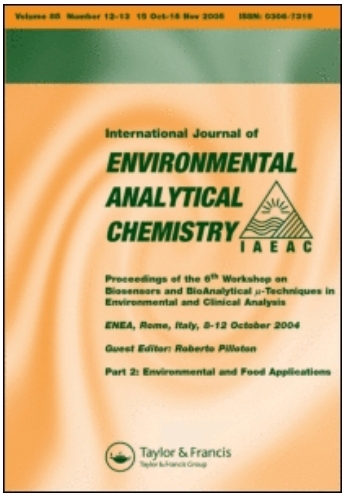

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Characterization of Nitro-PAH Adsorbed on Environmental Micro Particles: A Comparison of Lamma, Fourier Transform Mass Spectrometry Laser Microprobes and Gas Chromatography-Tandem Mass Spectrometry

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CHARACTERIZATION OF NITRO-PAH ADSORBED ON ENVIRONMENTAL MICRO PARTICLES: A COMPARISON OF LAMMA, FOURIER TRANSFORM MASS SPECTROMETRY LASER MICROPROBES AND GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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Characterization of nitro-PAHs has an important environmental interest. This work proposes a methodology for the systematic study of nitro-PAHs adsorbed on environmental aerosols, i.e. particles emitted by steel industry fumes. Direct analysis by LAMMA and FTMS has been combined with indirect characterization of nitro-PAHs by GC-MS-MS. The results suggest that LAMMA and FTMS laser microprobe analysis, used at very short wavelength and low energy (power densities about 9×10^6 W/cm^2) allows the *in situ* desorption of high-molecular-weight compounds (PAHs and nitro-PAHs). This work is the first qualitative and potentially quantitative analytical approach for the analysis of these toxic and carcinogenic compounds adsorbed on a complex matrix.

KEY WORDS: Dust, nitro-PAH, laser desorption, LAMMA 500, fourier transform mass spectrometry, gas chromatography-tandem mass spectrometry.

INTRODUCTION

The application of detection and characterization techniques to nitrated polycyclic aromatic hydrocarbons (nitro-PAH) in environmental samples is a priority in the field of pollution, since nitro compounds can be present in particles from various sources (industrial, domestic and natural combustions)[1–5] and have well known mutagenic and carcinogenic activities[6–8]. Analytical methods for nitro-PAH must usually exhibit both high sensitivity and selectivity. Firstly, nitro-PAH are typically present in low µg/g or ng/g concentration in samples which weigh a few hundred milligrams at the most. Secondly, most separation methods which isolate a nitro-PAH enriched fraction typically produce an isolate which contains many other compounds as well. Nitro-PAH can be detected by a variety of chromatographic detectors[9–11] and mass spectrometric methods[12–14]. While the mass specrometric methods, particularly chemical ionization with

negative ion detection (NCI) generally provide more certain qualitative information, the chromatographic detectors permit satisfactory quantitation at the μg/g and ng/g levels. In the last decade, applications of mass spectrometry combined with laser desorption (LDMS)[15,16] in environmental problems, revealed that it turns out to be the best performing and most adapted technique for direct analysis of nitro-PAH adsorbed on aerosols. In recent work, Muller *et al.*[17] showed the capabilities of LDMS for nitro-PAH detection on several substrates. In the present paper, we first demonstrate the effectiveness of laser microprobe analysis for rapid and accurate characterization of nitro-PAH adsorbed on microparticles from steel industry fumes. Furthermore, we compared laser microprobe methods with GC-MS and GC-MS-MS. Finally, we propose a methodology for the systematic study of nitro-PAH adsorbed on environmental matrices by direct (LDMS) and indirect (GC-MS and GC-MS-MS) analytical techniques.

EXPERIMENTAL

Collection and extraction

Particle collection was performed at a specific steelworks site by use of an Andersen impactor device with an air aspiration speed of 28 L/min, for 24 h. Aluminium filters of nine granulometric ranges from 0.4 to 9 μm were recovered and stored in the dark at –6°C. After removing particles from the aluminium filters for direct analysis by LDMS, the filters were subjected to methylene chloride soxhlet extraction for 24 h; extraction was performed in the dark, to avoid possible photooxidative reactions. Extracts were then evaporated to dryness, redissolved in methylene chloride and finally stored at –6°C before GC-MS and GC-MS-MS analysis.

