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Simultaneous Determination of 79 Polar and Non-Polar Polycyclic Aromatic Compounds in Airborne Particulate Matter by Gas Chromatography – Tandem Mass Spectrometry

Mathieu Galmiche^{a,b} , Alexandre Sonnette^a, Michel Wolf^a, Christophe Sutter^a, Olivier Delhomme^{a,c} , Yannis-Nicolas François^b , and Maurice Millet^a 

^aInstitut de Chimie et Procédés Pour L'Énergie, L'Environnement et la Santé (ICPEES) – Physico-Chimie de L'Atmosphère, Université de Strasbourg – CNRS, UMR 7515, Strasbourg, France; ^bLaboratoire de Spectrométrie de Masse Des Interactions et Des Systèmes (LSMIS), Université de Strasbourg – CNRS, UMR 7140, Strasbourg, France; ^cUFR Sciences Fondamentales et Appliquées, Université de Lorraine, Metz, France

ABSTRACT

Research on Polycyclic Aromatic Compounds (PACs) in the atmospheric environment has been mainly focused on the 16 EPA's PAHs. Due to toxicological relevance and particular emission sources, there is a research need in broadening the scope of PACs analysis to include polar and semi-polar PACs in new analytical methods. Here, we describe a single GC-MS/MS method to simultaneously determine 79 polar, semi-polar and non-polar PACs. Temperature gradient and injection conditions were optimized. Optimal Multiple Reaction Monitoring (MRM) and pseudo-MRM mass transitions were searched to enhance the detection. PACs were extracted from particulate samples by Pressurized Liquid Extraction (PLE). The choice of the optimal extraction solvent was carefully evaluated. Instrumental LOQ were from 1 to 2 ng. The method was validated against linearity of the calibration, intra-day and inter-day variability, LOQ and recoveries. The analysis of a Diesel Particulate Matter Certified Reference Material enabled a firm method validation. The method was applied to PM₁₀ samples from a residential parking lot. PACs total amount varied from 2.3 to 14 ng/m³. The most abundant PACs were phthalic anhydride, 1,8-naphthalic anhydride and benzo(b)fluoranthene. PAHs diagnostic ratios enabled the identification of fuel combustion and vehicular traffic as the main source of PACs.

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KEYWORDS


PAHs; polar PACs; polycyclic aromatic heterocycles; GC-MS; pressurized liquid extraction

Introduction

Airborne particulate matter (PM) is of great concern for its known health and environmental effects.^{1–4} PM in outdoor air pollution is registered by the International Agency for Research on Cancer (IARC) as carcinogenic to humans, and is suspected to cause millions of premature deaths in the world each year.^{3,5–7}

Among the organic pollutants of interest in airborne PM, Polycyclic Aromatic Hydrocarbons (PAHs) play a major role.^{6,8–11} They have been studied for decades, mainly according to the list of 16 priority pollutants from the U.S. Environmental Protection Agency.¹² Besides these PAHs, their polar derivatives such as nitrated PAHs (NPAHs) and oxygenated PAHs (OPAHs), their heterocyclic

CONTACT Maurice Millet  mmillet@unistra.fr  Institut de Chimie et Procédés pour l'Énergie, l'Environnement et la Santé (ICPEES) – Physico-Chimie de l'Atmosphère, Université de Strasbourg – CNRS, UMR 7515, 25 rue Becquerel, 67000 Strasbourg, France

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derivatives such as Polycyclic Aromatic Nitrogen Heterocycles (PANHs), also called Azaarenes (AZAs), and Polycyclic Aromatic Sulfur Heterocycles (PASHs), also called Thiaarenes (THIAs), were historically neglected, despite documented adverse effects.^{12,13} Nowadays, more and more studies aim to evaluate the health risks due to polar and non-polar Polycyclic Aromatic Compounds (PACs), broadening the scope of environmental monitoring of these compounds beyond PAHs.^{14–16} When a wide range of PACs were taken into account, the toxicity of the global PACs mixture was found to greatly increase compared to the toxicity of the sole 16 EPA PAHs.¹⁷ Generally, it is required that current and future analytical methods tend to involve an increasing number of individual PACs, including polar PACs as well as ‘parent’ PAHs outside the list of the 16 EPA priority PAHs, which can also exhibit considerable genotoxicity, mutagenicity and carcinogenicity.^{12,14,15,18,19}

