Chemical characterization of aromatic compounds in extra heavy gas oil by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry

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ARTICLE INFO

ABSTRACT

Comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC-TOFMS) was used for the characterization of aromatic compounds present in extra heavy gas oil (EHGO) from Brazil. Individual identification of EHGO compounds was successfully achieved in addition to group-type separation on the chromatographic plane. Many aromatic hydrocarbons, especially polycyclic aromatic hydrocarbons and sulfur compounds, were detected and identified, such as chrysenes, phenanthrenes, perylenes, benzonaphthothiophenes and alkylbenzonaphthothiophenes. In addition, triaromatic steroids, methyl-triaromatic steroids, tetrahydrochrysenes and tetraromatic pentacyclic compounds were present in the EHGO aromatic fractions. Considering the roof-tile effect observed for many of these compound classes and the high number of individual compounds identified, GC × GC-TOFMS is an excellent technique to characterize the molecular composition of the aromatic fraction from EHGO samples. Moreover, data processing allowed the quantification of aromatic compounds, in class and individually, using external standards. EHGO data were obtained in μg g^{-1}, e.g., benzo[a]pyrene were in the range 351 to 1164 μg g^{-1}. Thus, GC × GC-TOFMS was successfully applied in EHGO quantitative analysis.

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1. Introduction

Petrochemical products contain a large and diverse number of chemical classes, such as paraffins, naphthenes, aromatic and unsaturated hydrocarbons, as well as sulfur, oxygen and nitrogen compounds [1]. There are a great number of individual components within these classes, making these samples extremely complex. For analysis of these mixtures, Blomberg et al. [2] demonstrated the applicability of comprehensive two-dimensional gas chromatography (GC × GC) to the characterization of a complex petrochemical mixture and several aromatic hydrocarbons and sulfur compounds were identified in samples. Similarly, in extra heavy gas oil (EHGO) samples, the number of individual components is vast, and no single chromatographic technique is able to separate and characterize these complex mixtures completely. So, comprehensive two-dimensional gas chromatography (GC × GC) could be particularly useful in solving this problem [1,3,4].

EHGO samples are obtained by molecular distillation, a procedure usually used for the distillation of thermally unstable material,

which is the most economically feasible method of purification [5]. This technique is widely applied in fine chemistry, petrochemistry, pharmaceutical chemistry and oil and grease analysis, as well as in scientific research to concentrate and purify organic chemicals of high molecular weight, high boiling point, high viscosity or poor heat stability [5]. Moreover, since petroleum sources are progressively decreasing, the demand for upgrading heavy fractions is increasing.

Molecular distillation has been used for heavy petroleum processing and characterization [6,7]. In this way, GC × GC coupled to time-of-flight mass spectrometry (GC × GC-TOFMS) could be used for detailed chemical characterization of EHGO obtained by molecular distillation. The results regarding the chemical composition of EHGO is very important to petrochemical industries, giving information about the nature, chemical makeup and applicability of these materials.

Concerning aromatic compounds, there are few studies reporting the analysis of such substances in petrochemical samples by GC × GC. Table 1 shows some of the most important results obtained [3,8–13,14–20]. In particular, there is no work regarding EHGO analysis by the mentioned technique. Furthermore, the literature points to only one paper concerning the characterization of saturated biomarkers in Brazilian EHGO samples using GC × GC coupled to time-of-flight mass spectrometry [21].

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Table 1
Important works regarding aromatic compound analyses in petrochemical samples by GC × GC.

Sample	Detector used	Characterized molecules	Reference
BTEX	FID	Benzene, toluene, xylenes, alkylbenzenes, naphthalenes, methylnaphthalenes	[8]
Crude oils	FID	Naphthalenes, biphenyls, fluorenes, phenanthrenes, chrysenes, dibenzothiophenes, benzonaphthothiophenes, steranes, triterpanes, triaromatic steranes	[9]
Jet fuel	FID	Alkylbenzenes	[10]
Kerosene	TOF	Monoaromatic compounds and alkylbenzothiophenes	[11]
Naphtha	FID	Aromatic compounds	[12]
Crude oils and FCC products	TOF, AED	Aromatic thiols, alkylated benzothiophenes, dibenzothiphenes, benzonaphthothiophenes, phenanthrene, pyrene and methylpyrene, chrysene, carbazoles	[13]
Naphtha	FID	Mono- and diaromatics	[3]
Diesel	FID	Mono-, di- and triaromatics, naphthenic-diaromatics	[14]
Gasoline	FID, TOF	Benzene and alkylbenzenes, toluene, naphthalene, styrene, benzothiophenes	[15]
Gasoline	FID	Benzene, toluene, ethylbenzene, naphthalene, xylenes	[16]
Diesel	FID	Mono- and diaromatics	[17]
Source rocks	FID, SCD	Aromatic compounds, benzothiophenes, dibenzothiophenes	[18]
Downhole fluid	FID, TOF	Naphthalenes, phenanthrenes, alkylbenzenes	[19]
Heavy oil	TOF	Alkylbenzenes and polycyclic aromatic hydrocarbons (PAHs)	[20]

In the present study, the aromatic fractions of EHGO samples were analyzed using GC × GC-TOFMS and their molecular compositions characterized, providing a detailed report on the classes of compounds present in these samples. Moreover, the data processing allowed for a quantitative analysis of the aromatic extra heavy gas oil fractions, another objective of this work. Because of the limited information on the chemical constituents of EHGO, this study also enhanced the understanding of these samples and continued the study initiated by our group on Brazilian EHGO samples.

2. Experimental

2.1. Sampling and sample preparation

Three extra heavy gas oil (EHGO) samples were supplied by CENPES/PDP/TPAP, Petrobras (Brazil), and named RO-59, RO-82 and AL-35. Each of these EHGO samples was obtained by molecular distillation (10^{-3} mmHg) of the vacuum residue (ASTM D 5236). Molecular distillation is a process used to separate the fractions of different molecular weight in the vacuum residue at the lowest possible temperature to avoid damage. The EHGO samples were then fractioned into saturated (n-hexane), aromatic [n-hexane: CH_2Cl_2 (8:2)] and polar compounds [CH_2Cl_2:MeOH (9:1)] by liquid chromatography, using activated silica gel (Merck) [22,23].

