ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS BY ITD MASS SPECTROMETRY AND COMPARISON WITH GC AND LC CHROMATOGRAPHIC TECHNIQUES APPLICATIONS: AIRBORNE PARTICULATE

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ABSTRACT A method for the simultaneous analysis of nineteen Polycyclic Aromatic Hydrocarbons (PAH), 11 of which are included in the priority pollutants list of the US Environmental Protection Agency (EPA), was designed for their determination in airborne particulate. PAHs analysis was carried out by different analytical techniques: reversed-phase liquid chromatography with Ultraviolet detection and wavelength programming (LC-UV), capillary gas chromatography with Flame Ionisation (GC-FID) and Mass Spectrometry (GC-MS) with Ion Trap Detector (ITD). The minimum amounts detectable with the various techniques were determined for each compound. They lay respectively between 0.05 and 0.2 ng on LC-UV, between 1.5 and 5 ng on GC-FID and between 0.5 and 4 pg on GC-ITD-MS. PAHs separation was achieved on 5 µm polymeric C-18 column in LC and on two different capillary columns in GC. Samples were extracted by acetonitrile using Soxhlet extraction. The purification step was assessed for each analytical technique. These methods were applied for the determination of PAHs in three locations in Tunis. For studied samples, ten PAHs were detected and quantified. Moreover, PAHs levels were in relation ship with traffic rate in studied locations.

Key-words: PAH/ Mass Spectrometry/ Ion Trap Detector/ airborne particulate

RESUME Différentes techniques analytiques ont été étudiées afin de mettre au point une méthode permettant la détermination des HAP dans les particules aéroportées. 19 HAP ont été recherchés, 11 parmi eux appartiennent à la liste US-EPA. L'analyse de ces composés a été effectuée par: chromatographie liquide à polarité de phase inversée couplée à un détecteur UV (CPL-UV), chromatographie gazeuse couplée à un détecteur FID (CPG-FID) et la spectrométrie de masse à trappe d'ions (CPG-ITD-MS). Les quantités minimales détectables ont été déterminées pour chaque composé pour ces différentes techniques. Elles varient entre 0,05 et 0,2 ng en CPL-UV, entre 1,5 et 5 ng en CPG-FID et entre 0,5 et 4 pg en CPG-ITD-MS. La séparation des HAP a été réalisée en CPL sur une colonne C-18 à caractère polymérique (5 µm) et sur deux différentes colonnes capillaires en CPG. Les échantillons sont extraits par Soxhlet avec l'acétonitrile. L'étape de purification a été testée pour chacune de ces techniques analytiques. Ces méthodes ont été appliquées à la Détermination des HAP dans trois sites de la ville de Tunis. Dans les échantillons étudiés dix HAP ont été détectés et quantifiés. Les teneurs de ces composés sont en corrélation avec l'intensité du traffic.

Mots clés: HAP/ Spectrométrie de masse/ Détecteur à trappe d'ions/ Particules aéroportées.

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAH) currently form one of the groups of organic compounds of greatest environmental impact owing to their widespread distribution in the environment; this is because they are generated naturally (forest fires, volcanic activity, etc.) and by the incomplete combustion of fossil fuels [1,2] as well as other organic materials (motor vehicle exhaust) [2,4].

The mutagenic and/or carcinogenic [5-7] nature of these compounds means that their presence in different matrixes should be rigorously monitored, among such matrixes, of exceptional importance is air. In fact, atmospheric aerosol has been recognised as an important source of these compounds.

Many studies have been undertaken to characterise the PAH content of airborne particulate matter [8,9]. A major problem associated with the determination of PAH in complex mixtures in general, and in extracts of atmospheric aerosols in particular, is the separation and identification of individual PAH in the presence of the numerous other isomeric parent and alkyl-substituted PAH. Since the biological properties of many PAH are isomer specific, the determination of individual procedures and selective detection techniques are required for the characterisation of PAH in complex «real world» samples. The most studies were limited to the 16 priority PAHs and only qualitative information has been reported.

As a first step in analytical procedure for PAHs in airborne particulate, extraction of the target compounds retained on PTFE or glass-Fibber filters is necessary. Soxhlet extraction and ultrasonication using a variety of organic solvents including acetone, benzene, toluene acetonitrile are the most widely used processes [10-12].

The analysis of the purified extract can be carried out using liquid chromatography with ultraviolet [13-19] and /or fluorimetric [20,21] detection and gas chromatography with flame ionisation and /or mass spectrometry detection [9,22-24].

Many studies showed that fluorescence detection improves sensitive and selective detection for PAHs. However, C-18 bonded phases are classified as monomeric and polymeric. According to the data available in the literature, separation of the 16 priority PAHs is better carried out in of C-18 columns with a high polymerisation degree and with an acetonitrile-water mobile phase [24,25].

