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Preparation and characterization of micro-bore wall-coated open-tubular capillaries with low phase ratios for fast-gas chromatography–mass spectrometry: Application to ignitable liquids and fire debris

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A R T I C L E I N F O

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A B S T R A C T

Fast Gas Chromatography (GC) allows for analysis times that are a fraction of those seen in traditional capillary GC. Key modifications in fast GC include using narrow, highly efficient columns that can resolve mixtures using a shorter column length. Hence, a typical fast GC column has an inner diameter of 100–180 µm. However, to maintain phase ratios that are consistent with typical GC columns, the film thickness of fast GC stationary phases are also low (e.g., 0.1–0.18 µm). Unfortunately, decreased film thickness leads to columns with very low sample capacity and asymmetric peaks for analytes that are not sufficiently dilute. This paper describes micro-bore (50 µm i.d.) capillary columns with thick films (1.25 µm), and low phase ratios (10). These columns have greater sample capacity yet also achieve minimum plate heights as low as 110 µm. Hence, separation efficiency is much higher than would be obtained using standard GC columns. The capillary columns were prepared in-house using a simple static-coating procedure and their plate counts were determined under isothermal conditions. The columns were then evaluated using temperature programming for fast GC–MS analysis of ignitable liquids and their residues on fire debris exemplars. Temperature ramps of up to 75 °C min^{-1} could be used and separations of ignitable liquids such as gasoline, E85 fuel, and lighter fluid (a medium petroleum distillate) were complete within 3 min. Lastly, simulated fire debris consisting of ignitable liquids burned on carpeting were extracted using passive headspace absorption-elution and the residues successfully classified.

1. Introduction

Gas Chromatography coupled with Mass Spectrometry (GC–MS) is the dominant instrumental technique for the analysis of ignitable liquids and their residues on fire debris. Since GC has been in common use, however, there have been many studies on how to shorten analysis times without compromising resolution [1,2]. Traditional capillary GC achieves separations within one hour with peak widths at half height > 3 s [3]. "Fast" GC achieves separations within minutes with peak widths at half height of 1–3 s [1,3]. "Very fast" GC achieves separations within seconds with peak widths at half height of 30–200 ms. [3].

The most dramatic reductions in GC analysis times have come about via techniques such as Low Pressure Gas Chromatography (LP-GC) and Micro-Bore (MB) GC [1,4,5] [6–10]. The latter addresses the fact that typical wall coated open tubular GC columns have inner diameters of 0.25–0.53 mm. In contrast, "fast" GC uses MB columns with inner diameters of 0.10–0.18 mm [3,6]. However, one of the limitations of MB GC is decreased sample capacity, which scales with the square of column diameter [6,7,11]. One means to increase sample capacity is to increase stationary phase film thickness [12]. While very thick films have been used in the past [12,13], the application of thick films to MB columns and their use in forensic fire debris analysis has yet to be accomplished.

This study focuses on investigating the practicality of preparing MB GC columns coupled to a vacuum-outlet to produce "very fast" GC analyses. In-house prepared columns of 50 µm inner diameter were tested for suitability and efficiency. The application of interest for this technique is the analysis of ignitable liquid residues in fire debris. "Fast" or "very-fast" GC is advantageous in fire debris analysis due to the traditionally long run times, commonly upwards of 30 min [14,15]. Micro-bore GC columns can achieve similar separation performance in one fifth of the time. Decreased analysis time could also decrease case back-log in forensic laboratories.

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1.1. *Theory*

In general, chromatographic resolution is dependent upon column efficiency (N), retention (capacity factor, k) and selectivity (α). Of these, column efficiency offers potentially unlimited increases in resolution. Chromatographic efficiency is characterized by the height equivalent of a theoretical plate (H), which reflects the number of theoretical plates (N) for a column of certain length (L) [16]. For open-tubular columns, H depends upon physical factors such as column radius (r) and the thickness of the stationary phase film (d_f). In addition, H depends upon chemical factors such as the capacity factor of a retained peak (k), and the diffusivity of the analyte in the mobile phase (D_G) and stationary phase (D_S).

