

Optimization of the injection condition on comprehensive two-dimensional GC (GC x GC) for characterization of PAHs in tar

Ohba H¹, Ozawa S¹, Iwasaki K¹, Ieda T², Ochiai N², Kanda H² and Iwaki K³

¹ EBARA Research Co., Ltd., 4-2-1, Honfujisawa, Fujisawa-shi, 251-8502, Kanagawa, JAPAN;

² GERSTEL K.K., 2-13-18 Nakane, Meguro-ku, 152-0031, Tokyo, JAPAN;

³ School of Pharmaceutical Science, Ohu University, 31-1, Misumido, Tomita-machi, Koriyama-shi, 963-8611, Fukushima, JAPAN

Introduction

Comprehensive two-dimensional GC (GC x GC) is an interesting technique for applying multi componential analysis and high matrix contained samples analysis owing to its higher resolution. Also, it is expected to simplify analytical process. Generally on GC analysis of samples contained non- or semi-volatile compounds such as tars, complexly pre-treatment process for removing these compounds is necessary to keep capillary column performance. In this study, optimization of the injection method for characterization of PAHs in tars without pre-treatment process was attempted and compared with the conventional pre-treatment method.

Materials and Methods

(1) Optimization of injection method

Programmable Temperature Vaporization (PTV) system (GERSTEL CIS 4 [Cooled Injection System] with ALEX [Automated Liner EXchange]) was employed to optimize thermal condition. Three thermal conditions shown in Table 1 were evaluated by using the C₅-C₄₄ standard solution and 16 PAHs standard solution.

Table 1 The thermal conditions of PTV system

	Condition
(1)	10 °C → 12 °C/sec. → 150 °C (1 min.) → 10 °C
(2)	10 °C → 12 °C/sec. → 175 °C (1 min.) → 10 °C
(3)	10 °C → 12 °C/sec. → 200 °C (1 min.) → 10 °C

(2) GC x GC measurement

10 mg of tar sample was diluted with 10 mL of toluene and analyzed by following condition.

System: 6890 series (Agilent technologies) with KT2004 (Zoex), CIS4 (GERSTEL) and ALEX (GERSTEL)

Injection mode: Split (ratio 1:20) Gas saver on after 3min. (300 mL/min.)

Injection temperature: 10 °C → 12 °C/sec. → 200 °C (1 min.) → 10 °C

Carrier gas: 2.26 mL/min. (Constant flow mode)

1st column: HP-1MS (Agilent technologies) 30 m x 0.25 mm i.d., 0.25 μm thickness

2nd column: DB-17 (Agilent technologies) 2 m x 0.1 mm I.d., 0.1 μm thickness

Oven temperature: 40 °C (1 min.) → 5 °C/min. → 280 °C (12 min.)

Modulation period: 6 sec.

Hot jet gas duration time: 300 msec.

Detection mode: FID

Sample preparation and analysis

(3) Conventional pre-treatment method

The pre-treatment procedure was shown in Fig.1. After this procedure the fraction (3), (4), (5) and (6) were analyzed by using GC/MS with following condition.

GC.... 6890 series (Agilent technologies)

Column : HT5 aluminium-crad type (SGE), 30 m x 0.32 mm i.d.

Oven temperature : 50 °C (2 min.) → 5 °C/min. → 290 °C (10 min.) → 10 °C/min. → 400 °C

Injection temperature : 300 °C

Injection mode : split (ratio. 1:10)

Carrier gas : Herium, 5 psi (Constant pressure)

MS....5973 (Agilent technologies)

Detection mode : SCAN(m/z=50~550)

