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DEVELOPMENT AND VALIDATION OF A LC/APCI/TOF-MS METHOD TO QUANTIFY NITRATED AND OXYGENATED PAHS IN ATMOSPHERIC AEROSOLS

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Abstract: A new method for the analysis of 12 nitrated polycyclic aromatic hydrocarbons (NPAHs) and 9 oxygenated polycyclic aromatic hydrocarbons (OPAHs) has been developed using reversed-phase liquid chromatography (LC) coupled to mass spectrometry (MS). Validation has been carried out on NIST standard reference materials and compared with certified data. Results are briefly discussed.

Keywords: nitrated polycyclic aromatic hydrocarbons oxygenated polycyclic aromatic hydrocarbons, particulate organic matter, ultra-performance liquid chromatography (UPLC), time-of-flight mass spectrometry (ToF-MS).

1. INTRODUCTION

Atmospheric aerosols are complex matrices composed of different chemical species potentially harmful to human health. Polycyclic aromatic hydrocarbons (PAHs) are well-known carcinogenic and/or mutagenic compounds, emitted by incomplete combustion (e.g. [1], [2]). Once in the atmosphere, they redistribute between both the particulate and the gas phases.

PAHs derivatives, such as NPAHs and OPAHs, seem to be even more toxic than their related parent PAHs and are also found in airborne particulate matter [3-4]. They can be directly emitted by combustion processes or formed in the atmosphere by both gas and heterogeneous reactions of PAHs induced by atmospheric oxidants (OH, NO₃; NO₂, O₃). Little is known about their behavior and their typical concentrations in airborne particulate matter, as their analysis generally requires several purification and pre-concentration steps.

NPAHs and OPAHs have already been analyzed by gas chromatography/mass spectrometry methods (e.g. [5]). But this technique involves time-consuming procedures like sample purification and derivatization steps. LC generally requires less sample clean-up, and derivatization steps are usually not necessary. For some of these compounds LC coupled to mass spectrometry with atmospheric pressure ionization (LC/APCI/MS) has already been applied successfully [6-9]. To the best of our knowledge, few studies [8] have used ToF-MS to characterize and quantify PAHs derivatives in particulate matter. One of its main advantages is its accurate mass measurements which can prove very useful when analyzing air samples since it can lessen the matrix interferences from coeluting impurities and it allows unequivocal identification of target compounds

from complex matrices, as well as the possibility of quantification at low-level concentrations.

In this work, a new method for the simultaneous detection and quantification of 21 NPAHs and OPAHs (Figure 1) using LC/MS is reported.

2. EXPERIMENTAL

2.1. Materials

ULC-MS solvents (CH₃CN, CH₃OH, H₂O, CH₂O₂) were purchased from Biosolve (Valkenswaard, the Netherlands). Reference NPAHs and OPAHs were obtained from Aldrich (St-Quentin Fallavier, France) and Carlo Erba SDS (Peypin, France). If standard substances at different qualities were available, the highest purity was chosen. Leucine Enkephalin was purchased from Aldrich.

Stock solutions of NPAHs and OPAHs (0.02-10 mg.L⁻¹) were prepared in methanol. The stock solutions were further diluted between 10 and 40,000 times to give a series of standards.

Standard reference samples of Diesel Particulate Matter (SRM 1650) and Urban Dust (SRM 1649) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were used.

2.2. Extraction

Extractions of NPAHs and OPAHs were carried out by a pressurized solvent extractor (ASE 200, Dionex SA, Voisins-le-Bretonneux, France) with cells of 11 mL. Methanol was used as the extraction solvent. A cellulose filter (Ø = 1.923 cm, 049458, D28, Dionex SA) was inserted at the bottom of the cell. Then particles were weighted on a quartz fiber filter (Ø = 47 mm, PALLFLEX, VWR, Fontenay-sous-Bois, France) which was folded to be introduced into the cell. Finally, Fontainebleau sand (VWR) was added to fill up the cell. Extraction parameters were as follows: 120°C extraction temperature, 2,000 psi nitrogen pressure, 8-min static time, 60% flush, 40 s purge.

The extracts were concentrated by evaporation under a nitrogen stream (TurboVap, Zymark Corp., Hopkinton, MA, USA) at 60°C down to a volume of 1 mL.

