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Short communication

Direct determination of coronene in heavy oil fraction by high-performance liquid chromatography

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Abstract

A simple and selective HPLC method for the determination of coronene in hydrocracked vacuum gas oils is described. The method is based on normal-phase HPLC separation on a column packed with 3,5-dinitrobenzamidopropyl (DNBAP)-silica gel and on-line detection of the eluate with a diode-array detector. The diluted oil samples were injected directly on to the DNBAP column with a mixture of light petroleum (b.p. 60–90°C) and *o*-xylene as eluent. The absolute detection limit was 7.9 ng when using UV detection at 305 nm, corresponding to a concentration detection limit of 4.0 $\mu\text{g/g}$ in the original oil samples, if a 20- μl diluted sample with an oil concentration of 0.1 g/ml is injected. The relative standard deviation for ten replicate determinations was 2.8% at a coronene concentration of 7.02 $\mu\text{g/ml}$.

Keywords: Oil, hydrocracked; Coronene; Polynuclear aromatic hydrocarbons

1. Introduction

Process-side fouling is a serious problem in hydrocracking processes, especially when heavy feedstocks are processed. The formation and accumulation of heavy polynuclear aromatics (HPNAs) are considered to be the cause of hydrocracker fouling, which ultimately leads to coke formation in hydrocracking units [1]. In order to control HPNA accumulation in feedstocks, it is necessary to develop a simple method for the determination of HPNAs in hydrocracking products, particularly for the determination of coronenes and ovalenes, which are thought to

be the precursors of coke formation [1]. The method proposed in this paper is intended to be used for the rapid determination of coronene, the content of which is usually used as an indicator to evaluate the HPNA content in the oil.

There have been a number of reports dealing with the determination of HPNAs in various mixtures, including carbon black, coal tars, chimney soot, automobile and other airborne particulates, diesel particulate and high-boiling petroleum distillates [2–8]. Most of these studies utilized either HPLC or TLC. Fetzer and Biggs [8] utilized a non-aqueous reversed-phase HPLC technique coupled to a photodiode-array detector to determine the HPNAs in a diesel particu-

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late and identified components with up to ten rings. In their work [8], column chromatography was needed for sample pretreatment. Recently, they have published a review on the large PNAs [9].

The method described here allows the rapid determination of coronene in hydrocracked vacuum gas oils by HPLC with minimum sample pretreatment. The method is based on normal-phase HPLC with a 3,5-dinitrobenzamido-propylsilica gel packed column and on-line detection with a diode-array detector. The packing was previously synthesized for the determination of buckminsterfullerenes, C₆₀ and C₇₀. Compared with ODS, this packing is more retentive in fullerene analysis, and is expected to be so for HPNAs also owing to the stronger π - π interaction between the dinitrobenzamido moieties of the packing and the analyte HPNA molecules. With this packing an aromatic hydrocarbon solvent can be used as the strong solvent in the binary mobile phase to improve the solubility and detectability of HPNAs, making the analysis capable of being performed with direct injection after sample dilution.

2. Experimental

All chromatograms were measured on a Hewlett-Packard Model 1090 liquid chromatograph in the isocratic mode at ambient temperature, and a mixture of light petroleum (b.p. 60–90°C, containing ca. 90% hexane and 10% pentane) and *o*-xylene was used as the mobile phase at a flow-rate of 2.0 ml/min. A 20- μ l sample solution was introduced in each run with an autoinjector. Detection was performed with a Hewlett-Packard Model 1040 diode-array detector. The spectrum of the eluent was monitored in the wavelength range 290–600 nm. As the UV cut-off wavelength of *o*-xylene is 285 nm, the chromatographic monitoring wavelength was set at 305 nm.

A stainless-steel column (15 \times 0.4 cm I.D.) packed with 3,5-dinitrobenzamido-propyl (DNBAP)-silica gel using a conventional slurry packing procedure was used. The DNBAP

chemically bonded silica gel was synthesized according to Felix and Bertrand [10] with some modification. NH₂-silica gel was formed by reacting silica gel (5 μ m) (Qingdao Oceanic Chemical Factory) with γ -amino-*n*-propyltrimethoxysilane (Chemical Factory attached to Wuhan University), then the NH₂-silica gel was converted into DNBAP-silica gel with 3,5-dinitrobenzoyl chloride.

