*Petroleum and Coal, Vol. 43, **1**, 17–21*

HIGH TEMPERATURE GAS CHROMATOGRAPHIC ANALYSIS OF ASPHALT-POLLUTED SOIL

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Abstract. *High temperature gas chromatography is a very useful tool for separation of high boiling oil fractions. However, HTGC conditions cannot manage elution of high boiling asphaltic fractions. This work deals with the separation of asphalts into maltenes and asphaltenes precipitating asphaltenes and high temperature gas chromatographic determination of maltenic fraction. All fractionated as well as non-fractionated asphaltic samples were also characterized using gel permeation chromatography.*

Key words: *high-temperature capillary gas chromatography, asphaltenes precipitation, maltenes, high-boiling oil contamination*

Introduction

Contamination of soil with petroleum constituents represents one of the most frequent environmental pollution. Commonly used GC methods are focused mainly on soil analysis of "mobile" hydrocarbons to approximately C_{25}–C_{28} [1], because they are more dangerous due to possible contamination of ground waters. However, soil contamination often has character of lubricants. In this case, when GC analysis is performed under common conditions only lower boiling fractions up to approximately C_{30}–C_{40} can be determined. It means that higher boiling petroleum fractions such as heavy oils and asphalts contaminating soil are not determined. In analysis of soils contaminated with high boiling petroleum constituents, high temperature gas chromatography (HTGC) seems to be a suitable method due to the fact, it operates at column temperatures above 350 °C [2].

In the previous part of this work [3] high temperature gas chromatographic separation system has been elaborated using a 1.5 m x 0.53 mm i.d. fused silica capillary column coated with 0.075 μm of a cross-linked OV-1 stationary phase and with external high temperature polyimide coating. Operating with a cool on column injector and hydrogen carrier gas flow rate of 20 ml.min^{-1} (corresponding to approximately 250 cm.s^{-1}), n-alkanes up to C_{110} have been eluted within 20 minutes. This separation system allowed resolution of high boiling petroleum fractions (light oil, heavy oil, light and heavy asphalts) and individual n-alkanes as well. The baseline was not achieved within 20 minutes when asphalts were separated and the highest boiling fractions kept eluting out of the column. Comparing the areas of chromatographic bands for analyzed samples of oils and asphalts, approximately of 6% of light asphalt and 24% of heavy asphaltic constituents were guessed being retained in the column.

Asphalts are high molecular fractions of mineral oil, remaining as a residue after vacuum distillation of high boiling liquid fractions [4]. The main components of asphalt are petroleum resins – maltenes, i.e. substances soluble in light alkanes and asphaltenes that are insoluble in these solvents, form colloidal solutions from which they can be precipitated. Asphaltenes are formed during industrial processes by polycondensation reactions of molecules with high molecular weights. The structure of asphaltenic substances is not yet quite clear. They are meanly polyaromatic heterocycles with a rather broad range of molecular weights and also contain condensed naphthenic structures, closely connected with aromatic rings. The lower limit of molecular weights of asphaltenic substances is about 900, molecular weights of the main fraction of asphaltenes do not exceed several thousand, but the heaviest fractions have molecular weight 20 000 - 30 000. Maltenes contain 6 to 16 condensed rings arranging in one layer, whereas in asphaltenic molecules condensed 16-ringed layers repeat for several times, connected through saturated chain or ring.

From given information it follows that the use of gas chromatography cannot manage the elution of asphaltic high molecular fractions out of the chromatographic columns. This work deals with the separation of asphalts into maltenes and asphaltenes precipitating asphaltenic fraction using n-heptane and high temperature gas chromatographic determination of maltenic fraction. Gas chromatographic analysis of maltenic portion seems to be an appropriate approach, because the ratio of maltenes to asphaltenes can be determined.

Experimental

Materials

High boiling petroleum products (light oil R 932 and heavy oil R 953 and both light and heavy asphalts) were

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The major part of this work was presented at 39th International Petroleum Conference, September 20–23, 1999, Bratislava, Slovak Republic.

derived from Slovnaft Ltd. (Bratislava). In order to specify carbon number distribution, synthetic wax Polywax 655 (Supelco) and n-alkane C_{28} (VÚRUP Bratislava) were used.