The dependence of H on these variables as well as the linear velocity of the mobile phase (u) is given by the expanded Golay equation (Eq. (1)) [17].

$$H = \frac{2D_G}{u} + r^2 u \frac{1 + 6k + 11k^2}{24(1 + k)^2 D_M} + u \frac{2kd_f^2}{3(1 + k)^2 D_S} \tag{1}$$

The phase ratio (β) is the ratio of the total empty volume of the capillary to the volume of stationary phase. Given a known column inner radius and film thickness, the phase ratio can be calculated using Eq. (2), which can be simplified by assuming that in most cases column radius is much greater than film thickness (i.e., $r > > d_f$) [17].

$$\beta = \frac{(r - d_f)^2}{2rd_f} \approx \frac{r}{2d_f} \tag{2}$$

Setting the derivative of H with respect to u to zero allows for an expression for minimum plate height that will result in maximum efficiency. Ultimately, the key parameter that determines efficiency is column radius. To a lesser extent, the minimum plate height also decreases with increasing phase ratio (β), which manifests as a loss of column efficiency with increasing film thickness.

As an example, Fig. 1 displays a variety of commercially-available WCOT columns as a function of their inner diameter and film thickness. Most columns have phase ratios between 62.5 and 500. Other columns reported in the literature are also included, which clearly deviate from the norm. The columns by Steenackers and Sandra [13] and the columns described in this paper operate in a drastically different region than normal columns. The work by Steenackers et al. used a 5% phenyl stationary phase and columns at least 0.8 m longer than the ones described in this work.

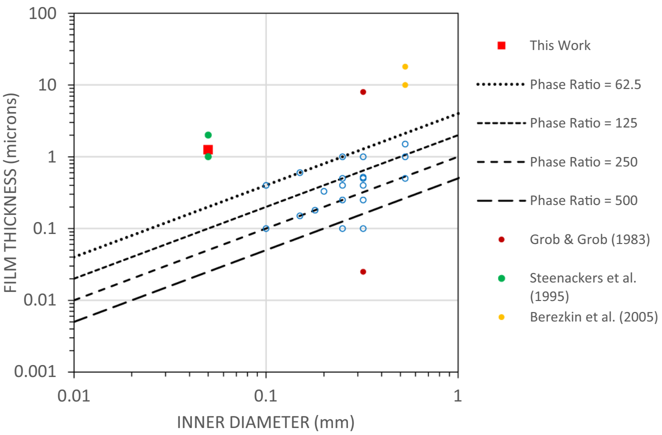

Fig. 1. Commercially available WCOT GC columns with a 100% PDMS stationary phase (plotted in open blue circles) displayed according to their inner diameter and stationary phase film thickness. Columns reported in the literature are also included, as well as the columns described in this paper (β = 10). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The mass of an analyte that can be loaded onto a column is related to the film thickness. A thin film column suffers from low loadability when compared to a thick film column of the same inner diameter. However, thicker films will have worse separation efficiency than thin films. Though the maximum separation efficiency is less for thick film columns, the maximum separation may not be necessary. For most applications, the separation efficiency of a thin film 0.25 mm or 0.18 mm inner diameter columns is enough. However, the time required for those analyses can be dramatically reduced using a thick film MB column.

An important limitation of micro-bore capillary columns is high inlet pressures and potential extra column broadening from the injector [3,4,18,19]. The high head pressure requirements can be offset to some extent by using a low-pressure or vacuum outlet such as with a mass spectrometer detector. The impact of a vacuum outlet on column head pressure is well known and can be seen in the Poiseuille equation for the flow of compressible fluids:

$$P_i = \sqrt{P_o^2 + \frac{F * L * P_o * \eta}{3.75 * \pi * r^4}} \tag{3}$$

where P_i is the column head pressure, r is the column inner radius, L is column length, F is the volumetric flow rate, η is carrier gas viscosity, P_o is the column outlet pressure, and T is temperature. For example, at low flow rates, changing from an atmospheric pressure outlet ($P_0 = \sim 15$ psi) to a vacuum outlet ($P_0 < 10^{-6}$ psi) can increase flow rates by ~10%. Extra-column broadening from the injector can be countered via the use of either high split ratios to reduce sample volume or retention gaps to aid in the separation of solutes from the solvent vapor [20].

