Contribution of Basic and Neutral N-Compounds to the Adverse Health Effects of Ambient Aersols

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This work is attributed to structures which can be deduced from the wide-spread structure of PAHs in aerosols. Amino- and Cyano-PAH as well as basic and neutral azaarenes were chosen as target components (fig. 1).

The low concentration level of these analytes and the complexity of the ambient aerosol matrix make the development of a selective and sensitive analytical method necessary.
LC hyphenated with tandem MS is the appropriate technique. To provide selectivity a triple-quadrupole instrument working in MS/MS mode was used.
Because the sensitivity of electrospray source (ESI) was not sufficient Atmospheric Pressure Photoionisation (APPI) as a new ionization technique was used. Fig.2 shows the ionization principle of APPI and APCI (Atmospheric Pressure Chemical Ionisation).
For Amino-PAH a 5-10-fold increase in sensitivity was achieved. Basic azaarenes exhibit the same effect for early eluting peaks. Late eluting peaks didn't show a similar effect. Fig. 3 gives an overview of the influence of the ionization source on sensitivity.

The characteristic fragmentation pattern of each compound, schematic depicted in fig. 4 for Amino-PAH, were used to build at least 2 MRMs. The first MRM was used for quantification whereas the second was used to qualify the first.
Fig. 5 shows these MRMs used for the investigation of the aerosol samples. Limits of quantification achieved are given in table 1.

Because many compounds occur as isomers described "two-dimensional" selectivity (select mass 1 in quad1, fragment and extract a characteristic daughter ion with mass 2 in quad2) provided by the mass spectrometer itself is not sufficient. Therefore a third dimension has to be established by means of chromatography. Optimisation of separation resolution is often time-consuming therefore Dry Lab(TM) as a software assisted approach was used. The computer optimized separations were in good agreement with measurements for basic and neutral azaarenes (Fig. 6). Due to a good initial resolution in the case of Amino-PAH optimisation was not necessary. For a different column (Phenyl instead of C-18) the computer assisted evaluation shows that a quick and straight optimisation was not possible.

The developed LC-MS methods were used to measure the atmospheric levels of these compounds at a high traffic volume road in the north of Munich.
Samples were collected on glass fiber filters by a high volume Anderson sampler equipped with a 2.5 µm head. The filters were extracted with methanol/methylene chloride in an ultrasonic bath. Samples were concentrated before injection. Fig. 7 with table 2 shows results of LC-MS measurement of a filter extract.

