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Pentafluorobenzyl derivatives for the gas chromatographic determination of hydroxy-polycyclic aromatic hydrocarbons in urban aerosols

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Abstract

A method for the analysis of hydroxy-substituted polynuclear aromatic hydrocarbons (hydroxy-PAHs), using gas chromatography with electron-capture (ECD) and mass spectrometric (MS) detectors, is described. Pentafluorobenzyl bromide (PFBBr) was used as derivatizing agent for the hydroxy-PAHs. Optimization of the derivatization conditions was performed, and electron impact and negative ion chemical ionization mass spectra were studied. Detection limits ranged from 0.01 to 3.3 pg in ECD and negative ion chemical ionization mode (NICI)-SIM-MS values that allowed the determination of these compounds in environmental samples. Samples of air particulate matter were collected for the analysis of hydroxy-PAHs. The concentrations found for 5-hydroxyindol, 2-nitro-1-naphthol, 2-hydroxy-1,4-naphthoquinone and 2-hydroxy-9-fluorenone ranged between 5 and 189 pg/m^3.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are obtained in the incomplete combustion of fuel and they constitute an important environmental hazard. Polar functional groups can be introduced in polycyclic aromatic hydrocarbons by incomplete combustion in diesel engines or by chemical reactions with O_x, SO_x and NO_x in ambient air combustion [1–5]. Substituted PAHs have been identified in diesel exhausts and atmospheric aerosols [3,6–12]. For instance, nitro- and oxy- compounds have been found at ng/m^3 levels in aerosol samples [13–16], and the mutagenicity of certain extracts has been attributed to the presence of these compounds rather than to the PAHs themselves. In addition, more polar compounds have been identified in these samples such as hydroxy-PAHs [17], nitrated lactone derivatives [18], and aliphatic and aromatic carboxylic acids and their hydroxy derivatives [19].

Due to their low concentration levels, nitro- and oxy- compounds are currently determined by GC with electron-capture detection (ECD) or mass spectrometry in the negative ion chemical ionization mode (NICI-MS), but few methods have been proposed for the analysis of the hydroxy derivatives. Free phenolic compounds can be analyzed by GC, but the hydroxyl groups cause difficulties in their analysis. The transformation of the hydroxyl groups into less polar derivatives facilitated the use of GC for the analysis of these compounds. This increases the number of useful stationary phases, leads to an improvement in the peak shape and improves

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separation and detection [20–23]. Thus, an increase in accuracy can be obtained.

Two of the most sensitive techniques for the determination of organic compounds at trace level are based on the process of gas-phase electron capture: the electron-capture detector in gas chromatography (GC–ECD) and the mass spectrometer in the electron-capture negative ion chemical ionization in the single ion monitoring (NICI-SIM-MS) [24]. In both cases, low detection limits (low femtogram) have been achieved [24,25].

Both the chromatographic behaviour and the relative response of electron-capture detectors can be enhanced by derivatization with halogen-containing reagents [20,26–28]. Phenols can be converted to pentafluorobenzyl ethers by reaction with pentafluorobenzyl bromide (PFBBr). These derivatives exhibit high electron affinity and, therefore, good response in ECD and NICI-MS [24,26,28–30]. Moreover, pentafluorobenzyl ethers have been shown to give NICI mass spectra with abundant analyte specific ions [24,31].

The aim of this study is to establish a simple and virtually quantitative derivatization procedure for hydroxy-PAHs. The method was optimized and quality parameters were established using ECD, NICI-MS and EI-MS operating in the positive mode as detectors. The procedure was applied to the analysis of hydroxy-PAHs in airborne particulate matter.