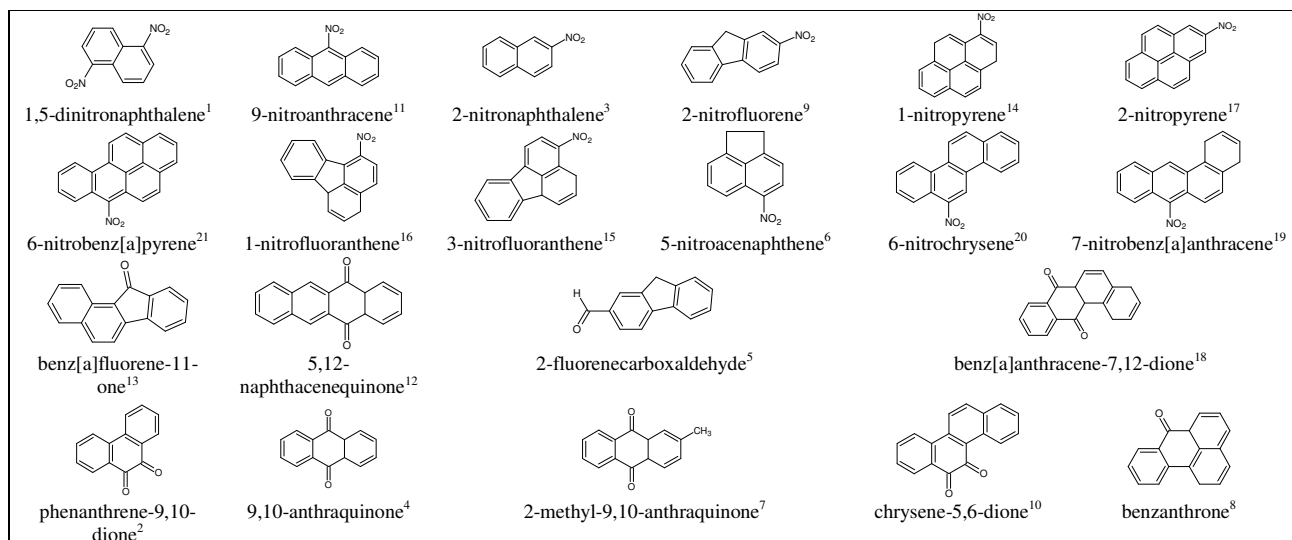


Fig. 1. Structures of the 12 NPAHs and 9 OPAHs studied
The superscript number refers to the elution order in Fig.2 chromatogram

2.3. Instrumentation

Analyses of the extracts were performed by a Waters Acquity UPLC[®] pump coupled to a PDA detector and a LCT Premier XE Time-of-Flight mass spectrometer (Waters, Millford, MA, USA). The MS detector was connected to the LC system through an atmospheric pressure chemical ionization (APCI) source running in negative mode. Instrument control, data acquisition and analysis were performed with MassLynx version 4.1.

The LCT Premier XE Time-of-Flight mass spectrometer was coupled to the UPLC[®] system with an atmospheric chemical ionization (APCI) interface, which consists of a heated nebulizer probe and an atmospheric pressure source equipped with a corona discharge pin. Accurate mass spectra for negative ions were recorded across the range from m/z 50–1000 each 0.2 s. Nitrogen was used as the drying gas. The instrument was tuned to provide a resolution of 12,000 FWHM. The mass axis was calibrated using a sodium formate solution over the m/z 50–1000 range. A lock-mass of leucine enkephalin ($[M-H]^- = 555.2645$ for the negative ion mode) at a concentration of 2.0 ng μL^{-1} in 50:50 acetonitrile:water containing 0.1% formic acid was infused at a flow rate of 0.05 mL min^{-1} via a lock spray ionization source with the help of a second HPLC pump (Waters Reagent Manager). Data were collected in the centroid mode and the lock-mass data were averaged over 50 scans for correction.

3. RESULTS AND DISCUSSION

3.1. Extraction procedure

The applicability of ASE for the extraction of PAHs from aerosol samples has been evaluated and optimized in a parallel study where it provides good repeatability and recoveries, as well as low time and solvent consumption. Similarly to the work carried out in the case of PAHs, blank filters ($n=5$) were spiked with a known amount of NPAHs

and OPAHs and were extracted keeping parameters the same as for PAHs extraction. Methanol, also the analysis solvent, was used for extraction. Possible evaporation losses from the concentration step were investigated and found to be less than 10% for almost all the standard compounds, except for 2-fluorencarboxaldehyde and 9,10-anthraquinone.

