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Analysis of high-molecular-mass polycyclic aromatic hydrocarbons in environmental samples using liquid chromatography–atmospheric pressure chemical ionization mass spectrometry

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) with molecular masses higher than 300 u were analysed using LC–atmospheric pressure chemical ionization (APCI) MS in extracts of environmental samples from Hamilton, Canada including zebra mussels from Hamilton Harbour, air particulate and coal tar. The LC–APCI-MS profiles of three molecular mass classes of PAHs (326 u, 350 u and 374 u) were compared to identify potential sources of PAH contamination in Hamilton Harbour. The Hamilton air particulate profile was also compared with an urban air reference standard (NIST SRM 1649) from Washington, DC, USA. Profiles of all extracts were similar and suggested an environmental predominance of PAHs within the three isomeric molecular mass classes studied. However, PAHs of molecular mass 326 u and 350 u were detected in extracts of coal tar and zebra mussels from Hamilton Harbour but were not detected in Hamilton air. These results indicated that some high-molecular-mass PAHs may be characteristic of contamination by coal tar. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

High-molecular-mass (higher than 300 u) polycyclic aromatic hydrocarbons (PAHs) are prevalent in a variety of matrices including carbon blacks, petroleum still bottoms, tars and ashphalts, and urban air particulates. A number of these compounds have been demonstrated to be potent mammalian carcinogens [1,2] and previous studies have shown that PAHs designated as priority pollutant compounds [3] may only be responsible for a fraction of the carcinogenic activity of some environmental mixtures [4]. Grimmer et al. [5] estimated that PAHs containing four and more rings were responsible for over 75% of the carcinogenic potential of diesel particulate, gasoline-engine particulate and coal combustion particulate. We have previously used a bioassay-directed fractionation methodology to iden-

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tify genotoxic PAHs in extracts of coal tar-contaminated sediments [6–8] and urban air particulate material [9]. In these studies, the PAH-rich extracts were separated by high-performance liquid chromatography (HPLC) into subfractions which were subjected to biological tests using the Ames *Salmonella*/microsome assay. Gas chromatography–mass spectrometry (GC–MS) analysis of subfractions exhibiting positive bioassay responses resulted in the identification of known mutagens and carcinogens including benzo[*a*]pyrene. In addition, subfractions containing PAHs of molecular masses 302 u, 326 u and 328 u, and 350 u and 352 u exhibited positive mutagenic responses which accounted for approximately 25% of the total genotoxic response of the extracts. The results of these studies showed that significant amounts of biological activity exhibited by extracts of PAH-contaminated samples were associated with high-molecular-mass PAHs that are not routinely detected using conventional analytical methods such as GC–MS.

Despite the demonstrated biological importance of some higher-molecular-mass PAHs, the determination of these compounds is seldom undertaken. The reasons for this include:

1. High-molecular-mass PAHs are generally present in environmental mixtures at much lower levels than priority pollutant PAHs.
2. High-molecular-mass PAHs have large numbers of possible isomers which increase with increasing molecular mass.
3. There is a paucity of authentic standards of high-molecular-mass PAHs for obtaining UV–Vis absorption spectra, fluorescence spectra, retention index data and for biological studies.
4. The isomers of high-molecular-mass PAH classes are difficult to separate using conventional GC or HPLC methods due to the number of isomers and structural similarities.
5. The biological effects of high-molecular-mass PAHs have commonly been thought to be of lesser importance than those of designated priority pollutant compounds.

The biological responses of some high-molecular-mass PAHs demonstrate the need for the development of methodologies that are capable of resolving and identifying these compounds. Capillary GC offers high chromatographic efficiencies but the analysis of PAHs with molecular masses greater than 300 u has proven difficult due to the low volatilities of these compounds. The most widely used technique for analysis of high-molecular-mass PAHs is HPLC coupled with fluorescence and/or UV absorption detection. Wise et al. [10] reported a normal-phase HPLC procedure for the isolation of PAHs from complex mixtures based on numbers of aromatic carbons, and subsequently used polymeric reversed-phase HPLC columns with high selectivities for PAHs coupled with fluorescence detection for the separation and identification of select PAHs with molecular masses of 300 u and 302 u. We previously applied a modification of Wise's normal-phase method for isolation of PAHs from coal tar-contaminated sediment to enable determination of mutagenic potencies of high-molecular-mass compounds [6]. These studies have shown that HPLC methods may currently afford an efficient method for separation of these compounds.

Authentic standards are not available for many high-molecular-mass PAHs. In addition, the chromatographic peaks resulting from the reversed-phase HPLC separation of high-molecular-mass PAH fractions are likely to contain a number of unresolved components. This illustrates the need for a sensitive method of detection offering molecular mass information, such as mass spectrometry. A number of LC–MS methods have been applied to the analysis of high-molecular-mass PAHs including moving belt LC–MS [11,12], LC–MS using a particle beam (PB) interface [13] and heated pneumatic nebulization atmospheric pressure chemical ionization (APCI) LC–MS [13]. Anacleto et al. [14] also compared the performance of the three aforementioned techniques and found that LC–APCI-MS afforded the best combination of detection limits and linear dynamic range for PAHs in a coal tar standard reference material. We have previously employed LC–APCI-MS for the profiling of high-molecular-mass PAHs in extracts of bottom sediments, suspended sediments and zebra mussels from Hamilton Harbour [15]. We have also investigated the optimisation of LC–APCI-MS operating parameters and mobile phase conditions for the analysis of high-molecular-mass PAHs [16].

Our previous work has shown that high-molecular-mass PAHs are present in the water column in

Hamilton Harbour and are being transported via suspended particulate material [15]. We have also shown that these compounds are bioavailable to aquatic organisms such as zebra mussels (*Dreissena polymorpha*) [15]. Two potential sources of high-molecular-mass PAH contamination in the Hamilton Harbour water column are suspended particulate originating from the resuspension of bottom sediments contaminated by coal tar and airborne particulate deposition. The objective of the current study was to use LC–APCI-MS for the characterisation of high-molecular-mass PAHs in extracts of Hamilton coal tar, Hamilton Harbour zebra mussels, and Hamilton air particulate material and to attempt to identify the primary source(s) of contamination. We also attempted to identify individual high-molecular-mass PAH isomers as potential source-specific indicators of contamination.

