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Development of novel fiber-packed needle interface for off-line reversed-phase liquid chromatography–capillary gas chromatography

Akira Abe, Yoshihiro Saito*, Ikuo Ueta, Kenichi Nakane, Tsutomu Takeichi, Kiyokatsu Jinno

School of Materials Science, Toyohashi University of Technology, Toyohashi 441-8580, Japan

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ABSTRACT

For two-dimensional reversed-phase liquid chromatography–gas chromatography (2D RPLC–GC), a specially-designed needle packed with a polymer-coated fibrous stationary phase was introduced as a novel interface. The bundle of synthetic fibers coated with polydimethylsiloxane (PDMS) was packed into the head section of the needle, and served as the extraction medium. Using the post-column dilution of the LC eluent by water and subsequent extraction with the needle interface, the analyte was successfully concentrated to the PDMS phase on the fibrous support in the needle. The concentrated analytes were directly injected to GC system by inserting the needle to a heated GC injector. 2D separations of aliphatic and aromatic hydrocarbons, and also kerosene-extract were performed with the off-line RPLC–GC system interfaced by the needle extractor. The results suggested that the fiber-packed needle interface could be one of the simple and effective approaches to develop an on-line coupled LC–GC system.

1. Introduction

In order to obtain a higher separation power, multi-dimensional chromatography has been widely investigated from almost beginning of the chromatographic history. Two-dimensional (2D) chromatography on planner stationary phases, such as a paper or a thin-layer porous stationary phase, could be regarded as the typical example, where more enhanced separation power and peak capacity have been realized. Extensive research and development of modern 2D chromatography and the corresponding applications have been also published especially in gas chromatography–gas chromatography (GC–GC) [1–11], liquid chromatography–liquid chromatography (LC–LC) [12–18] and LC–GC [19–21], along with the on-line coupling to supercritical fluid chromatography [22,23]. This is because the chromatographic performance of the single separation system could not be sometimes satisfactory, and on-line coupling of these separation systems should be carried out for the separation of very complex sample mixtures as found in peptides and natural petrochemicals [12,22].

For the hyphenation of two separation systems, an interface is commonly required, and the performance of the interface is one of the most important parameter to determine the entire performance of the 2D chromatography system. As the interface for 2D LC–GC, a manual/automatic multi-port valve equipped with two sample loops is commonly employed. The valve-based interface could offer a good performance for typical 2D LC–GC analysis. Alternative interfacing modulator is based on a solvent evaporation technique [24], however, the analytes having a boiling point similar to that of the mobile phase would be co-evaporated with the solvent during the modulation, resulting a discrimination problem. In addition, for water-containing LC eluent employed in reversed-phase LC (RPLC), an interface typically utilizing a concentration technique such as liquid–liquid extraction or solid phase extraction has been also developed [25]. The details of the 2D LC and GC systems are reviewed elsewhere [24–27].

Recently, novel chromatographic media have been developed with several synthetic organic high-performance fibers as the stationary phase. High temperature GC separations were successfully demonstrated with the fiber-packed column [28,29] and the polymer-coated fibrous support [30]. Selectivity tuning of the fibrous stationary phase was studied with surface-derivatized fiber, where the surface of the fibrous materials was chemically modified with several organic functional groups [31]. These fibrous materials were also introduced as the extraction medium for miniaturized sample preparation process [32–35], and the on-line coupling to liquid-phase separation system has been studied [36]. Introducing the fibrous materials to a needle-type extraction device, a simultaneous extraction and the subsequent GC separation of volatile organic compounds were carried out along with the derivatization and preconcentration of the analyte on the polymer-coated fibers packed into the needle device. The applications of the in-needle sample preparation could be found in our previous publications [37–40]. Taking advantage of the needle extraction device, such as easier operation to transfer the extracted analyte to GC system and

* Corresponding author. Fax: +81 532 48 5833.
E-mail address: saito@chrom.tutms.tut.ac.jp (Y. Saito).