2. Experimental

2.1. Materials

5-Indanol (5-IOH), 5-hydroxyindol (5-HI), 2-nitro-1-naphthol (2N-1N), 2-hydroxy-1,4-naphthoquinone (2-H-1,4-NQ), 2-hydroxy-9-fluorenone (2-H-9-FLO) were purchased from Aldrich (Steinheim, Germany) and 1,8-dihydroxy-9,10-anthraquinone (1,8-DH-9,10-AQ) from Scharlau (Barcelona, Spain). Hexachlorobenzene (Aldrich) was used as internal standard. Pentafluorobenzyl bromide was purchased from Sigma (St. Louis, MO, USA), and 18-crown-6 (18c6) from Merck (Darmstadt, Germany). Potassium carbonate (Panreac, Barcelona, Spain) was washed with dichloromethane and acetone, and then stored at 110°C. Organic solvents (dichloromethane, acetone, hexane, methanol and toluene) were of HPLC-grade (Merck). Bond Elut silica cartridges were provided by Varian (Harbor City, OR, USA) and a Supelco Visiprep (Supelco, Gland, Switzerland) was used for the clean-up.

2.2. Capillary gas chromatography

High-resolution gas chromatography (HRGC) analyses were carried out with two different chromatographic systems. A Carlo-Erba (Milan, Italy) 5300 Mega Series equipped with a ^{63}Ni electron-capture detector, autosampler and split–splitless injector was used for the GC–ECD determinations. The injection port and the detector temperatures were 290°C and 330°C, respectively. Chrom-Card data system was used for data handling. For GC–MS analyses a Hewlett-Packard Model 5988A instrument coupled to an HP-5890 gas chromatograph was used. A Hewlett-Packard 59970MS Chemstation data system was used to record the data. The injection port temperature was 250°C, and the transfer line interface was kept at 280°C and the ion source at 250°C. Data were acquired using electron-impact (EI) mode (70 eV) and negative ion chemical ionization (NICI) with methane (1 Torr) as reagent gas.

The separation was carried out on a DB-17 fused-silica capillary column (J&W Scientific, Rancho Córdova, CA, USA), 30 m × 0.25 mm I.D., 0.25-μm film thickness. Helium at 30 cm/s was used as carrier gas.

For the chromatographic analysis of the derivatives two temperature programmes were used with the two detection systems: (a) GC–MS: initial 100°C, hold 1 min, rate 6°C/min to 280°C, hold 20 min; (b) GC–ECD: initial 100°C, hold 2 min, rate 25°C/min to 125°C, hold 1 min, rate 6°C/min to 240°C, hold 1 min, rate 30°C/min to 300°C, hold 20 min.

2.3. Derivatization procedure

Pentafluorobenzyl (PFB) ethers were prepared by the Claisen method [21,26,28,32,33]. The hydroxy-PAH mixture in acetone (1 ml) was introduced into a 2-ml screw top vial, and 10 μl of 10% PFBBr in acetone, 50 μl of an 18c6 solution (4000 ppm in acetone) and 10 mg of powdered K_2CO_3 were added. The vial was stoppered and shaken in a sonication bath for 60 min, at a temperature below 25°C. After the reaction, the solution was filtered, dried on anhydrous Na_2SO_4, evaporated under nitrogen to dryness and dissolved in 1 ml of hexane. To eliminate the by-products that strongly interfere in GC–ECD analyses a clean-up on a silica cartridge was required. Hexane (10 ml) was used to condition the cartridge. The sample was quantitatively transferred to the column, washed with 3 ml of hexane and eluted with hexane (5 ml), hexane–toluene (5 ml) and toluene–methanol (5 ml). The PFB ethers were eluted in the first and third fractions, which were pooled, evaporated to dryness and redissolved with 1 ml hexane containing the internal standard.

2.4. Sample collection

Airborne particulate matter samples were collected in one of the main avenues of Barcelona, 10 m above ground level. A large volume of heavy traffic passes through this area. Four atmospheric aerosols were collected in one year, one sample per season, on a 20.3 × 25.4 cm glass fibre filter paper (Whatman EPM-2000) thermally treated (300°C for 2 h), using a Sierra Misco Model 650 high volume sampler. After sampling filters were stored at −20°C.

2.5. Sample extraction and clean-up procedure

The sample was cut into four pieces and each piece was extracted ultrasonically with 75 ml dichloromethane for 30 min followed by 75 ml of methanol for 30 min at a temperature below 30°C. Both extracts were combined, dried over anhydrous sodium sulphate, passed through a Whatman GF/A glass microfibre filter, evaporated at 25°C in a rotary evaporator under reduced pressure to near dryness and redissolved in 1 ml of hexane for clean-up.