Instrumentation

Laser microprobe mass analysis (LAMMA-TOF). All experiments were performed on a LAMMA 500 time of flight apparatus (Leybold Heraeus, Germany) with a transmission arrangement. In our modified system[18], the Nd Yag laser harmonic (532 nm) pumps a TDL50 dye laser (Quantel, France). Harmonic frequencies of the dye laser, as selected by a holographic network, may either be doubled (by a DCC crystal) or mixed (by a MCC crystal). It is possible to separate the various wavelengths with a quartz separator prism, and to align the selected laser beam either doubled or mixed with the optical pathway of the He-Ne pilot laser beam. Thus, the sample is ionized with a spatial resolution similar to that of the original LAMMA 500 instrument (1–3 μm). We can obtain any wavelength between 220 and 1080 nm with a precision of 0.1Å, by using the whole range of dyes and the appropriate doubling and mixing crystals, provided that the pumping energy is sufficient (400 mJ at 532 nm). We used 590 Exciton rhodamine, which lases between 565 and 604 nm when pumped by the doubled harmonic of the Nd Yag. The various wavelength ranges were obtained with this dye laser, after doubling and/or mixing. Desorption and ionization of molecules were realized using a pulsed dye laser at 222 nm with low power (10^6 W/cm^2). Ions produced by laser irradiation were extracted at an angle of 180° to the incident beam in the LAMMA 500 (transmission mode) whereas in the LAMMA 1000, ions are extracted at an angle of 45° to the

incident beam and 90° to the sample surface (reflection mode). All mass spectra were registered on a Nicolet 4094C transient recorder, connected with an Apple Macintosh II CX 40MB computer.

Fourier transform mass spectrometry analysis (FTMS). Analyses were performed by using a laser microprobe Fourier transform ion cyclotron resonance mass spectrometer[19,20]. This instrument is a modified, differentially pumped dual cell Nicolet Instrument FTMS 2000 (nowadays Extrell FTMS Millipore) operated at 3 T magnetic field strength and coupled with a reflection laser interface and special sample manipulation hardware. The ionization step was performed using an excimer laser charged with KrF mixture (λ = 193 nm; pulse duration, 23 ns; output energy, 250 mJ). The laser beam is focused on the sample, which is placed inside the source cell, by means of several internal lenses and an external adjustable telescope. This configuration allows the adjustment of the laser beam diameter from 5 μm to several hundreds of μm corresponding to a power density varying between 10^5 and 10^{10} W/cm^2 with an energy at the sample surface of approximately 60 μJ per pulse. Ions were extracted at 90° to the sample surface (reflection mode).

The viewing system using an inverted cassegrain optics design allowed the sample visualization with x300 magnification[19,20].

Particles of dust were fixed on an indium plate with a large sample surface for analysis (ca. 1 cm^2). Coarse and fine xyz manipulation of the sample stage was achieved by micromanipulators with a spatial resolution precise to micrometers.

The experimental sequence used for these analyses was as follows:

- Ions are formed by a laser-induced ionization in the source cell (residual pressure, 5 10^{-8} torr).
- During the ionization event, the conductance limit is kept at the trap potential (typically +1V) to confine ions in the source cell. This conductance limit can eventually be grounded to transfer ions in the analyser cell (residual pressure, 10^{-9} torr) to achieve better resolution in the heterodyne mode.
- A variable delay period follows, during which ion-molecule reactions can occur.
- Ions are then excited and the ion image current is detected, amplified, digitized and Fourier transformed to produce a mass spectrum.

Gas chromatography-mass spectrometry and tandem mass spectrometry analysis. GC-MS analysis was performed with a triple quadrupole mass spectrometer Finnigan MAT TSQ70 coupled with a Varian 3400 gas chromatograph equipped with a programmable on-column capillary injector. Different ionization and mass analytical methods were first performed using the standard solution and were then applied to dust extracts with enough caution to prevent any contamination. Detection in the electron capture negative ion chemical ionization mode (ECI) enhances specificity for nitro-PAH[21]. Moreover, ECI is more sensitive than electron impact (EI) or positive chemical ionization (PCI) because of the high electron affinity of nitro compounds. To reduce chemical noise and increase selectivity[22], nitro-PAH analysis was achieved by ECI and tandem mass spectrometry. The first quadrupole was set to transmit the molecular ion $[M]^{-\circ}$ which was then fragmented with argon in the collision cell, and the product ions were mass analysed by the third quadrupole. In selected reaction monitoring (SRM) experiments, only two daughter ions were monitiored with the third quadrupole, $[M\text{-}NO]^-$ and $[NO_2]^-$. SRM was applied for the trace-level detection of nitro compounds from dust extracts.

GC conditions were as follows: column, DB5MS (J&W), 60 m, 0.25 mm i.d.; film thickness, 0.1 μm; carrier gas, helium at 32 cm/s; column temperature programme, 35°C for 1 min, 35 to 150°C in 10°C/min, 150 to 300°C in 5°C/min. The injector temperature programme increased from 35°C to 300°C in 1 min and was then kept at 300°C for 32 min. Transfer line temperature, 300°C.

MS conditions were as follows : moderating gas, isobutane; source pressure, 2.8 torr; source temperature, 150°C. For tandem mass spectrometry : collision gas, argon; collision energy, 30 or 50 eV; collision cell pressure, 1 millitorr. Combined with ECI, SRM seems to be the best way to enhance the sensitivity in detection of nitro-PAH.