Separation of maltenes and asphaltenes

5 g of asphalt sample were shaked with 200 ml n-heptane for 20 hours. Precipitated asphaltenes were separated passing the slurry through a filter paper. Maltenes remained on a filter and/or maltenes occluded on asphaltenic particles were extracted for 6 hours in a Soxhlet apparatus using 200 ml n-heptane as the extraction agent. Both maltenic portions were accompanied and brought to dryness using vacuum rotary evaporator at 44 °C. Solvent from asphaltenic fraction was removed drying in oven at 50 °C. Both the maltenic and the asphaltenic fractions were weighted.

High temperature gas chromatography

Fused silica capillary tubes of inner diameter 0.53 mm with high temperature polyimide coating (Department of Physics, SAV Bratislava) were dried with nitrogen at 250 °C to remove surface moisture. A capillary column surface prior to coating with the OV-1 was deactivated by hexamethyldisilazane at 300 °C. Subsequently, columns were washed with dichloromethane and methanol and dried with nitrogen. The stationary phase was dissolved in hexane in appropriate concentration to provide a required film thickness by static coating method and suitable amount of dicumylhydroperoxide was added. 1% of peroxide (w/w based on the stationary phase) is required to produce a non-extractable coating. Once coating was complete, residual solvent was removed by purging with nitrogen. The polymethylsiloxane was immobilized with peroxide according to the procedure introduced by Grob [6]. The statically coated column was mounted in a gas chromatograph with the exit end disconnected, and was flushed for 5–10 minutes using twice the regular carrier gas flow rate. The flow rate was reduced to the minimum that can be reliably maintained (0.02–0.1 ml.min^{-1}). The oven was immediately heated to 160 °C and, after 1 h, was heated to 180 °C. After 1 h at 180 °C, still with a low carrier gas flow rate, the flow rate was increased to the normal level for at least 1–2 h. The column was conditioned by slowly heating to 420 °C. The column exit was then connected to the detector and a test was run.

GC measurements were performed on Hewlett-Packard Gas Chromatograph 5890 Series II fitted with FID. Data acquisition was performed using CSW software. A fused silica capillary column with length of 1.5 m, internal diameter of 0.53 mm coated with 0.075 μm OV-1 film thickness was used. The carrier gas was hydrogen with inlet pressure of 15 kPa. Cool on column injection mode was used. FID temperature was set at 425 °C.

Gel permeation chromatography

GPC measurements were performed on a Merck Lachrom liquid chromatograph equipped with a diode array detector and a refractive index detector. A gel column with length of 30 cm, internal diameter of 3 mm, filled with stationary phase Spheron 40 (hydroxyethylmetacrylate-ethylenedimethylmetacrylate copolymer) of < 25 μm particle size. Tetrahydrofuran pumped at a flow rate of 0.25 ml.min^{-1} was used as a mobile phase. A 2-μl aliquot of sample dissolved in tetrahydrofuran at concentration level of approximately 2000 μg.ml^{-1} was injected into the column. Column calibration was performed using polystyrene standards with molecular weights of 4000, 10 000, 37 000 and 2 million, and toluene.

Results and Discussion

Percentage contents of maltenes and asphaltenes in light and heavy asphalts are given in Table 1. Contents of individual fractions in asphalts were weighted. Light asphalt and heavy asphalt contain almost 5% and more than 30% of asphaltenic fraction, respectively.

Table 1. Percentage content of maltenes and asphaltenes in light and heavy asphalts.