The extract was transferred onto the silica cartridge previously rinsed with 10 ml of hexane, and sequentially eluted with 3 ml of hexane and 2 ml of hexane–dichloromethane (80:20) to give fractions enriched in alkanes and PAHs, respectively. Then an alumina cartridge rinsed with 5 ml of hexane and 5 ml of hexane–dichloromethane (80:20) was coupled to the bottom of the silica cartridge. Both cartridges were eluted with 6 ml dichloromethane to obtain the oxy- and nitro- PAHs. The hydroxy-PAH fraction was obtained by eluting the alumina and silica columns with 5 ml of methanol. The methanol fraction was evaporated under reduced pressure to dryness and dissolved in 1 ml of acetone for derivatization.

3. Results and discussion

3.1. Optimization of the derivatization conditions

The derivatization reaction needs a basic medium, which was obtained using K_2CO_3. A large number of degradation products from the derivatizing agent were obtained when aqueous solutions of this salt were used. To avoid this problem, the derivatization procedure was performed using solid K_2CO_3 and 18c6 as catalyst, as recommended for derivatization of phenols with PFBBr [29,33]. To optimize the procedure, the amount of derivatizing agent, the temperature and the time were studied. High concentrations of derivatizing agent increased both the number and the abundance of interfering peaks. So, an excess of PFBBr equivalent to 30 times the total amount of the hydroxy compounds was used. Although degradation of the derivatizing agent was reduced under these conditions, and no interference was observed in the GC–MS analysis, a large number of interfering peaks appeared in the GC–ECD chromatogram, as can be seen in Fig. 1. These by-products, which strongly interfere in the gas chromatographic