GC chromatography is the method with a high resolution power in PAH mixture separation. A recent comparison of some high temperature GC columns also illustrated their applicability to the analysis of moderately high-molecular-mass PAHs with a reasonable retention time. GC with capillary columns has been used in combination with FID. However the Ion Trap mass spectrometer allows selective and sensitive detection.

In a previous work [26], we have showed that liquid chromatography coupled to UV absorption with variable wavelength during elution improves the selectivity and sensitivity of detection by using for each PAH the wavelength of detection corresponding to its maximum of absorption. However, the LC-PAH Supelcosil column recommended for the separation of the 16 PAH's priority list does not allow the resolution of more studied PAHs, essentially for the alkyl-substituted PAHs.

The objectives of this study are to develop an efficient method for the determination of PAHs in air samples. For this different analytical techniques, LC-UV, GC-FID and GC-MS were assessed in their sensitivity and selectivity.

The separation of examined PAHs was checked on a polymeric C-18 column in LC and on two different capillary columns in GC. Limits of detection were determined for each compound on LC with an ultraviolet detector with variable wavelength, on GC-FID and on GC-ITD-MS

All optimised conditions of PAHs analysis by these chromatographic techniques were applied for their determination in atmospheric particulate taken at three different locations in Tunis.

MATERIALS AND METHODS

Chemicals reagents

Organic solvents; acetonitrile, methanol, and dichloromethane were of LC purity grade (Prolabo, Paris, France). Deionized water was distilled and further purified through a C-18 cartridge. Silica gel, 230-400 mesh (Fluka, Buchs, Switzerland), was activated at 450°C over night and stored in a desiccator. Acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, chrysene, 1-methylphenanthrene, 2-mehylanthracene, 2-methylnaphthalene, dibenzofuran, dibenz[a,c]anthracene, dibenz[a,h]anthracene, fluorene, 9-methylanthracene and 9-phenylanthracene were supplied by Janssen Chimica (Geel, Belgium) and benzo[ghi]perylene by Supelco (Bellefonte, USA). Phenanthrene, pyrene, perylene and fluoranthene were purchased from Merck (Darmstadt, Germany). These standards were dissolved in dichloromethane at 1 mg/mL. Stock mixtures of PAHs standards were made from the the individual solution in methanol. The solutions were protected from light and stored at a temperature of 4°C.

Chromatographic conditions

For LC, the analyses were achieved with a chromatographic system consisting of Waters (Milford, MA) Model 6000A solvent delivery systems, a Waters Model 660 solvent programmer, a Heweltt-Packard (Palo Alto, CA) Model 1050 UV-Vis detector (a programmable absorbance

detector), a rheodyne (cotati, CA) 7125 sample injector with 20 µL loop, a Hewelett-Packard Model 3395 integrator, a Supelcosil LC-PAH column (Supelco, Bellefonte, PA), 15 cm x 4.6 mm I.D., 5 µm particulate size and a Supelco LC-18 guard column.

The mobile phase (acetonitrile-Water) gradient: 60% acetonitrile + 40% water for 5 min, increasing linearly up to 100% acetonitrile in 15 min; isocratic 100% acetonitrile up to 30 min. The flow rate was 1 mL/min and the temperature was 25°C. During chromatography the mobile phase was degassed by passage of a continuous flow of helium through the solvents. UV detection was performed using programmable wavelength during the analysis: (time, λ); 0.01 min, 226 nm; 11.2 min, 254 nm; 15.8 min, 340 nm; 16.5 min, 329 nm; 18 min, 254 nm; 20.9 min, 285 nm; 21.99 min, 265 nm; 24.5 min, 254 nm; 28 min, 300 nm.

GC-FID analyses were performed using a Perkin Elmer gas chromatograph equipped with a flame ionisation detector and a Split-Splitless injector. A 25 m x 0.32 mm I.D. RTx-5 (film thickness 0.12 µm) fused-silica capillary column was used. The GC analyses were performed with an oven temperature program from 50 to 150°C at 20°C/min (held for 1 minute at the initial temperature), then from 150°C to 280°C at 8°C/min and held isothermal until all components were eluted. Injector and detector temperature were of 240 and 260°C respectively.

GC-MS analyses were achieved on a Varian star 3400 CX gas chromatograph coupled to Varian Saturn III, Ion Trap Mass spectrometer. Separation was performed on a DB-5 capillary column (30 m x 25 mm x 0.25 µm). Data were acquired in the EI mode (70 eV). The operating conditions of the mass spectrometer were: ion source temperature 200°C 12 µA for the emission current and the mass spectra was scanned from 40 to 450 u with 3µ scans/second.

All analyses were done using helium as the carrier gas and the injector was in the Splitless mode (2 µL), the Split valve closed for 1 minute.