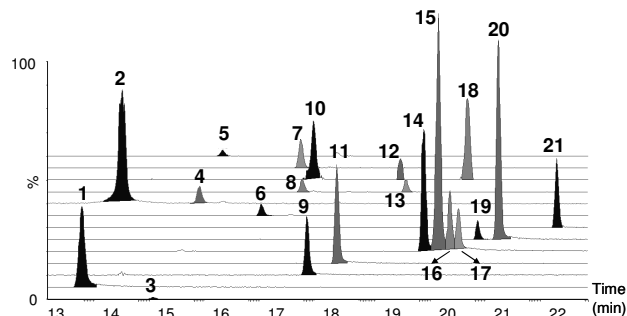


Fig.2. LC/ToF-MS ion chromatograms of a standard solution of NPAHs and OPAHs with APCI in negative mode

3.2. Suitable chromatographic conditions

A good chromatographic separation of the analytes (Figure 2) needed to be achieved, in order to differentiate isomeric compounds such as nitrofluoranthenes in the mass spectrometer. The chromatographic separation was performed on an Acquity UPLC[®] BEH C18 column (100 mm \times 2.1 mm i.d., 1.7 μm , Waters). Different elution conditions - with water, methanol and acetonitrile - and different concentrations of acid in the mobile phase have been tested. The addition of an acid to the mobile phase was required to enhance the sensitivity of the APCI. The two mobile phases were - phase A: acidified water (10 mM formic acid); phase B: methanol. A linear gradient was programmed - 0 min: 20% B; 20 min: 90% B; 27 min: 90% B; 30 min: 20% B. The flow rate was 0.2 mL min^{-1} . The column was held at 30°C. The injection volume was 5 μL . The Acquity UPLC[®] HSS T3 column (100 mm \times 2.1 mm

i.d., 1.8 μm , Waters) was also tested without improving the separation. UV chromatograms were monitored across the range 190-500 nm with a resolution of 1.2 nm.

3.2. LC/APCI/ToF-MS parameter optimization

The main instrumental parameters (corona current, cone voltage, probe gas flow and temperature, and aperture 1 voltage) were optimized to provide the best possible sensitivity within the recommended range of values (cf. Table 1).

Optimizations were carried out by chromatographic separation of a standard solution and the signal area obtained for each compound was plotted as a function of the settings value. Parameters were sequentially optimized, using the optimized values in the following optimization steps. For all compounds, the major peak in the mass spectra was either the $[\text{M}]^-$ or the $[\text{M}-\text{H}]^-$ molecule and for each parameter, a compromise providing the optimal sensitivity for all compounds was chosen.

Interestingly, in the higher range of aperture 1 voltages the fragmentation of the analytes is increased and allows the use of one or two specific fragments for confirmation purposes.

Table 1. Optimized parameter values of the APCI interface

Parameter	Test range	Optimum value
Corona current (μA)	3-35	25
Cone voltage (V)	0-100	30
Probe temperature ($^{\circ}\text{C}$)	100-650	400
Source temperature ($^{\circ}\text{C}$)	70-150	100
Probe gas flow (L h^{-1})	50-600	300
Cone gas flow (L h^{-1})	0-150	30
Aperture 1 voltage (V)	2-25	8
Ion guide 1 voltage (V)	2-15	2

3.3. Accurate mass measurements

Checking the accuracy of mass measurements was carried out using the following procedure. The m/z of the analytes (using a mass interval of 0.01 Da) was extracted from the total ion chromatogram (TIC), to obtain an extracted ion chromatogram. The accurate masses of the molecular ions $[\text{M}]^-$ were used for both identification and quantification purposes in all cases, except for 2-fluorene-carboxaldehyde, 5-nitroacenaphthene and 2-nitrofluorene, which showed deprotonated ions. Accurate mass data of the molecular ions were then processed through the software, which provided a list of molecular formula assignments based on the accurate mass and the isotopic intensity pattern (i-fit). For each compound, the best elemental formula corresponded to the expected molecule. Accuracy of mass measurements for a standard solution of the 21 PAH derivatives is shown in Table 2. Errors were less than 5 ppm in most cases with an average value of about 1 ppm. The widely accepted accuracy threshold for confirmation of elemental compositions has been established at 5 ppm. The

corresponding mass spectrum together with the characteristic retention time and UV spectrum provided unique elemental composition assignment.

