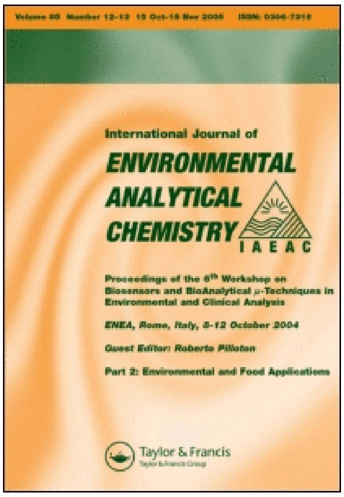

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Niessner, R. , Klockow, D. , Bruynseels, F. and Van Grieken, R.(1985) 'Investigation of Heterogeneous Reactions of PAH's on Particle Surfaces Using Laser Microprobe Mass Analysis', International Journal of Environmental Analytical Chemistry, 22: 3, 281 — 295

To link to this Article: DOI: 10.1080/03067318508076427

URL: http://dx.doi.org/10.1080/03067318508076427

Intern. J. Environ. Anal. Chem., 1985, Vol. 22, pp. 281–295
0306-7319/85/2204-0281 $18.50/0

Printed in Great Britain

Investigation of Heterogeneous Reactions of PAH's on Particle Surfaces Using Laser Microprobe Mass Analysis

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(*Received May 30, 1985*)

Artificially generated NaCl particles were coated with PAH's by using a condensation technique. These particles were exposed to reactive gases like ozone, bromine and nitrogen dioxide. The original as well as the exposed particles were investigated by fluorimetric analysis and by LAMMA (Laser Microprobe Mass Analysis) in the desorption mode, which allows the evaporation and characterization of surfaces of single particles. The results are interpreted in terms of possible heterogeneous atmospheric reactions. The reactivity of the considered PAH's towards nitrogen dioxide was found to be negligible. The structure of the reaction products formed with ozone was partially elucidated.

KEY WORDS: Laser microprobe mass analysis (LAMMA), PAH's, airborne particles, microstructure, heterogeneous atmospheric reactions, NaCl-particles.

INTRODUCTION

During recent years several new techniques were developed for characterization of airborne particles, and more and more knowledge on the microstructure of particles is being acquired. Microstructure is a term which refers to the topographical composition of a single particle; it considers, e.g. the presence and type of multilayers or agglomerates that might occur on a primary particle core, as illustrated in Figure 1.

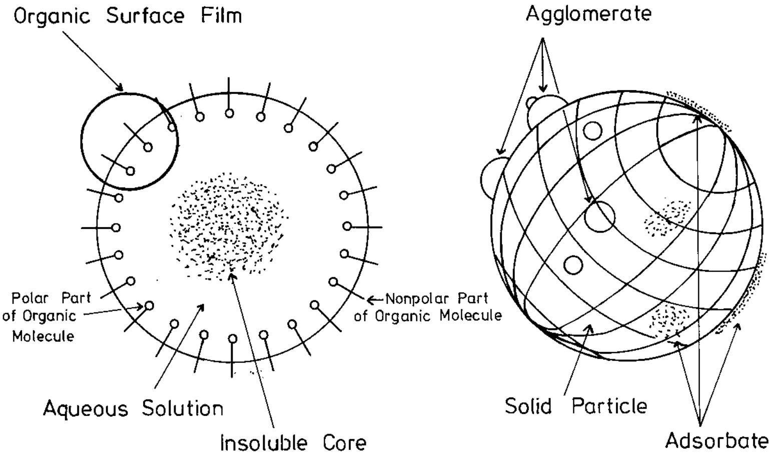


FIGURE 1 Schematic representation of the possible microstructure (compositional heterogeneity) of particles.

In many situations where aerosols are in an equilibrium with the surrounding gas phase, the existence of an organic surface layer governs the fate of a particle core, e.g. by influencing the condensation behaviour or the kinetics of reactions with the gas-phase. Also the toxicological assessment of inhalable particles strongly depends on their microstructure.

In this respect one of the most relevant topics today is the behaviour and life-time of surface enriched polycyclic aromatic hydrocarbons (PAH's) under various atmospheric conditions.