Sampling

Airborne particulate were collected on a weighted glass fibre filter (0.7µm; Whatmann GF/B) with a pump Gilian, Hi Flow Sample Model HFS 113 APN/0800070.

After sampling, the filter was weighted again, covered with aluminium and stored at 4°C until analysis.

Extraction and clean-up procedures

The filter was extracted 12 h with 300 mL of acetonitrile (recycled approximately every 15 min) in a glass Soxhlet apparatus. The organic extract was concentrated to 20 mL in a rotary

evaporator, then under a gentle stream of nitrogen in a Kuderna-Danish (K-D) evaporator (at a temperature of 30-35°C on water bath).

To clean-up the extract before analysis, it was initially changed into 1mL of n-hexane and the organic extract was transferred on top of a glass column (25 x 0.9 cm I.D.) packed with 2g of activated silica. The sequence of eluents were as follows: 12 mL of n-hexane (aliphatic hydrocarbons). Then 12 mL of n-hexane/toluene (V:V, 1:2) (aromatic hydrocarbons). The second fraction was evaporated to dryness in K-D and redissolved in methanol. Chromatographic analysis was achieved with LC-UV, GC-FID and GC-MS.

RESULTS AND DISCUSSION

LC determination

The nineteen PAHs studied contain from two to five rings. Eleven of those PAHs are on the US-EPA Priority List. The literature data suggest that C-18 polymeric stationary phase yields to the PAHs best selectivity in LC. Thus, the 16 PAHs' Priority List are totally separated on a LC-PAH Supelcosil column with an acetonitrile-water gradient [24-25].

However, for the studied compounds, two coelutions are observed as it can be seen from the retention times of table I. The 2-methylnaphthalene and dibenzofuran peaks overlap as those of 2-methylanthracene, 1-methylphenanthrene and fluoranthene too.

Nevertheless, despite many changes in chromatographic conditions such as the mobile phase flow rate and the elution gradient rate, it was not possible to improve the resolution. Other investigators have reported difficulties in separating these two PAHs groups [27,28].

The UV absorption spectra of the studied PAHs obtained in the range 200 and 400 nm show that this compounds have no maximum absorbance at the same wavelength (λ_{max}). It is to be noted that PAH λ_{max} increases when its aromaticity increases. Most of the obtained λ_{max} lay in the ranges: from 208 to 230 nm; from 252 to 258 nm and from 280 to 300 nm. Thus, using a single detection wavelength, such as λ = 254 nm which is often called upon for PAH analysis does not permit the best sensitivities. However, the variation during the chromatographic elution improves both sensitivity and selectivity. For the former quality, the best is to select for each compound the detection wavelength (λ_{det}) which corresponds to its maximum absorbance through the detector programming in terms of retention times. But, for the sake of reaching accurate quantitative results, the chromatographic resolutions must equal 1.5 or better. The resolutions can be obtained when few PAHs are analysed, and in the absence of interfering compounds. When the analysis of samples

extracted from complex matrixes is carried out, it is only possible to change the detector parameters a few times during the elution of the chromatogram. Various PAH are therefore detected at the same wavelength. Table I, gives the λ_{det} chosen for this work.

Table I. Retention Times (RT) and limit of detection (LOD) on LC-UV

Compound	RT (min)	λ det (nm)	LOD (ng)
Acenanphtylene	8.69	226	0.1
Dibenzofurane	10.39	226	N.E
2-Methyl naphtalene	10.39	226	N.E
Acenaphthene	10.93	226	0.05
Fluorene	11.59	254	0.4
Phenanthrene	13.22	254	0.2
Anthracene	14.91	254	0.2
1-Methyl phenanthrene	16.46	340	N.E
2-Methyl anthracene	16.46	340	N.E
Fluoranthene	16.46	340	4
Pyrene	17.61	239	4
9-Phenyl anthracene	18.41	254	0.1
9-Methyl anthracene	19.16	254	0.1
Benz[a]anthracene	21.36	285	0.1
Chrysene	22.44	265	0.1
Perylene	25.19	254	0.2
Dibenz[a,c]anthracene	25.72	254	0.1
Dibenz[a,c]anthracene	31.72	300	0.2
Benzo[ghi]perylene	33.62	300	0.1

Under such conditions, the λ_{det} for each of the fourteen separated PAHs, the detection limits estimated, based on the signal-noise ratio, (S/N = 3) lay between 0.05 and 4 ng (Table I). For the coeluted PAHs, the determination become impossible when the UV absorption spectra are similar as in the dibenzofuran and 2-methylnaphthalene case. For the three other coeluted (Viz. 1-methylphenanthrene, 2-methylanthracene and fluoranthene) they display very different UV spectra. Moreover, the former compounds do not absorb at 340 nm and that is why this wavelength was selected in this study. This wavelength is suitable for the fluoranthene determination even when the two other hydrocarbons are present.