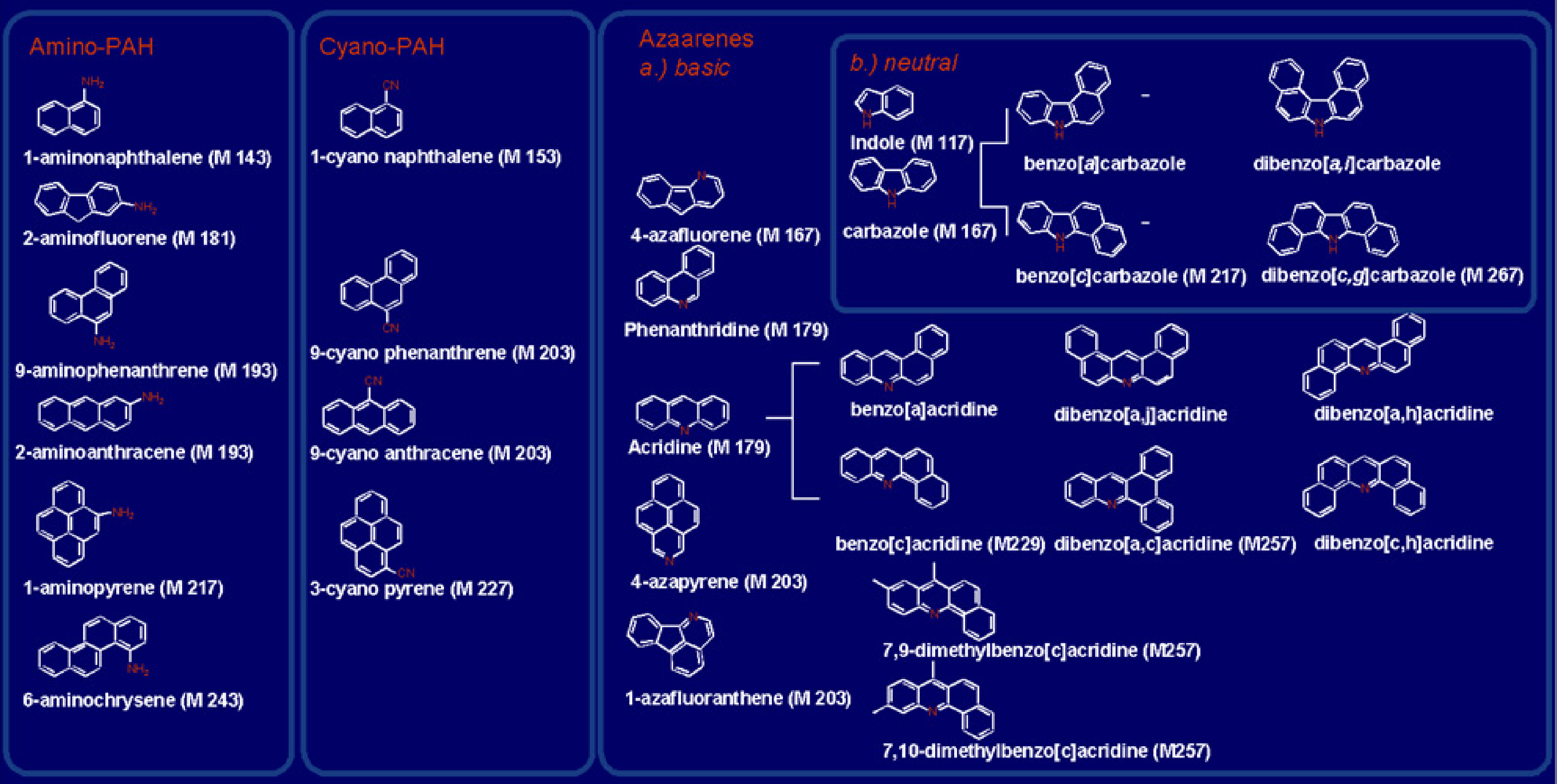