2. Materials/methods

2.1. *Materials*

All capillary tubing was purchased from Polymicro Technologies (Phoenix, AZ). Polydimethylsiloxane (PDMS) with a viscosity of 100 cSt was purchased from Acros (Bridgewater, NJ). Pentane (pesticide grade) was purchased from Fisher Chemical (Fair Lawn, NJ) and used in all dilutions. Hexadecane (ReagentPlus) was purchased from Sigma-Aldrich (Milwaukee, WI) All analyses used hydrogen as a carrier gas unless otherwise stated.

2.2. *Instrumentation*

An Agilent (Wilmington, DE) 6890 N Gas Chromatograph (GC) with a Flame Ionization Detector (FID) and an Agilent (Wilmington, DE) 7890A gas chromatograph (GC) with 7693 autosampler connected to an Agilent 5975C mass spectrometer were used to obtain chromatographic data from prepared capillary columns. All liquid injection vials and caps were purchased from Fisher Scientific (Hanover Park, IL).

2.3. *Column preparation*

Three capillary columns were prepared using a static coating procedure. Although slow, this method has been in use for many decades [12,13]. In general, the film thicknesses of columns prepared in this way are uniform, repeatable and predictable using Eq. (4) [21].

$$d_f = \frac{d_c \times C}{400} \tag{4}$$

where d_f is stationary phase film thickness, d_c is capillary inner diameter, and C is the volume percent of PDMS in the coating solution.

The capillary columns were filled with a solution of 10% PDMS in pentane using a Nanobaume apparatus (Western Fluids Engineering & Mfg, LLC, Wildomar, CA). The capillary was then disconnected from the apparatus and one end was plugged into a rubber septum as a “cap” and the other end was left uncapped so solvent could evaporate off for 16 h.

Based upon Eq. (4) the columns prepared for this study had a film thickness of 1.25 µm. The columns were inspected under 10 × magnification for plugs, voids or other irregularities. After inspection, the ends of the columns were clipped. One end of the column was installed into the inlet of the GC and purged with helium gas to remove excess solvent followed by heating the column in the GC oven at 200 °C for 4 h.

2.4. Column testing

Columns were tested with either pentane or 0.25% hexadecane in pentane with different head pressures. Testing was done to confirm column efficiency and to determine the optimum head pressure for each column. The optimum head pressure was designated as the pressure at which the calculated plate height was smallest.

A column with an inner diameter of 50 µm and a length of one meter was tested at 40 °C. Column efficiency as a function of column head pressure was determined with pure pentane. A constant split ratio of 2000 was used to introduce an analyte mass of 1.6 ng on column. Hexadecane was analyzed under varying isothermal conditions where the capacity factor was calculated.

A second column with an internal diameter of 50 µm and a length of five meters was tested with pentane and hexadecane at head pressures from 5 to 50 psi, split 200, injection volume 200 nL, inlet temperature 280 °C, transfer line temperature 280 °C, oven temperatures isothermal and varied at 85, 90, 92, 95, 97, and 100 °C. Testing continued with separations of an n-alkanes (C_6–C_{20}) mixture, a sample of E85 automotive fuel, and an ASTM E1618 test mixture. The solution of n-alkanes (C_6–C_{20}) was analyzed using an isothermal method at 120 °C oven temperature under constant head pressure of 75 psi. The ASTM E1618 mix was analyzed with a constant flow of 0.3 $\mathrm{mL\,min^{-1}}$, injection volume 200 nL, split 850, oven program starting at 50 °C ramped to 200 °C at 75 $\mathrm{°C\,min^{-1}}$ hold 1.5 min. The E85 fuel sample was analyzed at constant flow 0.3 $\mathrm{mL\,min^{-1}}$, oven ramped at 15 $\mathrm{°C\,min^{-1}}$ from initial temperature 35 °C to 200 °C final temperature.