The accuracy and the linearity of the detector response were checked for each solute at the corresponding λ_{det}. The relative standard deviations of the peak heights for the five 20 µL consecutive injections originating from a standard solution lay between 1.5% for acenaphthene and 2.5% for benzo[ghi]perylene. A good linearity is observed for all the solutes. The regression coefficients obtained vary from 0.999 for acenaphthylene and 0.995 for 9-methylanthracene.

GC Determination

The separation of studied PAHs was tested on two different columns, RTx-5 and HP-1701. These two columns have different stationary phases polarity: the first column is non-polar and the second has medium polarity. Retention times observed in the two cases were reported in Table II. All analysed solutes were separated on the two columns at the same elution range with an acceptable resolution. An exception was observed for the dibenz[a,c]anthracene and dibenz[a,h]anthracene. The chromatographic peaks of this two isomers were overlap in the HP-1701 column and they have low resolution in the RTx-5 column. Hence, increasing the polarity of the column stationary phase does not improve the resolution of PAHs. These results were in accordance with the conclusions of C. Escriva and al. work [11]. These authors, have observed many coelutions for the sixteen priority PAHs in polar phase columns such as BP-20 and RSL-400.

The influence of the column length on the separation of PAHs peaks was also studied by using a SE-54 column with a length of 50 m. The stationary phase of the column is identical to the phase of RTx-5 column. Increasing the column length makes time longer but did not improve the resolution of the chromatographic peaks of studied PAHs. Figure 1, shows the chromatogram of all examined PAHs.

As a result of this study, the RTx-5 column was selected for routine analyses because it provided the best separation between the PAHs with shortest analysis time. This column was similar to DB-5 column recommended by US-EPA for the analysis of priority PAHs. However, the film thickness of DB-5 column used for GC-MS in this study was greater than that of RTx-5 column (film thickness; 0.12 µm). Hence, chromatographic peaks of the more retained PAHs (Dibenz[a,c]anthracene, dibenz[a,h]anthracene and benzo[ghi]perylene) were broader, so the sensitivity decreased.

In this study, two detectors were used in GC for PAH analyses: Flame Ionisation Detector (FID) and Mass Spectrometry using Electron Impact ionisation mode (MS-EI).

Detection limits using FID were determined in the range between 1.5 and 5 ng (table II). Inside a domain of injected quantity between 10 and 100 ng (5 points), a good linearity is observed for all the solutes. The regression coefficients obtained vary from 0.998 for fluorene and 0.968 for benzo[ghi]perylene.

Table II. Retention times (RT) and limit of detection (LOD) on GC-FID.

Compound	N°	RT (min)		LOD (ng)
		RTx-5	HP-1701	
2-Methylnaphthalene	1	4.75	14.90	1.5
Acenaphthylene	2	6.25	17.80	1.5
Acenaphthene	3	7.00	18.74	1.5
Dibenzofurane	4	7.75	19.40	1.5
Fluorene	5	8.00	20.85	1.5
Phenanthrene	6	10.50	24.20	1.5
Anthracene	7	10.75	25.18	2.5
1-Methylphenanthrene	8	12.50	27.00	2.5
2-Methylanthracene	9	12.75	27.11	2.5
9-Methylanthracene	10	13.50	28.41	2.5
Fluoranthene	11	15.00	30.28	2.5
Pyrene	12	15.75	31.22	2.5
9-Phenylanthracene	13	20.50	36.00	2.5
Benz[a]anthracene	14	21.00	37.02	5
Chrysene	15	21.50	37.75	5
Perylene	16	26.30	39.25	5
Dibenz[a,c]anthracene	17	31.52	41.75	5
Dibenz[a,h]anthracene	18	31.75	41.75	5
Benz[ghi]perylene	19	34.02	42.35	5