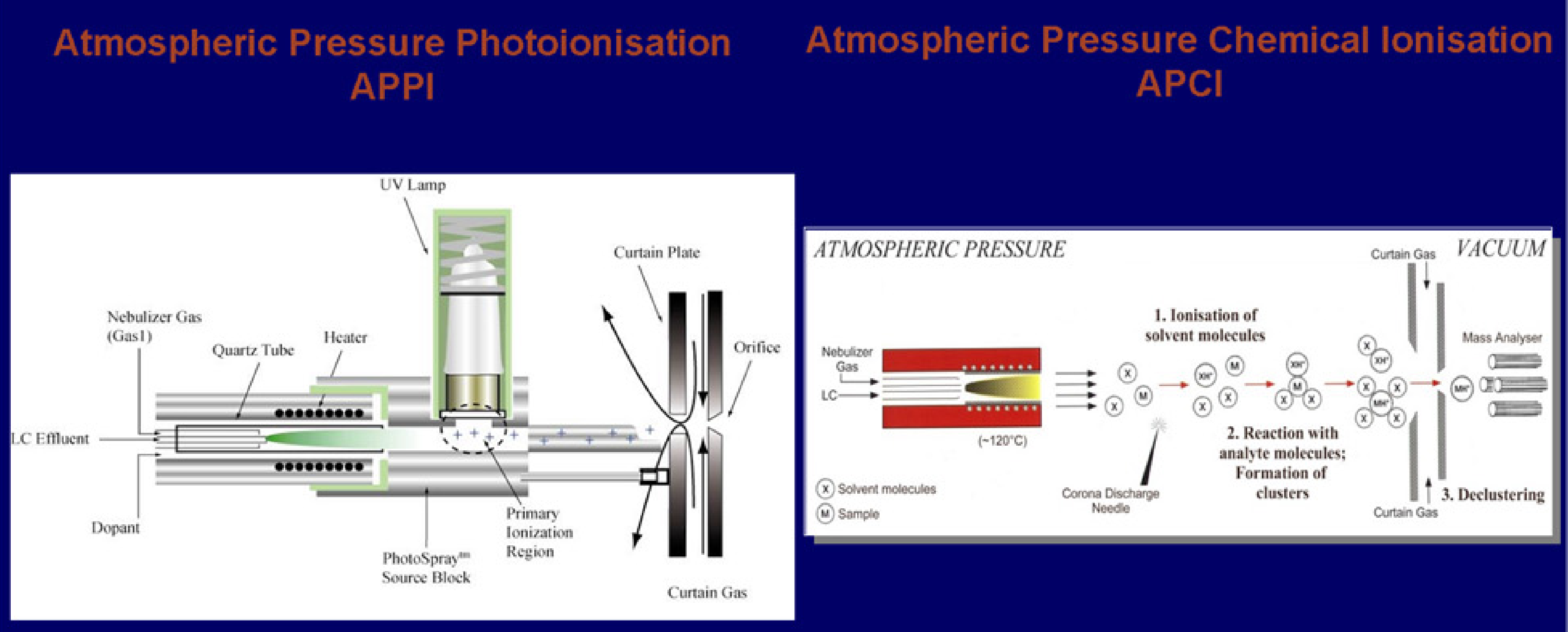