2. Experimental

2.1. Field methods and instrumentation

The Hamilton air particulate sample was collected on PTFE-coated glass-fibre filters (Pallflex Tx40M120WW, twenty 24-h samples equivalent to 1630 m^3 of air each) using an Anderson PM-10 air sampler (General Metal Works, Village of Cleves, OH, USA). A diesel particulate reference standard (SRM 1650) and an urban air particulate reference standard (SRM 1649, Washington, DC, USA) were obtained from the National Institute of Standards and Technology (Gaithersburg, MD, USA). Ultrasonic extractions were performed using a 300 W Sonic Dismembrator Model 300 with a 3/4 in. diameter titanium horn (Fisher Scientific, Fairlawn, NJ, USA) (1 in.=2.54 cm). Reversed- and normal-phase HPLC was performed on a Model 1090 liquid chromatograph with a built-in diode array detector and equipped with a Chemstation data system (Hewlett-Packard, Mississauga, Canada). A Model 110A HPLC pump equipped with a Model 153 UV detector (Beckman Instruments, Fullerton, CA, USA) was used in the Sephadex LH-20 gel column clean-up described below. The LC–MS experiments were performed using the Model 1090 liquid chromatograph interfaced with a Fisons Platform benchtop

quadrupole instrument equipped with a MassLynx data system.

2.2. Extraction and clean-up

Freeze–dried zebra mussel tissue was ground to a fine powder in a vegetation grinder; this powder was homogeneous enabling rapid and accurate sample mass measurements. Organic solvent-soluble material was prepared using an ultrasonic extraction method [17]. Samples were suspended in 50 ml of dichloromethane in a glass beaker and eight consecutive ultrasonic pulses (15 s duration each) were applied at full power. The suspension was filtered and the procedure was repeated with 50 ml of fresh dichloromethane. Air filters were extracted individually using a Soxhlet apparatus with dichloromethane for 24 h followed by extraction with methanol for 24 h.

Air particulate and zebra mussel organic solvent extracts were adsorbed onto neutral alumina (3 g, Brockman activity 1, 80–200 mesh) by solvent evaporation under reduced pressure; the alumina containing the adsorbed organic extract was then applied to the top of fresh alumina (6 g) contained in a glass column. A sample of coal tar was applied directly to the top of the alumina in the column. Organic components were eluted using solvents of increasing polarity. Hexane (60 ml), afforded an aliphatic fraction. Non-polar polycyclic aromatic compounds (PACs), which include PAHs, sulphur heterocylces, aza and keto compounds, were eluted by the sequential addition of benzene (50 ml) followed by dichloromethane–ethanol (70 ml, 99:1, v/v), which were combined to afford a single non-polar PAC fraction. This PAC fraction was then subjected to a gel column [30×4 cm glass packed with Sephadex LH20 gel (Pharmacia, Uppsala, Sweden)] clean-up step using a hexane–methanol–dichloromethane (6:4:3, v/v) mobile phase at a flow-rate of 3 ml/min to remove any remaining aliphatic compounds.

2.3. Liquid chromatography–mass spectrometry

A 5 μm, 25 cm×4.6 mm I.D. Vydac 201TP54 reversed-phase analytical column (Separations Group, Hesperia, CA, USA) was used with the

following linear gradient elution program at a flow-rate of 1.0 ml/min: initial, 100% acetonitrile; 10 min, 100% acetonitrile; 35 min, acetonitrile–dichloromethane (75:25); 45 min, acetonitrile–dichloromethane (45:55); 50 min, 100% dichloromethane; 55 min, 100% dichloromethane. The column temperature was maintained at 35°C.

The mass spectrometer was operated in positive ion APCI mode. Source temperature was 120°C and the APCI probe temperature was maintained at 500°C. The full scan mass range was 170 u to 520 u with a scan rate of 2.96 s/scan. The APCI drying gas was nitrogen at 300 l/h and the sheath gas was nitrogen at 80 l/h. The corona discharge voltage and cone voltage were maintained at 3 kV and −25 V, respectively. Mass spectrometer instrument parameters including probe temperature, source temperature, corona discharge voltage and cone voltage were optimised during constant infusion into the source of a 1 μg/ml standard solution of dibenzo[a,l]pyrene in acetonitrile at 1 ml/min. Following the optimization procedure, the estimated LC–MS detection limit for dibenzo[a,l]pyrene in 100% acetonitrile was 5 ng injected in full scan mode and 200 pg in selected ion monitoring (SIM) mode (signal-to-noise ratio of 5:1). The linear dynamic range exhibited by dibenzo[a,l]pyrene was at least two-orders of magnitude (10 ng to 1000 ng injected).

3. Results and discussion

The gradient elution program employing acetonitrile–dichloromethane was designed to achieve optimum separation and APCI mass spectrometric detection of high-molecular-mass PAHs [16]. Analyses of PAHs with molecular masses less than 300 u under these gradient conditions were characterised by poor APCI signal intensity and poor HPLC resolution of compounds (data not shown). A gradient elution program starting in acetonitrile–water was necessary for satisfactory separation of lower-molecular-mass PAHs; water-modified mobile phases have been used to aid in proton transfer to high-molecular-mass PAHs [18,19]. However, we observed five-fold to 10-fold lesser instrument response for all PAHs in acetonitrile–water mobile phases, compared to 100% acetonitrile. Based on the poor

APCI response to PAHs in mobile phases containing water, we determined GC–MS to be a superior methodology for routine analysis of priority pollutant PAHs with molecular masses less than 300 u.