RESULTS AND DISCUSSION

LAMMA TOF analysis

A systematic LAMMA study of aluminium filters for different granulometric ranges of dust (0.4–10 μm) revealed that only the dust fraction from 0.4 μm filters contains nitro-PAH. Information on the mineral composition of the matrix was obtained from the mass spectra at high irradiance level (10^8 W/cm^2) in both the positive and negative ion detection mode. The positive ion mass spectra revealed that the dust matrix contains sodium, potassium, calcium and iron (Figure 1). In the negative ion mass spectra (Figure 2), the observation of SiO_x^-, NO_x^-, SO_x^-, PO_x^- and FeO_x^- indicates that the matrix contains silicates, nitrates, sulphates, phosphates and iron oxides. Because the matrix is polyphasic, the spectral interference would mask the isotopic patterns. Detection of organic substances was realized by laser desorption (LD) at low irradiance (10^6 W/cm^2). A positive ion LAMMA spectrum of particles, presented in Figure 3 shows the specific distribution of high-mass PAH (MW > 220 amu). The simultaneous observation of peaks corresponding to iron and PAH in the LD spectrum

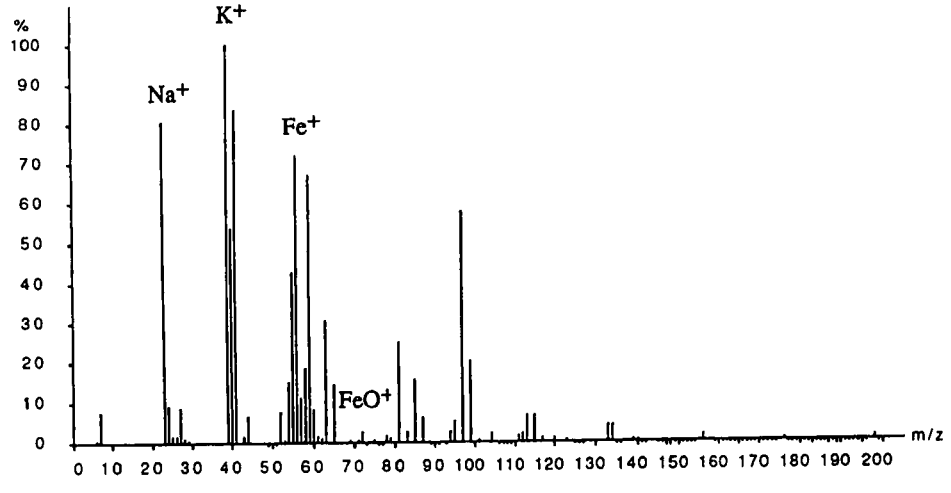

Figure 1 Positive ion LAMMA-TOF mass spectrum of particles smaller than 0.4 μm.

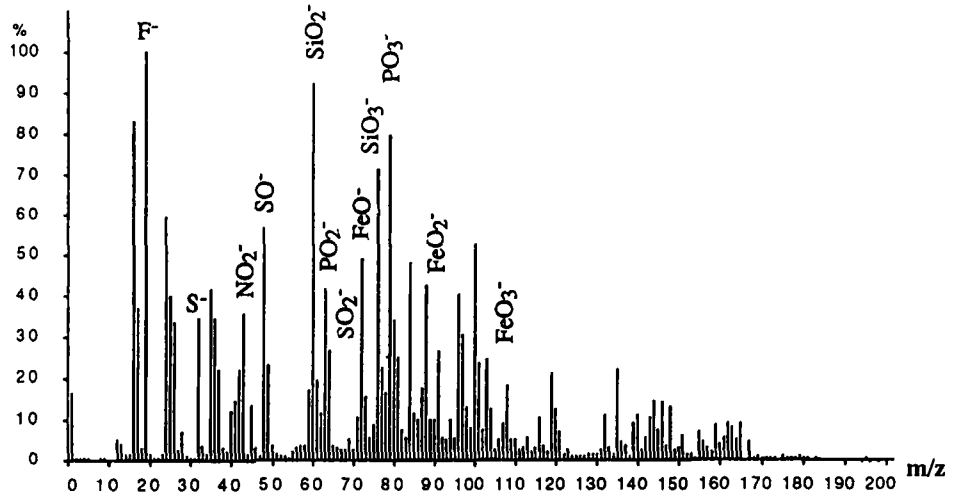

Figure 2 Negative ion LAMMA-TOF mass spectrum of particles smaller than 0.4 μm.