Fig. 1: Target Components


Atmospheric Pressure Photoionisation APPI

Atmospheric Pressure Chemical Ionisation APCI

Fig. 2: Ionisation principle of APPI and APCI

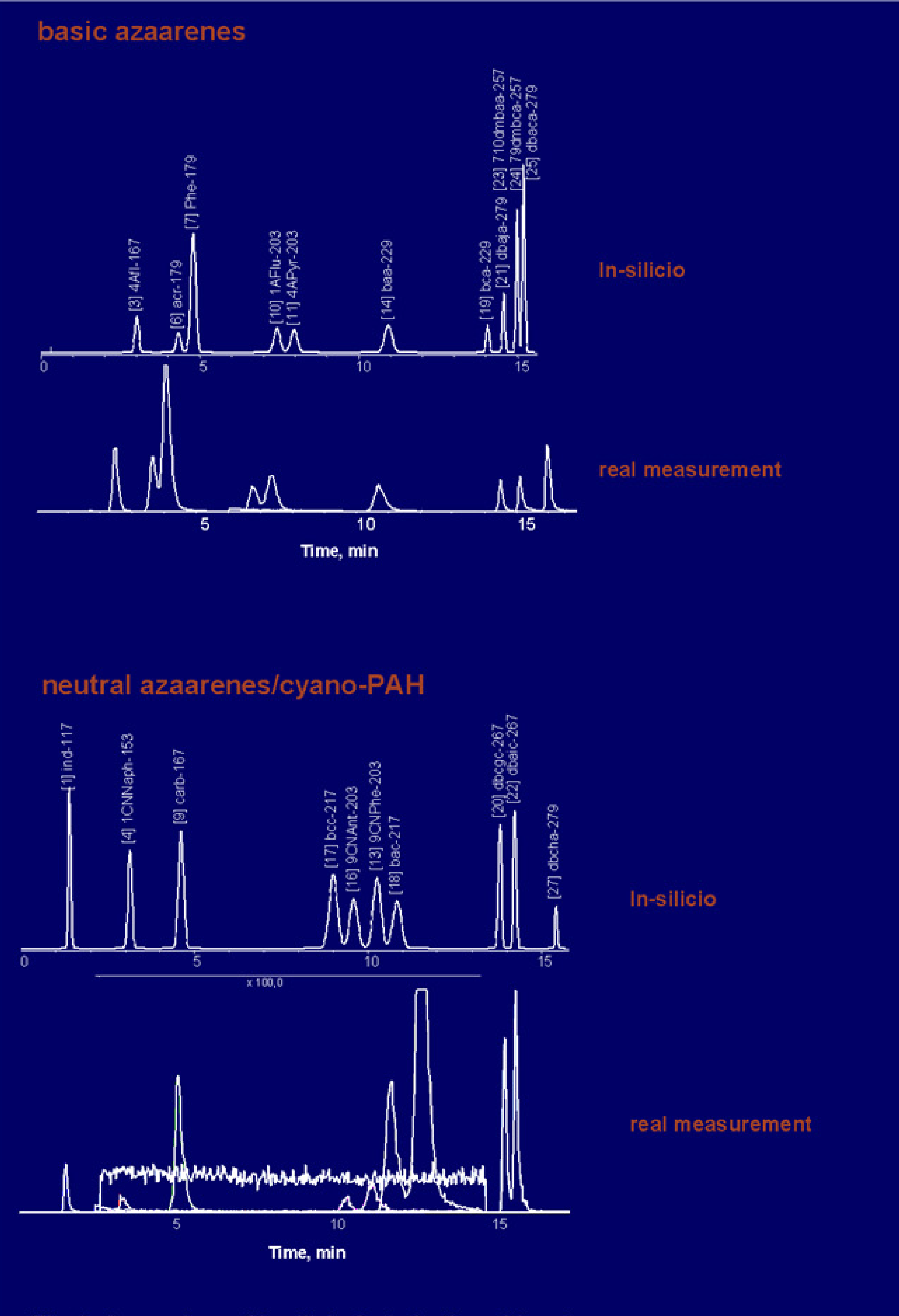


Fig. 6: Comparison of In-silicio Optimization with real measurement

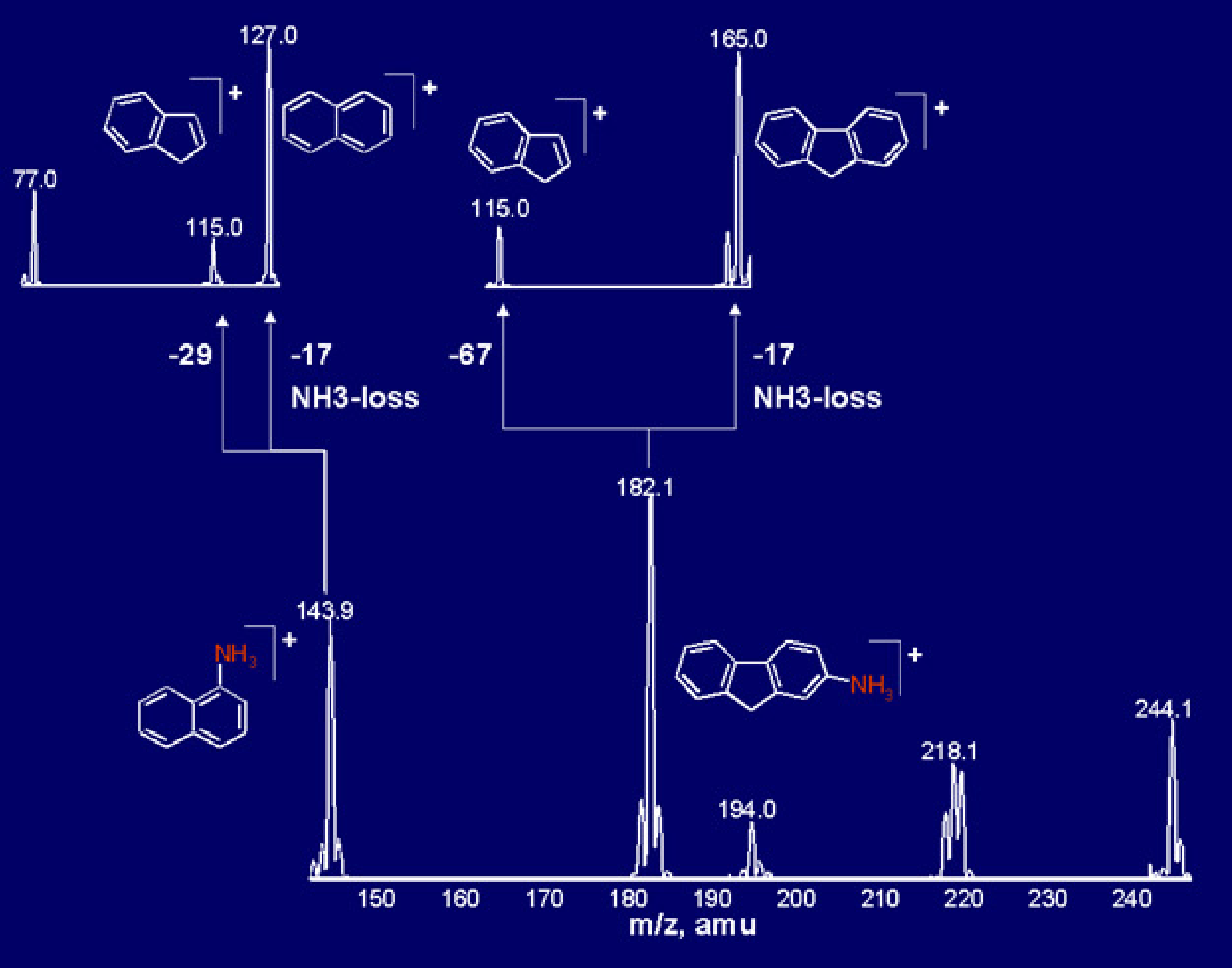


Fig. 4 Scheme of characteristic fragmentation

