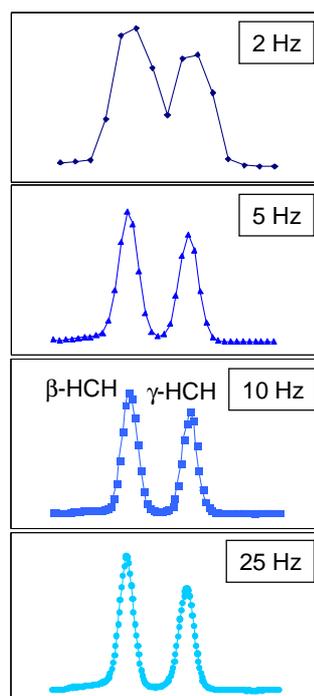


Figure 2 The changes of the chromatogram peaks shape depend on data acquisition speed for β -HCH and γ -HCH.

The calibration curves of α -HCH and Mirex measured by EI and NICI ionization were shown in figure 4 and 6. In both case of EI and NICI, a good linearity of calibration curve at the concentration ranges that were investigated in this study were observed.

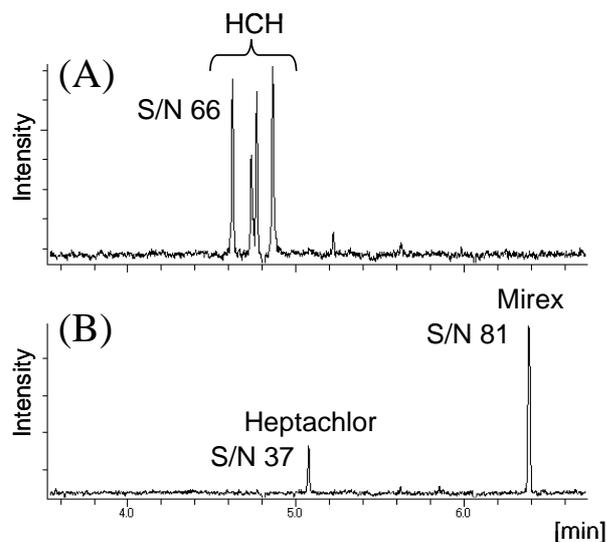


Figure 3 High-resolution mass chromatograms of 0.3 pg/ μ L for GC/EI measurement. (A) m/z 218.9116 \pm 0.025, (B) m/z 271.8102 \pm 0.025.

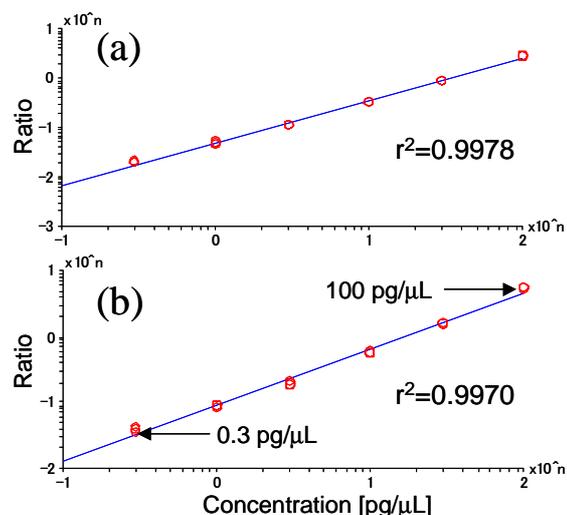


Figure 4 Calibration curves for GC/EI measurement. (a) α -HCH, (b) Mirex.

Table 2 GC/EI measurement results.

No.	Compound	Retention time [min]	Exact mass of quantitative ion [m/z]	Coefficient of correlation	Mass chromatogram (exact mass \pm 0.025) of 0.3 pg/ μ L	
					C. V. [%] (n=3)	S/N (r.m.s.)
1	α -HCH	4.627	218.9116	0.9978	3.4	66
2	β -HCH	4.738	218.9116	0.9979	8.7	36
3	γ -HCH	4.770	218.9116	0.9960	1.6	58
4	δ -HCH	4.864	218.9116	0.9947	8.4	63
5	Heptachlor	5.080	271.8102	0.9968	7.2	37
6	Aldrin	5.226	262.8570	0.9974	4.9	61
7	4,4'-DDE	5.599	246.0003	0.9978	3.4	87
8	Dieldrin	5.632	262.8570	0.9974	4.2	32
9	2,4'-DDT	5.780	235.0081	0.9989	5.3	34
10	4,4'-DDT	5.906	235.0081	0.9994	6.2	15
11	Methoxychlor	6.127	227.1072	0.9993	8.0	18
12	Mirex	6.393	271.8102	0.9970	8.6	81

In figure 3 and 5, mass chromatograms of HCHs and Mirex measured by EI and NICI were shown. In case of NICI measurement, the clear peaks correspond to both compounds were detected even in 10 times lower concentration range comparing to the results from EI.