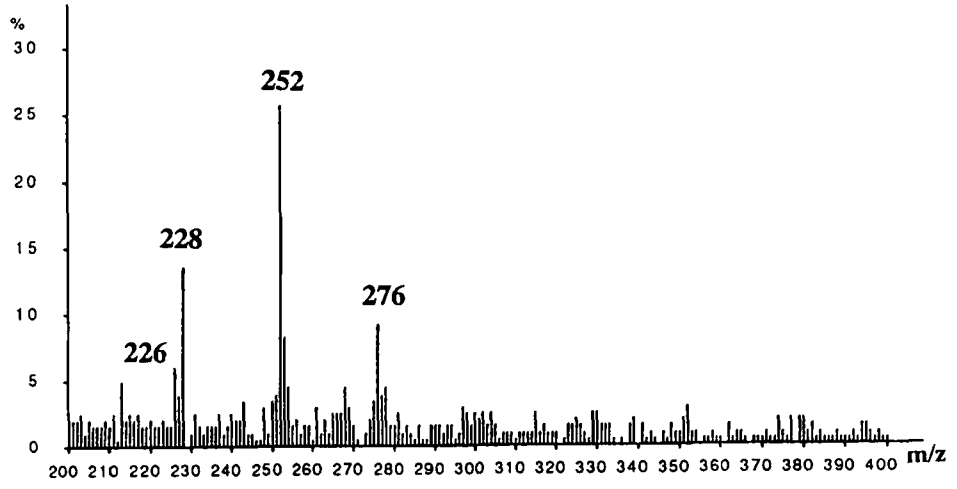

Figure 3 Positive ion LAMMA-TOF mass spectrum of particles smaller than 0.4 μm, showing the signals which may be attributed to PAH.

shows that this atom is intimately linked to the chemical environment of PAH. The negative ion spectrum (Figure 4) shows that nitrated compounds are present; they are characterized by specific $M^{-\bullet}$ ions (m/z 223 and 247) and $[M\text{-}NO]^-$ ions (m/z 193 and 217), with associated low mass ions CN^- (m/z 26), CNO^- (m/z 42), NO_2^- (m/z 46) and CNO_2^- (m/z 58). Early observation led us to investigate a possible confirmation of the presence of nitro-PAH in the particles. By LD at a wavelength of 1.064 μm. Hercules *et al.*[15,16,23] first showed that nitro-PAH could be characterized by the specific

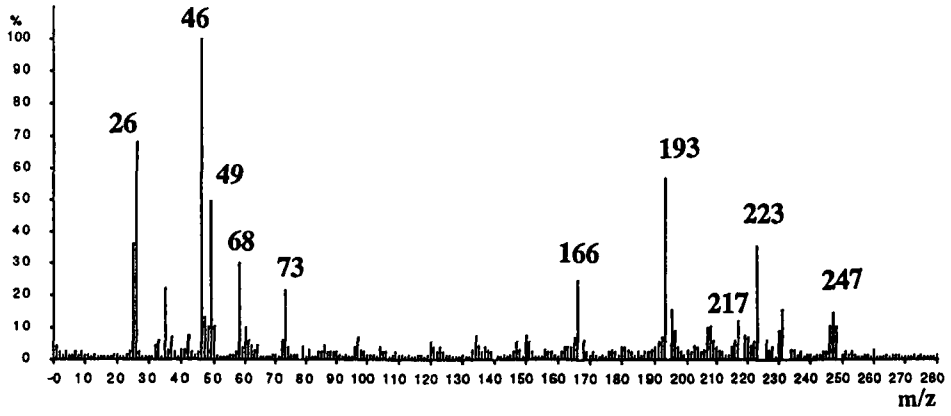

Figure 4 Negative ion LAMMA-TOF mass spectrum of particles smaller than 0.4 μm, showing the signals which may be attributed to nitro-PAH.

detection of $[M\text{-}NO]^-$ and $[M+15]^-$ in negative ion mass spectra, but that $M^{-\circ}$ was not detected with their LAMMA 500 intrumentation. Later, the $M^{-\circ}$ was detected with LAMMA 1000 and FTMS 1000 instruments. The authors also confirmed by FTMS 1000 that the $[M+15]^-$ ion could be assigned to $[M+O\text{-}H]^-$. To be sure that the nitrated compounds detected by LAMMA 500 were not produced by combination of NO_2^- and PAH under the influence of the laser pulse, the dust samples were further analysed by laser desorption FTMS 2000 in the reflection mode at 193 nm and by GC-MS.

Laser desorption FTMS analysis

PAH and their derivatives are commonly detected in laser desorption FTMS experiments at a wavelength of 266 nm or 1.064 μm. However, we used the short UV wavelength of 193 nm in order to detect high-mass PAHs (MW > 252 amu), and to detect the Fe^+ ion as the main ionized element in the positive ion mode (Figure 5). Moreover, these experiments confirmed the presence of nitro compounds by the detection of $[M\text{-}NO]^-$ ions (m/z 193, 217 and 352) and of the corresponding $M^{-\circ}$ ions (m/z 223, 247 and 382) (Figure 6). However, $[M+O\text{-}H]^-$ ions were not detected in our experiments. Exact mass calculation (Table 1) of specific ions confirmed the presence of nitro-PAH like nitrofluorene (m/z 211), nitroanthracene (m/z 223) and nitrofluoranthene (m/z 247). Low-mass compounds can in principle not be detected by laser desorption FTMS because they sublime under the high-vacuum conditions (10^{-8} torr) and therefore, a complementary GC/MS analysis is required. It should be noted that more abundant nitro-PAH commonly detected in environmental analysis are the low-mass compounds 1- and 2-nitronaphthalene[24]. Moreover, light PAH are the more abundant compounds in the atmosphere and light nitro-PAH are potentially formed in larger abundance than their heavy homologues.