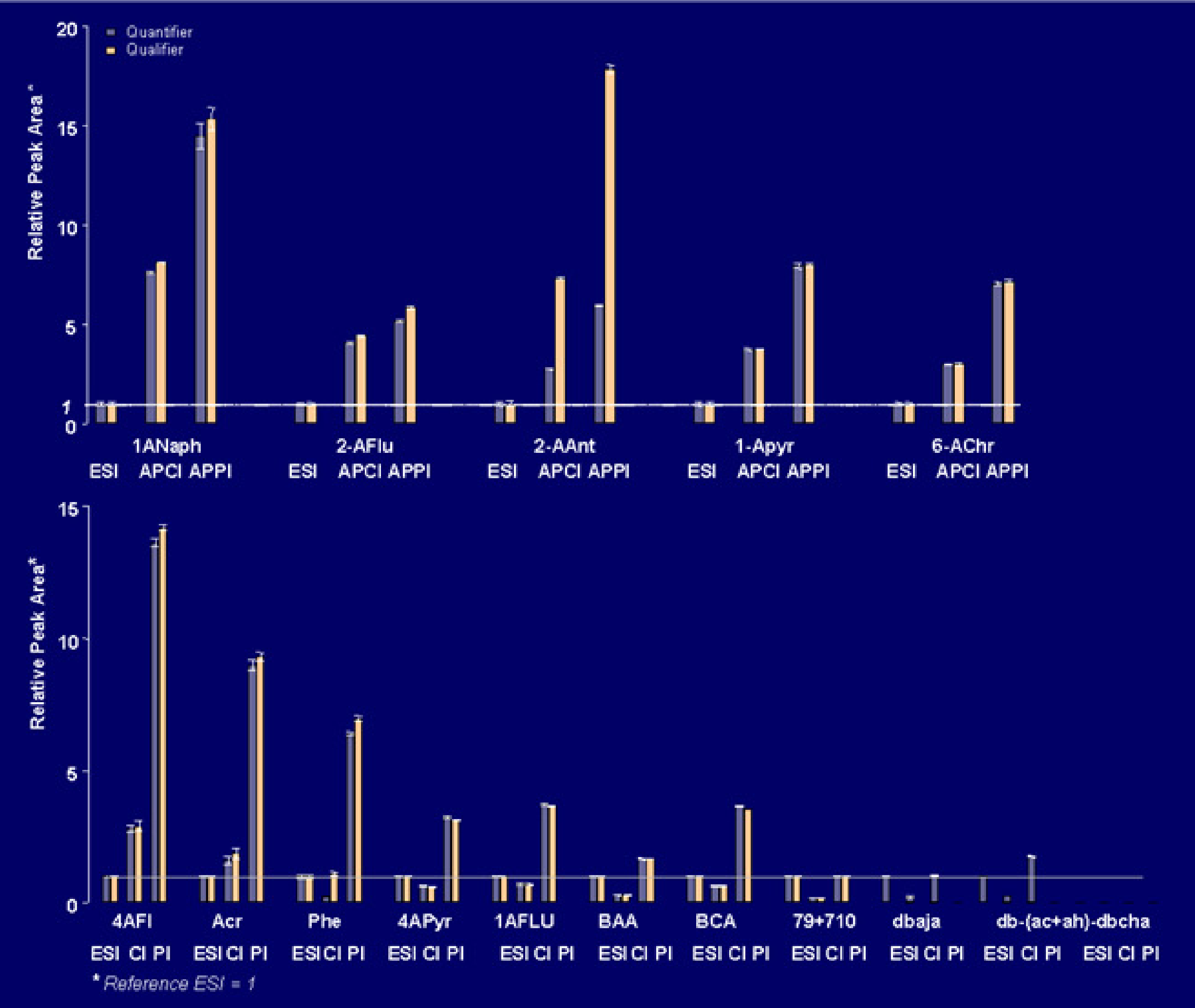


Fig. 3 Influence of ionisation source on sensitivity

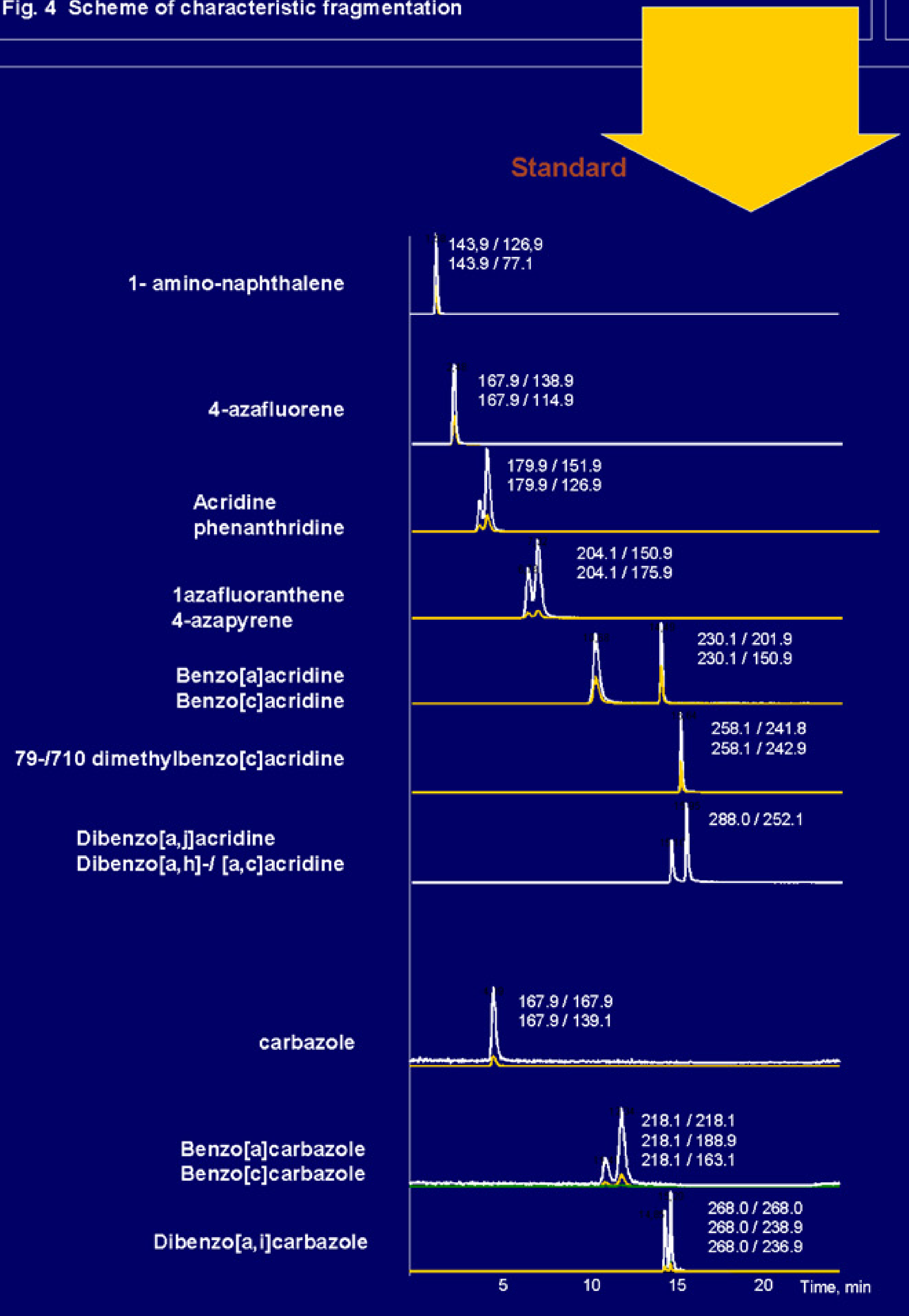


Fig. 5 MRMs used for measurement

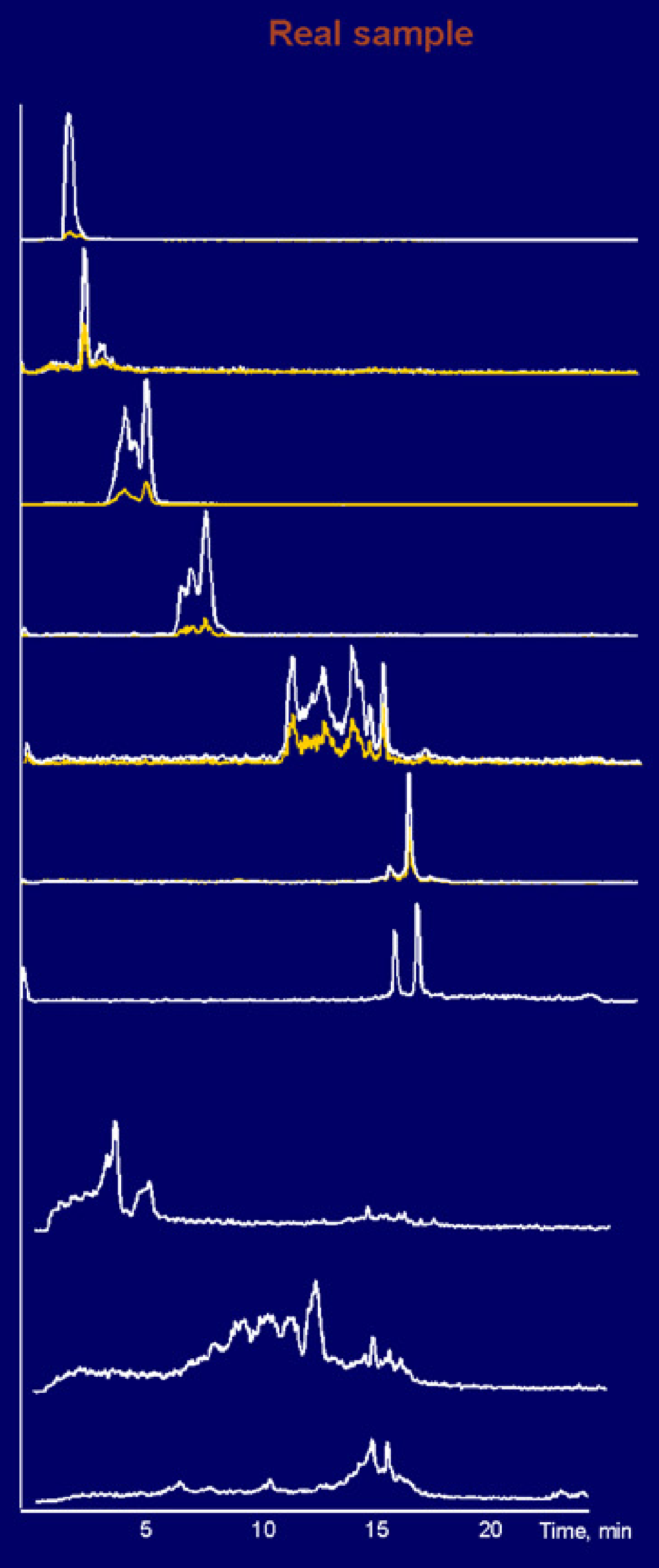


Fig. 7 LC/MS/MS of ambient aerosol

Compound	LOQ* (pg/µl)
4-azafluorene	3,5
Acridine	0,5
Phenanthridine	1.0
1-azafluoramthene	4.0
4-azapyrene	4
Benzo[a]acridine	0.5