The competing ionization mechanisms in APCI are reported to be proton transfer to form $[M+H]^+$ from water clusters, and charge transfer to form $M^{\cdot+}$ from $N_2^{\cdot+}$ and $O_2^{\cdot+}$ species [14,20]. Using our instrument and the described experimental conditions, the greatest ion intensities were observed through proton transfer. The corona discharge and cone voltages were held constant throughout the HPLC gradient elution program as variation of these instrument parameters to induce fragmentation was thought to offer no practical advantage in the analysis of PAHs. The proton transfer capability of the acetonitrile–dichloromethane mobile phases decreased with increasing dichloromethane content which also resulted in decreased APCI response of PAH, compared to 100% acetonitrile. Mass spectra of high-molecular-mass PAHs in acetonitrile–dichloromethane mobile phases were dominated by the $[M+H]^+$ ion, indicating that proton transfer was still the primary mechanism of ionization. Fig. 1 shows the relative intensity of the $[M+H]^+$ ion for dibenzo[a,l]pyrene using a range of LC–APCI-MS mobile phase compositions. A mobile phase of 100% dichloromethane was required to elute some high-molecular-mass PAHs from the HPLC column; mass spectra of PAH that eluted in 100% dichloromethane exhibited a charge transfer product ion $[M]^{\cdot+}$ that was approximately equal in intensity to the proton transfer product ion (data not shown); we now routinely monitor both the $[M]^{\cdot+}$ and $[M+H]^+$ ions during SIM runs.

Hamilton Harbour zebra mussels were sampled from a navigation buoy that was anchored in close proximity to sediments contaminated by coal tar. The resuspension and transport of contaminated sediment from this area is thought to be a vector for the distribution of PAHs to other areas of the harbour. The PAH content of Hamilton air particulate is influenced both by mobile emissions (i.e., cars and trucks) and industrial emissions including emissions from coking operations at the two steel mills. Fig. 2 shows the ion m/z 327 LC–APCI-MS ion chromatograms of the non-polar PAC fractions of the extracts of Hamilton Harbour zebra mussels, Hamilton air particulate and Hamilton coal tar. Although the
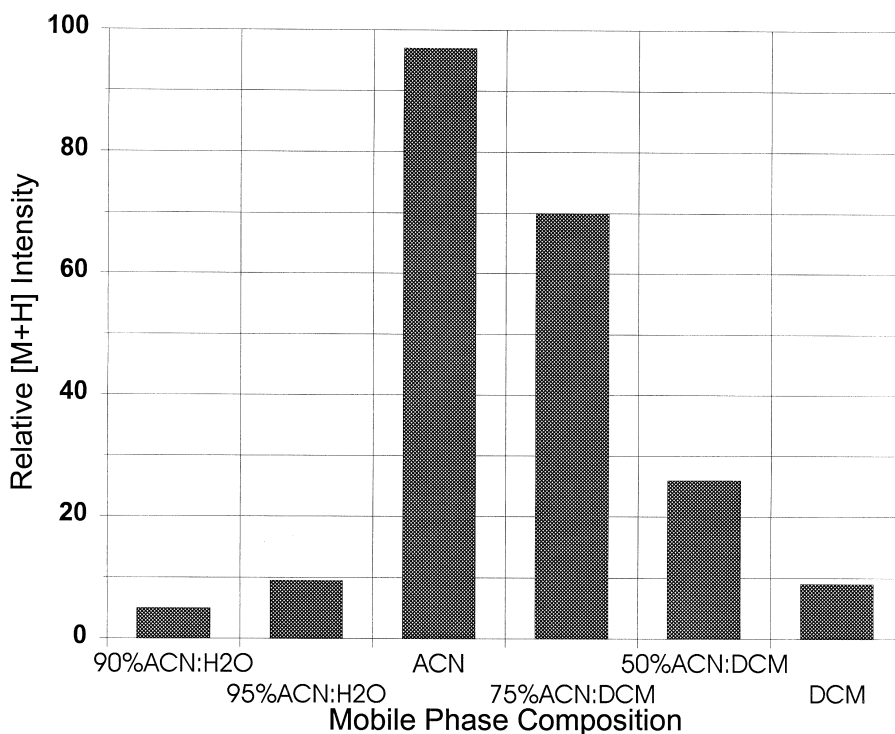
Fig. 1. Relative intensity of the $[M+H]^{+}$ ion for dibenzo[*a,l*]pyrene for a range of LC–APCI-MS mobile phase compositions. Both the charge exchange and proton transfer products were observed in 100% dichloromethane at an approximate 1:1 ratio. ACN=acetonitrile, H2O=water, DCM=dichloromethane.

comparison of the chromatograms revealed some differences in the profiles, the PAHs present in both the coal tar and Hamilton air particulate extracts were also detected in the zebra mussel extract. Two molecular mass 326 u PAHs were tentatively identified in the LC–MS chromatograms (Fig. 2) based on retention time, UV/fluorescence and mass spectral matches with authentic standards (Fig. 3). Compound 1 was identified as naphtho[1,2,3,4-*ghi*]perylene and compound 4 was identified as dibenzo[*cd,lm*]perylene.

Fig. 4 shows the sum of the ion *m/z* 351 and ion *m/z* 375 LC–MS chromatograms of the extract of Hamilton Harbour zebra mussels, Hamilton air particulate and Hamilton coal tar. The chromatographic profiles of the three extracts exhibited strong similarities. Four individual PAHs were tentatively identified in the LC–MS chromatograms (Fig. 4) based on retention time, UV/fluorescence and mass spectral matches with authentic standards. Compounds 6

and 7, which were poorly resolved, were identified as benzo[*a*]coronene (350 u) and dinaphtho-[*cde,lmn*]pyrene (350 u), respectively. Compounds 8 and 10 were identified as benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene (350 u) and naphtho[8,1,2-*abc*]coronene (374 u), respectively. Based on LC–MS analysis of the standards, the levels of PAHs of molecular masses 326 u, 350 u and 374 u were estimated to range from 400–750 μg/g in Hamilton coal tar, 0.3–0.7 ng/m^{3} in Hamilton air particulate, and 75–125 ng/g in whole wet zebra mussels from Hamilton Harbour.