The first attempts to use Laser Microprobe Mass Analysis (LAMMA) for single particle analysis were published by Kaufmann and Wieser.[1] Since that time the application of LAMMA for detecting aerosol microstructures was reported by several authors.[2-7] Employing LAMMA at high laser power a microscopic particle can be evaporized completely and ionized for mass analysis, but microstructure analysis is also possible because the applied laser power can be varied by an optical filter system. At excitation energies below $0.09\,\mu J/\mu m^2$ (i.e. in the so-called laser desorption mode) particles larger than about $1\,\mu m$ are not completely destroyed in favourable cases. The particle under study receives a "thermal shock", and the most instable compounds, like those of an organic layer on the particle surface, are evaporated. This results in the selective excitation and analysis of the surface material. The mass spectrum recorded for a second high-power laser pulse on the same particle yields information about the particle core.

The intention of the present work was to demonstrate the usefulness of LAMMA in studying heterogeneous gas-phase reactions of PAH's artificially deposited on NaCl-particles.

The PAH/NaCl-system was chosen because of its similarity to man-made emissions: a primary thermodynamically stable particle acts as a condensation nucleus in a PAH-supersaturated exhaust gas stream. From *in situ* photoemission studies of garage aerosols or burner aerosols[8] it is known that condensed higher PAH's are non-uniformly enriched at particle surfaces. One explanation for this finding might be the fact, that once the PAH is deposited at an irregularity of a particle surface the further PAH-growth continues at the same site. The PAH/NaCl-system is also advantageous for LAMMA. At low laser energy, PAH's give rise to intense molecular ion peaks which can easily be identified, while complicating recombination reactions between NaCl and PAH's are not observed.

EXPERIMENTAL

LAMMA instrument

For a full description of the LAMMA-500 instrument (Leybold-Heraeus GmbH, Köln, F.R.G.) we refer to other publications.[9,10] To work in the desorption mode, the energy delivered by the laser beam to the particle can be varied by a set of attenuating filters. The laser energy is monitored by an energy meter. The working pressure of the instruments is $<10^{-8}$ bar. The laser generated ions are accelerated into a time-of-flight mass spectrometer, that can be operated either in the positive or negative ion mode. The ions are detected by an open Cu-Be secondary electron multiplier, and the signals are fed into a Digital Minc-11 computer for storage, mass calibration and integration.

Aerosol generation

For production of artificially PAH-coated particles a system was used as already described by Niessner.[11] The experimental set-up is given in Figure 2. An atomizer was employed for production of NaCl-condensation nuclei. A small vessel in a temperature controlled oil bath contains the PAH. Nitrogen, which is pre-heated by passing it through a spiral type glass tube in the oil bath, enters the vessel and takes up PAH-vapour. The gas is then mixed with NaCl-aerosol in a heated ring-gap mixing nozzle. In the following cooling section the vapour condenses on the primary particles, thus forming an agglomerate, whose thickness depends on the PAH vapour pressure and thus on the temperature of the oil bath.

The primary NaCl-aerosol had a number concentration around $5 \cdot 10^4\,\text{cm}^{-3}$ and a number median diameter of 0.1–0.2 μm ($\sigma_g \simeq 1.8$). After the coating procedure an increase in particle diameter between 5 and about 100% was observed depending on the PAH-supersaturation. As a typical example anthracene coated NaCl-particles are shown in Figure 3. The anthracene crystallization typically starts at the edge of a particle.

The relative humidity in the experimental setup was kept close to 0%. After having passed the condensation section the coated particles were mixed with a reactive gas. Bromine and NO_2 were delivered from a permeation system[12] with known permeation rates. Ozone as a reactive gas was generated by use of a Welsbach O_2-discharge unit. The ozone concentration was determined by iodometric analysis.[13] The mixture of the reactive gas and the coated aerosol was conducted through a plastic chamber (60 L) allowing a residence time of about 10 min. From this a known sample volume was drawn for impactor sampling.