The effect of matrix complexity from standard reference samples and filters was evaluated and no significant differences were observed in the accuracy compared to those prepared with pure solvents, keeping the relative error below 5 ppm. Therefore the method can be considered as specific and selective.

3.4. Method validation

Sensitivity, accuracy, precision and linearity of the method were investigated for validation.

Instrumental limits of detection (LOD) were calculated for all standard compounds and were defined as three times the signal-to-noise ratio ($S/N=3$). LOD ranged from 10 to 295 pg for NPAHs, and from 45 to 1185 pg for OPAHs. Values of instrumental LODs obtained for NPAHs were in the same order of magnitude as those obtained by [8]. Those obtained for OPAHs were less sensitive than those obtained by [9]. However in this latter work an LC-APCI-MS-MS was used which produced some selective fragmentation patterns leading to an increase of selectivity and sensitivity. Quantitation limits (LOQ) were considered as the analyte concentration that gives $S/N = 10$.

Accuracy was estimated with the determination of recovery factors from the extraction of five blank filters spiked with a standard mixture. The extraction method presented here gives acceptable recovery values ($> 80\%$) for almost all the standard compounds. However the obtained value for chrysene-5,6-dione and phenanthrene-9,10-dione were as low as 39% and 41%, respectively, but with estimated concentrations comparable to the detection limits, where small area variations strongly affect the measured concentrations. Recovery corrections were applied to the NPAHs and OPAHs measurement values.

The repeatability of the response was checked by injecting the same standard solution seven times in one day. The reproducibility of the response was carried out for three successive days using the same solution. From the results obtained, the developed method was found to be precise (with run-to-run instrumental RSD $< 7\%$ and day-to-day RSD $< 13\%$). In addition, RSD values of retention time (R_t) were less than 0.1% for repeatability and reproducibility.

Calibration plots were drawn from six different concentration levels up to 3 orders of magnitude, using standard solutions ranging from 0.02 to 10 mg L^{-1} . Excellent linearity was observed for all compounds with determination coefficients $R^2 > 0.992$ in most cases. Due to some disadvantages and limitations, such as the narrow dynamic range, LC/ToF-MS has been applied mainly for confirmatory analyses rather than for quantification in the past few years. A Dynamic Range Enhancement (DRE) is used in this work providing thus an enhanced linear dynamic range and this makes possible its successful applicability to NPAHs and OPAHs analyses.

2-Methyl-9,10-anthraquinone	1661 (216)	-	-	-	-	-	-	-	-	1200
Benz[a]fluoren-11-one	3232 (259)	-	3512 (284)	1890 (300)	1900 (210)	-	-	-	-	-
Benzenanthrone	6414 (577)	-	3715 (872)	1310 (20)	4500 (340)	-	-	-	-	6700 ⁱ
Chrysene-5,6-dione	<5369	-	-	-	-	-	-	-	-	-
2-Fluorene-carboxaldehyde	<1833	-	-	-	-	-	-	-	-	-
Benz[a]anthracen-7,12-dione	7520 (226)	-	8459 (797)	7465 (1100)	2400 (250)	-	-	-	-	-
5,12-Naphthacene-quinone	<6915	-	-	-	-	-	-	-	-	2600
1-Nitrofluoranthene	613 (43)	-	-	-	-	-	-	<2	-	-
3-Nitrofluoranthene	<115	4.5 (1.8) ^b	-	-	-	-	-	4.5 (1.8)	1.9 (0.15)	-
9-Nitroanthracene	<100	33.4 (6.1) ^b	39.1 (4.2)	-	-	-	34.0 (1.0)	35.9 (0.6)	70 (11)	-
7-Nitrobenz[a]anthracene	<80	27.8 (6.7) ^b	11.1 (7.2)	-	-	-	25.0 (1.0)	35.1 (3.6)	15 (2.0)	-
6-Nitrochrysene	<57	4.01 (0.52) ^b	1.8 (0.3)	-	-	-	3.0 (0.6)	4.4 (0.2)	2.5 (0.6)	-
1-Nitropyrene	<802	70.9 (4.3) ^b	104.5 (6.4)	-	-	-	78.0 (8.0)	71.5 (5.2)	40 (3.6)	-
2-Nitropyrene	<225	24.4 (4.0) ^c	190.0 (51.4)	-	-	-	-	24.4 (4.1)	7.0 (0.1)	-
2-Nitronaphthalene	<2529	10.0 (0.5) ^c	12.0 (2.4)	-	-	-	-	10.0 (0.5)	12 (1.7)	-
5-Nitroacenaphthene	<993	3.1 (0.3) ^c	-	-	-	-	-	3.1 (0.3)	4.2 (3.1)	-
1,5-Dinitronaphthalene	<98	-	-	-	-	-	-	-	nd	-
2-Nitrofluorene	<439	-	<0.4	-	-	-	<2	<3	2.6 (3.4)	-
6-Nitrobenz[a]pyrene	<58	-	25.0 (6.7)	-	-	-	<0.8	<40	nd	-