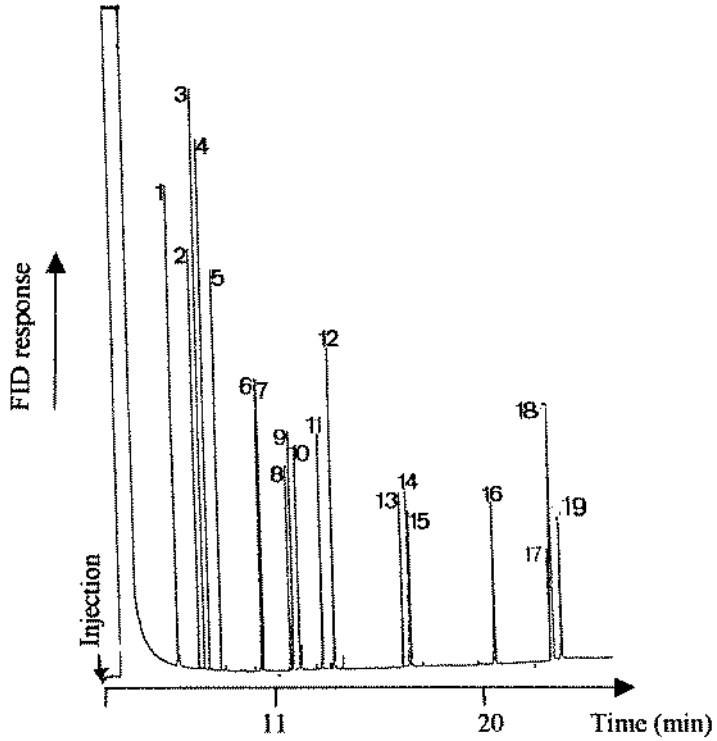

Fig 1. Chromatogram of the studied PAHs obtained in RTx-5 column. For chromatographic conditions see text.

On other hand, PAH determination was performed by GC-MS. Figure 2, gives total ion chromatogram (TIC) and the reconstructed ion chromatogram (RIC) for some of the examined PAH. Selected ion for each PAH corresponded to $M^{+\cdot}$ ion (table III). In fact, electron impact spectra of PAHs all exhibit the molecular ion $M^{+\cdot}$ as the base peak [29-31]. Fragment ions corresponding to $(M-H)^+$, $(M-H_2)^+$ and $(M-H_3)^+$ were hardly observed. In this study, selected ions were not specific of the researched compounds. Many PAH isomeric were characterised by the same selected ion. For the detection of 9-methylanthracene, for example, our choose was based on the ion corresponding to m/z = 192. This ion was also used to characterise 1-methylphenanthrene and 2-methylanthracene. Hence, this three PAHs were represented by peaks in the reconstructed ion chromatogram of m/z = 192. Distinguishing between this three PAHs isomeric was based on their retention times. Detection limits of examined PAHs determined on MS mode varied between 0.5 and 4 pg (table III). Regression coefficients lay between 0.984 for fluoranthene and 0.998 for phenanthrene and this for a domain of injected quantity between 0.2 and 5 ng.

