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Preliminary Study on Some Contaminant Hydrocarbons in Settled Particles in Caracas City, Venezuela

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Organic compounds reach the atmosphere from widely differing anthropogenic and natural sources. The variety of organic compounds present in the aerosol must be enormous. The measurement of low concentration of organic compounds in the atmosphere has been a subject of research for many years (Farmer and Wade 1986; Benner et al 1989 ; Dannecker et al.1990; Salazar et al.1991 Heintzenberg 1994).

The carcinogen effect of high molecular weight hydrocarbons, such as polyaromatic hydrocarbons (PAHs) is very well known (Farmer and Wade 1986; Venkataraman and Sheldom 1994). The anthropogenic sources of these compounds are mostly particles and gas emission from motor vehicles. Hence, the importance of determining these pollutants in the atmosphere.

The sampling of particles in highway tunnels, being a semi-closed environment, provides an opportunity to analyze automobile emissions under more favorable conditions. Emissions are not affected by dilution effects, as it is presented with sampling in the environment air (Danneker et al. 1990). An additional advantage of sampling in these places, is that the results obtained can be compared with those from urban aerosoles studies in order to asses the impact of motor vehicle emissions on urban pollution. Gas chromatography with mass spectrometric detection (GC/MS) is the technique usually established for analysis of these compounds after high volume sampling or size-fractionation.

Very little information about this subject have been published at the present in Venezuela (Jaffé et al. 1993). The main objective of this preliminary work was to carry out a qualitative analysis of saturated and polyaromatic hydrocarbons (PAHs) on settled particles collected in different tunnels located in Caracas, a large capital city. This study aims to determine the possible causes for the chemical composition changes in the saturated and aromatic compounds associated to settled particles.

MATERIALS AND METHODS

Settled particles samples were collected in three tunnels named: La Trinidad, El Valle and El Paraiso. Sampling was carried out using a clean, new brush and a

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plastic dustpan. They were kept in plastic bags. Samples were dried at room temperature and sieved through stainless steel sieves of 35, 60, 120, 230 and 325 mesh. The analytical procedure for the extraction was the following: the collected samples were refluxed with a mixture of KOH and CH_3OH (5% in vol) (Salazar et al. 1991) for two hours and the resulting solutions passed through a silica-gel chromatography column (dimensions of column 30 cm large , 1 cm diameter, packed with a silica gel) The fraction corresponding to the saturated and aromatic hydrocarbons was separated using n-hexane and a chloromethane / n-hexane mixture respectively. All solvents used were analytical grade (Merck).

The analysis of the different compounds present in the collected samples was done using Gas Chromatography-Mass Spectrometry (GC-MS) with SIM (ion selection method) and full scanning methods detection for the saturated and the aromatic fractions respectively. A Perkin-Elmer, model Q-MASS 910 GC-MS equipped with a 60 m capillary column (i.d. 0.25 mm and 0.25 μm thickness) was used. Chromatographic conditions were: starting temperature: 80 ^{0}C, heating velocity 4^0/min up to 280 ^{0}C. Helium was the carrier gas. The identification of the organic compounds was carried out by matching the retention time with a sample of crude oil from Venezuela, whose n-alkanes distribution is known (Cassani and Eglinton 1991), and also by comparison of the mass fragment with respect to mass spectral data supplied by the NIST library. The detection limit is 0.1 ppm .

RESULTS AND DISCUSSION

Figure 1 shows the distribution of n-alkanes in the C_{18}-C_{35} interval for each tunnel sample. A hump or a non resolved hydrocarbons mixture (UCM) at long retention times (≅ 43-50 minutes) is also obtained in each sample. Fragmentograms m/z 217 and m/z 218 of the saturated fraction for samples collected in each tunnel under study is shown in figure 2. These fragmentograms correspond to a typical distribution of regular steranes with a maximum peak at C_{27}. As can be seen the chromatograms and fragmentograms showed similar distribution in each sample , which indicate a common origin for these type of hydrocarbons similar to those reported for many crude oils from Venezuela (Alberdi et al. 1996 ; Tocco R ; 1996).