2.2. GC × GC-TOFMS

The GC × GC-TOFMS system was a Pegasus 4D (Leco, St. Joseph, MI, USA), which is an Agilent Technologies 6890 GC (Palo Alto, CA, USA) equipped with a secondary oven and a non-moving quad-jet dual-stage modulator. Data acquisition and processing was carried out using ChromaTOF software version 4.0 (LECO Corp., St. Joseph, MI). The GC column set consisted of a HP-5 ms, 5%-phenyl–95%-methylsiloxane (30 m, 0.25 mm i.d., 0.25 μm d_f) as the first dimension (^{1}D) and a BPX-50 (Austin, Texas, USA), 50%-phenyl–50%-methylsiloxane (1.5 m, 0.1 mm i.d., 0.1 μm d_f) as the second dimension (^{2}D). The second column was connected to the TOFMS by an empty deactivated capillary (0.5 m × 0.25 mm i.d.). The columns and the empty deactivated capillary were connected by SGE unions using SilTite metal ferrules (Austin, Texas, USA) for 0.10–0.25 mm i.d. GC columns.

GC conditions followed published experimental settings [21]. Briefly, the primary oven temperature program was 70 °C for 1 min, ramp at 20 °C min^{-1} to 170 °C, and then ramp at 2 °C min^{-1} to 325 °C. The secondary oven temperature program had a temperature 10 °C higher than that of the primary one. Carrier gas flow rate was 1.5 mL min^{-1} using helium. A previous analysis was made using the same modulation period for saturated hydrocarbons (8 s), but several wrap around peaks were observed. Therefore, the modulation period was altered for 10 s with a 2.5 s hot pulse duration and a 30 °C modulator temperature offset versus the primary oven temperature.

The MS transfer line was held at 280 °C, and the TOFMS was operated in the electron ionization mode with a collected mass range of 50-600 m/z. The ion source temperature was 230 °C, the detector was operated at 1650 V, the applied electron energy was 70 eV, and the acquisition rate was 100 spectra s^{-1}.

2.3. Data processing

GC × GC-TOFMS data acquisition and processing were performed by ChromaTOF software version 4.0 (Leco, St. Joseph, MI, USA). After data acquisition, samples were submitted to a data processing method where the individual peaks were automatically detected on the basis of a 10:1 signal to noise ratio. Individual peak areas were automatically acquired, and compound identification was performed by examination and comparison with literature mass spectra, retention time, authentic standards and elution order.

A standard mixture solution of PAHs (EPA 610) was acquired from Supelco (Bellefonte, USA). After dilution, the injected solution contained 1.6 ng μL^{-1} of anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[k]fluoranthene, chrysene, indene[1,2,3-cd]pyrene, phenanthrene and pyrene; 3.2 ng μL^{-1} of benzo[b]fluoranthene, benzo[g,h,i]perylene, dibenzo[a,h]anthracene, fluoranthene and fluorene; and 32 ng μL^{-1} of acenaphthene, acenaphthylene and naphthalene. These compounds were used as external standards for compound identification and external quantification, and were analyzed applying the same analytical conditions used for extra heavy gas oil samples. Any response factor was used, being the quantification relative to the respective external standards.

Quantification of identified compounds was achieved from the relation between the sum of peak areas in respect to the PAH standards and its concentration in the external standard mixture. For example, triaromatic steroid compounds and alkylbenzonaphthothiophenes were quantified relative to pyrene and chrysene standards, respectively. Therefore, it was possible to calculate the relative concentrations (ng μL^{-1}) of each compound identified by the relationship between its peak area and the peak area of the external standard of known concentration. Later, this concentration was corrected to the initial EHGO mass (μg g^{-1}).

Table 2
Diagnostic ions (*m/z*) used to identify aromatic compounds in the Brazilian extra heavy gas oils.

Compound name or compound classes	Diagnostic ions (*m/z*)
Alkylbenzenes	105, 119, 120, 134, 148
Naphthalene and alkylnaphthalenes	128, 142, 156
Phenanthrene and alkylphenanthrenes	178, 192, 206, 220, 234, 248, 262, 276
Alkylpyrenes	216, 230, 244, 258, 272, 286, 300, 314
Benzo[a]anthracene and chrysene	228
Alkylchrysenes	242, 256, 270, 284, 298
Benzo[k]fluoranthene and benzo[a]pyrene	252
Alkylbenzo[k]fluoranthenes or alkylbenzo[a]pyrenes	266, 280, 394, 308, 322
Dibenzo[a,h]anthracene and C1-alkyldibenzo[a,h]anthracenes	278, 292, 306, 320
Benzo[g,h,i]perylene	276
Alkylbenzo[g,h,i]perylenes	290, 304
Benzonaphthothiophenes and alkylbenzonaphthothiophenes	234, 248, 262, 276
Triaromatic steroids	231
Methyl-triaromatic steroids	245
Tetrahydrochrysenes	259, 273
Tetraromatic triterpenoids	281

3. Results and discussion

Aromatic compounds in EHGO samples were analyzed on extracted ion chromatograms (EIC) using the diagnostic ions indicated in Table 2. The three samples were very similar in regards to their molecular composition. Their aromatic fractions contained a large diversity of alkylbenzenes, polycyclic aromatic hydrocarbons (PAHs), benzonaphthothiophenes, alkylbenzonaphthothiophenes, triaromatic steroids, methyl-triaromatic steroids, tetrahydrochrysenes and tetraromatic triterpenoids. The chemical structures are given in Appendix A.

3.1. Chromatographic aspects

The results obtained allowed the identification of at least fifteen compound classes in the chromatographic plane, representative of alkylbenzenes, several PAHs classes, a series of triaromatic steroids and methyl-triaromatic steroids, tetrahydrochrysenes and tetraromatic terpenoids.

A previous analysis was made using the same modulation period for saturated hydrocarbons in EHGO samples (8 s), as reported in our previous work [21]. However, several wrap around peaks were observed. Therefore, the modulation period was altered to 10 s, which enabled the best analytical results. Fig. 1 illustrates these results for the AL-35 sample and shows benzo[k]fluoranthene and benzo[a]pyrene identified in two of the modulation periods used.