GC-MS and tandem mass spectrometry analysis of dusts

Figure 7 shows a total ion current chromatogram of a standard mixture of six reference nitro-PAH. The reference compounds are sufficiently separated, but tailing

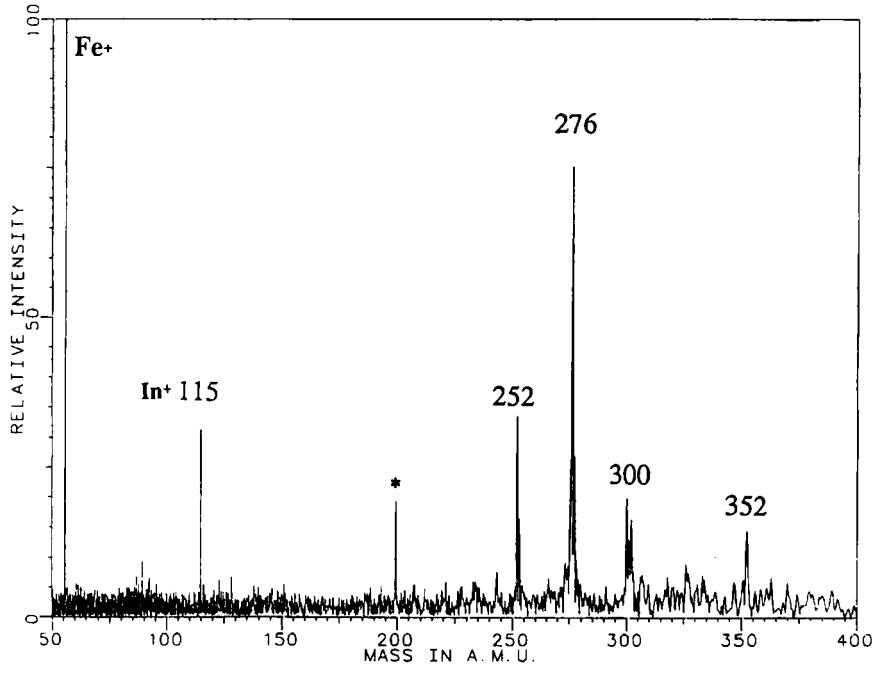

Figure 5 Positive ion LD-FT-ICR mass spectrum of particles smaller than 0.4 μm (λ = 193 nm), I = 9×10^6 W/cm^2), showing the signals which may be attributed to PAH (* radiofrequency artefact).

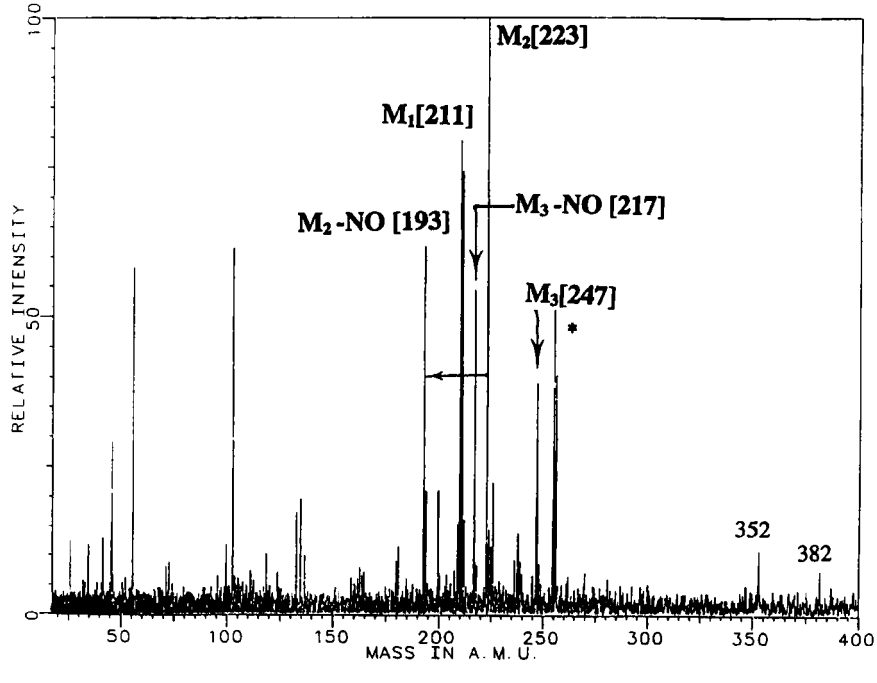

Figure 6 Negative ion LD-FT-ICR mass spectrum of particles smaller than 0.4 μm (λ = 193 nm), I = 9×10^6 W/cm^2), showing the signals which may be attributed to nitro-PAH (* radiofrequency artefact).