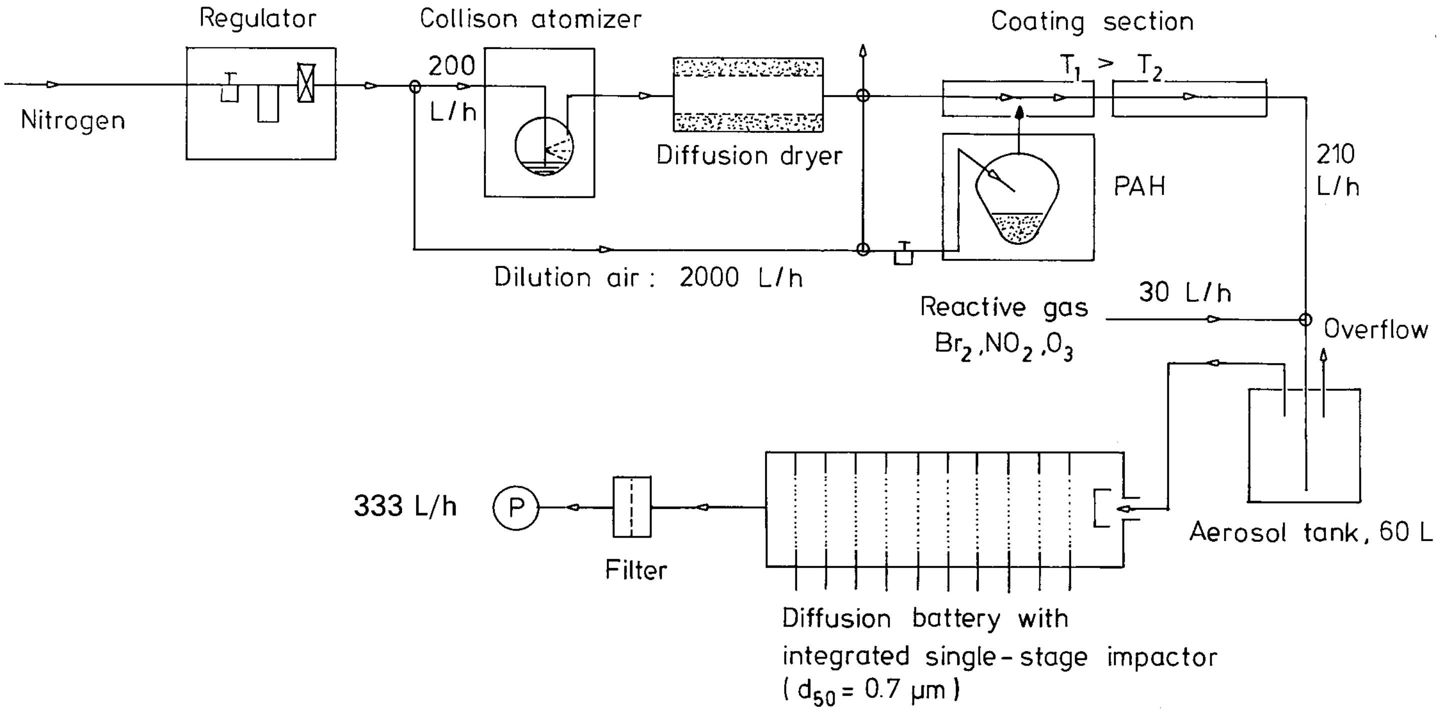


FIGURE 2 Experimental setup for aerosol generation.