It is also observed from this figure, that signal intensity of the sterane pregnane (C_{21}) and the methyl pregnane (C_{22}) peaks from El Paraiso tunnel, is more intensive compared with that obtained from other locations. This intensity increase (C_{21} and C_{22} signals) in relation to that given by C_{27}-C_{29} peaks for the same sample, may be related to a preferential removal of the heaviest molecular hydrocarbons. This probably due to an enhancement on the biodegradation process due to the presence of bacterias coming from a continuous domestic waste flow through the tunnel.

The terpanes pattern from the three locations is shown in figure 3. It can be observed a similar distribution for the tricyclic terpanes in the range of (C_{20}-C_{26})

Paraiso samples a significative increase of tricyclic terpenes with respect to the pentacyclic hopane series.

Table 1 . Ratio of the different compounds for each tunnel

Sample	La Trinidad	El Valle	El Paraiso
C_{21}/C_{22}	1.00	1.06	1.33
C_{27}/C_{29}	1.63	1.60	2.80
C_{29}/C_{30}	1.21	1.20	1.20
$C_{23}/C_{23+}C_{30}$	0.40	0.66	1.20
Tt/tp	0.90	1.34	4.22

tt : tricyclic terpane ; tp : pentacyclic terpane ; C_{23} : tricyclic terpane with 23 atoms of carbon ; C_{29} , C_{30} hopanes 17 α (H), 21β(H) (m/z 191) ; C_{27}/C_{29} : steranes 14 α (H), 17α (H) y 14 β (H), 17β (H), (m/z 217) ; C_{21}/C_{22} pregnane y methyl pregnane

Table 1 summarized the molecular ratio for the different steranes and terpenes from the three areas studied. The greatest ratios of C_{21}/C_{22} (1.33), C_{27}/C_{29} (2.80) and the terpene ratios C_{29}/C_{30} (1.20) and $C_{23}/C_{23+}C_{29}$ (1.20) were obtained from El Paraiso tunnel . This indicates that these samples have been preferentially altered respect to those from other tunnels. It is also observed from this table, that the tricyclic to pentacyclic terpanes (ttp/tp) ratio is quite different for the three tunnels studied: 0.90, 1.34 an 4.22 for La Trinidad, El Valle and El Paraiso respectively. All the changes in the molecular ratios and in the sterane and terpanes distribution may be related to biodegradation process as it has been postulated by several researches (Tissot and Welte 1978; Seifert and Moldowan 1979; Connan 1984; Grbic'-Galic' 1989 ; Omon et al. 1992; Goncalves et al. 1995) in crude oil subjected to a natural and in-vitro biodegradation.

The aromatic fraction, and specifically the phenantrene series (m/z 178), dibenzothiophene (m/z 184) and methyldibenzothiophene (m/z 198) show significant changes in the signal intensities for the three tunnels samples. This results could be assigned to similar variations as it was noted for the saturated fraction (biodegradation). In general these results suggest important alterations in both: saturated and aromatic fractions for the three tunnels. The most relevant changes occur in the saturated fraction for El Paraiso tunnel samples and in the aromatic fraction for La Trinidad tunnel. These observed variations seem to be related to an unique process or mechanism associated to the microbial attack on the organic matter adsorbed on this kind of particles.