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the robustness that should be necessary for the repeatable use at the heated GC injector during the desorption/injection, one can find the possibility of the developed needle device as the interfacing device between LC and subsequent GC separations.

In this paper, the polymer-coated fiber-packed needle was introduced as the novel interface for the off-line coupling of conventional RPLC and capillary GC. For the successful trapping of the analyte by the needle interface, the LC eluent was diluted by water to decrease the solubility of the solute. The resulting aqueous solution was transferred to the needle, and then the analyte was extracted by the PDMS phase on the fibrous support in the needle. After a period of time, the needle interface was detached from the LC line, and inserted into a heated GC injector to desorb/inject the extracted analytes for GC separation. Several experimental parameters for the extraction were studied to optimize the trapping performance. Under the optimized conditions, 2D separation of standard compounds and a real complex sample were performed, and the results suggested a further application of the developed needle-type 2D RPLC–GC interface.

2. Experimental

2.1. Materials

All reagents and solvents were purchased either from Wako Pure Chemicals (Osaka, Japan) or Tokyo Chemical Industry (Tokyo, Japan), and used without further purification. Water was purified with Milli-Q water purification system (Millipore, Bedford, MA, USA). Kerosene was purchased at a local gas station in Toyohashi, Japan. Poly(*p*-phenylene-2,6-benzobisoxazole) fiber, commercialized as Zylon (Toyobo, Ohtsu, Japan), was used as the fibrous support material. The nominal average diameter of the Zylon filament was about 11.5 μm. A specially-designed lure-lock needle having the dimensions of 0.5 mm i.d., 0.7 mm o.d., 85 mm length, and polydimethylsiloxane (PDMS) coating were provided from Shinwa Chemical Industries (Kyoto, Japan). As the tubing material for liquid lines, a polyetheretherketone (PEEK) tube of 0.13 mm i.d., and a polytetrafluoroethylene (PTFE) tube of 0.25 mm i.d. were purchased from GL Science (Tokyo, Japan) and used with the appropriate length.

2.2. LC and GC systems

LC system (JASCO, Tokyo, Japan) was consisted of PU-1585 HPLC pump and UV-970 UV/VIS detector, while MD-915 photodiode-array detector was used if necessary. All LC separations were carried out with Develosil ODS UG-5 packed with 5 μm particles, 4.6 mm i.d., 150 mm length (Nomura Chemical, Seto, Japan). The flowrate of the LC mobile phase (methanol) was set at 0.1 mL/min, and the column temperature was controlled at 24 ± 0.5 °C. The flowrate of the LC eluent was determined from preliminary experiments, where the total operation time of the fractionation, GC analysis time and the pressure generated by the fiber packing were considered. A high pressure tended to a failure of the operation due to the leakage from the connector between the syringe and the needle.

As the GC system, a HP 6890N GC system (Yokogawa Analytical Systems, Tokyo, Japan) equipped with DB-1 column of 0.32 mm i.d., 15 m length, d_f: 0.25 μm (J & W Scientific, Folsom, CA, USA), a split injector and a flame ionization detector (FID) was employed through this work. Nitrogen was used as the carrier gas and the column head pressure was set at 20 kPa. The split ratio was typically set at 20:1, and the injector and detector temperature were set at 300 °C based on the preliminary experiments for the optimization of these parameters. The other operation conditions will be described in the following section when necessary. A ChromNav software (JASCO) was used for the data collection from both RPLC and GC system on personal computers.