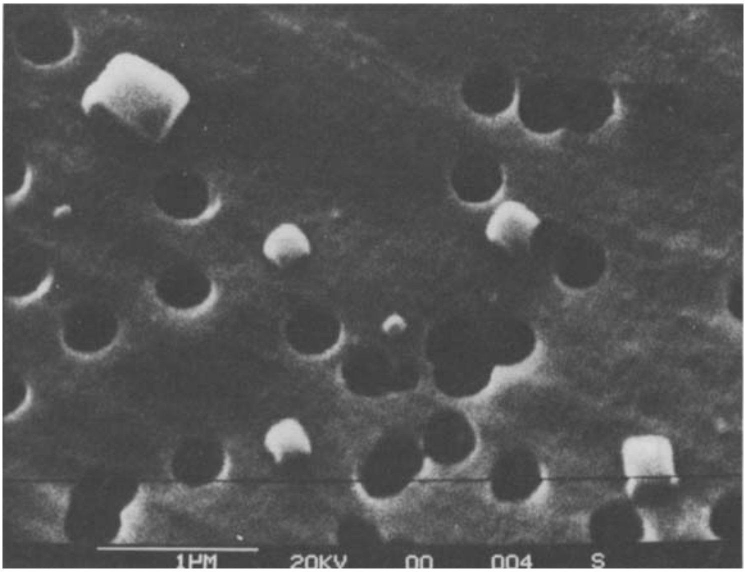


FIGURE 3 Electron micrograph of anthracene-coated NaCl-particles on a Nuclepore filter.

Sampling procedure

For LAMMA analysis a one-stage impactor with an effective cut-off diameter of 0.7 μm[14] was used as a sampling instrument. Particles larger than 0.7 μm diameter were collected on a <100 nm thick foil of Formvar^R (Polyvinyl formal) supported by 300 mesh electron microscope grids which were mounted on Parafilm backings. The sampling time was restricted to 10 minutes to avoid overloading; this corresponded to a sampled air volume of 55.5 litre.

In order to obtain the average PAH-content of the generated aerosol parallel samples were collected using glass fibre filters (Whatman GFC). The filters were extracted for 10 min by a known volume of *n*-heptane employing ultrasonic treatment. After the extraction the mixture was centrifuged for 3 min at 15,000 rpm. An aliquot of the supernatant extract was taken for fluorimetric analysis.

Fluorimetric analysis

Fluorimetric analysis was performed by means of a Zeiss PMQ II spectrophotometer equipped with the fluorimetric device ZFM4. Excitation and emission wavelengths according to Jurgensen *et al.*[15] were used. Calibration standards of the PAH's under study were prepared in *n*-heptane and stored in a dark and cool place.

RESULTS AND DISCUSSION

Fluorimetric analyses of the coated particles were carried out before and after their exposure to the reactive gases, in order to assess whether a heterogeneous gas-solid reaction had taken place or not. Each reaction system was investigated several times at different concentration ranges. The "yes/no" decision with respect to a reaction between PAH and reactive gas was based on a statistical treatment of data at the 95%-confidence level. The results are compiled in Table I. As can be seen the fluorescence behaviour of fluoranthene and chrysene was not altered by the attack of ozone. A bromination reaction under the applied experimental conditions was observed only in case of anthracene and perylene. No reaction of nitrogen dioxide with any of the PAH's under study was observed. Considering the PAH's used and data like the first ionization potential or aromaticity index (see Table II), one can expect a high reactivity of antracene and perylene against NO_2 as predicted by Nielsen.[16] Although a high NO_2-concentration was applied, no difference between the NO_2-treated and untreated aerosol was found. This seems to corroborate the conclusions of Grosjean *et al.*[17] that a nitration of PAH's takes place only in the presence of nitric acid. Similar results were obtained by Pitts[18] and Nielsen.[16] Opposite findings were published by Sine,[19] who reported a reaction between NO_2 and pyrene on carbon black as a carrier.

LAMMA was applied to the investigation of aerosol samples collected on Formvar^R membranes. One advantage of using LAMMA in the desorption mode is the possibility of progressively analysing deeper layers of a particle in repetitive laser shots. This is demonstrated in Figure 4. At first only the molecular ion of the PAH is observed. After three soft-energy shots, a fourth pulse at

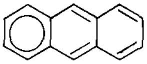
TABLE I

Results of fluorimetric analysis ($n=6$) of aerosols before and after exposure to reactive gases.