3.2. Molecular composition

3.2.1. Alkylbenzenes

Several alkylbenzenes were detected by Frysinger et al. [8] by GC × GC in gasoline samples, such as ethylbenzene, xylene, isopropylbenzene and propylbenzene. In the same way, Mullins et al. [19] detected C5-substituted alkylbenzene isomers in oil samples. Alkylbenzenes, represented by C3 and C4-alkylbenzenes, were detected in all the samples analyzed (Fig. 2), despite the oil samples being subjected to three distillation processes before chemical analysis.

3.2.2. Polycyclic aromatic hydrocarbons and sulfur compounds

Polycyclic aromatic hydrocarbons (PAHs) and sulfur compounds have been analyzed in various petrochemical samples, such as crude oils, kerosene, gasoline and source rocks [9,11,13,15,18,19]. These compounds were detected in all aromatic fractions of the EHGO samples, represented by naphthalene and alkylnaphthalenes (Fig. 2), phenanthrene and
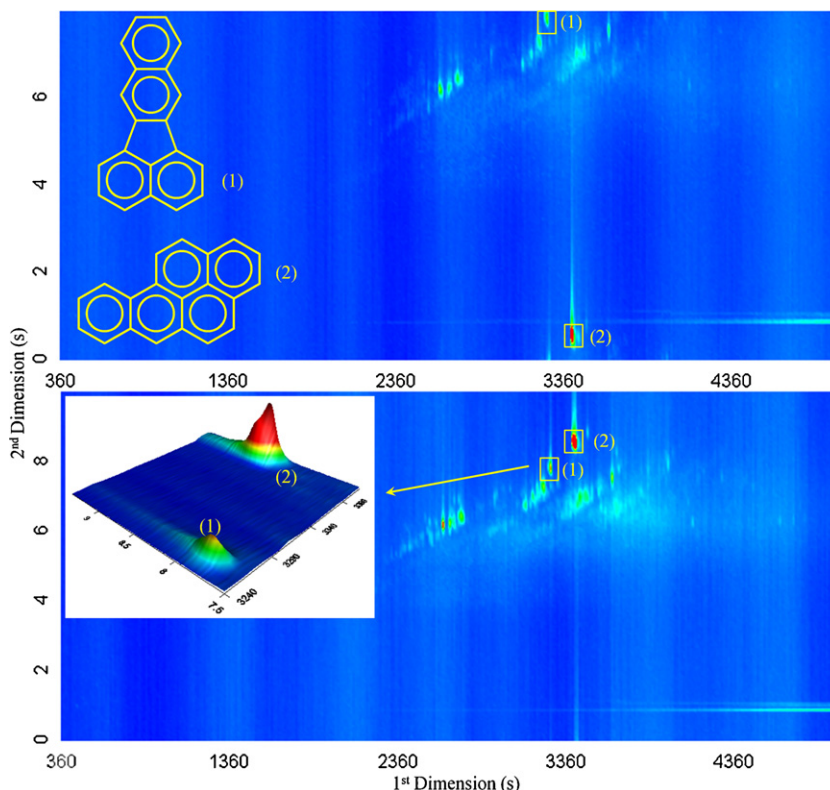
Fig. 1. Mass chromatograms (*m/z* 252) showing benzo[k]fluoranthene and benzo[a]pyrene detected with a modulation period of 8 s (A) and a modulation period of 10 s (B).
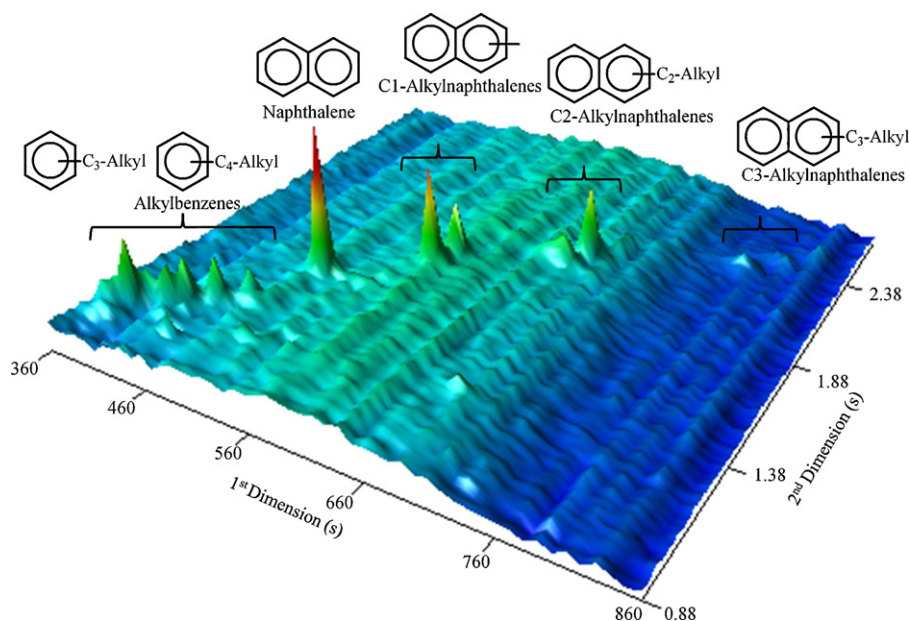
Fig. 2. Alkylbenzenes and naphthalenes detected in the aromatic fraction of the AL-35 EHGO sample.

alkylphenanthrenes, alkylpyrenes, benzo[a]anthracene, chrysene and alkylchrysenes, benzo[k]fluoranthene, benzo[a]pyrene and alkylbenzo[k]fluoranthene or alkylbenzo[a]pyrene, dibenzo[a,h]anthracene and alkyldibenzo[a,h]anthracenes, benzo[g,h,i]perylene and alkylbenzo[g,h,i]perylenes, benzonaphthothiophenes and alkylbenzonaphthothiophenes.

Fig. 3 shows some of the sulfur compounds and phenanthrenes identified in the RO-82 sample and the roof-tile effect observed for such compounds. The roof-tile effect was also clearly observed

for the other PAH classes detected, as illustrated in Fig. 4 for alkylpyrenes in the RO-59 sample.