The observed similarities in the high-molecular-mass PAH profiles of all three samples may have indicated a common source of PAH contamination in the Hamilton area sample extracts, or an environmental predominance of the PAH isomers detected within the three molecular mass classes profiled. An environmental predominance of isomeric PAHs within molecular mass classes would detract from the use
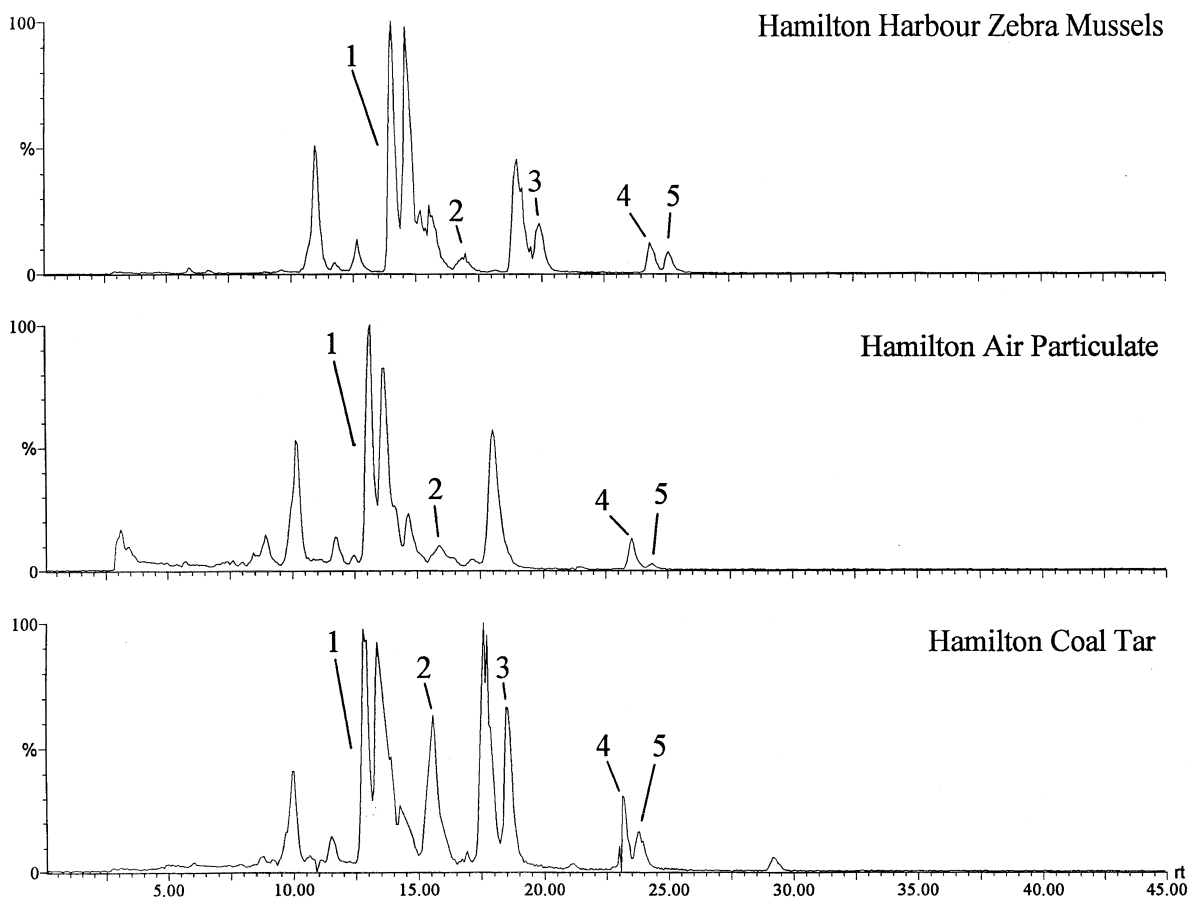
Fig. 2. LC–APCI-MS ion chromatograms (*m/z* 327) showing some molecular mass 326 u PAH from extracts of Hamilton Harbour zebra mussels, Hamilton air particulate and Hamilton coal tar. Numbered peaks were (1) naphtho[1,2,3,4-*ghi*]perylene; (2) unidentified; (3) unidentified; (4) dibenzo[*cd,lm*]perylene and; (5) unidentified. rt=Retention time in min.

of LC–MS profiling as a source apportionment tool. Pace and Betowski [13] also observed similarities in the particle beam LC–MS profiles of molecular mass 326 u, 352 u and 376 u PAHs in extracts of contaminated soils from two different hazardous waste sites and Wise et al. [21] observed similarities in the profiles of select molecular mass 302 u PAHs in four environmental reference materials. Figs. 5 and 6 show the LC–APCI-MS profiles of the high-molecular-mass PAHs from extracts of an urban dust standard reference material (SRM 1649) collected in Washington, DC, USA and Hamilton air particulate. With the exception of the relative abundances of the compound(s) eluting immediately after the PAH tentatively identified as naphtho[1,2,3,4-*ghi*]perylene