A Restek (Bellefonte, PA) Rxi-1 ms column with length 30 m, 0.25 mm column inner diameter and with a 0.25 µm stationary phase film thickness was used for comparison. Samples analyzed for comparison were the same C_6-C_{20} alkane mixture, ASTM E1618 test mix and E85 automotive fuel as the five-meter column. The alkane mixture was analyzed isothermally at 120 °C with a constant pressure of 7.0 psi. The ASTM E1618 test mixture was analyzed using the Rxi-1 ms column at a flow of 1.5 $\mathrm{mL\,min^{-1}}$, oven temperature program starting at 35 °C for 1 min then ramped at 10 $\mathrm{°C\,min^{-1}}$ to 300 °C, injection volume 200 nL, splitless injection. The E85 auto fuel was analyzed using a split of 10, flow rate of 1.25 $\mathrm{mL\,min^{-1}}$, oven temperature program started at 35 °C held for 1 min and ramped at 15 $\mathrm{°C\,min^{-1}}$ to 300 °C held for two minutes.

2.5. Preparation of simulated fire debris samples

A sample of carpet was cut into four square pieces 3 in. long, each piece was then placed in a clean metal can. One was burnt to char without an accelerant, one with 1.0 mL of 87 octane gasoline, one with 10.0 mL of 87 octane gasoline, and one with 5.0 mL of charcoal lighter fluid (all purchased locally). The three samples with accelerant burned until they self-extinguished. Samples were sealed with the metal lid then sat for 42 h at room temperature. An activated charcoal strip was hung in each can then resealed and placed in an oven for 23 h at 65 °C. Strips were placed in 2.0 mL of pentane and vortexed for 10 s each. 250 µL of sample was then placed into GC vials and analyzed with GC–MS.

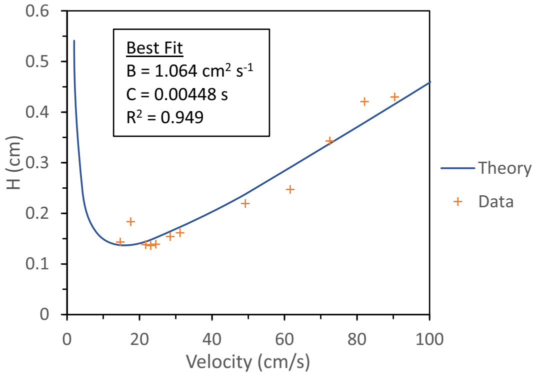

Fig. 2. The Height Equivalent of a Theoretical Plate (H) for a non-retained solute (pentane, $k < 0.05$) at 40 °C is plotted against the mobile phase velocity at which the chromatograms were produced. The pressures used were 10, 12, 15, 16, 17, 20, 22, 36, 46, 55, 63, and 70 psi on a 1 m × 50 µm × 1.25 µm column.

3. Results/discussion

3.1. Assessing chromatographic efficiency

Column efficiency testing was performed under isothermal conditions so that analyte retention is dictated by a constant distribution coefficient and peak dispersion abides by the kinetic model as established in the van Deemter equation. However, this necessarily limits the boiling point range of compounds that can be separated in a reasonable time. In practice, almost all GC separations utilize a temperature ramp, which drastically increases peak capacity and allows for the separation of analytes with a broad range of boiling points [16,17,21].

As a proof of concept, a column with an inner diameter of 50 µm, and length of one meter was prepared with a 1.25 µm film thickness. Pentane eluted at the calculated dead time at the corresponding inlet pressure. Using pentane, the column was tested to determine the dependence of H upon inlet pressure for a non-retained solute. As pressure is directly proportional to the mobile phase velocity, this allows us to produce a Van Deemter curve. The results of the measured separation efficiency versus calculated linear velocity can be found in Fig. 2. The data was fit to the Van Deemter equation using an unweighted least-squares approach as described by Harris [22].

A column with a length of five meters was prepared and evaluated. A solution of n-alkanes (C_6-C_{20}) was analyzed using an isothermal method to determine chromatographic efficiency. The alkanes C_6-C_{16} are well-resolved in under 3.25 min. Due to the isothermal conditions, however, later-eluting straight-chain alkanes were broadened and undetectable in the TIC.

A Restek Rxi-1 ms column was used to analyze the same mixture isothermally with constant pressure of 7.0 psi. 7.0 psi was used to maintain the same gas linear velocity as the five-meter column. Chromatographic efficiency was measured from the data collected. Eicosane (C_{20}) was retained beyond 120 min and was excluded from the chromatogram in Fig. 4.