3.2.3. Triaromatic steroids, tetrahydrochrysenes and tetraromatic triterpenoids

Studies on the GC × GC analysis of triaromatic steroids in crude oils have been reported by only a few authors [9]. We undertook an analysis of these compounds, however, and all the samples presented a series of triaromatic steroids ranging from C19 to C28,
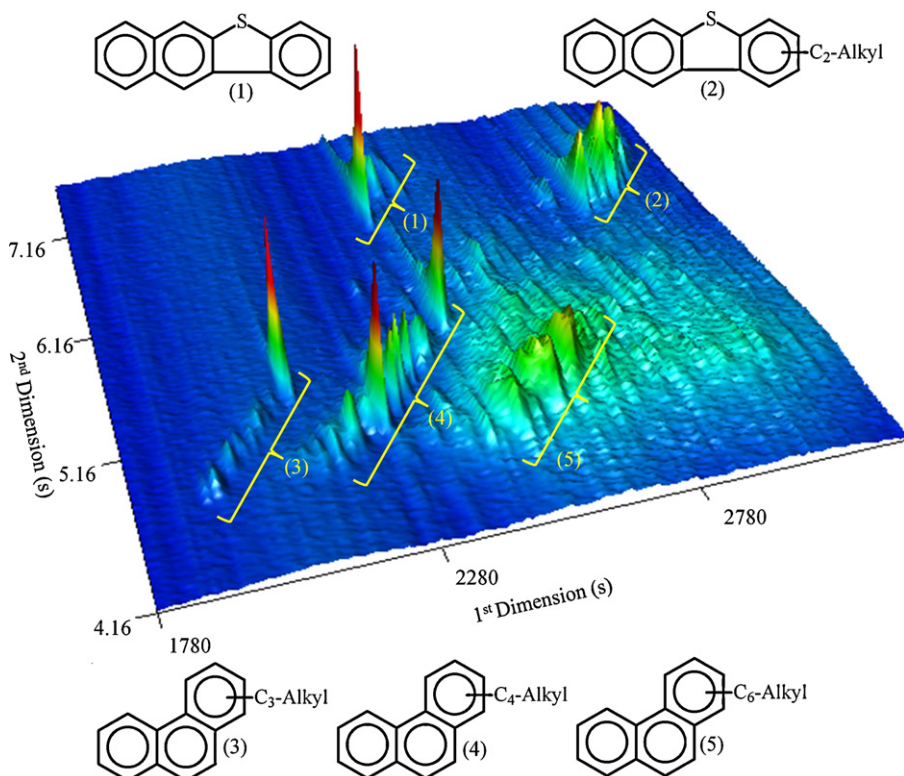

Fig. 3. Benzonaphthothiophenes and phenanthrenes detected in the aromatic fraction of the RO-82 EHGO sample.
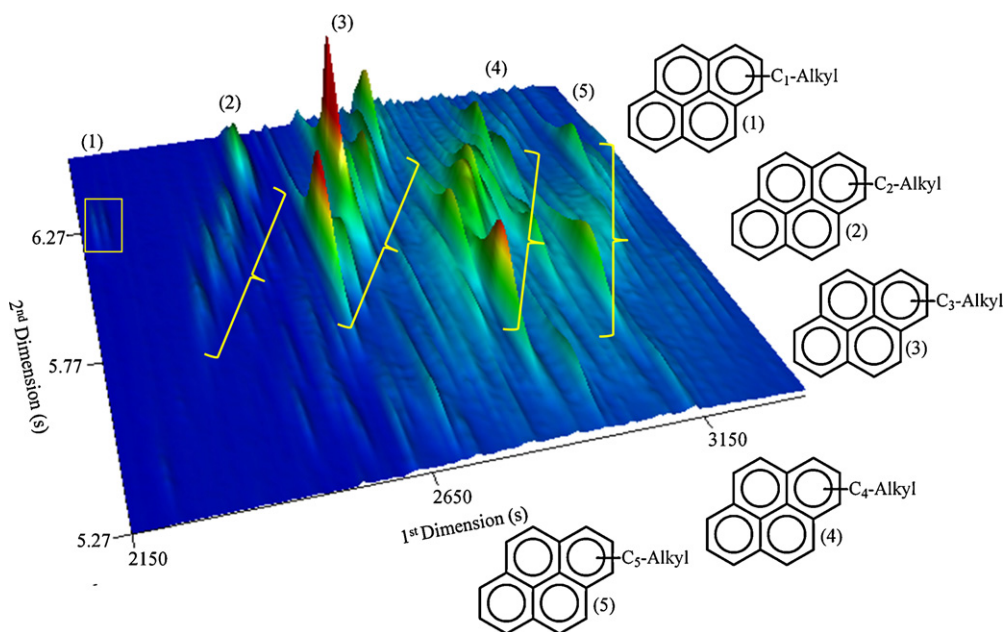
Fig. 4. Roof-tile effect observed for alkypyrenes detected in the aromatic fraction of the RO-59 EHGO sample.

as detected by the m/z 231 ion (Fig. 5). These compounds, usually called biomarkers, are very widespread in crude oil and sediment samples [20].

Using the m/z 245 ion, a series of methyl-triaromatic steroids ranging from C20 to C29 were observed in all the samples (Fig. 6), according to fragmentation patterns observed previously [24]. Regarding the compounds with the diagnostic m/z 259 and m/z 273 ions, they were associated with methyl-tetrahydrochrysenes, as represented in Fig. 7.

Finally, three alkyl tetraromatic triterpenoids, represented by the structures illustrated in Fig. 8, were also identified in all the

samples. Philp reported similar mass spectra with a m/z 281 diagnostic ion corresponding to lupane derivatives [25]. However, several geochemical studies have demonstrated the absence of such a compound class in Brazilian oil samples. Therefore, the mass spectra represented in Fig. 8 were interpreted as alkyltetraromatic terpenoids not related to the lupane class, but from hopanoid compounds. As evidence, the fragmentation patterns observed clearly proved the loss of methyl, ethyl and isopropyl groups.