Table 1 Calculated and measured masses of nitro-PAH detected by LD-FT-MS after confirmation by GC/EC-MS/MS.

Nitro-PAH	*Calculated mass*	*Measured mass*
Nitrofluorene	211.06392	211.04731
Nitroanthracene	223.06392	223.04393
Nitrofluoranthene (M-NO)$^-$	217.06592	217.08325

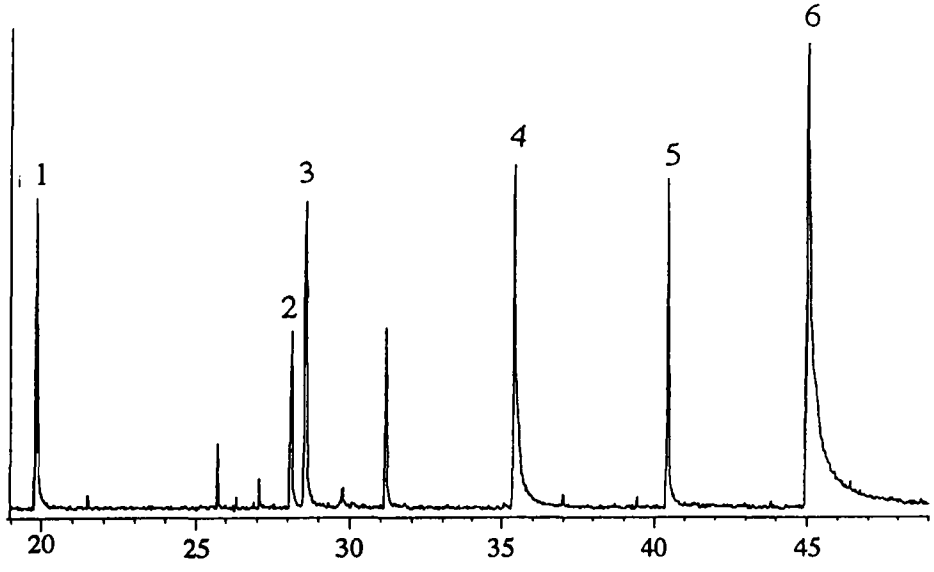

Figure 7 Total ion current chromatogram from a mixture of six reference nitro-PAH, obtained under full scan GC/EC-MS conditions; 1: 2-nitronaphthalene, 2: 2-nitrofluorene, 3: 9-nitroanthracene, 4: 3-nitrofluoranthene, 5: 6-nitrochrysene, 6: 6-nitrobenzo[a]pyrene (time scale in min).

occurs for compounds 4 and 6. When modified GC conditions were applied, in particular by decreasing the temperature, peak tailing remained. This phenomenon probably arises from thermal decomposition of nitro-PAH and not from overloading of the reference compounds. This is supported by the fact that only several nanograms were injected and that mass spectra were indeed different at the beginning and at the end of the peak and that the molecular ion $M^{-\circ}$ disappeared while the [M-30] ion increased. Thermal decomposition can occur either in the column at 250°C (although its surface is deactivated) or in the mass spectrometer during contact of the reference compounds with the wall of the ion source at 150°C. GC-MS-MS in ECI mode (full-scan CID daughter spectra) was applied to the six reference nitro-PAH in order to optimize detection and selective identification of these compounds. Three nitro-PAH could unequivocally be detected in dust extracts by GC-MS-MS in the ECI mode : 2-nitrofluorene, 9-nitroanthracene and 3-nitrofluoranthene (Figure 8). As the signal