To this end, different analytical strategies can be considered:

- Several analytical methods complementing one another can be implemented concurrently to measure separately various PAC classes: for instance, GC-EI-MS for PAHs and carbonyl-OPAHs, GC-EI-MS with prior derivatization for hydroxyl- and carboxyl-OPAHs, and GC-NICI-MS for nitro-PAHs.^{20–22}
- Thanks to the current development of high-resolution mass spectrometry (HRMS) methods, non-target screening is getting particularly powerful and adapted to environmental analysis of PACs.^{23–27} Two-dimensional gas chromatography is an additional tool to facilitate this non-target approach.²³ However, the enormous number of existing isomers among PACs can be a major obstacle to the unambiguous identification of PACs individuals, and quantitative determination of each compound is not possible when commercial standards are not available.
- To our knowledge, only three research groups reported the simultaneous determination in a single analytical method of many polar and non-polar PACs,^{28–30} knowing that one of them implemented two-dimensional gas chromatography to this purpose.²⁹ Moreover, in those articles, groups of compounds such as AZAs and PASHs, as well as other critical individual PACs, were not analyzed.

In this article, a single GC-MS/MS method enabling the simultaneous determination of 79 polar and non-polar PACs spread out among the PAHs, OPAHs, NPAHs, AZAs and PASHs groups is described, including the optimization of GC-MS/MS instrumental parameters and of the Pressurized Liquid Extraction (PLE), the validation of the method and its application to a Certified Reference Material and to real-world PM₁₀ samples.

Materials and methods

Chemicals

Analytical HPLC grade solvents were purchased from VWR Chemicals (Fontenay-sous-Bois, France). Certified standards of polar and non-polar PACs were purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France), LGC Standards (Molsheim, France), Cluzeau Info Labo (Sainte-Foy-la-Grande, France) and BCP Instruments (Oullins, France). Deuterated PACs internal standards (ISTDs) were purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France), Cluzeau Info Labo (Sainte-Foy-la-Grande, France) and BCP Instruments (Oullins, France).

Samples

PM₁₀ samples were collected from February to March 2022 in a parking lot from a residential building in the urban area of Strasbourg (Alsace, France, 48°35′30″ N, 7°43′32″ E). This building

was located close to a motorway (<500 meters), directly beside an urban roadway on one side and beside a tramway line on the other side. The parking lot was semi-closed and had two levels: ground and underground. PM₁₀ samples were collected thanks to a Sven Leckel LVS6-RV medium-volume air sampler (Sven Leckel Ingenieurbüro GmbH, Berlin, Germany) operated at 2.3 m³/h for a whole week. This sampling was performed during six consecutive weeks. Because of noise disturbance from the sampling device, ground-level samples (Week 1, 2 and 3) could only be collected during daytime (from 08:00 to 21:00), whereas underground-level samples (Week 4, 5 and 6) were collected 24 hours a day.

All PM₁₀ samples were collected on glass fiber filters (GFFs) (Ø 47 mm, GF6, Whatman, GE Healthcare, Little Chalfont, United Kingdom). Before sampling, the GFFs were rinsed with n-hexane and dichloromethane and conditioned at 50 °C for at least 48 hours to remove traces of organic contaminants.

Between collection and extraction, PM₁₀ samples were stored in aluminum foil at -20 °C.

Extraction and sample preparation

Aerosol samples had to be extracted by solid-liquid extraction. Beforehand, ISTDs (Table 1) were spiked onto the samples at a level consistent with their mid-range calibration level.