The separation efficiency for four alkanes are compared for the five-meter column and the Rxi column in Table 1. The data for Table 1 was obtained from the analyses that produced Fig. 3 and Fig. 4 above. The lowest height equivalent of a theoretical plate (H) for the five-meter column was found to be 0.11 mm, which compares well to previous literature [9,13]. Overall, under similar conditions, the in-house 50 µm column produced plate heights less than one tenth of the commercial column.

Table 1
Chromatographic efficiency for four n-alkanes on a 50 µm i.d. column with length five meters and a 1.25 µm stationary phase and the same four compounds analyzed on an Rxi-1 ms 0.25 mm i.d. column, length 30 m, with a 0.25 µm stationary phase.

Compound	t_r	W	N	N/m	H (mm)
Heptane (50 µm)	0.167	0.002	38,000	7700	0.12
Octane (50 µm)	0.181	0.002	45,000	9000	0.11
Nonane (50 µm)	0.206	0.003	26,000	5200	0.19
Decane (50 µm)	0.249	0.004	21,000	4200	0.23
Heptane (250 µm)	0.837	0.019	11,000	360	2.8
Octane (250 µm)	0.913	0.027	6300	210	4.7
Nonane (250 µm)	1.043	0.041	3600	120	8.4
Decane (250 µm)	1.269	0.030	9900	330	3.0

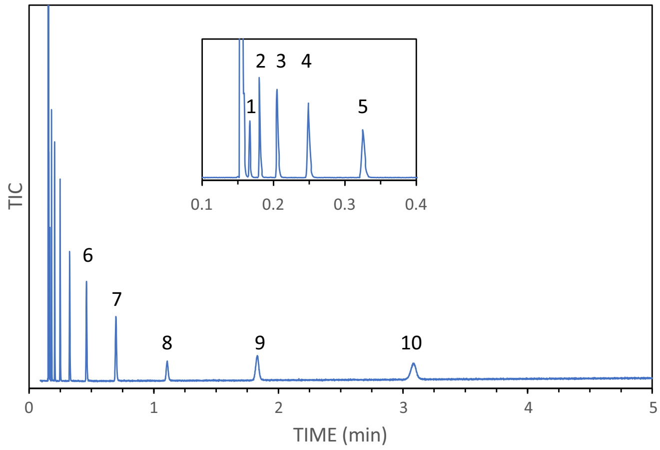

Fig. 3. An isothermal separation of an n-alkanes sample at 120 °C and constant 75 psi on a 50 µm i.d. column with length five meters and a 1.25 µm stationary phase, 200 nL injection volume, split 200, transfer line and inlet temperature 280 °C. Peaks: 1. heptane, 2. octane, 3. nonane, 4. decane, 5. undecane, 6. dodecane, 7. tridecane, 8. tetradecane, 9. pentadecane, 10. hexadecane.

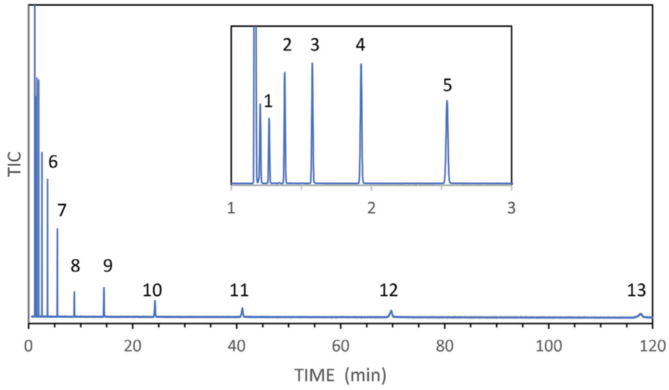

Fig. 4. An isothermal separation of an n-alkanes sample at 120 °C and constant 7.0 psi using a commercial 30 m × 0.25 mm × 0.25 µm column, split 100, inlet and transfer line temperature 280 °C. Peaks: 1. heptane, 2. octane, 3. nonane, 4. decane, 5. undecane, 6. dodecane, 7. tridecane, 8. tetradecane, 9. pentadecane, 10. hexadecane, 11. heptadecane, 12. octadecane, and 13. nonadecane.