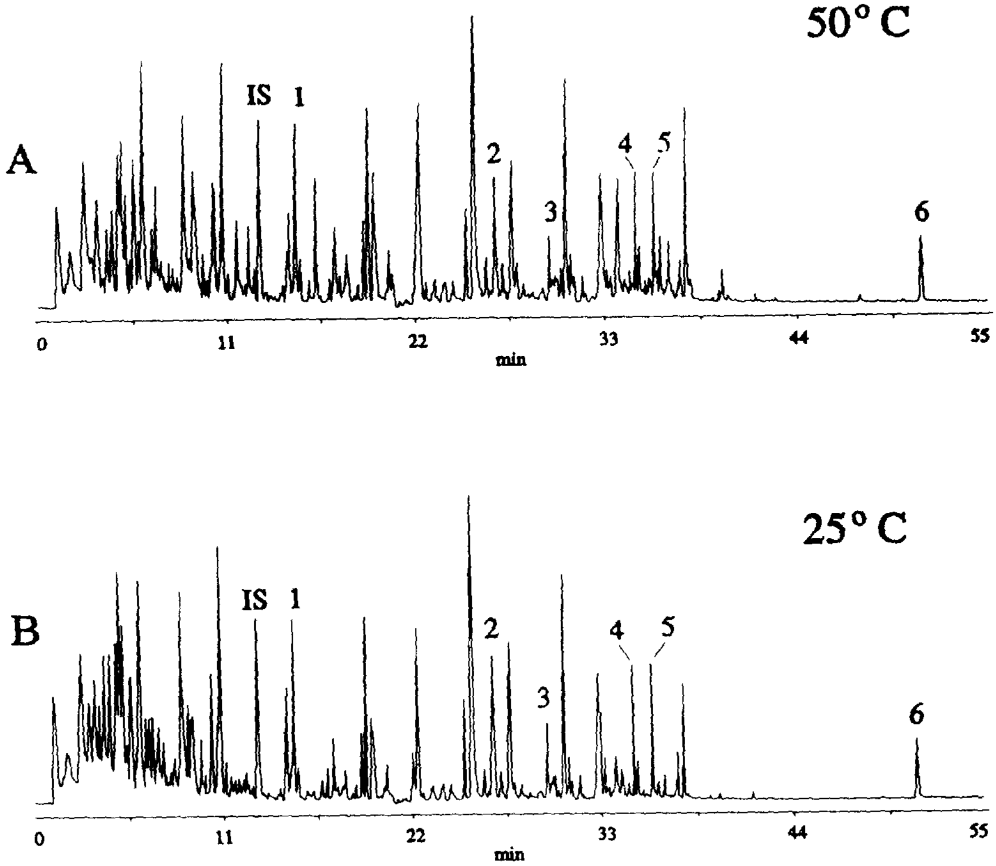

Fig. 1. GC–ECD chromatograms of a standard solution of hydroxy-PAHs (120 μg/l) after derivatization at different temperatures: (A) 50°C; (B) 25°C. Peaks: 1 = 5-IOH; 2 = 5-HI; 3 = 2N-1N; 4 = 2H-1,4-NQ; 5 = 2H-9-FLO; 6 = 1,8-DH-9,10-AQ. Chromatographic conditions as indicated in the text.

analysis with ECD, may originate from the decomposition of PFBBr, and probably have the structure $(C_6F_5CH_2O)_n$, as has been indicated by Davis [33].

Temperature also affects the decomposition of PFBBr. Derivatization at 80°C gave a larger number of interfering peaks in the chromatogram than derivatization at lower temperatures; the GC–ECD chromatograms of the PFB ethers obtained at 50°C and 25°C are given in Fig. 1.

Different derivatization processes were carried out with different reaction times, ranging from 15 to 120 min, to optimize reaction time, showing that reaction times of 60 min at 25°C are needed to obtain maximum responses. At higher temperatures a large decrease in the reaction time was observed: 15 and 35 min for 80°C and 50°C, respectively; however under such conditions a greater number of interfering peaks was obtained. The optimum conditions for the derivatization process were 25°C, 60 min and 10 μl of 2.5% derivatizing agent in acetone. Although these conditions gave a relatively clean chromatogram, an additional clean-up procedure was needed to eliminate most of the interferences and obtain a chromatogram with higher resolution, which would be suitable for the identification and determination of the hydroxy-PAHs. To clean the derivate solution a solid-phase extraction procedure was used. Silica was the adsorbent, as has been recommended for the derivatization of phenols [21,26,28]. The solvent composition and the volume of each fraction were optimized. After a cleaning step with 3 ml hexane, in the second fraction eluted with 5 ml hexane the pentafluorobenzyl ether of 5-IOH was recovered. The third fraction eluted with 5 ml hexane–toluene (90:10) was discarded, and the rest of the compounds was eluted in the fourth fraction with 5 ml toluene–methanol (95:5). A GC–ECD chromatogram of a standard sample (120 μg/l) obtained after derivatization and clean-up is given in Fig. 2.

3.2. Gas chromatography–mass spectrometry

The PFB derivatives were studied by gas chromatography–mass spectrometry with EI and NICI. Mass spectra were recorded in both ionization techniques. The relative abundances of the main fragment ions are given in Table 1. The EI spectra of the ether derivatives showed two different patterns. Compounds such 5-indanol, 5-hydroxyindol and 2-hydroxy-9-fluorenone without electronegative groups in the aromatic rings or low electronegativity gave the phenoxyde ion $[ArO]^+$ as base peak and some fragment ions, such as the loss of CO group, characteristic of phenolic compounds. Compounds with electronegative groups such 2-nitro-1-naphthol, 2-hydroxy-1,4-naphthoquinone and 1,8-dihydroxy-9,10-anthraquinone gave the ion *m/z* 181 corresponding to the pentafluorobenzyl ion $[C_6F_5CH_2]^+$ as base peak, so no characteristic ions of the original hydroxy-PAH were observed. The derivative molecular ions generally showed low relative abundance, except for the 5-hydroxyindol, 2-hydroxy-9-fluorenone and 2-hydroxy-1,4-naphthoquinone, whose relative abundances were higher than for the other compounds.

Under NICI conditions the pentafluorobenzyl derivatives underwent a dissociative electron-capture process to produce the phenoxide anion $[ArO]^-$ as a sole peak in the mass spectrum. Low relative abundance of the ion at *m/z* 181 and other fragments were observed for all the compounds (Table 1). The 2-hydroxy-1,4-naphthoquinone gave ions at *m/z* 174 and 175 due to the quinone group. For the hydroxy compound 1,8-dihydroxy-9,10-anthraquinone the loss of a PFB group gave the base peak, although the loss of two PFB groups and the molecular ion were also observed.