(compound 1), the profiles of the molecular mass 326 u PAHs were very similar (Fig. 5). The profiles of the molecular mass 350 u PAH and 374 u PAH exhibited an even more striking similarity (Fig. 6). These data provide evidence that for the isomeric molecular mass classes profiled, high-molecular-mass PAHs detected in Hamilton air particulate are also characteristic of PAHs found in air particulate samples from other urban centres. However, we are presently unable to speculate as to the source(s) of high-molecular-mass PAHs in these samples. Our LC–MS analysis of the PAC fraction of a reference standard characteristic of mobile emissions (diesel SRM 1650) failed to detect any PAHs of molecular masses 326 u, 350 u or 374 u (data not shown).
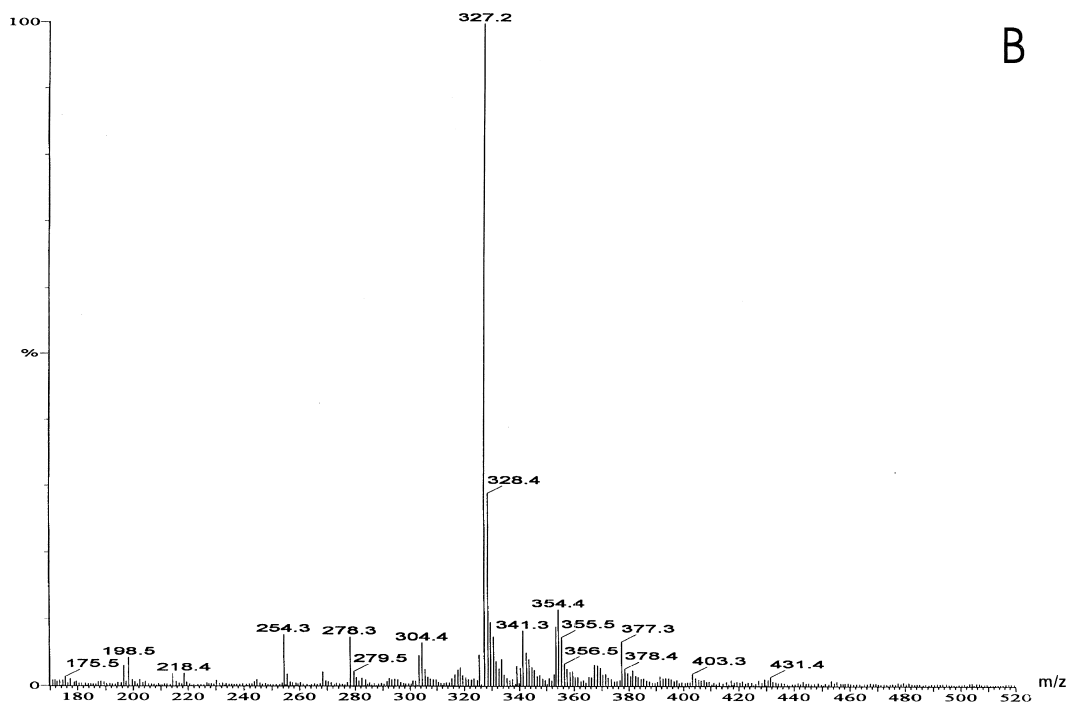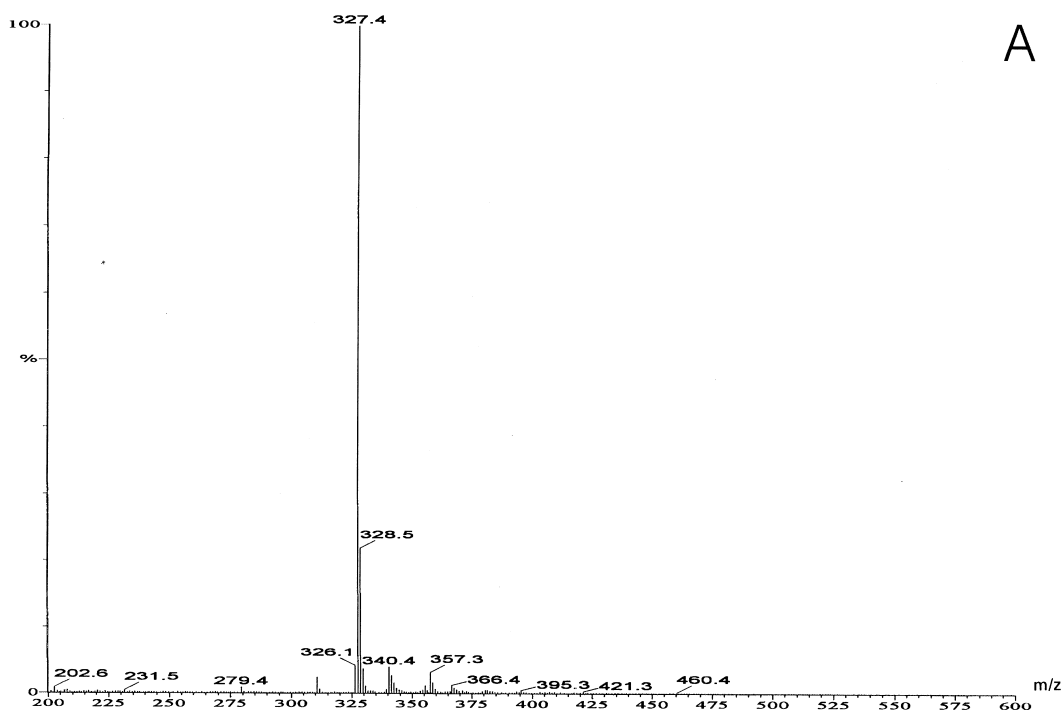
Fig. 3. LC–APCI-MS spectra of a dibenzo[*cd,lm*]perylene standard (A) and dibenzo[*cd,lm*]perylene tentatively identified in Hamilton Harbour coal tar (B).
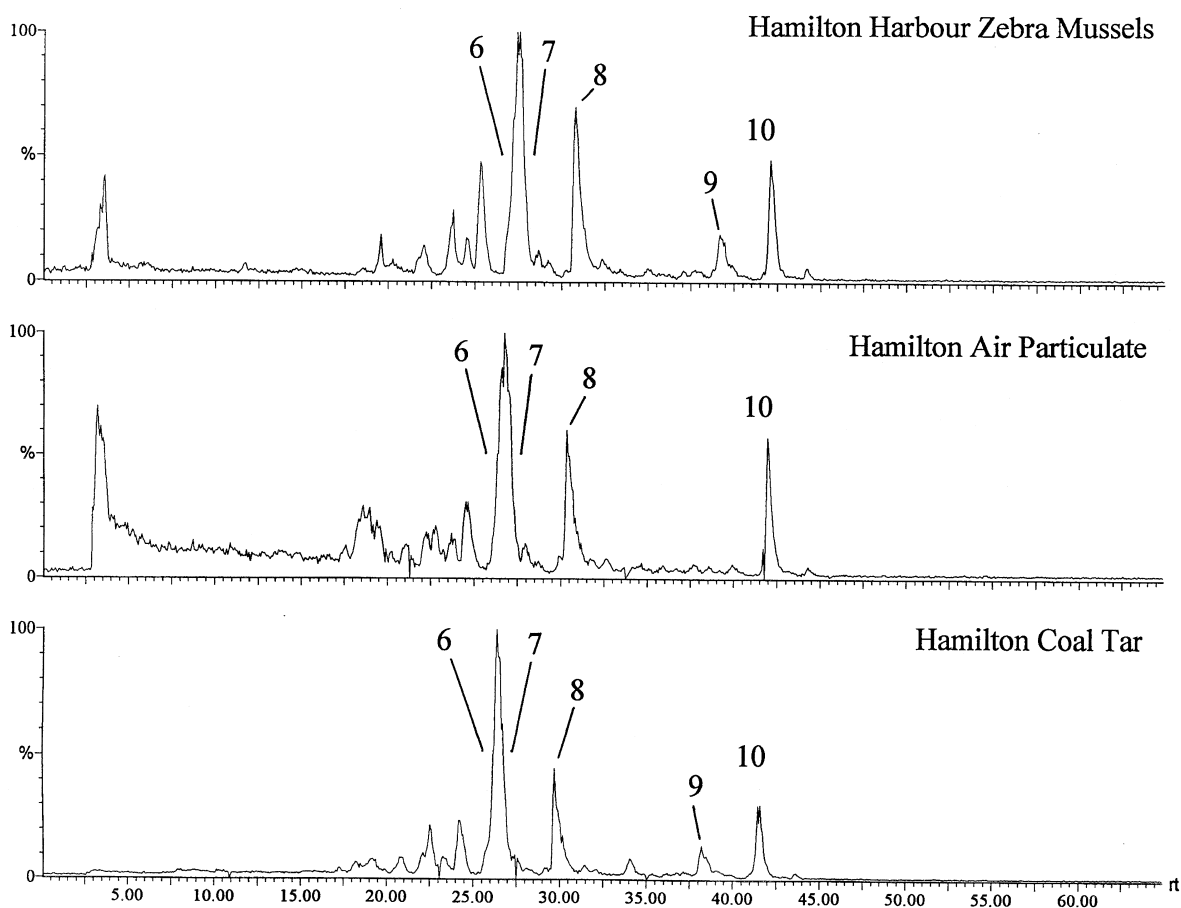
Fig. 4. LC–APCI-MS ion chromatograms (summation of ions m/z 351 and m/z 375) showing some molecular mass 350 u and 374 u PAHs from extracts of Hamilton Harbour zebra mussels; Hamilton air particulate and Hamilton coal tar. Numbered peaks were; (6) benzo[a]coronene (350 u); (7) dinaphtho[cde,lmn]pyrene (350 u); (8) benzo[pqr]naphtho[8,1,2-bcd]perylene (350 u); (9) unidentified and (10) naphtho[8,1,2-abc]coronene (374 u).