2.3. Preparation and preconditioning of the extraction needle

The polymeric coating onto the fibrous support material was accomplished as the following procedures: the bundle of 332 Zylon filaments was packed into a fused-silica capillary (0.32 mm i.d., 1 m length) and the coating process was done in a similar manner to the liquid stationary phase coating for conventional open-tubular fused-silica capillary for typical GC separation [28]. First, the fiber-packed fused-silica tubing was connected to the pressure-proof vessel containing 10 mL of acetone and washed with the solvent pumped by nitrogen gas at the pressure of 500 kPa, and washed sequentially by the following solvents: water, acetone and chloroform. Then, the fiber-packed capillary was allowed to dryness at room temperature for approximately 2 h under the flow of nitrogen. Secondary, the capillary was heated from room temperature to 300 °C at the ramp of 2 °C/min, and the temperature was maintained for 10 h in the GC oven with the nitrogen flow. Next, the solution of PDMS (7 wt% in hexane), cross-linking reagent and benzoyl chloride was pumped into the capillary. After the 5 mL of the coating solution was pumped, nitrogen flow was maintained for more than 5 h. Then, the column was installed in the GC oven again and heated at 300 °C for more than 48 h to ensure the completion of the cross linking reaction. As described previously [41], the film thickness has been calculated with several standard solutes based on the comparison of the retention factors obtained with the polymer-coated fiber-packed columns and conventional open-tubular columns. Assuming a uniform coating onto all the surface of the packed fiber, the estimated film thickness is about 2.0 μm for 7%-PDMS coating, and the results have a good agreement with that in several previous studies.

The obtained polymer-coated filaments were taken out from the capillary, and the bundle was cut and rearranged to form the bundle of 996 Zylon filaments of 3 cm length, followed by the packing procedure to the needle device as similar to that reported previously [37–40]. Fig. 1A shows the illustration of the needle extraction device. In order to ensure the removal of any impurities in the polymeric coating on the fibrous material, the needle was washed with both methanol and dichloromethane, and then heated up to 300 °C in the GC injection port. After this preconditioning procedure, the needle device allowed to be used for more than 100 times without any significant deterioration on the extraction performance along with no observable bleeding of the polymer coating.

2.4. Needle extraction and 2D RPLC–GC conditions

The eluent from LC was diluted with water at the tee-connector as shown in Fig. 1B, where two PEEK tube from the LC column and another pump for water delivery were attached to the connector, and the PTFE tubing to the modified syringe attached to the needle device was also linked to the tee. The post-column dilution enabled effective extraction of the analyte and consecutive GC separation by the needle-type interface. As the probe molecule for the concentration process by the needle interface, hexylbenzene was used through this section because the compound exhibited high $\log P_{o/w}$ value, low solubility in water and a satisfactory UV response. This feature would be suitable as a representative of real samples such as petrochemicals.

The extraction time was first set at 4 min to transport the injected analyte thoroughly from the injector to the outlet of the needle interface without LC column at the flowrate of methanol (0.1 mL/min), although the extraction efficiency was almost at constant over the extraction time from 4 to 5 min in the preliminary experiments. On the 2D analysis, the extraction time of 5 min was