PAH	PAH-concentration of aerosol (in $\mu g/m^3 \pm$ s.d. per meas.) Before	After	Reaction ($p=0.95$)
Exposure to O_3 (3.32 mg/m^3)			
Anthracene	393 ± 13	253 ± 25	Yes
Perylene	45.5 ± 4.5	2.8 ± 0.5	Yes
Phenanthrene	12.1 ± 1.6	7.3 ± 1.6	Yes
Pyrene	94.8 ± 5.1	57.1 ± 5.0	Yes
Fluoranthene	3.8 ± 1.1	4.3 ± 0.4	No
Chrysene	33.8 ± 1.1	31.2 ± 1.9	No
Exposure to Br_2 (187 $\mu g/m^3$)			
Anthracene	9.5 ± 2.2	1.1 ± 0.6	Yes
Perylene	7.0 ± 0.1	5.2 ± 0.3	Yes
Phenanthrene	2.3 ± 0.2	2.1 ± 0.6	No
Pyrene	17.9 ± 1.4	17.7 ± 1.1	No
Fluoranthene	0.4 ± 0.1	0.4 ± 0.1	No
Chrysene	61.6 ± 6.7	57.3 ± 4.9	No
Exposure to NO_2 (1.79 mg/m^3)			
Anthracene	140 ± 6	147 ± 2	No
Perylene	0.5 ± 0.1	0.5 ± 0.1	No
Phenanthrene	6.5 ± 1.3	5.3 ± 2.4	No
Pyrene	5.5 ± 0.6	6.1 ± 0.5	No
Fluoranthene	11.9 ± 0.9	11.5 ± 1.2	No
Chrysene	85.4 ± 8.1	80.7 ± 5.9	No

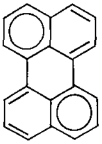
TABLE II

Aromaticity index (22) and ionization potential (23) for the considered PAH's.



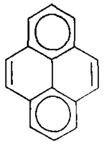
Aromaticity Index : 0.71
Ionization Potential : 7.47 eV

Anthracene



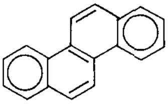
AI : 0.83
IP : 7.00 eV

Perylene



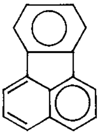
AI : 1.25
IP : 7.45 eV

Pyrene



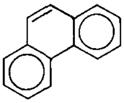
Chrysene

AI : 0.93
IP : 7.60 eV



Fluoranthene

AI : 1.25
IP : 7.80 eV



Phenanthrene

AI : 1.43
IP : 7.86 eV

higher power onto the same particle reveals the thermodynamically stable particle core. All coatings of the PAH's used in this study were observed in the mass spectra, by occurrence of their molecular ions.

In the experiments with NO_2 no reaction products could be found by LAMMA. This is in agreement with the results obtained by fluorimetric analysis. Also from the bromination study no reaction products were observed, but possibly some products might have volatilized in the vacuum of the instrument before the analysis.

In the ozone-PAH experiments an agreement existed between the results of LAMMA and fluorimetry, except for perylene.

The mass spectra found before and after O_3 treatment of the anthracene-coated particles are given in Figure 5. Also shown for comparison are the mass spectra of anthrachinone enriched onto NaCl-particles. The mass peaks at m/z = 180 and 152 are due to single and double loss of CO ($M = 28$) from the anthrachinone molecule ($M = 208.23$). While in electron impact mass spectrometry, anthrachinone yields a molecular ion mass peak at m/z = 208, in the LAMMA-spectrum a quasi-molecular ion at m/z = 209 of $(M+H)^+$