Profiles of all the PAH classes determined in this study were similar, however, some peaks were observed in the profiles of the coal tar extract that may potentially be characteristic of contamination from this source. Compound 2 (Fig. 2) was detected in the coal tar extract but was only observed at or below the detection limit in the air particulate and zebra mussel extracts. Compounds 3 and 5 (Fig. 2) and compound 9 (Fig. 4) were prevalent in the extracts of coal tar and zebra mussels but were not detected (compound 3 and compound 9) or detected near the detection limit (compound 5) in the air particulate sample. The interpretation of these data

was that compound 3 and compound 9, which were not observed in the Hamilton air particulate extract, may have been accumulated by zebra mussels as a result of exposure to coal tar-contaminated sediment in the water column in Hamilton Harbour. The APCI mass spectrum of compound 3 exhibited a dominant m/z 327 ion indicating that the major component was a PAH of molecular mass 326 u while compound 9 exhibited a dominant m/z 351 ion indicating a molecular mass 350 u PAH (Fig. 7). Other ions in the spectrum of the compound 3 LC–MS peak were tentatively assigned to co-eluting compounds as follows: m/z 340 and m/z 341 assigned to [M]$^{+}$ and
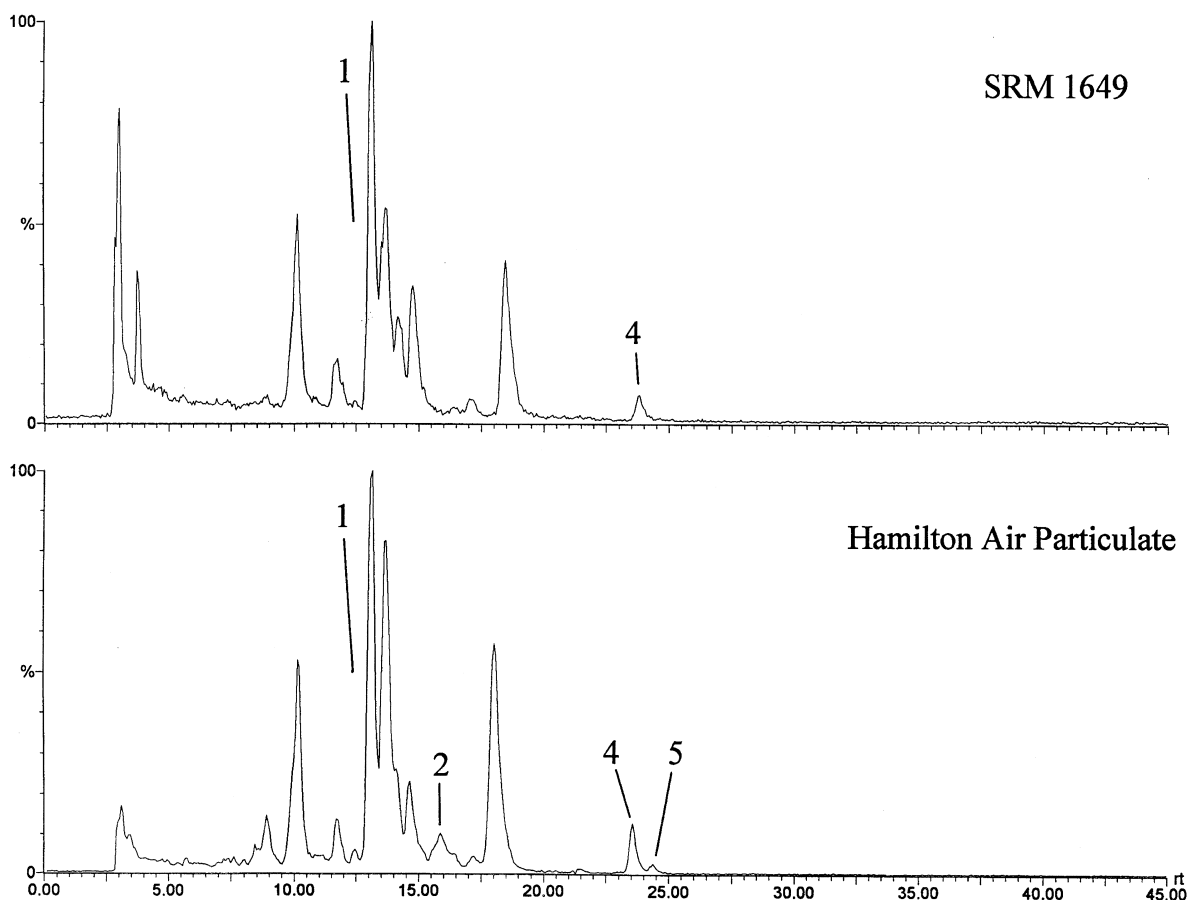
Fig. 5. LC–APCI-MS ion chromatograms (*m/z* 327) of some molecular mass 326 u PAHs from extracts of an urban air reference standard (SRM 1649, Washington, DC, USA) and Hamilton, Canada air particulate. Numbered peaks were; (1) naphtho[1,2,3,4-*ghi*]perylene; (2) unidentified; (4) dibenzo[*cd,lm*]perylene, and (5) unidentified.