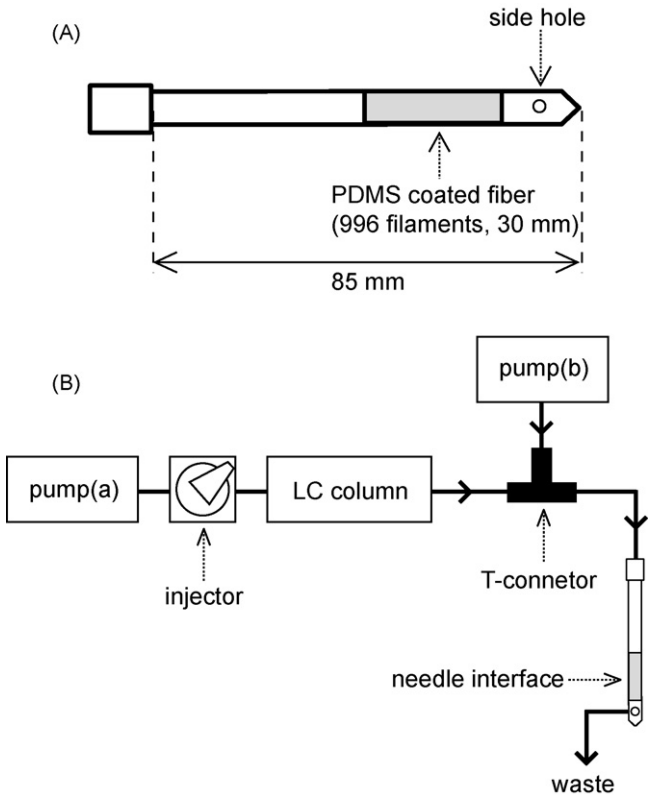

Fig. 1. Illustrations of the fiber-packed needle interface (A) and the post-column extraction system for LC eluent (B). LC pump(a) pumped the eluent, while water was delivered from pump(b).

used, where the other operation requirements for 2D separations were also considered in the preliminary experiments. After the fractionation, the needle extractor was attached to the other syringe, and inserted to the heated GC injection port. After 5 s from inserting the needle to the injection port, the sample was injected to GC column by flushing inside of the needle with 50 μL of methanol and 450 μL of air at 300 °C within 3 s. The dead volume of the needle packed with the coated-fiber was ca. 30 μL. Hence, the needle should be flushed out by a volume of solvent larger than the dead volume. In addition, the desorption solvent remaining in the needle should be also flushed out by nitrogen to ensure the injection of the analytes and fluids therein. From these reason, the desorption conditions were determined. For washing and re-conditioning the needle interface, the thermal desorption with the solvent as the same procedure with the GC injection were performed two times.

For 2D analysis, the eluent coming from the LC column was diluted by water and introduced to the PDMS-coated polymer-packed needle via the T-shape connector at the constant flow rate (0.3 mL/min) of water for the dilution with the system configuration shown in Fig. 1B. The collection time of the LC eluent was set for 5 min. The injection of the analyte to GC column was done with the same way mentioned in the above section. During the GC injection and the conditioning of the needle, LC mobile phase was paused for about 8 min, and then re-pumped for the next fractionation. All GC measurements were performed under the same conditions. GC oven temperature was programmed from 70 °C (1 min) to 250 °C (1.5 min) at the ramp of 40 °C/min. The other separation conditions were found in the section above.

For data processing, house-made short programs were used. The data sets generated from 2D LC–GC system were processed to visualize in three-dimensional plot with gnuplot software (version 4) on a Linux operating system.

3. Results and discussion

3.1. Validation of the extraction process

To transfer the analyte from LC to GC, the needle packed with polymer-coated fibers (Fig. 1A) was served as the extraction interface. For the successful trapping of the organic compounds, the LC mobile phase should be diluted by the poor solvent like water as described in Section 2. The LC column outlet was connected to the needle with T-connector which also connected the pump for water supply (Fig. 1B). During the experiments for the evaluation of the extraction and concentration performance, the needle extraction was performed without the LC column and the UV detector.

The needle which extracted the analyte was subjected to the thermal desorption with the plug of 50 μL of methanol and the 450 μL of air. The amounts of the organic solvent and air were determined based on our previous studies [37–40] and preliminary experiments. Considering the stability of the polymeric coating phase in the needle interface, the desorption temperature was set at 300 °C for the sequential 2D analyses.

For the determination of the adequate amount of water which mixed at T-connector, hexylbenzene was extracted with the different flow rate of the dilution water. The resulted peak areas after the desorption and the GC separation are shown in Fig. 2. The amount of extracted hexylbenzene from the water–methanol solution had the maximum around 0.3 mL/min of the dilution water, where the high flow rate of water would be expected to give a high recovery. This result could be explained by following reason: at a higher flowrate, the diffusibility of the analyte in the diluted eluent was decreased compared with the one expected on a lower flowrate, and then a part of the solute in the diluted eluent could not access to the PDMS phase and would pass the needle without the extraction. From these results, the flowrate of the dilution water was set at 0.3 mL/min which afforded the highest trapping performance. On the dilution process, the pressure caused by the packings in the needle was typically under 1 MPa (measured from the indication of the LC pump).