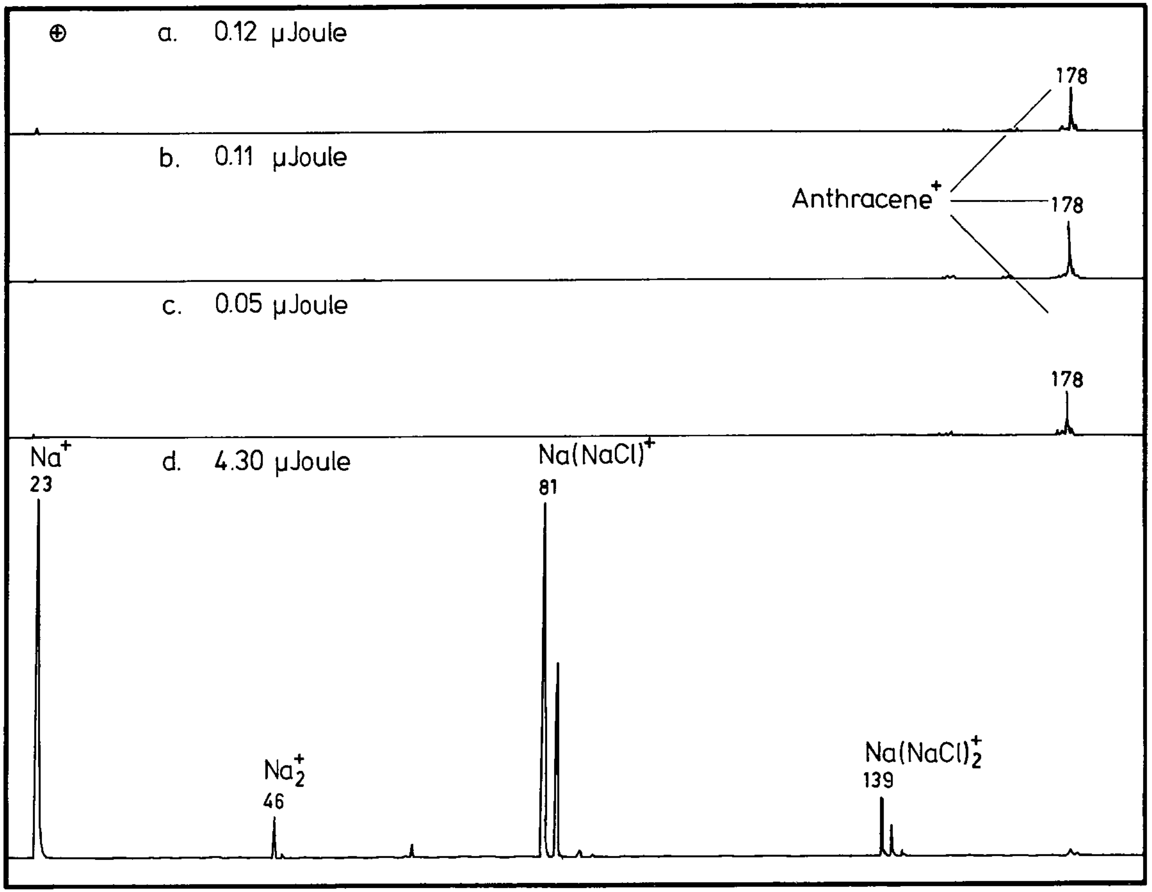


FIGURE 4 LAMMA-spectrum after subsequent laser shots onto an anthracene-coated NaCl-particle.