The values of S/N for all target compounds measured by EI (0.3 pg/ μ L) and NICI (0.03 pg/ μ L) were summarized in Table 2 and 3. Except for 2,4'-DDT and Methoxychlor by NICI measurement, S/N values for all target compounds were more than 10 and its C. V. (%) values were less than 20%. Those results suggested that the detection limit for all target compounds that were investigated in this study by EI and NICI were sub picogram (pg) level and several dozen femtogram (fg) levels respectively.

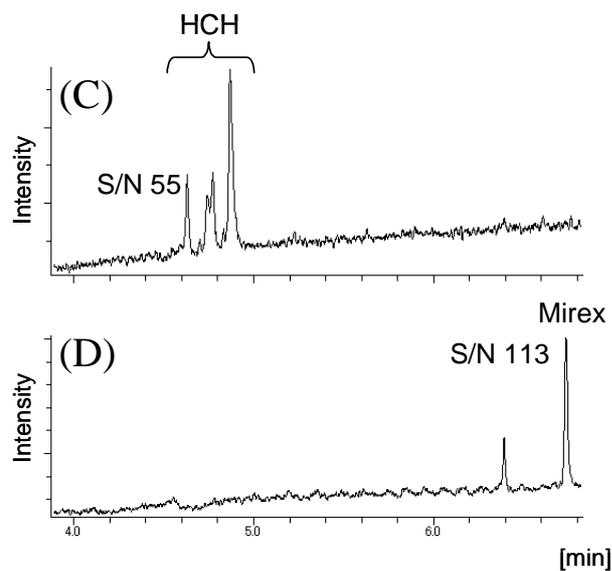


Figure 5 High-resolution mass chromatograms of 0.03 pg/ μ L for GC/NICI measurement. (C) m/z 69.93771 \pm 0.025, (D) m/z 403.74497 \pm 0.025.

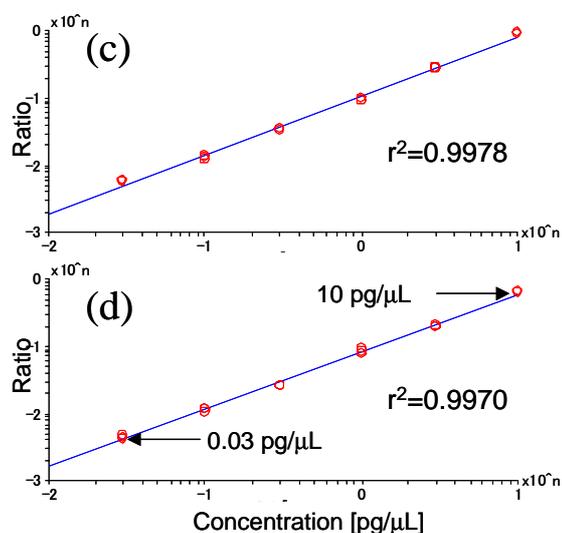


Figure 6 Calibration curves for GC/NICI measurement. (c) α -HCH, (d) Mirex.

Table 3 GC/NICI measurement results.

No.	Compound	Retention time [min]	Exact mass of quantitative ion [m/z]	Coefficient of correlation	Mass chromatogram (exact mass \pm 0.025) of 0.03 pg/ μ L	
					C. V. [%] (n=3)	S/N (r.m.s.)
1	α -HCH	4.629	69.9377	0.9972	5.8	55
2	β -HCH	4.740	69.9377	0.9885	4.5	42
3	γ -HCH	4.772	69.9377	0.9971	12.7	63
4	δ -HCH	4.867	69.9377	0.9971	0.3	149
5	Heptachlor	5.081	265.9038	0.9993	12.1	64
6	Aldrin	5.229	236.8413	0.9904	10.4	67
7	4,4'-DDE	5.603	34.9689	0.9955	6.5	17
8	Dieldrin	5.636	236.8413	0.9963	2.1	44
9	2,4'-DDT	5.784	34.9689	0.9929	10.3	11
10	4,4'-DDT	5.912	34.9689	0.9943	16.4	7
11	Methoxychlor	6.132	34.9689	0.9828	13.0	4
12	Mirex	6.397	403.7450	0.9954	1.1	113

References

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