Under the optimized trapping condition, the recovery of the analyte from the liquid phase was evaluated based on the comparison with the direct injection, where the obtained extraction yield calculated by the comparison with the peak area for the direct injection of hexylbenzene was 71% (RSD < 5.0%; $n = 5$).

The relationship between the sample concentration and the extraction was also examined. The mixture of hexylbenzene and

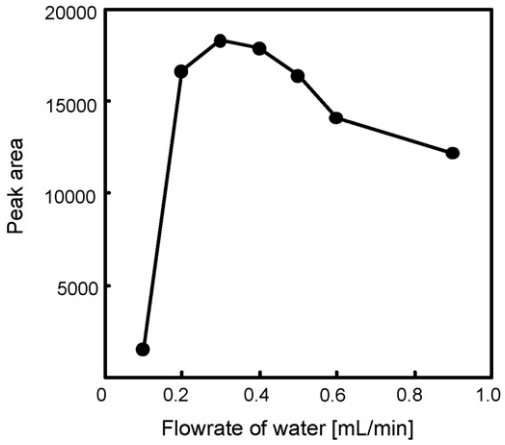

Fig. 2. Effect of the flowrate of dilution water on the extraction of hexylbenzene. The extract was desorbed at 300 °C in GC injector. The GC separation was carried out with the temperature programming of 110 °C (1 min) to 200 °C at the ramp of 20 °C/min.

Table 1
Linear range of the correlation curve and the correlation coefficient (r) for the extraction of two compounds.

Sample	Linear range (ppm)	r
Hexylbenzene	2.5–500	0.995
Dodecane	2.5–500	0.998

dodecane with different concentration was extracted and injected to GC. At the concentration ranging from 2.5 to 500 ppm for each compounds, the linear relationship between the extracted amounts and the analyte concentrations was observed and the results are summarized in Table 1. Typical chromatogram for the separation of the extracted hexylbenzene and dodecane is illustrated in Fig. 3, where a simultaneous extraction of these compounds by the needle device could be confirmed. As the typical examples of the needle extraction, Fig. 4 shows the chromatograms of five *n*-alkane mixture (A) and four alkylbenzene mixture (B) extracted and injected to GC by the needle interface. The chromatograms also elucidated the fiber-packed needle could concentrate the samples having a range of $\log P_{o/w}$ values, indicating a possibility for the simultaneous extraction/injection of a more complex mixture, although the selectivity of the needle extraction device as the interface between RPLC and GC should be further studied in detail along with the real applications based on the selectivity studies with various compounds having different polarity and molecular structure.

3.2. 2D LC–GC with the needle-type interface of the standards

For the evaluation of the total 2D system with the needle type extractor as the interface for LC–GC, the standard samples were chromatographed under the optimized extraction conditions. Alkanes mixture and alkylbenzenes mixture were used as the standard compounds. The conventional RPLC and the temperature-programmed capillary GC that found on the common laboratory were served as the first and second dimensions, respectively, without any complex instrument. Fig. 5 illustrates the overlaid 2D chromatograms for the separation of alkanes mixture and alkylbenzenes mixture. The samples were first separated into the groups which having similar $\log P_{o/w}$ value by ODS column, and then separated further by temperature-programmed GC mainly according to their boiling points. Alkanes and alkylbenzene were successfully separated by the off-line coupling of the conventional LC and the capillary GC by this interface, which demonstrated a further possibility of the developed 2D separation system consisted of the solvent dilution and the needle extraction system. The orthogonality of both dimensions employed in this work was not so high, however, it was satisfactory for the group analysis of the aromatic and aliphatic hydrocarbons with the combination of the separation system employed here.