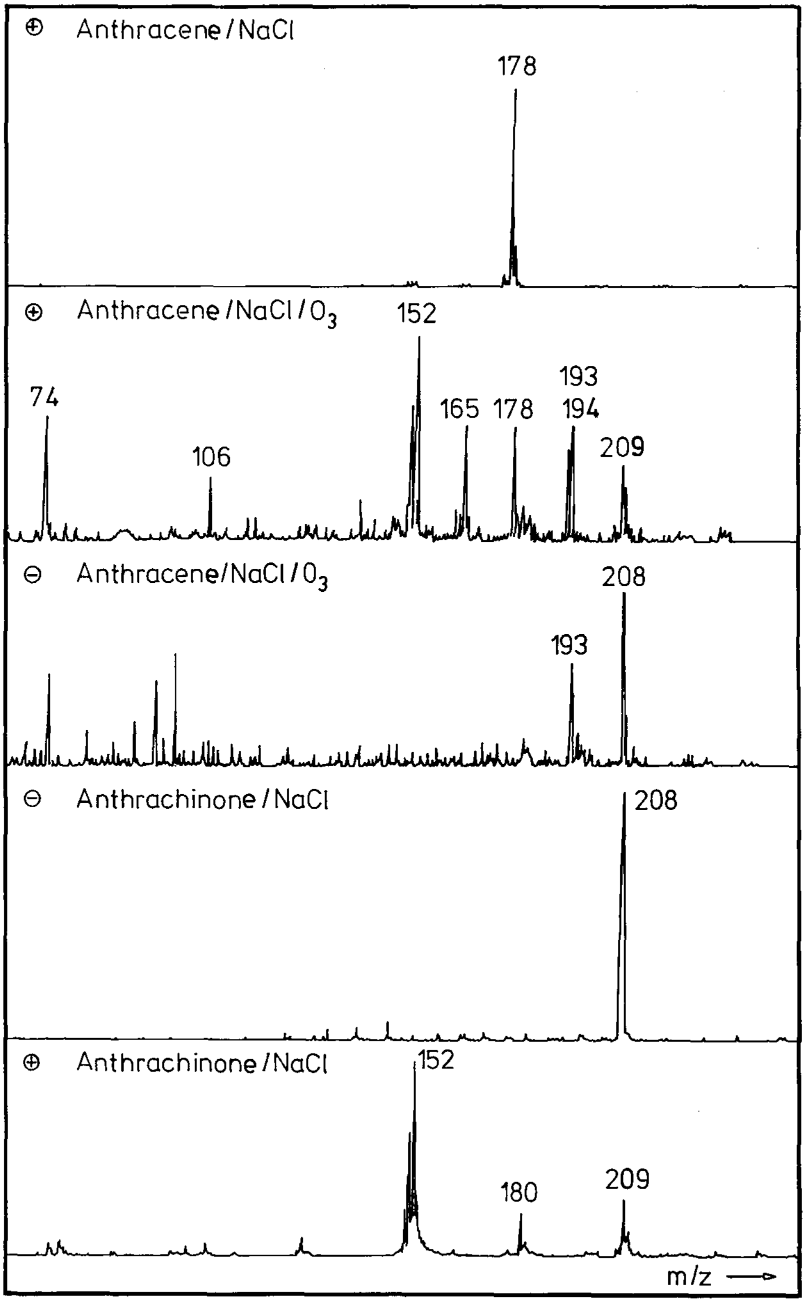
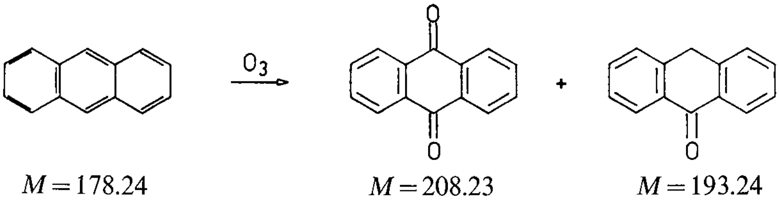


FIGURE 5 LAMMA-spectra of an untreated anthracene-coated NaCl-particle (in the positive ion mode), of an anthracene/NaCl-particle after reaction with O_3 (in the positive and negative ion mode) and of an anthrachinone-coated NaCl-particle (in the positive and negative ion mode).

shows up.[20] From the interpretation of the spectra in Figure 5, we assume the following reaction.



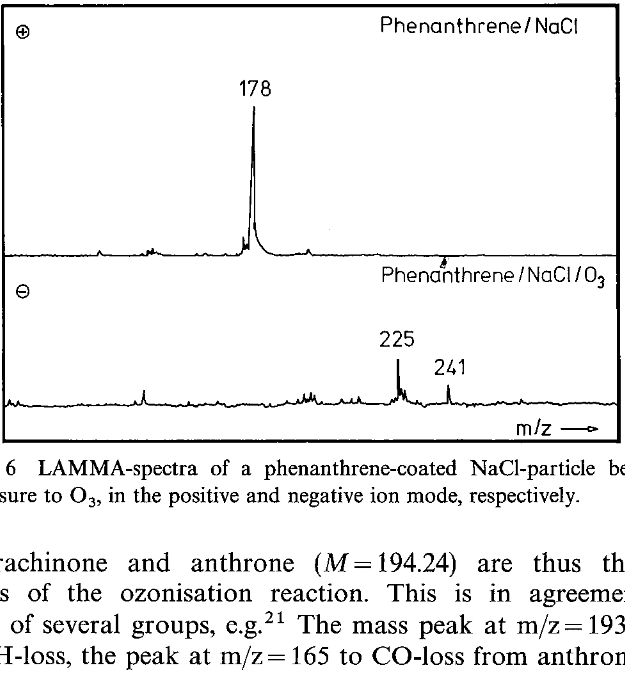
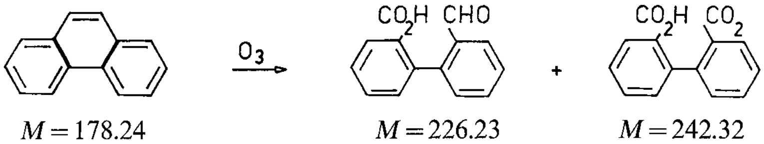