Some real hydrocracked vacuum gas oil samples taken from hydrocracking facilities at various petroleum processing plants in China were provided by the Research Institute of Petroleum Processing of China (Beijing). The samples and coronene standard were dissolved in a minimum amount of *o*-xylene and then diluted with light petroleum, to ensure solubilization of the sample. To remove insoluble material, the diluted samples were centrifuged at 4000 rpm for 2 min and the supernatant was used for analysis.

All reagents were of analytical-reagent grade and were used as obtained.

3. Results and discussion

To determine coronene directly in hydrocracked vacuum gas oils, it is important to select a mobile phase with increased solubility towards HPNAs. Usually, aqueous RPLC on an ODS column is recommended for small PNAs and non-aqueous RPLC on an ODS column for large PNAs [11,12]. However, for the direct determination of coronene in hydrocracked vacuum gas oils, both aqueous and non-aqueous RP-HPLC are limited owing to the poor solubility of HPNAs in the relevant mobile phases. In this work, in order to increase the load of the HPNA-containing sample and decrease the detection limit of the analytical method, *o*-xylene-containing light petroleum was selected as the mobile phase, which was found to have better solubility for HPNAs in the hydrocracked vacuum gas oils, as the solubility of HPNAs in an aliphatic hydrocarbon mobile phase can be considerably increased with the addition of an aromatic hydrocarbon solvent. DNBAP-silica gel, which has been used successfully in fullerene separation

[13,14] with a better retentive power than ODS phase, should be used instead of the latter to counteract the decrease in capacity factor of the analytes due to the presence of *o*-xylene in the mobile phase. Here, a charge-transfer complexation mechanism between the bonded dinitrobenzamido moieties and the PNA solutes is expected.

Fig. 1a shows the chromatogram of a typical hydrocracking tail oil on the normal-phase DNBAP column when the flow-rate of eluent consisting of light petroleum–*o*-xylene (9:1, v/v) was kept at 2.0 ml/min. For comparison, the chromatogram of coronene under the same conditions is depicted in Fig. 1b. The retention time of peak A in the sample chromatogram was always in excellent agreement with that of the

coronene standard when the composition of the mobile phase was varied. The presence of coronene was also confirmed by spiking aliquots of the sample with coronene standard, resulting in an increase in peak A. These results indicate that peak A in Fig. 1a probably represents coronene in hydrocracking tail oil.

It is well known that for each aromatic ring arrangement the locations and relative intensities of the UV–visible absorption peaks form a unique fingerprint [15]. For further identification of peak A in Fig. 1a, a comparison of its UV–visible absorption spectra (trace a) with that of the coronene standard (trace b) was made (see Fig. 2), and these two spectra were in excellent agreement with each other. In addition, an excellent spectral match for the rising, falling and maximum points of peak A in Fig. 1a was obtained, suggesting that a pure compound was responsible for this peak.

Similarly, the presence of some alkyl-substituted coronenes and six-ring PNAs in the hydrocracked vacuum gas oil samples was also confirmed. To this end, a comparison of the UV absorption spectra of peaks A, B and C in Fig. 1a was made, as shown in Fig. 3. It can be seen that for these three peaks the number of bands and their shapes and relative intensities agree well with each other; nevertheless, the locations of the bands shift slightly (ca. 5 nm). It is known that alkyl substitution of the ring does not greatly alter the unique UV spectral pattern of PNAs as only bathochromic shifts of a few nanometres are generally observed [16,17]. Therefore, it can be inferred that peaks A, B and C in Fig. 1a come from the same parent ring structure, i.e., peaks B and C result from alkyl-substituted coronenes. Similarly, the almost identical spectral characteristics for peaks D and E in Fig. 1a (see Fig. 4) imply the identical parent ring structure for these two peaks. As compared with the standard spectra [15], this spectral pattern might represent the benzo[*ghi*]perylene ring structure. However, other evidence is required for the definitive identification of peaks B–E in Fig. 1a.