[M+H]$^+$ of a 326 u PAH methyl derivative, and; *m/z* 354 and *m/z* 355 assigned to [M]$^{\cdot+}$ and [M+H]$^+$ of a 326 u PAH dimethyl derivative. Ions in the spectrum of the compound 9 LC–MS peak were also assigned to other compounds: *m/z* 377 assigned to [M+H]$^+$ of a 376 u PAH; *m/z* 401 assigned to [M+H]$^+$ of a 400 u PAH; *m/z* 402 and *m/z* 403 assigned to [M]$^{\cdot+}$ and [M+H]$^+$ of a 402 u PAH; *m/z* 427 assigned to [M+H]$^+$ of a 426 u PAH, and; *m/z* 428 and *m/z* 429 assigned to [M]$^{\cdot+}$ and [M+H]$^+$ of a 428 u PAH or a 400 u PAH dimethyl derivative.

The two spectra shown in Fig. 7 provide evidence for the minor presence of other PAHs and PAH alkyl derivatives co-eluting with the predominant PAHs;

work to identify additional compounds in these samples is currently underway. The non-polar PAC fraction of the coal tar extract was further separated using normal-phase HPLC to isolate the molecular mass 326/328 u PAH and 350/352 u PAH fractions. Preliminary analysis of the 326/328 u PAH fraction by reversed-phase HPLC with a 4.6 mm I.D. column packed with a polymeric 3 μm C$_{18}$ stationary phase and diode array UV and fluorescence detection provided additional evidence for the presence of co-eluting compounds in Figs. 3–6. However, these co-eluting compounds were estimated to be present at five- to 10-fold lower concentrations than the PAHs tentatively identified in this study. We are
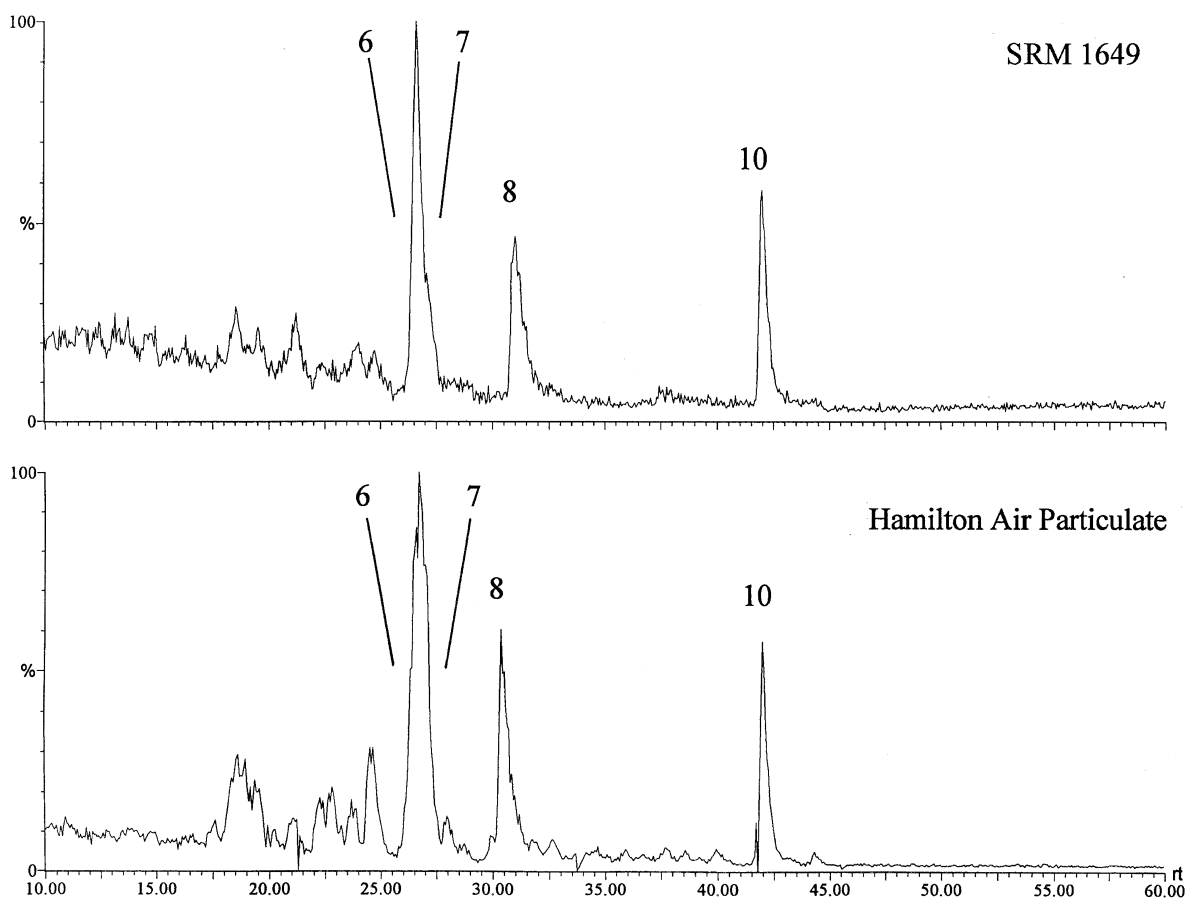
Fig. 6. LC–APCI-MS ion chromatograms (summation of ions m/z 351 and m/z 375) of some molecular mass 350 u and 374 u PAHs from extracts of an urban air reference standard (SRM 1649, Washington, DC, USA) and Hamilton, Canada air particulate. Numbered peaks were; (6) benzo[*a*]coronene (350 u); (7) dinaphtho[*cde,lmn*]pyrene (350 u); (8) benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene (350 u); (9) unidentified and (10) naphtho[8,1,2-*abc*]coronene (374 u).