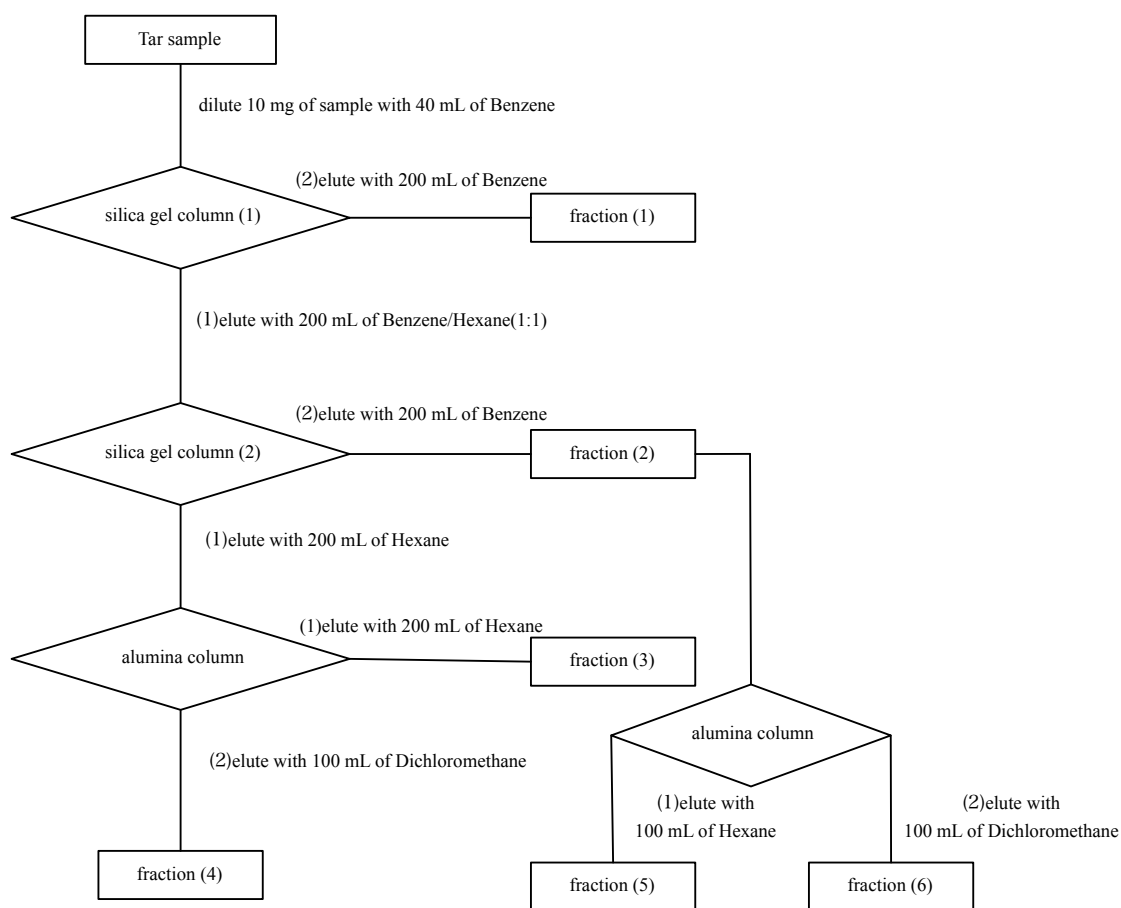


Fig. 1 The pre-treatment procedure of tar sample analysis

Sample preparation and analysis

Results and discussion

1) Optimization of injection method

The chromatograms of C₅-C₄₄ standard solution at each condition were shown in Fig. 2. C₅-C₁₈ were detected at all conditions. These peak strength of the condition (3) were equivalent to the result when the injection temperature was 350 °C. Focused on the peak of C₂₀H₄₂, the peak strength on condition (3) is better than others. Also the chromatogram of 16 PAHs standard at the condition (3) was shown in Fig. 3. It was found that the compounds smaller than Pyrene were detected at this condition. From these results, the condition (3) was employed in this study.

2) Comparison of GC x GC method with conventional pre-treatment method

The chromatogram of the tar sample by GC x GC was shown in Fig 4. Di ~Tetra aromatic compounds were detected. As for the peaks, the identification of the group type by the number of aroma rings was also possible according to the comparison with the 16 PAHs standard. Moreover, the peaks from impurities or obstructors were placed in the bottom of Y-axis in the chromatogram. It means that there is no obstacle in qualitative of PAHs. On the other hand, at conventional pre-treatment method, the peaks of PAHs were detected only in the chromatogram of fraction (4), shown in Fig. 5. Compared with these chromatograms, there are differences in the number and the strength of the peaks. It seems that the differences were caused by the loss of the target compounds in the pre-treatment and the peak separation ability with the column system.

3) Conclusion

From these results, the PAHs analysis in tars was improved in simplicity, high sensitivity, and high selectivity by the combination of PTV and GC x GC with optimization of the condition.