Recently, Dutriez et al. performed an important analysis of vacuum gas oil using GC × GC-FID and GC × GC-TOFMS [26,27]. Concerning aromatic fractions, the results reported by these
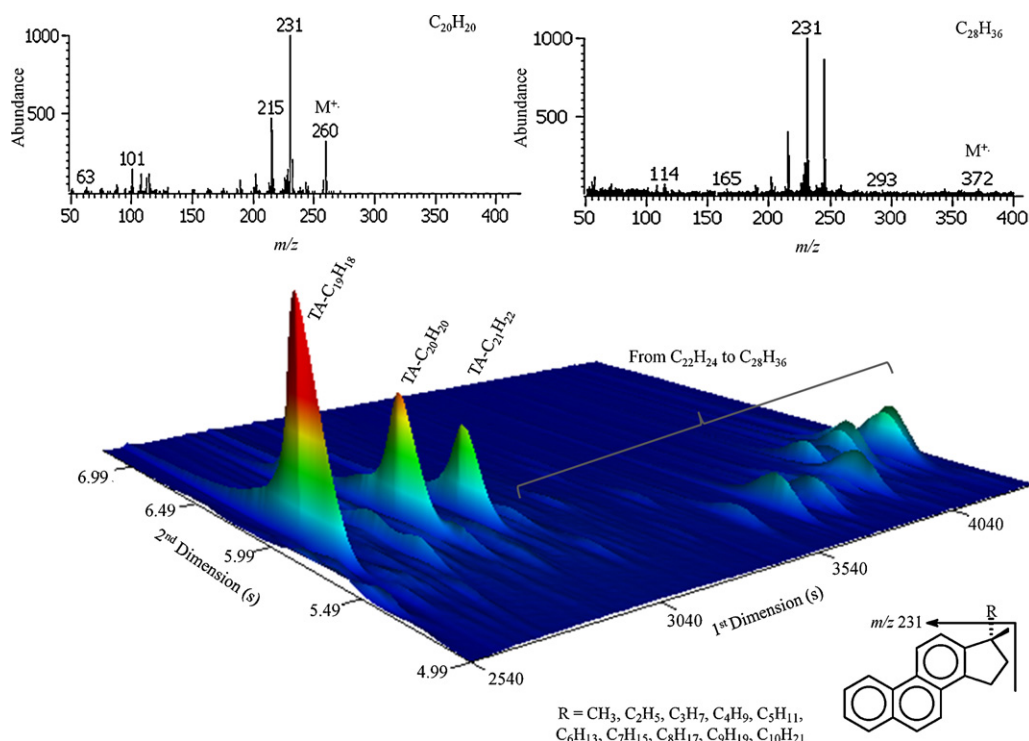

Fig. 5. Triaromatic steroids identified from the m/z 231 ion detected in the aromatic fraction of the RO-82 EHGO sample.
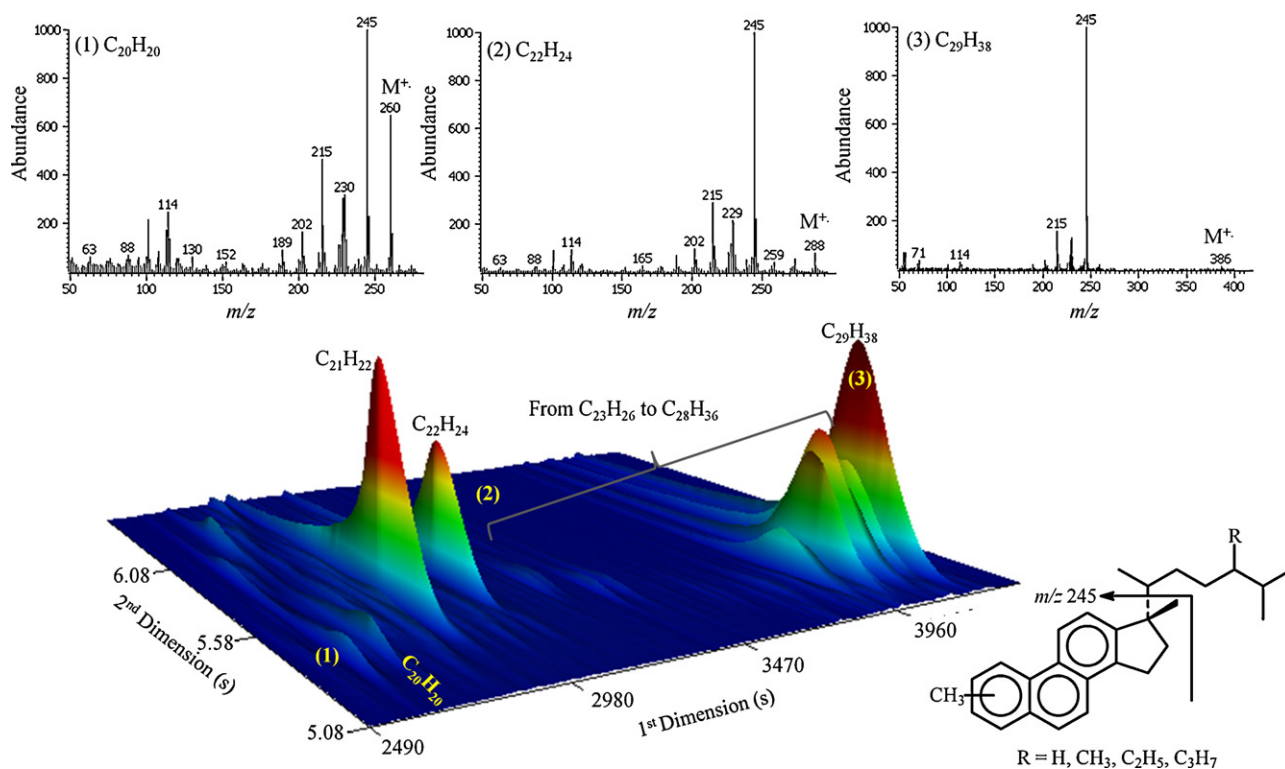
Fig. 6. Methyl-triaromatic steroids identified from the m/z 245 ion detected in the aromatic fraction of the RO-82 EHGO sample.
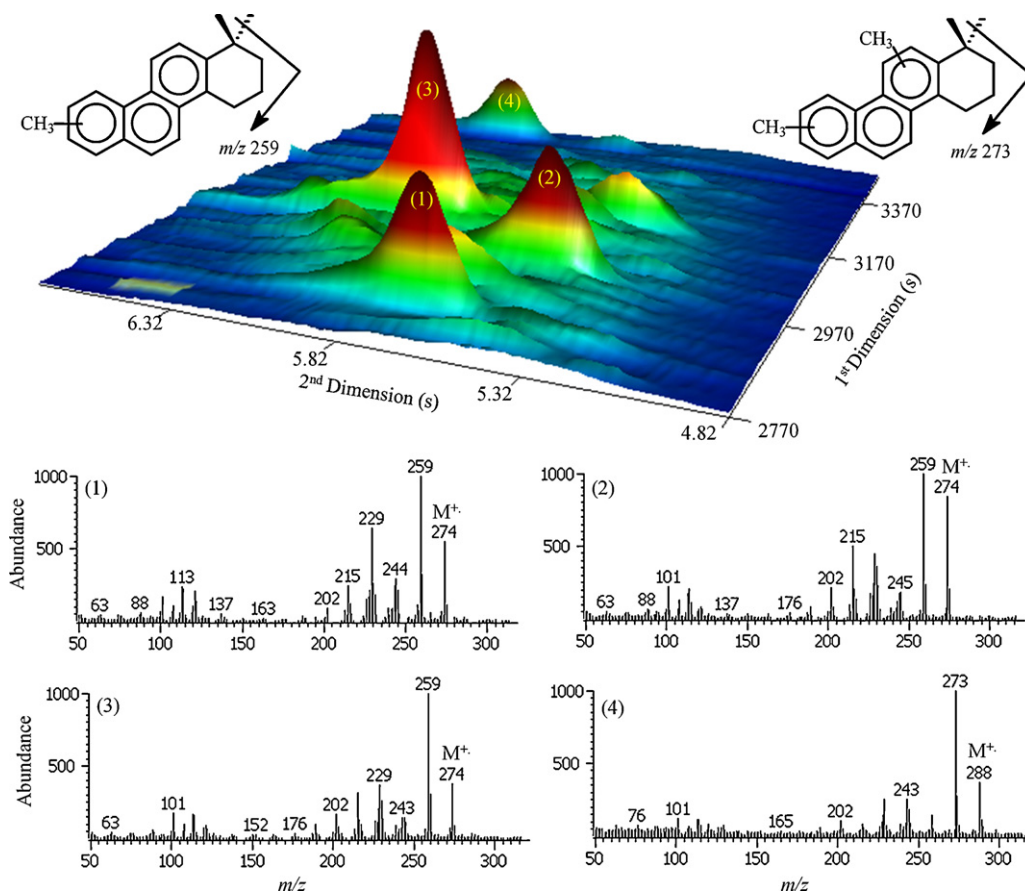