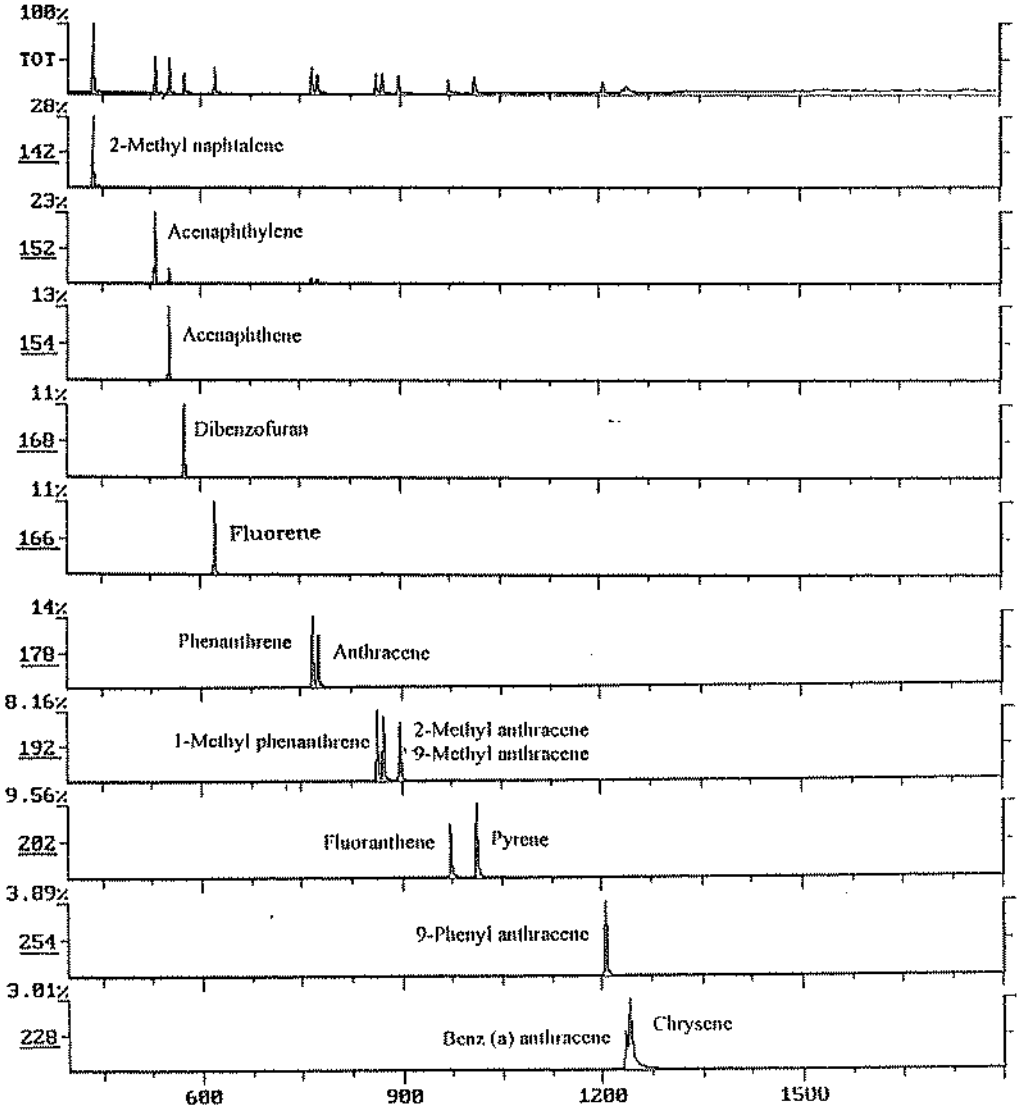

Fig 2. Total Ion Chromatogram (TIC) and Reconstructed Ion Chromatogram (RIC) for PAHs.

Table III. Retention times (RT) and limit of detection (LOD) on GC-MS.

N°	RT (min)	Selected Ion (m/z)	LOD (pg)
1	8.79	142	0.5
2	11.37	152	0.5
3	11.91	154	0.5
4	12.46	168	1
5	13.49	166	1
6	16.32	178	1
7	16.58	178	1
8	18.18	192	1
9	18.35	192	1
10	18.80	192	2
11	20.12	202	2
12	20.80	202	1
13	24.12	254	1
14	24.61	228	2
15	24.71	228	2
16	29.20	252	2
17	38.08	278	4
18	38.18	278	4
19	4018	276	4

All optimised analytical conditions of separation and detection of PAHs with the three studied techniques LC-UV, GC-FID and GC-MS have been used for the determination of PAHs in atmospheric samples.

APPLICATION : ANALYSIS OF AIRBORNE PARTICULATE SAMPLES

Sample handling

PAHs analysis in airborne particulate collected on filters must go through two steps: extraction then clean-up. The last step is useful in the case of heavily contaminated samples. The clean-up level depends mainly on the selectivity of the detection step. In this study, we have firstly assessed the necessity of the clean-up step for the studied atmospheric samples analysed by the three analytical techniques LC-UV, GC-FID and GC-MS.

Figure 3, gives the chromatograms of the analytical blank without cleaning and those of a raw extract, as well as of a purified extract sample. Two points must be stressed: (i) the blank chromatogram (figure 3A) shows no interfering peaks with the PAHs under study. (ii) The chromatogram of the purified extract and of the raw sample (figure 3 B and C) are qualitatively

similar. As a consequence, the clean-up step was not necessary in the PAH analysis on airborne particulate with LC-UV.