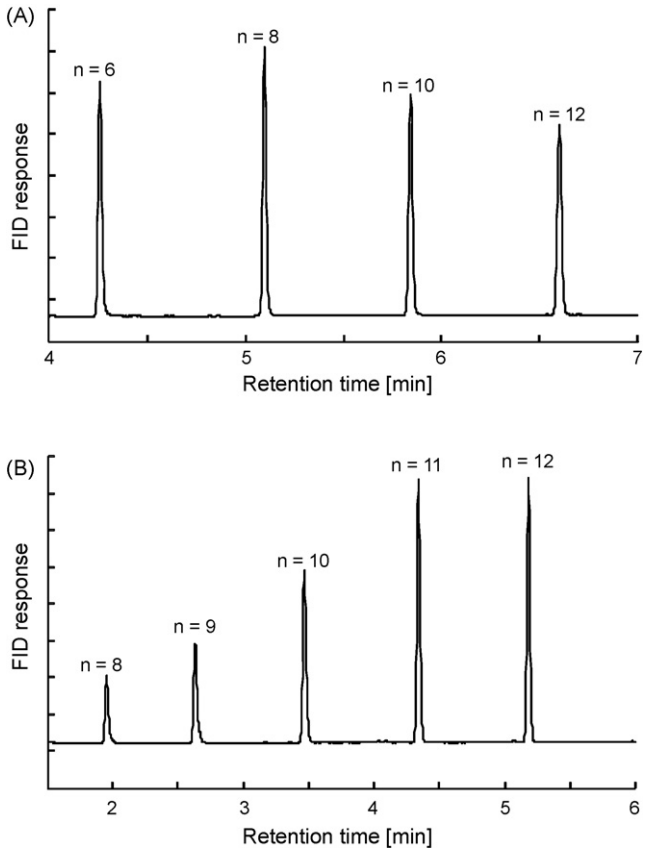

Fig. 4. Gas chromatograms for alkylbenzenes (A) (carbon number of the side chain n = 6, 8, 10, 12) and *n*-alkanes (B) (carbon number n = 8–12). Oven temperature: 70 °C (1 min) to 250 °C (1.5 min) at 40 °C/min (A), 70–200 °C at 20 °C/min (B). The other GC conditions are the same as in Fig. 2.

3.3. 2D chromatography of a real sample

The 2D separation of the petrochemicals was performed with the polymer-coated fiber-packed needle interface by the eluent-

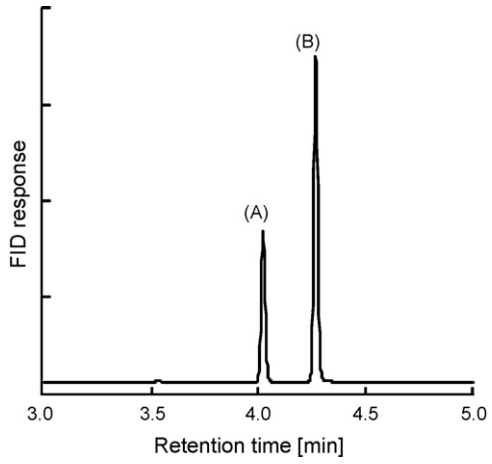

Fig. 3. Typical chromatogram of dodecane (A) and hexylbenzene (B) extracted by the needle extraction device. GC conditions are the same as in Fig. 2.

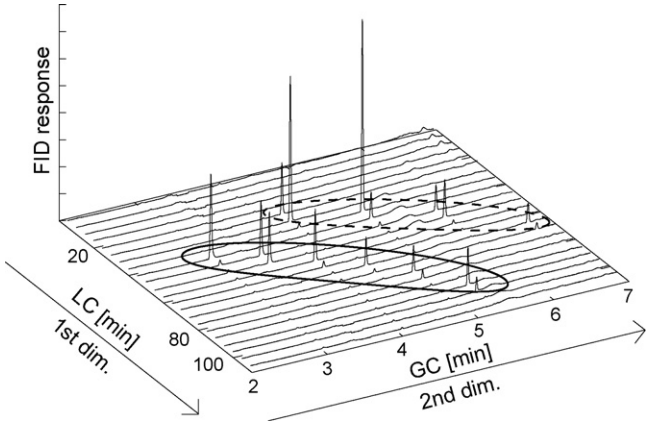

Fig. 5. Overlaid 2D chromatogram of *n*-alkanes (solid line, carbon number = 10–15) and alkylbenzenes (dashed line, carbon number of the side chain = 6, 8, 10, 12). Chromatographic conditions are found in the text.