^a standard deviation for n=1(7 injections) in brackets. Less than values are the analytical limits of detection; ^b certified value; ^c reference value; ^d n=1; ^e n=6; ^f n=1(3 injections); ^g n=12; ^h n=3; ⁱ benzenanthrone and 1-pyrenecarboxaldehyde were co-eluted. nd: not detected.

Table 4. OPAHs and NPAHs concentrations (ng g⁻¹) in SRM 1650 (diesel particulate)

	This work ^a	NIST	Schauer <i>et al.</i> [8] ^d	Bamford <i>et al.</i> [14] ^d	Crimmins & Baker [15] ^d	Turrio-Baldassarri <i>et al.</i> [16] ^d	Oda <i>et al.</i> [17]
9,10-Anthraquinone	82853 (4143)	-	-	-	-	-	62000
Phenanthrene-9,10-dione	146046 (5842)	-	-	-	-	-	-
2-Methyl-9,10-anthraquinone	54106 (2705)	-	-	-	-	-	46000
Benz[a]fluoren-11-one	6975 (907)	-	-	-	-	-	-
Benzenanthrone	13920 (2088)	-	-	-	-	-	24000 ^e
Chrysene-5,6-dione	<24437	-	-	-	-	-	-
2-Fluorene-carboxaldehyde	<8343	-	-	-	-	-	-
Benz[a]anthracen-7,12-dione	<10212	-	-	-	-	-	-
5,12-Naphthacene-quinone	<31473	-	-	-	-	-	16000
1-Nitrofluoranthene	<526	272 (6) ^c	-	274 (12)	-	-	-
3-Nitrofluoranthene	<525	65.1 (3.4) ^c	<30	65.2 (7.4)	54 (3.8)	180 (20)	-
9-Nitroanthracene	8139 (407)	5890 (310) ^b	930(150)	6080 (190)	13000 (350)	-	-
7-Nitrobenz[a]anthracene	<363	967 (42) ^b	2230(130)	995 (68)	390 (48)	-	-
6-Nitrochrysene	<258	45.5 (1.9) ^b	<30	44.4 (3.4)	36 (3.4)	-	-
1-Nitropyrene	13722 (1098)	18200 (200) ^b	16100(1200)	18330 (340)	16000 (1200)	20200 (400)	-
2-Nitropyrene	<1024	-	-	<4	nd	-	-
2-Nitronaphthalene	<11510	236 (3) ^c	140(30)	238 (3)	116 (2.9)	240 (10)	-
5-Nitroacenaphthene	<4520	36.9 (1.3) ^c	-	37 (2.9)	46 (5.5)	-	-
1,5-Dinitronaphthalene	<448	-	-	-	nd	-	-
2-Nitrofluorene	<2000	45.5 (1.4) ^c	240(10)	46.2 (2.6)	44 (3.3)	580 (40)	-
6-Nitrobenz[a]pyrene	<262	1390 (100) ^b	1440(60)	1442 (47)	970 (300)	-	-

^a standard deviation for n=1(7 injections) in brackets. Less than values are the analytical limits of detection; ^b certified value; ^c reference value; ^d n=3; ^e benzenanthrone and 1-pyrenecarboxaldehyde were co-eluted. nd: not detected.

4. CONCLUSION

In this work, a new method for the simultaneous detection and quantification of 21 NPAHs and OPAHs by LC/APCI/ToF-MS has been developed. The resolving power, accurate mass measurement capability and full spectral sensitivity allowed for the determination of the target compounds in complex matrices. So far, the analytical procedure has been applied to NIST SRM1649 and SRM1650, giving results in good agreement with the few data available in the literature and leading to the first determination of NPAHs and OPAHs in the Diesel particulate. This method will be used to investigate NPAHs and OPAHs concentrations in ambient air samples.

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