3.2. Complex samples

A sample of the ASTM E1618 test mixture was analyzed on a five-meter, 50 µm i.d. column with a 1.25 µm film to determine the shortest analysis time while maintaining baseline resolution. The chromatogram shows full separation of all 13 components and undecane within 3 min (see Fig. 5).

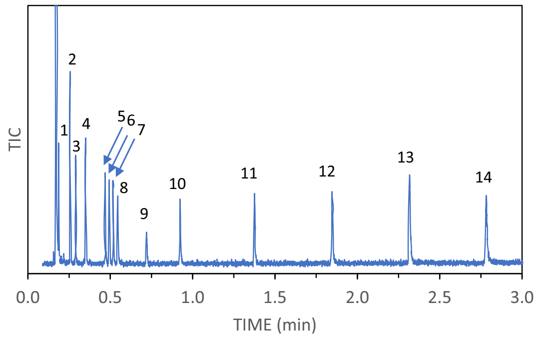

Fig. 5. Chromatogram of the ASTM E1618 mixture with oven program starting at 50 °C and ramped at 75 °C min^{-1} to 200 °C then held for 1.5 min, constant flow of 0.3 mL min^{-1}, 200 nL injection volume, and split 850 on a 5 m × 50 µm × 1.25 µm column. Peaks: 1. hexane, 2. toluene, 3. octane, 4. p-Xylene, 5. 2-ethyltoluene, 6. 3-ethyltoluene, 7. 1,2,4-trimethylbenzene, 8. decane, 9. undecane, 10. dodecane, 11. tetradecane, 12. hexadecane, 13. octadecane, 14. eicosane.

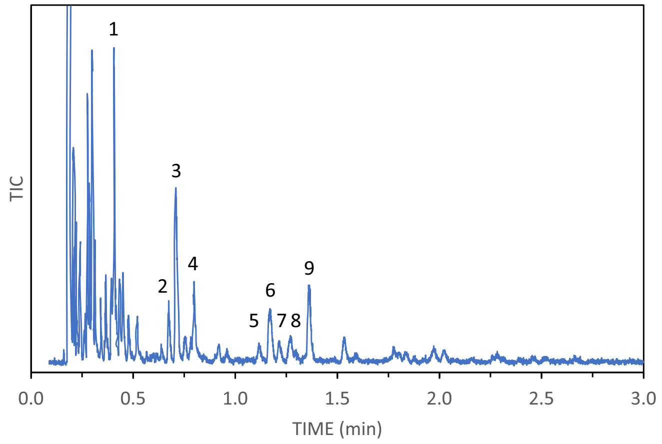

Fig. 6. Chromatogram of an E85 fuel sample analyzed at constant flow 0.3 mL min^{-1} with a ramp of 15 °C min^{-1} from 35 °C to 200 °C, split 850. Peaks: 1. toluene, 2. ethylbenzene, 3. m- and p-xylene, 4. o-xylene, 5. n-propylbenzene, 6. ethyltoluene, 7. 1,3,5-trimethylbenzene, 8. 2-ethyltoluene, 9. 1,2,4-trimethylbenzene.

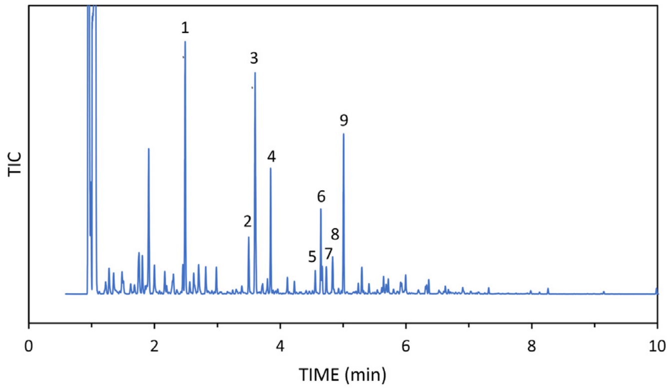

Fig. 7. Chromatogram of an E85 fuel sample analyzed on a 0.25 mm i.d. column at constant flow 1.25 mL min^{-1}, split 10, oven 35C for 1 min then ramped at 15 °C min^{-1} to 250 °C held 2 min. Peaks: 1. toluene, 2. ethylbenzene, 3. m- and p-xylene, 4. o-xylene, 5. n-propylbenzene, 6. ethyltoluene, 7. 1,3,5-trimethylbenzene, 8. 2-ethyltoluene, 9. 1,2,4-trimethylbenzene.