Acknowledgements

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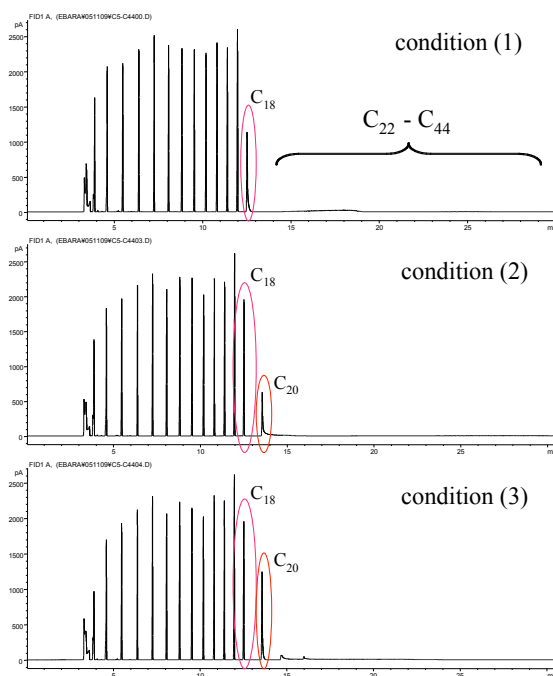


Fig. 2 The chromatograms of C₅-C₄₄ standard at each conditions

Sample preparation and analysis

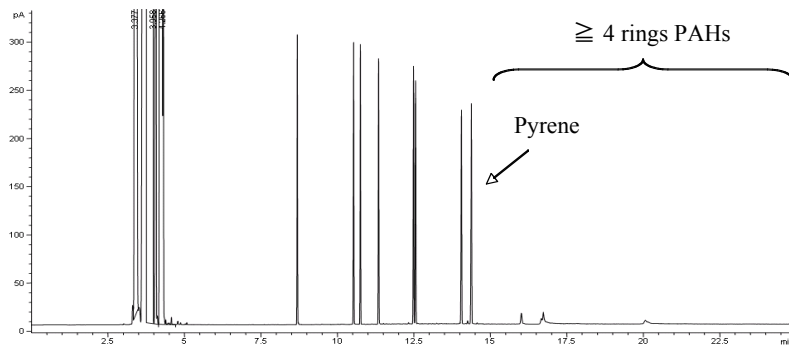


Fig. 3 The chromatogram of 16PAHs standard at condition (3)

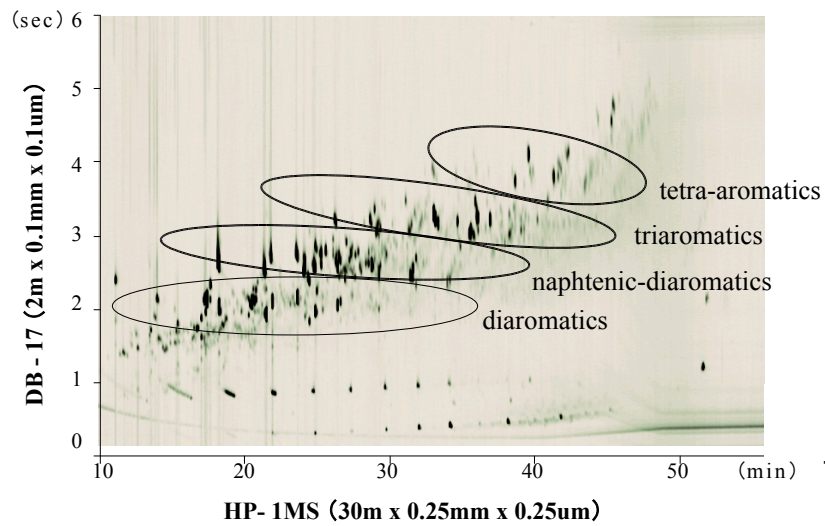


Fig. 4 The GC xGC chromatogram of the tar sample

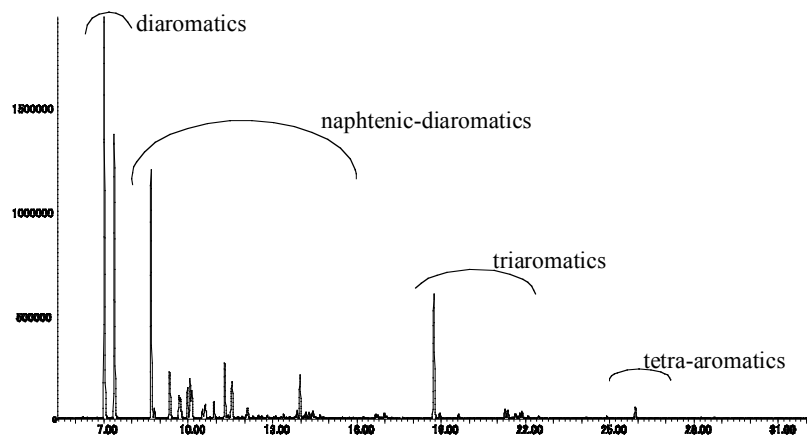


Fig. 5 The chromatogram of the fraction (4) from pre-treatment of the tar sample