	Maltenes [%]	Asphaltenes [%]
Light asphalt	95.1	4.9
Heavy asphalt	68.7	31.3

Both the whole asphaltic fraction and the maltenic as well as asphaltenic portions were separated using high temperature capillary gas chromatographic separation system that allows elution of n-alkanes up to C_{110}. Chromatograms of the HTGC separation of the samples are shown in Figures 1 and 2. The chromatograms of light asphalt sample (1A) and maltenic fractions (1B) are almost the same, in agreement with only 5% of asphaltenes present in this sample. The chromatogram of maltenic fraction of heavy asphalt (2B) is characterized with lower ratio of higher high-boiling fractions to lower high-boiling fraction in comparison with the chromatogram of the nonfractionated heavy asphalt (2A). Elution of asphaltenic-derived compounds starts in the C_{70} n-alkane region for both asphalt samples that corresponds to the initial limit of molecular weights of asphaltenic substances (≈ 900) published in literature. Approximately 97% of maltenic fraction were estimated being eluted out of the column under given conditions. Eluted fraction of asphaltenes represents no more than 30%. This is also proved comparing GC-FID signals of nonprecipitated light and heavy asphalt samples. Since the peak areas in chromatograms of asphaltenic fraction in light and heavy asphalts are similar, the content of components over molecular weight range approximately from 900 to several thousand (corresponding to the elution region of n-alkane C_{110}, that is molecular weight approximately under 2000) is comparable. From this fact follows that the asphaltenic fraction precipitated from asphalt samples consists mainly (at least of 70%) of compounds with molecular weight over several thousand (over approximately 2000).

All fractionated as well as nonfractionated asphaltic samples were characterized using gel permeation chromatography. GPC column parameters, specifically about column size exclusion limit of approximately 40 000, were selected with regard to molecular weights of heaviest

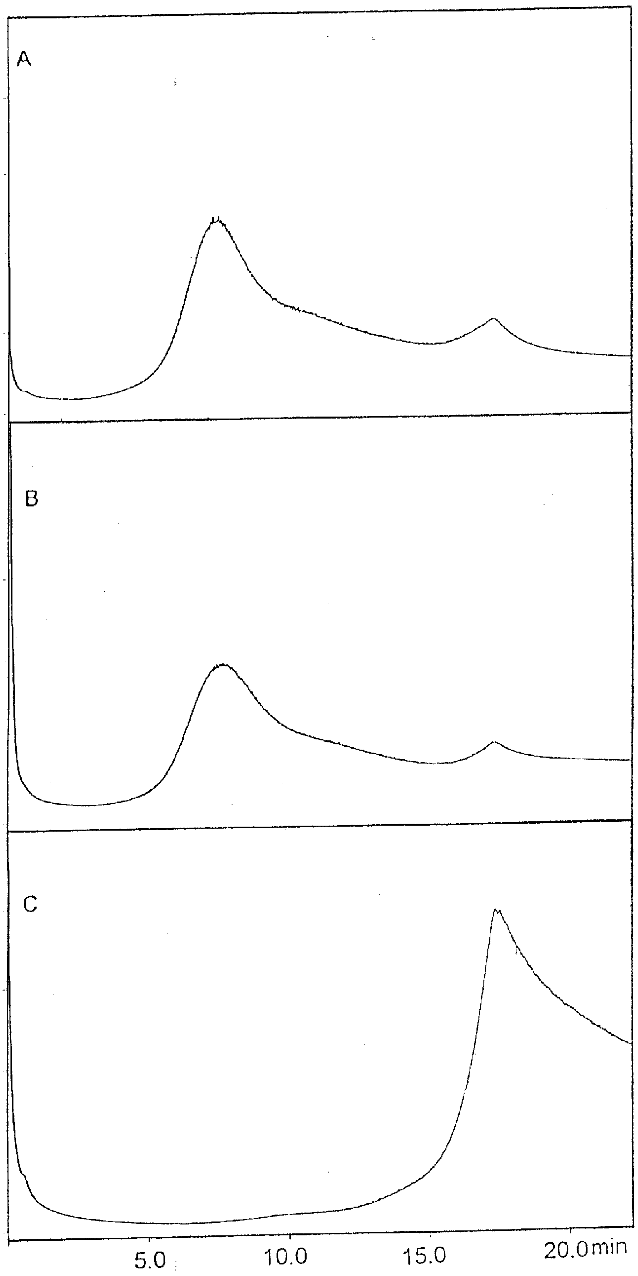

Figure 1. HTGC-FID chromatograms of light asphalt performed on a 1.5 m x 0.53 mm x 0.075 μm OV-1. Initial temperature 80 °C, program rate 20 °C.min^{-1}, final temperature 425 °C, then 5 min hold. Hydrogen inlet pressure 15 kPa. Cool on column injection mode. A-light asphalt sample (10 000 mg.kg^{-1}), B-maltenic fraction (12 930 mg.kg^{-1}), C-asphaltenic fraction (10 400 mg.kg^{-1}).