3.3. Quality parameters

Linearity and reproducibility of the GC–ECD system were determined (Table 2). Linearity between 7 and 185 pg, and correlation coefficients better than 0.999 for all the PFB ethers were obtained. To determine reproducibility of

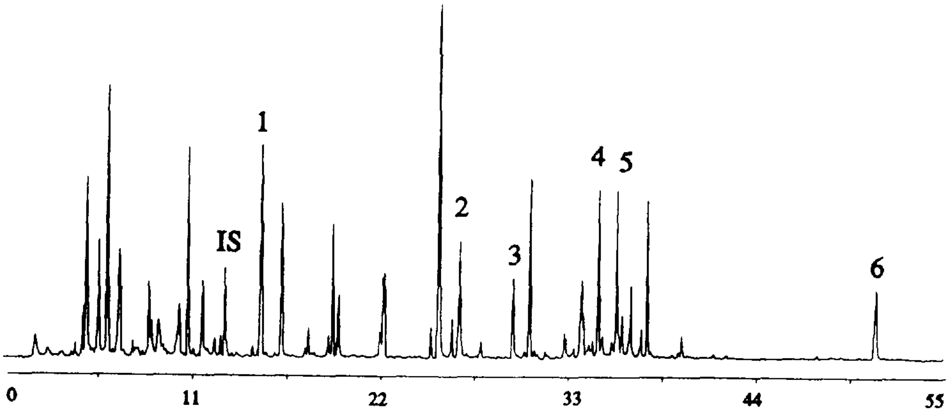

Fig. 2. GC–ECD chromatogram of a standard solution of hydroxy-PAHs (120 μg/l) after derivatization (25°C) and clean-up. Peaks: 1 = 5-IOH; 2 = 5-HI; 3 = 2N-1N; 4 = 2H-1,4-NQ; 5 = 2H-9-FLO; 6 = 1,8-DH-9,10-AQ. Chromatographic conditions as indicated in the text.

Table 1
Electron-impact and negative ion chemical ionization mass spectra data for the hydroxy-PAHs PFB derivatives

Compound	MW		*m/z* (relative abundance, %)								
	A	D	Electron-impact					Negative ion chemical ionization			
			$[M]^{+}$	$[ArO]^{+\cdot}$	$[ArO\text{-}CO]^{+}$	$[R]^{+}$	$[ArO\text{-}2CO]^{+}$	[M]	[ArO]	[R]	[ArO-NO]
Monohydroxy											
5-IOH	134	314	314(33)	133(100)	105(50)	181(69)	–		133(100)		
5-HI	133	313	313(7)	132(100)	104(45)	181(18)	–	-	132(100)	-	
2N-1N	189	369	369(3)	–	–	181(100)	–	–	188(100)	181(8)	158(23)
2-H-1,4-NQ	174	354	354(20)	173(9)	145(7)	181(100)	117(2)	–	173(100)	181(4)	
2-H-9-FLO	196	376	376(23)	195(100)	167(21)	181(35)	139(45)	–	195(100)	181(5)	–
	A	D	$[M]^{+}$	$[ArOO]^{+\cdot}$		$[R]^{+}$		$[M]^{-}$	$[ArOO]^{-}$	[R]	$[ArOOR]^{-}$
Dihydroxy											
1,8-DH-9,10-AQ	240	600	–	239(49)		181(100)		600(17)	239(51)	181(26)	419(100)

A = hydroxy-PAH; D = PFB ether; M = PFB ether derivative; R = derivatizing agent; ArO = phenoxide ion [M – R].