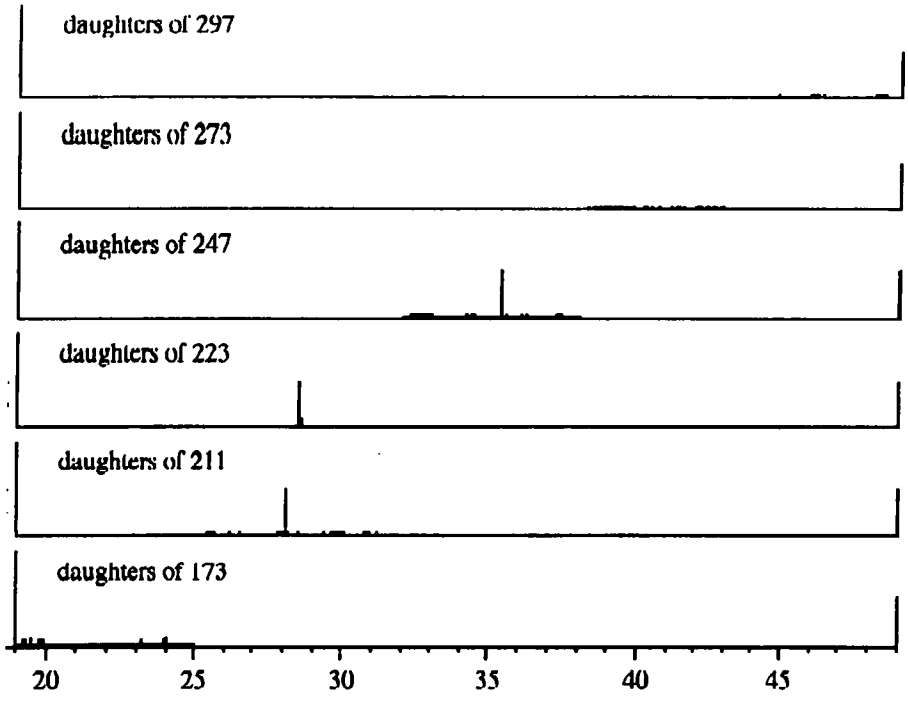

Figure 8 Selected reaction chromatograms from time-scheduled GC/MS/MS in ECI mode analysis of dust extracts (time scale in min).

intensity was not sufficient to detect and identify the three other nitro-PAH, an SRM GC/ECI-MS experiment was performed for the dust extracts. Of the three selected ions for each compound (Table 2), the molecular ion peak invariably had the highest intensity and fragment ions were used for confirmation. In this way, 2-nitronaphthalene, 6-nitrochrysene and traces of 6-nitrobenzo[*a*]pyrene were identified in dust extracts (Figure 9), in addition to the three nitro compounds mentioned above. SRM GC/ECI-MS seems to be the best way to enhance sensitivity of detection of nitro-PAH.

Table 2 Time programme for SRM detection of nitro-PAH.

Nitro-PAH	*Time window (min)*	*Selected ions (m/z)*
2-Nitronaphthalene	0–25	46, 143, 173
2-Nitrofluorene	26–32	46, 181, 211
9-Nitroanthracene	26–32	46, 193, 223
3-Nitrofluoranthene	33–38	46, 217, 247
6-Nitrochrysene	39–43	46, 243, 273
6-Nitrobenzo[*a*]pyrene	44–end	46, 267, 297