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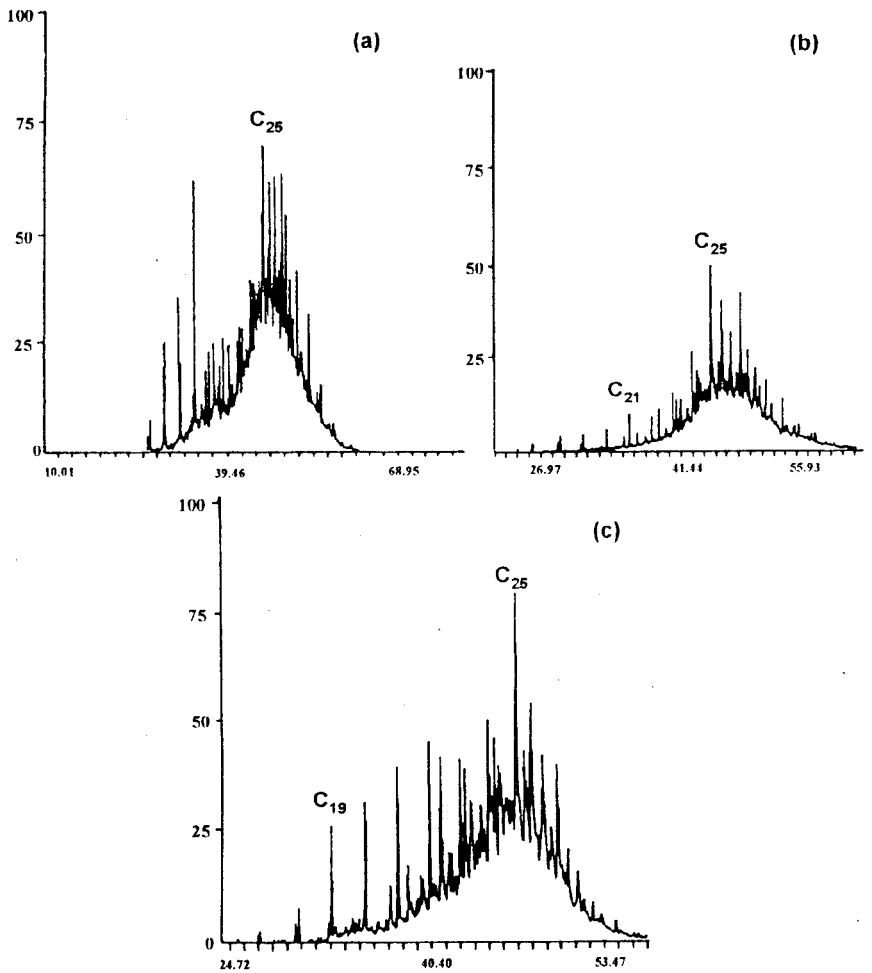

Figure 1. Analysis of saturate fraction. n-alcanes (m/z=113). (a) La Trinidad sample. (b) El Valle sample. (c) Paraiso sample.

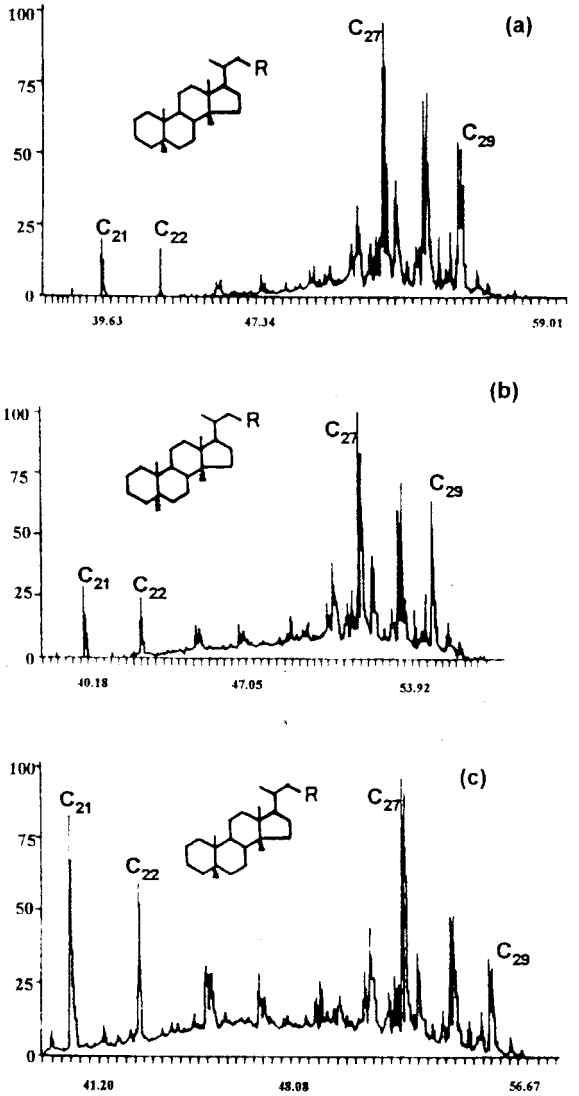

Figure 2. Analysis of saturate fraction. Steranes (m/z=218). (a) La Trinidad sample. (b) El Valle sample. (c) Paraiso sample.