FIGURE 6 LAMMA-spectra of a phenanthrene-coated NaCl-particle before and after exposure to O_3, in the positive and negative ion mode, respectively.

Anthrachinone and anthrone ($M = 194.24$) are thus the main products of the ozonisation reaction. This is in agreement with findings of several groups, e.g.[21] The mass peak at $m/z = 193$ can be due to H-loss, the peak at $m/z = 165$ to CO-loss from anthrone.

Phenanthrene/NaCl-aerosols sometimes show a complete conversion of phenanthrene by O_3. On some particles we found also residual unreacted phenanthrene. The reaction seems to be the following (Figure 6):



The mass peaks at m/z = 225 and 241 are due to H^+-loss from the acids.

LAMMA-spectra related to pyrene/NaCl-particles are shown in Figure 7. The mass peaks at m/z = 218, 234 and 250 are due to incorporation of oxygen atoms in the pyrene molecule ($M = 202.26$).

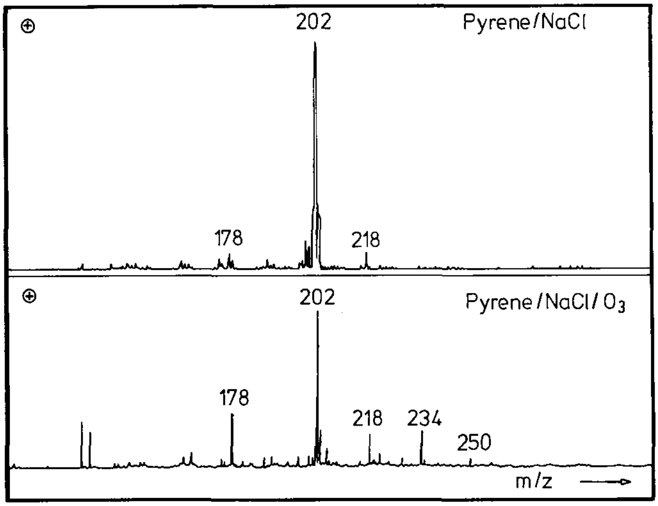


FIGURE 7 LAMMA-spectra (in the positive mode) of a pyrene-coated NaCl-particle before and after exposure to O_3.

Further unambiguous structural interpretation is not possible at present.

For the most reactive PAH used in experiments, perylene, no reaction product could be observed by LAMMA after exposure to O_3. The fact, however, that also no molecular ion was detectable in the corresponding mass spectra, strongly indicated that an efficient transformation of perylene had taken place.

CONCLUSIONS

The following conclusions can be drawn from the results presented above:

1. By application of soft consecutive laser pulses ($< 0.09\ \mu J/\mu m^2$) it is possible to elucidate the microstructure of aerosol particles by

LAMMA. For a system like PAH/NaCl, it is further possible to study gas-solid reactions and to identify reaction products at the femtogram-level by employing LAMMA in the desorption mode.

2. In case of formation of weakly-bound or thermally instable reaction products LAMMA analysis is not applicable.
3. Within the short reaction time used for the aerosol/gas mixture O_3 is more reactive than are Br_2 or NO_2. Fluoranthene and chrysene seem to be stable under all the experimental conditions described.

Further studies on the behaviour of PAH's enriched onto graphite particles, as a model for diesel exhaust aerosol, are planned.

Acknowledgement

This work was partially supported by the Belgian Ministry for Science Policy under grants 80-85/10 and 84-89/69.

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