Benzo[c]acridine	0.5
Dimethylbenzo[c]acridine	0.5
Dibenzo[a,j]acridine	0.5
Dibenzo[a,h]acridine Dibenzo[a,c]acridine	2.5
1-amino naphthalene	0.1
2-amino fluorene	0.5
9-amino phenanthrene	1.0
1-amino pyrene	1.5
6-amino chrysene	2.0
indole	1.5
1-cyanonaphthalene	200.0
Carbazole	12.5
9-amino phenathrene	300.0
2-amino anthracene	300.0
Benzo[a]carbazole	15.0
Benzo[c]carbazole	10.0
Dibenzo[c,g]carbazole	12.0
Dibenzo[a,i]carbazole	12.0

Table 1: Limits of Quantification

Compound	LOQ* (pg/m3)
4-azafluorene	detected
Acridine	2.0
Phenanthridine	1.7
1-azafluoramthene	4.8
4-azapyrene	detected
Benzo[a]acridine	detected
Benzo[c]acridine	detected
Dimethylbenzo[c]acridine	detected
Dibenzo[a,j]acridine	detected
Dibenzo[a,h]acridine Dibenzo[a,c]acridine	detected
1-amino naphthalene	0.2
2-amino fluorene	./.
9-amino phenanthrene	./.
1-amino pyrene	./.
6-amino chrysene	./.
indole	./.
1-cyanonaphthalene	./.
Carbazole	42.1
9-amino phenathrene	./.
2-amino anthracene	./.
Benzo[a]carbazole	detected
Benzo[c]carbazole	8.0
Dibenzo[c,g]carbazole	1.2
Dibenzo[a,i]carbazole	detected

Table 2: Concentration in ambient aerosol