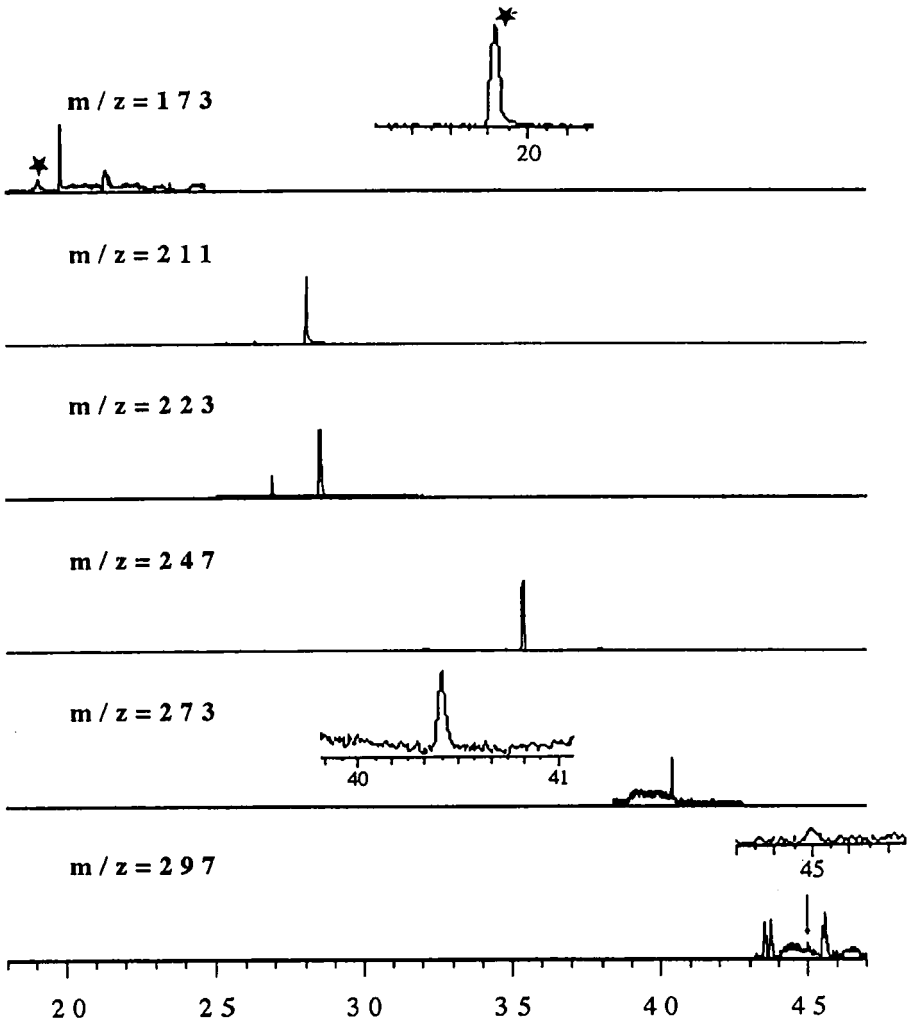

Figure 9 Ion chromatograms, for molecular ions of nitro-PAH, from dust extracts, obtained under SRM GC/ECI-MS conditions; m/z 173 for $M^{-\cdot}$ of nitronaphthalene, m/z 273 for $M^{-\cdot}$ of nitrochrysene, m/z 297 for $M^{-\cdot}$ of nitrobenzo[a]pyrene (time scale in min).

Comparison of LAMMA and laser desorption FTMS analysis of nitro-PAH in dust

The LAMMA TOF microprobe operates in the transmission mode and is mainly used for the analysis of microparticles or very thin films. The laser desorption FTMS microprobe allows the analysis of raw material or powder samples, after deposition on a support. The low-mass cut-off for the detection of compounds is better for LAMMA-TOF than for laser desorption FTMS analysis; whilst a compound with a molecular weight of 226 amu is detected by the first method, the second method would

not give any indication of the presence of such a light compound. This is probably due to differences in the vacuum conditions (typical source pressures are 10^{-8} torr in FTMS and 10^{-6} torr in TOF-MS), which influences sublimation of low-mass compounds. In the positive ion mode, both methods give molecular ions probable for PAH, at m/z 252, 276, and 352 (for $C_{20}H_{12}$, $C_{22}H_{12}$ and $C_{28}H_{16}$, respectively) and laser desorption FTMS also produces ions probably corresponding to PAH at m/z 300 and 302 (for $C_{24}H_{14}$ and $C_{24}H_{16}$, respectively). In the negative ion mode, two nitro-PAH were detected by both laser microprobe methods, as evidenced from the presence of the $M^{-\circ}$ and $[M\text{-}NO]^-$ ions; in addition, the detection of m/z 382 and 352 ions by laser desorption FTMS suggests the presence of a dinitro- or tetranitro-PAH with a molecular weight of 382 amu. Hercules *et al.* observed the same fragments, $[M\text{-}NO]^-$ and $[(2M\text{-}O)\text{-}NO_2]^-$, corresponding to the molecular weight of 2,3,5-trinitronaphthalene, by LAMMA 1000 analysis[15,16]. Results obtained by both methods show that PAH and nitrated derivatives are adsorbed on dust with fine granulometry (0.4 μm) and that the particles are mainly composed of iron oxides. Laser desorption mechanisms depend on interactions between adsorbed molecules and supports[25,26]. Indeed, Muller *et al.*[26] have shown that carbonaceous substrates, and particularly hematite, should be matrices of choice for laser desorption since the detection thresholds of PAH are then decreased.

Comparison of direct (laser microprobes) and indirect (GC-MS) analysis

Indirect analysis method by SRM GC-ECI MS allowed the detection of five nitro-PAH compounds (2-nitrofluorene, 9-nitroanthracene, 3-nitrofluoranthene, 2-nitronaphthalene and 6-nitrochrysene, and traces of 6-nitrobenzo[*a*]pyrene). Thus, this technique is complementary to direct mass spectrometrie methods for a confirmation of the presence of nitro-PAH, by GC-MS-MS in the ECI mode. If also presents the district advantage of the possibility of quantification of the results obtained in the SRM mode, and of the detection of additional nitro-PAH present at trace levels.

CONCLUSIONS

This study of particles emitted by steel industry fumes, has several implications. It authorizes the establishment of a methodology of combined analysis of nitro-PAH adsorbed on complex matrices. It is also the combination of firstly, a rapid direct analysis by LAMMA and FTMS microprobes of particles with different granulometries in order to detect adsorbed nitro-PAH and, secondly, an indirect analysis by GC-MS in the ECI mode that allows the quantification of nitro compounds adsorbed on particles. This work presents the first qualitative approach of an environmental analysis of organic compounds adsorbed on complex matrices containing metal oxides and capable of being inhaled and absorbed by human beings. Moreover, Muller *et al.*[17] have demonstrated that PAH adsorbed on a mineral support containing iron are particularly reactive and sensitive to air oxygen and ozone. Upon contact, this kind of matrix could have a catalytic function which can cause degradation of PAH and the formation of derivatives. It is therefore necessary further to develop a combined methodology of nitro-PAH analyses involving direct and indirect techniques which takes into account interactions of matrix and adsorbed compounds. Such a study should provide a good approach to understand the toxicological effect of nitro compounds.

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