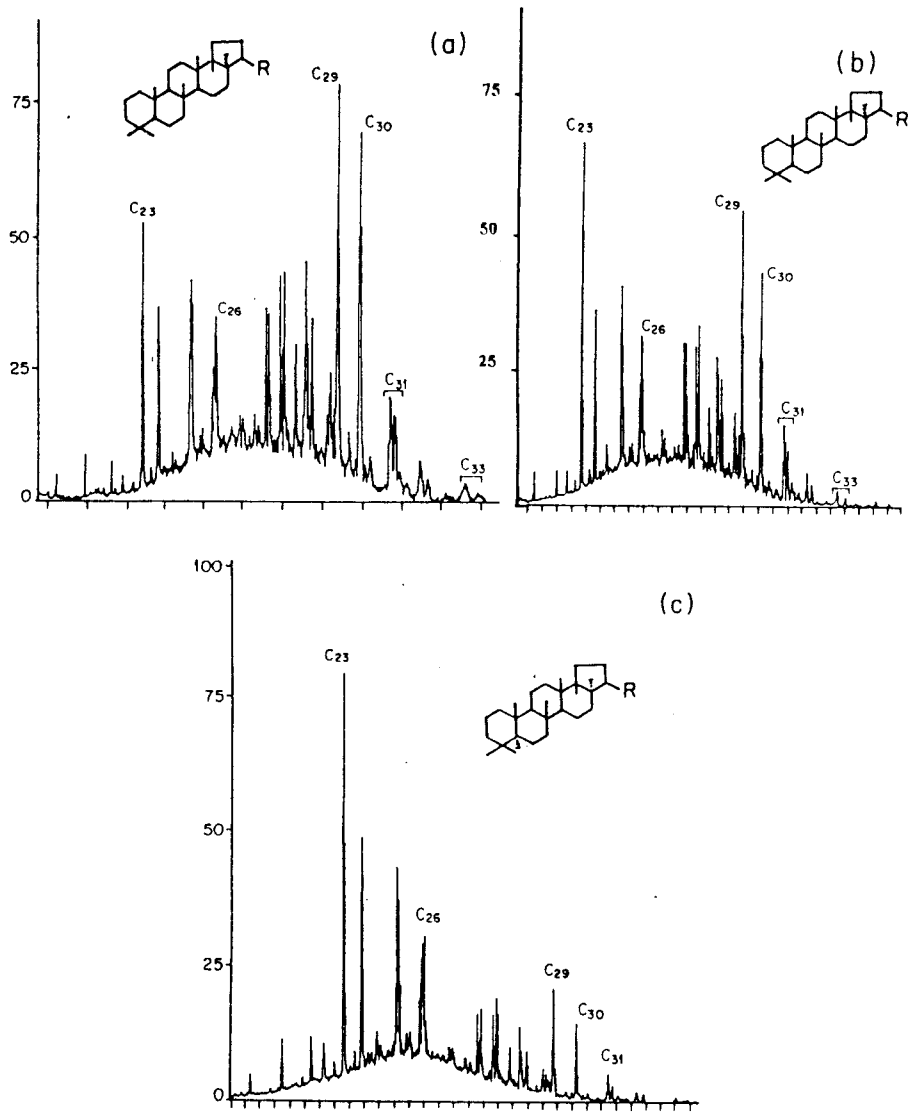

Figure 3. Analysis of saturate fraction.Hopanes (m/z=191).(a) La Trinidad sample. (b) El Valle sample. (c) Paraiso sample.

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