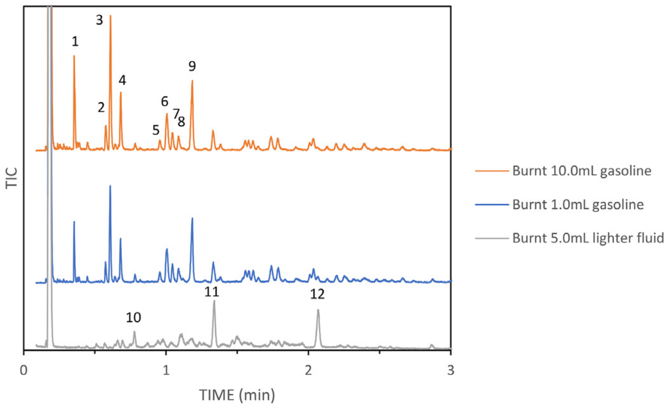

Fig. 8. Analysis of ignitable liquid residues from test burns. Oven 35 °C to 200 °C at 15 °C min^{-1}, constant flow 0.3 mL min^{-1}, split 200, inlet 280 °C, 50 µm i.d. column 4.99 m long with a 1.25 µm thick PDMS film. Chromatograms were normalized to 350,000 abundance. Peaks: 1. toluene, 2. ethylbenzene, 3. m- and p-xylene, 4. o-xylene, 5. n-propylbenzene, 6. ethyltoluene, 7. 1,3,5-trimethylbenzene, 8. 2-ethyltoluene, 9. 1,2,4-trimethylbenzene, 10. nonane, 11. decane, 12. undecane.

Further reducing the analysis time for the ASTM mixture was not possible in this case due to several instrumental limitations: the GC oven could not run a temperature ramp > 75 °C min^{-1} and the GC inlet could not exceed 100 psi, limiting the flow rate to 0.3 mL min^{-1}at the upper programmed temperature of 200 °C.

Gasoline is a common accelerant used in arson, E85 is also used [14]. E85, a complex mixture with lower concentrations of traditional gasoline compounds, was used as a representative sample for neat accelerants. A sample of E85 gasoline was analyzed on the 5 m column to confirm the ability of the method to separate and characterize such a complex sample (Fig. 6).

The micro-bore fast GC method was able to separate the E85 mixture for clear determination of toluene, xylenes, and C3-alkylbenzenes as required for gasoline identification. While a ramp of 15 °C min^{-1} is much slower than the 75 °C min^{-1} shown in the analysis of the ASTM standard, limited coelution of peaks was prioritized. The same E85 auto fuel analyzed on the 50 µm i.d. column was analyzed on the Rxi-1 ms column. The results are shown in Fig. 7.

3.3. Ignitable liquid residue analysis – Fire debris exemplars

Four fire debris exemplars were analyzed. Three of the samples contained ignitable liquids, two with gasoline at varying volumes and one with lighter fluid. The fourth exemplar was a comparison sample of carpet burned to a char. The debris samples were processed using a passive-headspace absorption-elution method. The extracts were analyzed by GC–MS using the prepared 50 µm i.d. column with length of five meters and the results are shown in Fig. 8.

Typical gasoline classifiers can be easily observed such as toluene, the “group of three” C2-benzenes, and the “castle group” of the C3-benzenes in both gasoline residue samples. The lighter fluid residue sample showed typical n-alkanes and the patterning of a medium petroleum distillate. The chromatograms in Fig. 8 show that the five-meter column was adequate to separate and classify the ignitable liquids at a fraction of the traditional analysis time.

4. Conclusions

An in-house process for static coating glass capillaries was shown to be effective, and column efficiency that surpassed conventional 0.25 mm i.d. columns. The ability to conduct “very fast” chromatographic analyses was demonstrated via separations of the ASTM E1618 test mix, E85 fuel samples, and gasoline. This column was also used to analyze residues of gasoline and a medium petroleum distillate on carpeting. Analysis time was less than three minutes for all samples.

Conflict of interests

The authors declare no conflict of interest.

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