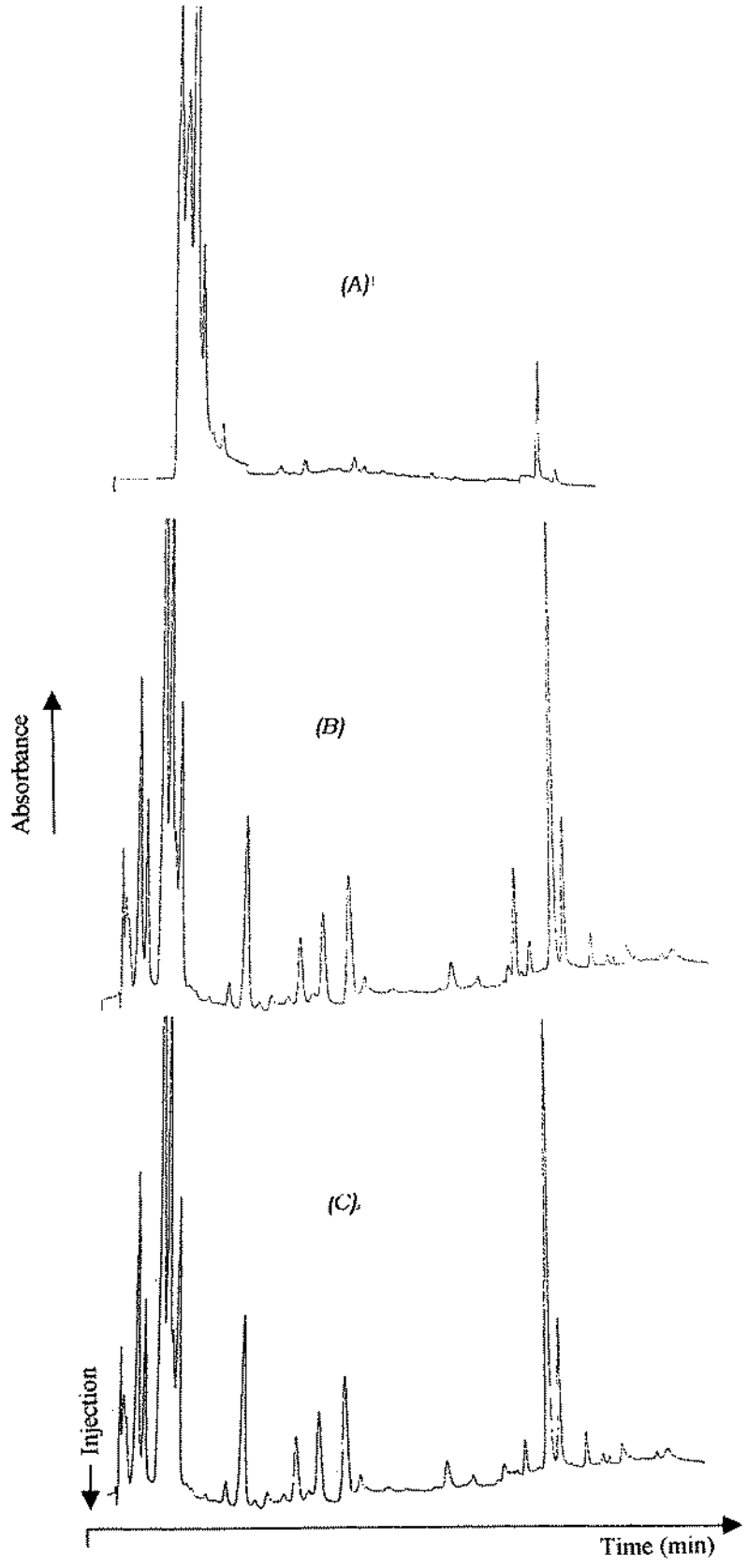

Fig 3.LC-UV chromatogram of A: Blank and B & C : with clean-up and without clean-up extracts respectively. For conditions see experimental section.

Analysis

Table IV, shows the concentrations of PAHs detected in atmospheric samples analysed by the three studied methods (LC-UV, GC-FID and GC-MS).

Table IV. Values of PAHs (ng/g) in an atmospheric sample analysed by the three studied methods (LC-UV, GC-FID and GC-MS)

Compound	GC-FID	GC-MS	LC-UV
Acenaphthylene	2.90	2.20	2.28
Acenaphthene	N.D	0.75	N.D
Dibenzofurane	13.38	11.01	N.E
Fluorene	N.D	2.51	2.65
Phenanthrene	20.66	19.86	15.55
Anthracene	10.55	9.31	9.52
Fluoranthene	6.42	5.96	5.42
Pyrene	5.99	6.04	7.35
Chrysene	N.D	1.61	N.D
9-Phenylanthracene	N.D	Tr	N.D

N.D : Non detected
N.E : Non estimated
Tr : Trace

We have to note that differences between levels obtained by this three analytical techniques were less than 5%. However, concentration of many PAH was not evaluated because of chromatographic interference such as dibenzofuran on LC-UV and also when the PAHs levels were less than the limit of detection of used method, essentially in the case of GC-FID because of losses due to purification step. GC-MS, should be the detection method of choice, for routine analysis of PAHs at low levels in complex matrixes. Hence, in this work we have used this method for the determination of PAH in atmospheric samples.

Results of quantitative analyses of nine atmospheric samples taken at three different locations in Tunis (table V) show that acenaphthene, fluorene and phenanthrene are the most abundant hydrocarbons in airborne particulate. It is worthy to note that these compounds are also the major compounds in exhaust Diesel engine [26]. In fact, PAH were usually found in the Diesel motor as survive the combustion processes [32-39]. This results are in accordance with the literature reports which say that traffic exhausts are the major source for the PAHs in the air [32]. Moreover, the levels of PAHs found in the samples taken at different locations of Tunis (table V) showed a relation ship between these concentrations and the traffic intensity at the three locations.

Analysis of the same raw extract by GC-MS and GC-FID revealed firstly that obtained chromatograms in the both cases were similar. The chromatographic profiles shows an unresolved complex mixture (UCM) corresponding to aliphatic hydrocarbon (TIC, figure 4). The physical and chemical behaviour of these compounds were similar to that of PAH, they interfere so, with researched compounds and can not allow their determination.

On GC-MS, reconstructed ion current allows to obtain chromatograms less complex and so permit an adequate determination of researched PAH on the raw extract. Identification of these compounds was based on their retention time and their mass spectra. However, a post separation PAH-alcanes was necessary on GC-FID. This cleaning step was achieved by silica gel adsorption chromatography. This supplementary treatment of the extract decrease recoveries, essentially, for more volatile PAHs.