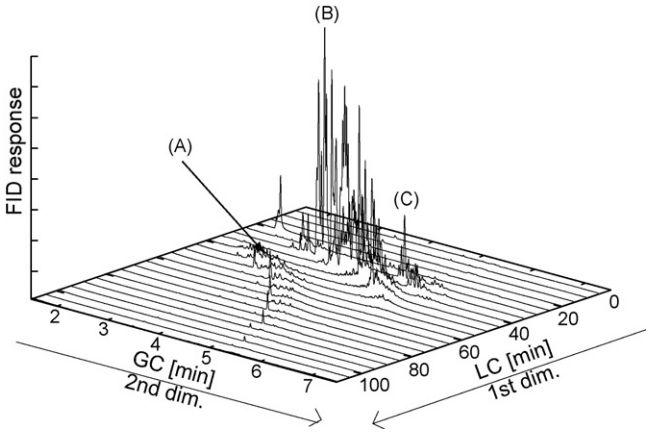

Fig. 6. 2D chromatogram for the separation of DMSO-kerosene extract. Group separation of alkanes (A), alkylbenzenes (B) and naphthalenes (C) and their derivatives was successfully performed. The other separation conditions are the same as Fig. 5.

dilution process. To obtain an UV-detectable sample, components in kerosene were extracted by dimethyl sulfoxide (DMSO) which selectively dissolved the aromatics and the polar compounds. The separated DMSO phase was used directly as the sample for the 2D separation. The three-dimensional plot for the 2D LC–GC of the DMSO-kerosene extract is shown in Fig. 6, where it takes about 4 h to complete the entire operation. DMSO was eluted as the same time as the dead volume of the LC column, although which would often be a source of an interference in the single GC analysis due to its high boiling point. In Fig. 6 alkanes, alkylbenzenes, naphthalenes, and their isomers and derivatives, were well separated. Each group were identified from the retention time of the abundant peak assigned on both dimensions. In spite of the low separations power of the LC system, the complex mixture was successfully separated by the assist of the high resolution capillary GC. One of the main aim for the 2D separation, the group analysis of the petrochemicals, was attained by this needle-type interface packed with the PDMS-coated Zylon fibers.

4. Conclusions

The polymer-coated fibrous material was packed into the head section of the specially-designed needle, and served as the interface for 2D RPLC–GC with the eluent-dilution system for trapping the analyte coming from ODS column. The PDMS-coated fiber-packed needle could be successfully produced without any frits by simply inserting the bundle of the thermally and mechanically stable fibers into the needle. The pressure generated by the packed fibers was sufficiently low to inject the sample with an easy manual operation. Under the optimized conditions, the 2D separation of aliphatic and aromatic hydrocarbons were performed successfully with the needle interface. The results indicated that the fiber-packed needle, coated with PDMS phase on the fiber surface, possessed a high extraction capacity, suggesting a successful application of the fibrous materials in the chromatographic techniques. The fibrous support and the polymeric stationary phase showed the excellent durability over a hundred times of the extraction and thermal desorption without any deterioration in the performance. This is the most advantageous feature of the developed needle interface toward the silica or ODS packings which could not be durable under such conditions.

As an application of this study, the development of the automatic valve-type modulator, which having the capillary packed with polymer-coated fibers, is now on progress in our laboratory to develop a more sophisticated 2D LC–GC system.

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