Although some alkyl-substituted coronenes may also exist in the hydrocracked vacuum gas oil, the quantitative analysis was focused only on

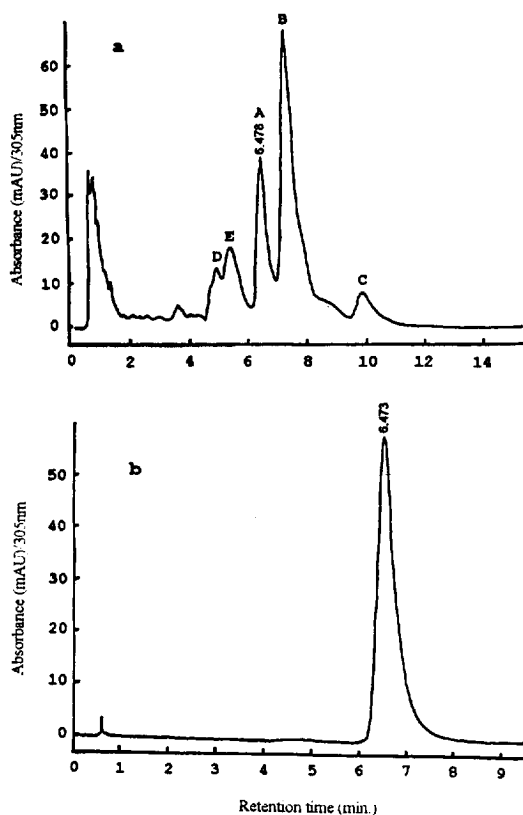


Fig. 1. Chromatograms of (a) a hydrocracked vacuum gas oil with dry point of 576°C and (b) coronene on DNBAP column (15 × 0.4 cm I.D.), 5- μ m packing, with light petroleum (b.p. 60–90°C)–*o*-xylene (90:10) as eluent at 2.0 ml/min.

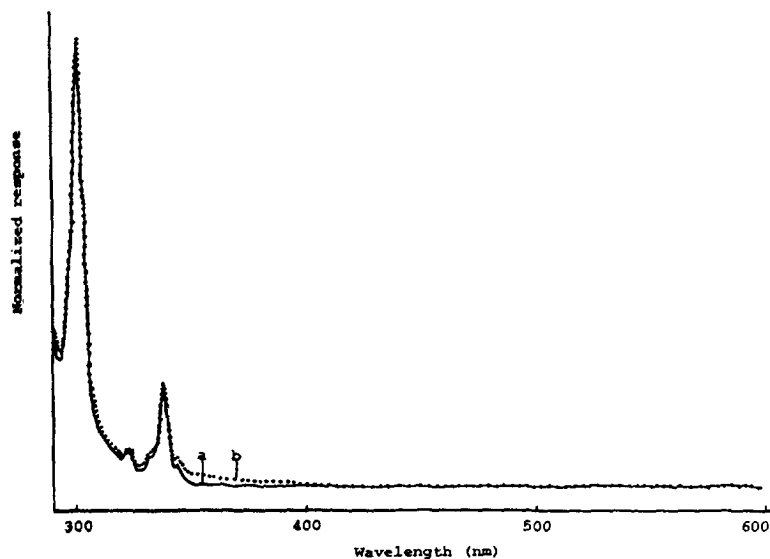


Fig. 2. Comparison of UV spectra of coronene (trace a) and peak A in Fig. 1a (trace b).

coronene as no alkyl-substituted coronene standard samples are currently available. Calibration was performed by injection of a series of coronene solutions with different concentrations (7–40 $\mu\text{g/ml}$), giving the calibration equation $y = 3.79x + 0.92$ with a correlation coefficient of

0.9995, where y is peak height (mAU) and x the concentration of coronene injected ($\mu\text{g/ml}$). The content of coronene in one hydrocracked vacuum gas oil sample (dry point 562°C) was found to be $205.7 \pm 5.9 \mu\text{g/g}$, and $95.1 \pm 3.0 \mu\text{g/g}$ for the other (dry point 527°C), based on four