Table 2
Linearity and reproducibility of the PFB ether of hydroxy-PAHs

Compound	Linearity (pg)	Reproducibility[a] (R.S.D., %)	Reproducibility of the method[b] (R.S.D., %)
5-IOH	7–92	0.94	2.04
5-HI	25–145	2.21	5.26
2-N-1-N	40–185	1.61	4.04
2-H-1,4-NQ	25–135	4.22	6.43
2-H-9-FLO	15–135	2.26	4.57
1,8-DH-9,10-AQ	15–180	3.17	5.04

[a] Three daily injections on four different days.
[b] Four derivatizing processes.

the chromatographic analysis three replicate injections of a derivatized hydroxy-PAH standard solution (120 pg each) were carried out on four different days. Relative standard deviations (R.S.D.) in the range of 0.94–4.22%, based on the peak area, were obtained. To determine the reproducibility of the entire method four independent derivatization processes of a standard solution of hydroxy-PAHs (120 μg/l of each compound) were carried out. The relative standard deviations ranged from 2.04 to 6.43%.

Detection limits of pentafluorobenzyl derivatives using ECD, EI-MS and methane NICI-MS based on a signal-to-noise ratio of 3:1 are shown in Table 3. Scan mode and selected-ion monitoring (SIM) using the base peak ions given in Table 1 were used to record the respective mass spectrometric responses. Detectors based on electron capturing (ECD and NICI-MS) gave low detection limits, ranging between 0.01 and 3.3 pg for ECD and 0.02 and 1 pg for NICI-SIM-MS. For NICI-MS, detection limits are higher for those compounds which showed higher fragmentation, such 1,8-dihydroxy-9,10-anthraquinone, 2-nitro-1-naphthol and 2-hydroxy-1,4-naphthoquinone. Values obtained with either technique are 10^2 times lower that those obtained with EI-SIM-MS for PFB ether derivatives.

3.4. Application

The analytical method studied in this paper was developed mainly to determine hydroxy-PAHs in airborne particulate matter. Four urban

Table 3
Detection limits of the PFB ethers of hydroxy-PAHs

Compound	Detection limits (pg)				
	ECD	MS			
		EI		NICI	
		SCAN	SIM	SCAN	SIM
5-IOH	0.01	20	5	0.5	0.02
5-HI	0.05	50	10	1	0.03
2-N-1-N	0.7	50	15	15	0.3
2-H-1,4-NQ	3.3	80	20	15	0.4
2-H-9-FLO	2	25	5	2	0.08
1,8-DH-9,10-AQ	3.3	400	100	25	1

aerosol samples, one in each season, were analyzed. A GC–NICI-MS chromatogram of an atmospheric aerosol is shown in Fig. 3. Only some of the hydroxy-PAHs studied were detected in the extracts. These compounds were identified from the NICI mass spectra and determined by GC–ECD, using hexachlorobenzene as internal standard. 2-Hydroxy-9-fluorenone was identified in all samples, at concentrations of 20, 5, 31 and 75 pg/m^3 in spring, summer, autumn and winter, respectively. Concentration in summer was the lowest probably due to the high temperatures which caused evaporation of the compounds. 2-Hydroxy-1,4-naphthoquinone was identified in winter and spring at concentrations of 13 and 14 pg/m^3, respectively. 2-