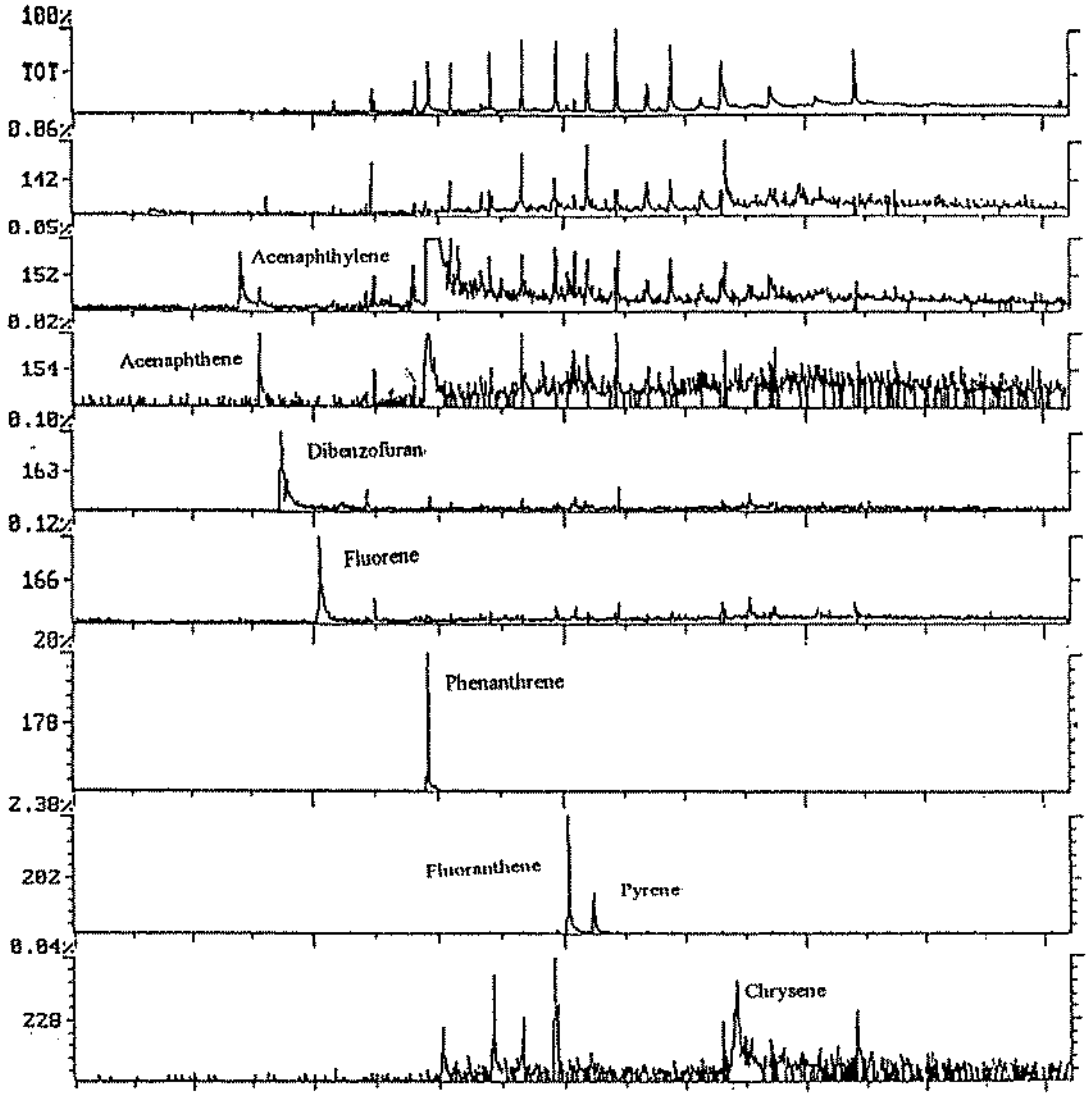

Fig 4. TIC and RIC of a raw extract of atmospheric sample.

Table V. Values of PAHs (ng/g) in air samples in Tunis obtained by GC-MS.

Compound	Site 1	Site 2	Site 3
Acenaphthylene	83.25	1.8	42.86
Acenaphthene	105.40	0.61	22.20
Dibenzofurane	419.61	13.75	41.34
Fluorene	4.53	1.99	15.77
Phenanthrene	459.28	21.66	55.58
Anthracene	50.23	6.11	10.33
Fluoranthene	29.41	4.54	1.47
Pyrene	10.49	4.53	1.61
Chrysene	10.25	1.26	*Tr*
9-Phenyl anthracene	22.43	*Tr*	*Tr*
PAH	1194,88	56,25	191,16

Tr : Trace
Site 1: Fuel distributors
Site 2: Middle traffic
Site 3: Heavy traffic

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