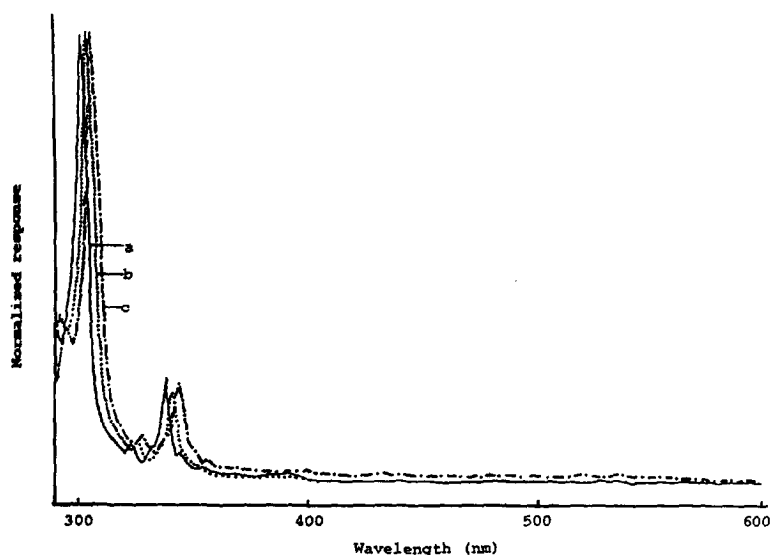


Fig. 3. Comparison of UV spectra of peaks A (trace a), B (trace b) and C (trace c) in Fig. 1a.

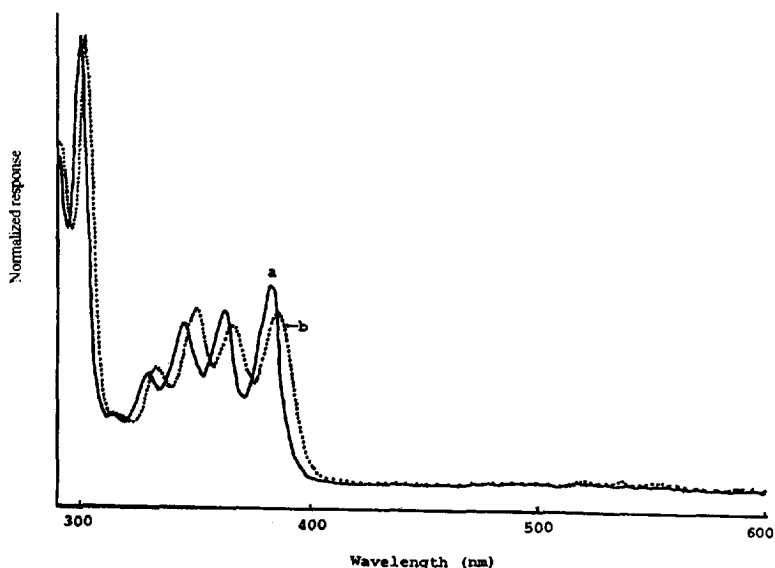


Fig. 4. Comparison of UV spectra of peaks D (trace a) and E (trace b) in Fig. 1a.

replicate determinations. An R.S.D. of 2.8% was obtained for a coronene concentration level of $7.02 \mu\text{g/ml}$, based on ten replicate determinations. The absolute detection limit was 7.9 ng at a signal-to-noise ratio of 3, corresponding to a concentration detection limit of $4.0 \mu\text{g/g}$ in the original oil if $20 \mu\text{l}$ of diluted sample solution containing 0.1 g/ml of the original oil are injected. As the mobile phase contains *o*-xylene, which has a UV cut-off wavelength of 285 nm , the detection sensitivity for coronene suffers slightly at the detection wavelength of 305 nm . However, this can be compensated for by the increased sample concentration. The concentration detection limit of the method can be improved by increasing the sample volume injected and the column efficiency. In addition, the content of alkyl-substituted coronenes was evaluated to be $651.1 \pm 19.3 \mu\text{g/g}$ for the first oil sample (dry point 562°C) and $262.8 \pm 10.6 \mu\text{g/g}$ for the second (dry point 527°C), if the same calibration factor in terms of peak height was assumed for coronene and alkyl-substituted coronenes.

The above results were typical for all the real samples we have investigated. The peaks eluted before coronene were probably PNAs with six

rings or fewer and those eluted after coronene including B–E might be impure, consisting of more than one component. The simple liquid chromatograms with only limited peaks by no means indicates that the sample is simple in composition. On increasing the solvent strength of the mobile phase with increasing *o*-xylene content, no additional peaks were found, showing that in these samples ovalene did not exist in a detectable amount. Therefore, the method proposed here is especially suitable for the determination of coronene, the content of which is usually used as an indicator to estimate the HPNA content in oil.

4. Conclusion

A simple and selective HPLC method for the determination of coronene in hydrocracked vacuum gas oils has been described. The method is based on normal-phase HPLC separation on the column packed with DNBAP-silica gel. The diluted oil samples are injected directly on to the DNBAP column with a mixture of light petroleum (b.p. $60\text{--}90^\circ\text{C}$) and *o*-xylene as eluent.

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