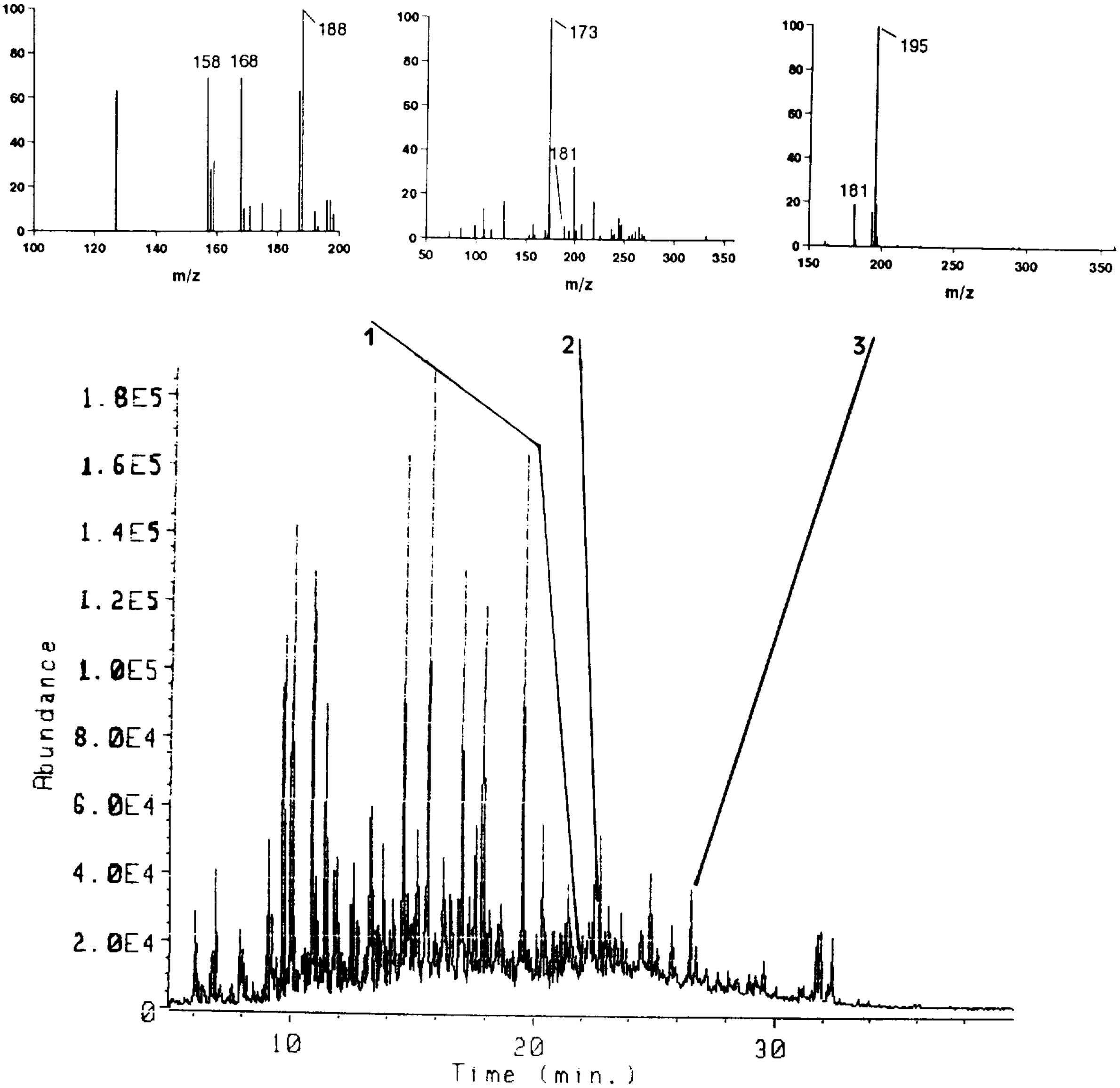

Fig. 3. Chromatogram (GC–NICI–MS) and mass spectra of the identified compounds of an atmospheric winter aerosol registred from m/z 100 to 250. Identified compounds: 1 = 2-N-1-N; 2 = 2-H-1,4-NQ; 3 = 2-H-9-FLO. Conditions as indicated in the text.

Nitro-1-naphthol was also identified in autumn and winter at levels of 24 and 189 pg/m^3, respectively. 5-Hydroxyindole was only identified in the autumn sample at very low levels (5 pg/m^3). Although very few studies deal with these compounds in atmospheric aerosols, our results agree with published values. For instance, Nishioka et al. [17] reported concentrations for hydroxy-nitro-PAHs in urban air particulate extracts between 10 and 600 pg/m^3. Bayona et al. [34] give similar values for nitronaphthol isomers (10–30 pg/m^3), and Tomingas and Mönch [35] reported 200 pg/m^3 for 9-hydroxyfluorene.

4. Conclusions

A procedure to obtain the PFB ethers of hydroxy-PAHs and the clean-up for the GC–ECD has been established. EI and NICI gas chromatography–mass spectrometry of the derivatives was used for the identification of these compounds in real samples. Electron-capture techniques (ECD and NICI) gave the best detection limits. The procedure proposed was used for the determination of some hydroxy-PAHs in urban aerosol samples.

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