currently endeavouring to couple this improved RP-HPLC separation methodology and microbore LC techniques with LC–APCI-MS.

4. Conclusions

LC–APCI-MS is an effective method for the analysis of the predominant high-molecular-mass PAHs in environmental samples. The LC–MS analyses were performed on non-polar PAC fractions without additional separation of PAHs into isomeric molecular mass classes. The LC–MS profiles of the ion m/z 327, m/z 350 and m/z 374 chromatograms from Hamilton air particulate and SRM 1649 (Washington, DC, USA) were very similar suggesting that high-molecular-mass PAH profiles of urban air particulate material may not be regionally or source specific. The comparison of profiles from three environmental samples from Hamilton indicated that high-molecular-mass PAHs in Hamilton coal tar and Hamilton air particulate are being accumulated in tissues of zebra mussels in Hamilton Harbour. The mechanisms by which zebra mussels are exposed to PAHs are unclear, but the LC–MS data indicated that some high-molecular-mass PAH contamination in zebra mussels may have originated from coal tar-contaminated sediment.
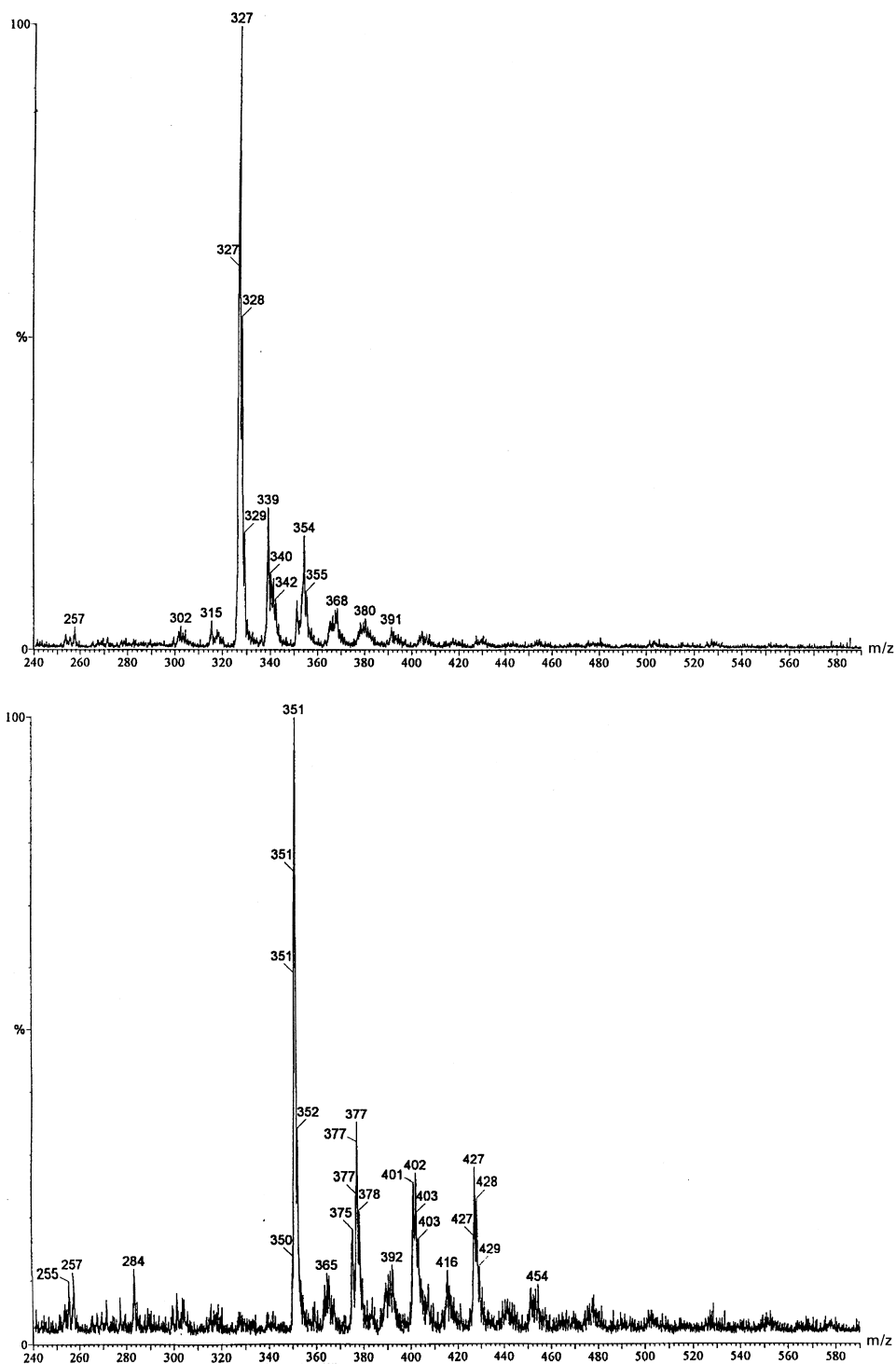
Fig. 7. APCI mass spectra of compound 3 (molecular mass 326 u PAH) and compound 9 (molecular mass 350 u PAH) from the LC–APCI-MS analysis of an extract of Hamilton coal tar.

Acknowledgements

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