Fig. 7. Methyl-tetrahydrochrysenes identified from the m/z 259 and m/z 273 ions detected in the aromatic fraction of the RO-82 EHGO sample.
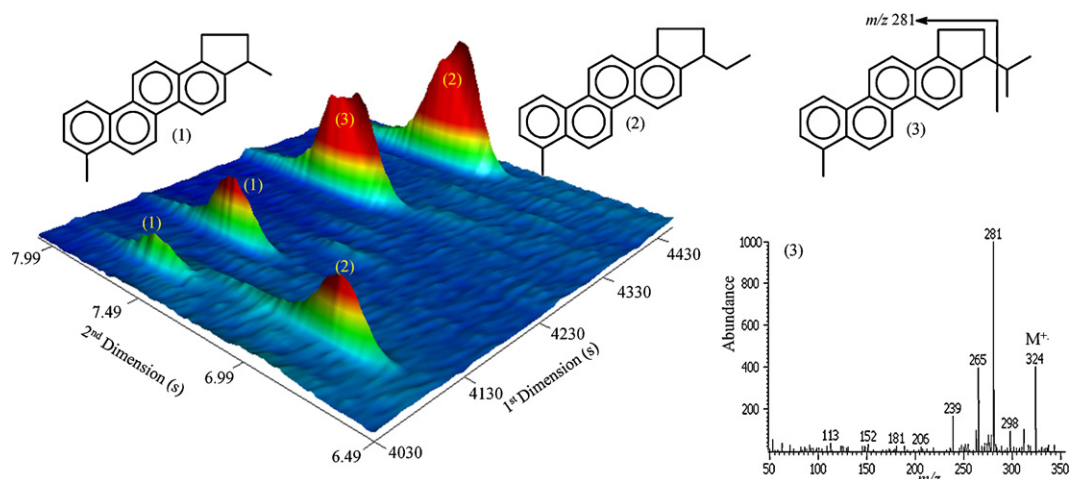
Fig. 8. Tetraromatic terpenoids identified by the *m/z* 281 ion detected in all EHGO samples.

Table 3
Concentrations ($\mu g\,g^{-1}$) of compounds identified in Brazilian EHGO samples.