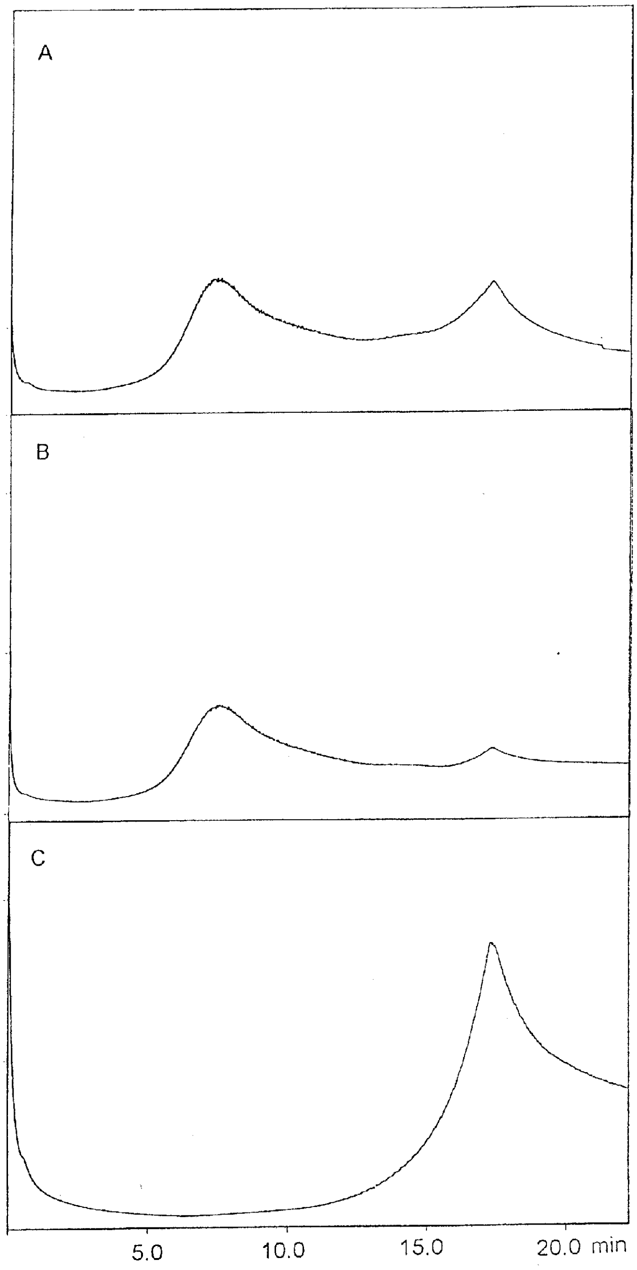

Figure 2. HTGC-FID chromatograms of heavy asphalt performed on a 1.5 m x 0.53 mm x 0.075 μm OV^{-1}. Initial temperature 80 °C, program rate 20 °C.min^{-1}, final temperature 425 °C, then 5 min hold. Hydrogen inlet pressure 15 kPa. Cool on column injection mode. A-heavy asphalt sample (10 000 mg.kg^{-1}), B-maltenic fraction (8 820 mg.kg^{-1}), C-asphaltenic fraction (11 110 mg.kg^{-1}).

asphaltic constituents (up to 30 000). Sample constituents were detected at 215, 260, 350, and 410 nm. For the detection of compounds not seen under UV light, the refractive index detector (RI) was used. No responses were recorded at 215 nm for all samples. GPC chromatograms of light and heavy asphalt samples detected at 260 nm are shown in Figure 3 and Figure 4, respectively. Contents of compounds with molecular weight of above the column size exclusion limit in all light asphaltic samples can be considered negligible. Heavy asphaltic sample consists of almost 15% of this fraction, and was practically removed after precipitation of asphaltenes with n-heptane. Asphaltenic fraction obtained from the heavy asphalt contains over 30% of excluded fraction. Table 2 gives the data on molecular weight of the main fraction determined from UV signal at 260 nm and RI signal for all the analyzed samples, calculated from the position of elution maximum. Besides calibration curve for UV data, a second curve was generated for the RI signal, to compensate for the retention time shift that occurs as the peaks travel through to the second detector, connected in-series. It is obvious, that MW data, particularly in the samples with prevailing content of maltenes (i.e. light asphalt and its maltenic fraction, as well as heavy asphalt and its maltenic fraction) show significant