Compound name or classes	Composition	Concentration ($\mu g\,g^{-1}$)		
		AL-35	RO-59	RO-82
C3-Alkylbenzenes	C_9H_{12}	2134.2	1521.2	1372.0
C4-Alkylbenzenes	$C_{10}H_{14}$	2131.8	921.9	800.6
C5-Alkylbenzenes	$C_{11}H_{16}$	359.6	nd	230.2
Naphthalene	$C_{10}H_8$	2612.3	940.8	5261.6
C1-Alkylnaphthalenes	$C_{11}H_{10}$	2179.8	504.2	988.7
C2-Alkylnaphthalenes	$C_{12}H_{12}$	1757.3	262.8	1045.9
C3-Alkylnaphthalenes	$C_{13}H_{14}$	957.4	nd	868.0
Phenanthrene	$C_{14}H_{10}$	1.9	0.2	1.8
C1-Alkylphenanthrenes	$C_{15}H_{12}$	nd	nd	3.1
C2-Alkylphenanthrenes	$C_{16}H_{14}$	nd	nd	2.0
C3-Alkylphenanthrenes	$C_{17}H_{16}$	74.7	35.7	46.1
C4-Alkylphenanthrenes	$C_{18}H_{18}$	199.8	108.6	130.0
C5-Alkylphenanthrenes	$C_{19}H_{20}$	209.8	1277.2	98.8
C6-Alkylphenanthrenes	$C_{20}H_{22}$	157.0	100.5	144.2
C7-Alkylphenanthrenes	$C_{21}H_{24}$	88.1	19.1	161.8
Pyrene	$C_{16}H_{10}$	0.5	nd	nd
C1-Alkylpyrenes	$C_{17}H_{12}$	45.2	8.7	20.9
C2-Alkylpyrenes	$C_{18}H_{14}$	342.7	239.2	402.4
C3-Alkylpyrenes	$C_{19}H_{16}$	786.9	1378.3	1374.0
C4-Alkylpyrenes	$C_{20}H_{18}$	555.5	1616.1	1011.7
C5-Alkylpyrenes	$C_{21}H_{20}$	109.9	395.4	282.8
C6-Alkylpyrenes	$C_{22}H_{22}$	6.6	11.5	14.5
C7-Alkylpyrenes	$C_{23}H_{24}$	0.7	6.9	8.1
C8-Alkylpyrenes	$C_{24}H_{26}$	nd	1.9	1.7
Benzo[a]anthracene	$C_{18}H_{12}$	33.3	56.2	36.1
Chrysene	$C_{18}H_{12}$	702.4	1633.2	1328.3
C1-Alkylchrysenes	$C_{19}H_{14}$	1462.1	3959.9	2611.4
C2-Alkylchrysenes	$C_{20}H_{16}$	1784.2	5503.7	3572.3
C3-Alkylchrysenes	$C_{21}H_{18}$	920.4	4943.4	2675.3
C4-Alkylchrysenes	$C_{22}H_{20}$	140.6	801.1	434.2
C5-Alkylchrysenes	$C_{23}H_{22}$	12.1	106.1	7.3
Benzo[k]fluoranthene	$C_{20}H_{12}$	50.7	197.5	93.5
Benzo[a]pyrene	$C_{20}H_{12}$	351.1	1163.9	726.7
C1-Alkylbenzo[k]fluoranthenes or C1-Alkylbenzo[a]pyrenes	$C_{21}H_{14}$	684.9	2558.6	1202.5
C2-Alkylbenzo[k]fluoranthenes or C2-Alkylbenzo[a]pyrenes	$C_{22}H_{16}$	322.3	1562.5	1067.1
C3-Alkylbenzo[k]fluoranthenes or C3-Alkylbenzo[a]pyrenes	$C_{23}H_{18}$	128.6	754.4	554.0
C4-Alkylbenzo[k]fluoranthenes or C4-Alkylbenzo[a]pyrenes	$C_{24}H_{20}$	8.7	309.2	188.9
C5-Alkylbenzo[k]fluoranthenes or C5-Alkylbenzo[a]pyrenes	$C_{25}H_{22}$	22.4	31.9	101.8
Dibenzo[a.h]anthracene	$C_{22}H_{14}$	31.1	145.6	9.1
C1-Alkyldibenzo[a,h]anthracenes	$C_{23}H_{16}$	15.6	360.9	209.2

Table 3 (*Continued*)

Compound name or classes	Composition	Concentration ($\mu g\,g^{-1}$)		
		AL-35	RO-59	RO-82
C2-Alkyldibenzo[a,h]anthracenes	$C_{24}H_{18}$	10.7	3.6	285.7
C3-Alkyldibenzo[a,h]anthracenes	$C_{25}H_{20}$	nd	109.6	109.5
Benzo[g.h.i]perylene	$C_{22}H_{12}$	19.3	75.4	45.1
C1-Alkylbenzo[g,h,i]perylenes	$C_{23}H_{14}$	10.8	53.6	46.4
C2-Alkylbenzo[g,h,i]perylenes	$C_{24}H_{16}$	2.4	28.1	23.4
Benzonaphthothiophenes	$C_{16}H_{10}S$	121.9	62.6	119.8
C1-Alkylbenzonaphthothiophenes	$C_{17}H_{12}S$	450.9	1.8	732.4
C2-Alkylbenzonaphthothiophenes	$C_{18}H_{14}S$	346.1	451.9	759.5
C3-Alkylbenzonaphthothiophenes	$C_{19}H_{16}S$	116.4	215.4	445.5
Tetrahydrochrysene-C21	$C_{21}H_{22}$	212.0	163.0	440.4
Tetrahydrochrysene-C22	$C_{22}H_{24}$	7.6	26.0	27.8
Tetraromatic triterpenoid-C23	$C_{23}H_{20}$	128.8	686.3	1.9
Tetraromatic triterpenoid-C24	$C_{24}H_{22}$	44.9	164.0	2.1
Tetraromatic triterpenoid-C25	$C_{25}H_{24}$	31.2	63.0	125.8
Triaromatic steroid-C19	$C_{19}H_{18}$	244.3	193.1	364.7
Triaromatic steroid-C20	$C_{20}H_{20}$	106.7	104.1	170.1
Triaromatic steroid-C21	$C_{21}H_{22}$	29.8	38.2	97.9
Triaromatic steroid-C22	$C_{22}H_{24}$	3.8	3.0	16.2
Triaromatic steroid-C23	$C_{23}H_{26}$	0.4	0.3	9.2
Triaromatic steroid-C24	$C_{24}H_{28}$	10.2	2.3	38.3
Triaromatic steroid-C25	$C_{25}H_{30}$	35.9	7.9	52.9
Triaromatic steroid-C26	$C_{26}H_{32}$	7.8	5.5	98.8
Triaromatic steroid-C27	$C_{27}H_{34}$	9.9	0.5	33.5
Triaromatic steroid-C28	$C_{28}H_{36}$	0.4	7.1	248.6
Methyl-triaromatic steroid-C20	$C_{20}H_{20}$	44.7	72.6	82.1
Methyl-triaromatic steroid-C21	$C_{21}H_{22}$	136.4	551.0	448.2
Methyl-triaromatic steroid-C22	$C_{22}H_{24}$	76.5	252.6	261.6
Methyl-triaromatic steroid-C23	$C_{23}H_{26}$	4.5	0.2	40.1
Methyl-triaromatic steroid-C24	$C_{24}H_{28}$	2.2	nd	36.3
Methyl-triaromatic steroid-C25	$C_{25}H_{30}$	3.0	18.1	7.4
Methyl-triaromatic steroid-C26	$C_{26}H_{32}$	54.8	0.2	25.7
Methyl-triaromatic steroid-C27	$C_{27}H_{34}$	40.7	6.4	20.8
Methyl-triaromatic steroid-C28	$C_{28}H_{36}$	2.7	5.0	326.7
Methyl-triaromatic steroid-C29	$C_{29}H_{38}$	304.4	0.3	1104.2
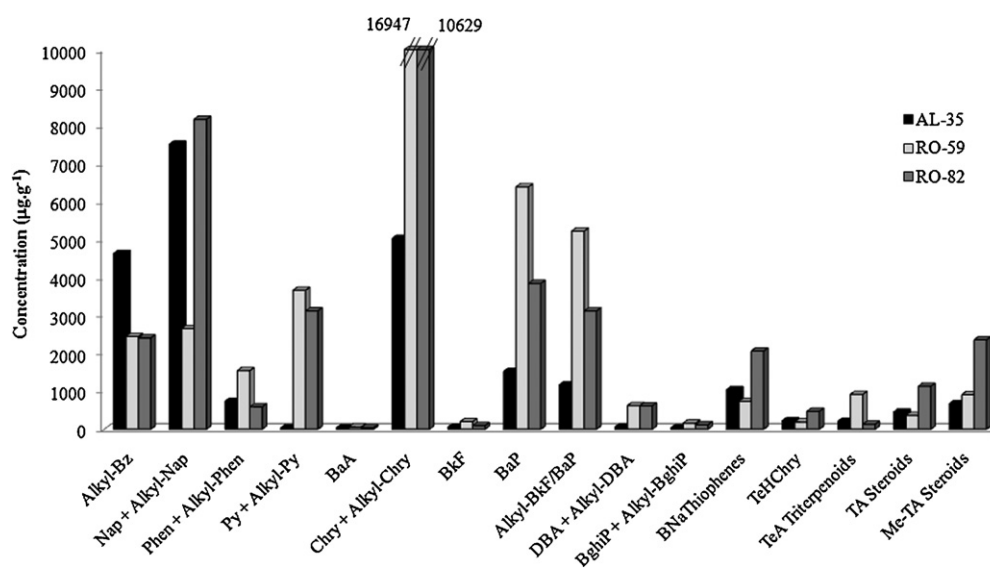
Fig. 9. Concentrations ($\mu g\,g^{-1}$) of compound classes identified in Brazilian EHGO samples. Alkyl-Bz: Alkylbenzenes; Nap+Alkyl-Nap: Naphthalene and Alkylnaphthalenes; Phen+Alkyl-Phen: Phenanthrene and Alkylphenanthrenes; Py+Alkyl-Py: Pyrene and Alkylpyrenes; BaA: Benzo[a]anthracene; Chry+Alkyl-Chry: Chrysene and Alkylchrysenes; BkF: Benzo[k]fluoranthene; BaP: Benzo[a]pyrene; Alkyl-BkF/BaP: Alkylbenzo[k]fluoranthenes or Alkylbenzo[a]pyrenes; DBA+Alkyl-DBA: Dibenzo[a,h]anthracene and Alkyldibenzo[a,h]anthracenes; BghiP+Alkyl- BghiP: Benzo[g,h,i]perylene and Alkylbenzonaphthothiophenes; BNaThiophenes: Benzonaphthothiophenes and Alkylbenzonaphthothiophenes; TeHChry: Tetrahydrochrysenes; TeA: Tetraromatic; TA: Triaromatic; Me-TA: Methyl-triaromatic.

authors allowed the group-type separation in mono-, di-, tri- and tetraromatic compounds. Furthermore, the identification of each vacuum gas oil compound was a huge task, made difficult by the heterogeneity of the sample composition (i.e., complex chemical structures, isomers and heteroatoms) [26]. However, in the present work it was possible to separate and identify several individual aromatic components of EHGO samples, as well as saturated compounds characterized in our previous work [21]. In this way, although individual identification was an exhaustive task, the results obtained proved that it was possible to identify compounds from a complex oil mixture using authentic standards, elution order, mass spectra and the roof-tile effect.

3.3. Quantitative analysis

The data processing method performed by the ChromaTOF Software allowed a quantitative analysis of various individual and compound classes.

After processing, the different peak areas were acquired by selection of a specific ion, such as the molecular ion or the base peak ion. In this work, for alkylbenzenes, PAHs and alkylbenzonaphthothiophenes, the molecular ion was used to determine their areas, while for triaromatic steroids, methyl-triaromatic steroids and tetraromatic terpenoids, the base peak ion was considered. It is important to note that all peak areas related to a specific class of compounds were summed.

Table 3 shows the compound concentrations ($\mu g\,g^{-1}$) identified in the samples. These results proved that it was possible to determine the relative percentages, and most important, the concentrations, for each individual substance or compound class, after processing. Selected quantitative data are illustrated in Fig. 9.

3.4. Importance of chemical characterization of EHGO samples

The results regarding the chemical data of EHGO are very important to petrochemical industries, and give information about the nature, chemical makeup and applicability of these materials. The understanding of the chemical composition of EHGO samples has a great importance in lumping procedures, allowing predictions about several properties. Lumping procedures have been used in the kinetic modeling of gasification, partial oxidation and combustion of hydrocarbon mixtures [28], and in modeling of visbreaking affected by naphthenic compounds [29], just to name a few applications. Moreover, our results are useful to guide for a petroleum conversion process that generates more products with higher added value.

4. Conclusion

This work highlights new information regarding the molecular composition of three EHGO samples from Brazilian oils, particularly their aromatic fractions. GC × GC-TOFMS was the technique used to analyze the samples, which allowed the group-type separation and identification of several individual compounds, as well as a quantitative analysis after data processing. The success in the acquisition of these results was due to the use of GC × GC-TOFMS, which proved to be ideal to elucidate the EHGO molecular composition and the relative abundance of each compound class detected. Polycyclic aromatic hydrocarbons, sulfur compounds, triaromatic steroids, tetrahydrochrysenes and tetraromatic triterpenoids were

the main compound classes identified in this study. In regards to the petrochemical industry, the results obtained are useful to guide for a petroleum conversion process that generates more products with higher added value.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.09.051.

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