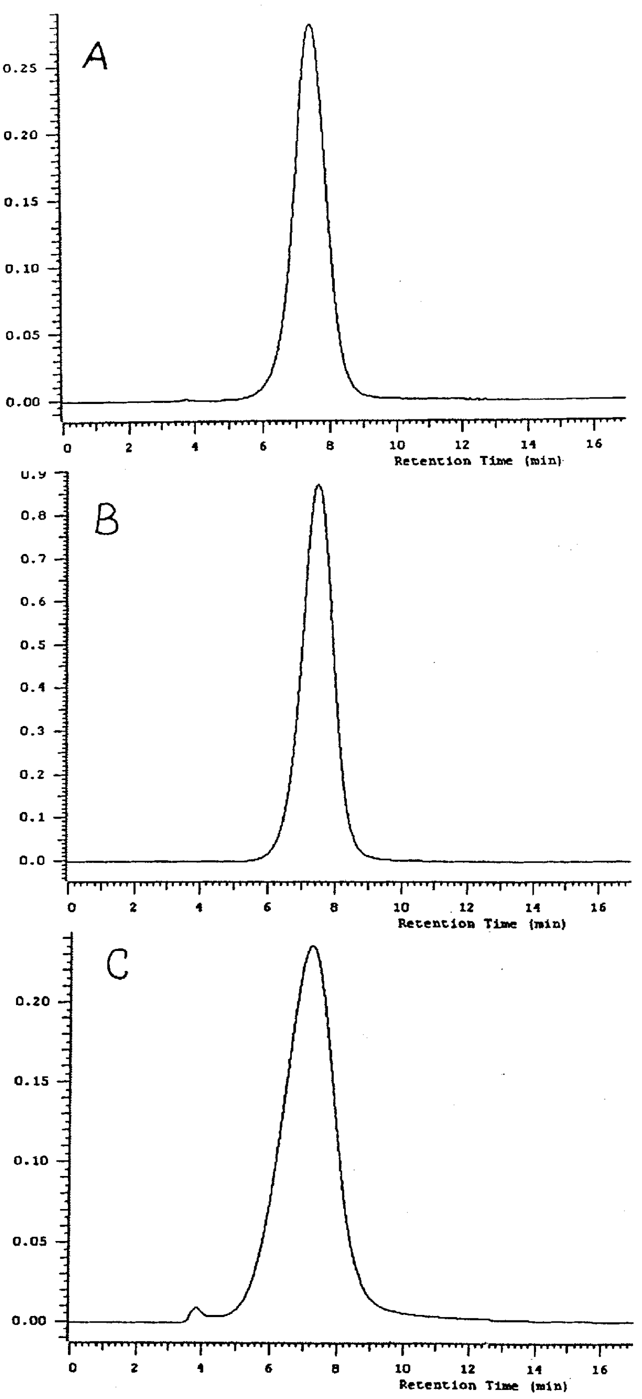

Figure 3. GPC-UV (260 nm) chromatogram of light asphalt performed on a 30 cm x 3 mm x < 25 μm Spheron 40. Tetrahydrofuran mobile phase with 0.25 ml.min^{-1} flow rate. A-light asphalt sample, B-maltenic fraction, C-asphaltenic fraction.

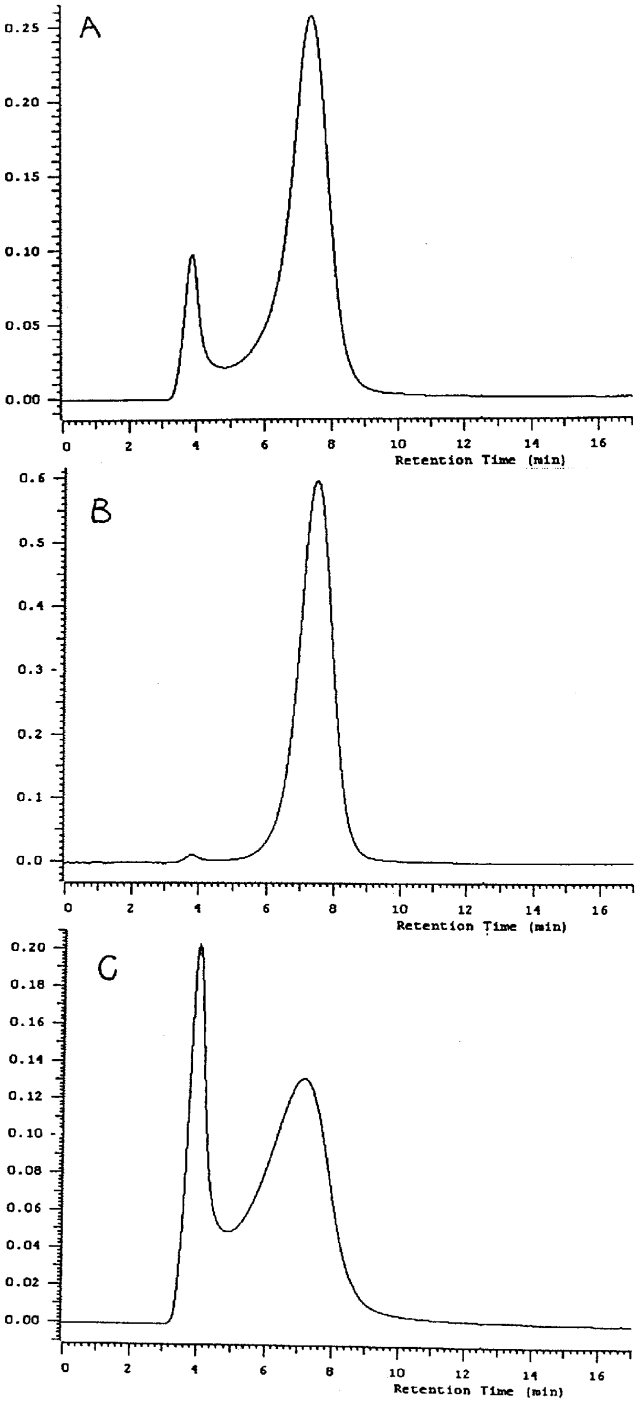

Figure 4. GPC-UV (260 nm) chromatogram of heavy asphalt performed on a 30 cm x 3 mm x < 25 μm Spheron 40. Tetrahydrofuran mobile phase with 0.25 ml.min^{-1} flow rate. A-heavy asphalt sample, B-maltenic fraction, C-asphaltenic fraction.

differences between UV and RI signal. These are caused probably due to the compounds having poor or no response at UV zone that are present mainly in lower region of molecular weights.

Generally, the system utilizing separation of asphalts into maltenic and asphaltenic fractions prior to high temperature capillary gas chromatographic analysis of maltenes allows determination of soil contamination with all oil types as well as asphaltic contamination. The total contamination can be calculated in term of known ratio of maltenes and asphaltenes in soil. This procedure eliminates the drawback of the previous system, namely accumulation of asphaltenic fraction in the column and resulting shortening of column lifetime.

Conclusion

High temperature gas chromatography is used for the separation of high boiling petroleum fractions. However, either high temperature conditions cannot manage the

Table 2. Molecular weight (MW) of the main fraction in analyzed samples determined from UV signal at 260 nm and RI signal.

Sample	Fraction	UV (260 nm) - MW	RI - MW
Light asphalt	Total	4 000	2 100
	Maltenes	4 000	2 100
	Asphaltenes	5 400	5 000
Heavy asphalt	Total	4 300	3 000
	Maltenes	4 050	2 150
	Asphaltenes	6 100	5 900

complete elution of asphaltenic portion of asphalts. Asphalts were separated into maltenes and asphaltenes precipitating asphaltenes with n-heptane and maltenic fraction was analyzed using capillary gas chromatography. Approximately 97% of maltenic fraction are eluted out of the column under given conditions. Eluted fraction of asphaltenes represents no more than 30%. This system allows determination of soil contamination with all oil types as well as asphaltic contamination after separation of asphalts into maltenes and asphaltenes. The total contamination can be calculated in term of known ratio of maltenes and asphaltenes in soil.

Acknowledgement

The authors thank Grant Agency VEGA (Grant No. 1/6108/99), Slovakia for the support of this research.

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