Among the available techniques, Pressurized Liquid Extraction (PLE) was selected for a time-efficient and automatable extraction, and for its robustness and repeatability.^{14,31,32} PLE was performed on an ASE 300 instrument (Dionex Corp., Sunnyvale, CA, USA) in 33 mL cells. Pressure was 1500 psi, temperature was 110 °C, and two static cycles of 10 minutes each were performed.

In this work, we compared various solvents in order to assess their extraction ability: acetonitrile, dichloromethane, toluene, ethyl acetate, toluene/acetonitrile (1:1, v/v), toluene/dichloromethane (1:1, v/v), n-hexane/acetone (1:1, v/v), n-hexane/dichloromethane (1:1, v/v). The use of these solvents and solvent mixtures in previous works was presented in a literature review.¹⁴

After PLE, the solvent was evaporated under a gentle stream of nitrogen down to 0.5 mL using a TurboVap II concentrator (Biotage, Uppsala, Sweden) and further two-fold diluted with ethyl acetate for a better suitability of the GC injection.

Instrumental method

PACs were separated with a CP-3800 Gas Chromatograph (Varian Inc., Walnut Creek, CA, USA) on a 60 m × 0.25 mm × 0.10 µm Rxi-PAH column (Restek, Bellefonte, PA, USA).

A Split/Splitless (SSL) injector was operated at 250 °C in splitless mode for the first two minutes of the run, then the split valve was opened at a 1:10 ratio to clean up the injector from remaining nonvolatile species which could be deposited. Moreover, a pressure pulse was applied during the first minute of the run, i.e. a flow rate of 4.0 mL/min carrier gas permitted to maximize the volatilization of the compounds and their transfer to the head of the column. The volume of liquid injected was 2 µL.

Helium was used as the carrier gas at a constant flow rate of 1.5 mL/min. The oven temperature was held at 60 °C for 1 min, then raised to 150 °C at 30 °C/min, slowly ramped up to 300 °C at 5 °C/min, a temperature held for 5 min before a final ramp up to 320 °C at 10 °C/min, and 9 min at a constant temperature of 320 °C. The total run time was 50 minutes. The temperature of the transfer line was set at the final oven temperature, i.e. 320 °C.

After their GC separation, compounds were ionized by Electron Ionization (EI) at 70 eV and 250 °C. Then, a 320MS triple quadrupole (Varian Inc., Walnut Creek, CA, USA) was used as the analyzer in MRM and pseudo-MRM modes. Pseudo-MRM mode was presented in detail in a previous article.³³ The optimal MS/MS transitions are reported in the 'Results and Discussion' section. Argon was used as collision gas at a pressure of 1.5 mtorr.

Table 1. List of the 79 compounds of interest and 7 internal standards of this work, classified into their respective chemical group, with their abbreviation, molecular mass (in Da), retention time (in min), MS/MS transitions including collision energy (in V), and instrumental limit of quantification (in pg).

Group	Compound Name	Abbrev.	MM (Da)	RT (min)	Quantitation transition (Q) (CE, V)	Qualification transition (q) (CE, V)	iLOQ (pg)	
PAHs <i>n</i> = 25	Naphthalene	NAP	128	7.05	128 → 128 (10)	128 → 102 (35)	5	
	Acenaphthylene	ACY	152	10.65	152 → 152 (15)	152 → 151 (25)	5	
	Acenaphthene	ACE	154	11.10	154 → 154 (15)	154 → 153 (25)	2	
	Fluorene	FLU	166	12.80	166 → 166 (15)	166 → 165 (25)	2	
	Phenanthrene	PHE	178	17.15	178 → 178 (15)	178 → 152 (25)	2	
	Anthracene	ANT	178	17.30	178 → 178 (15)	178 → 152 (25)	2	
	Fluoranthene	FLT	202	22.85	202 → 202 (15)	202 → 200 (30)	2	
	Pyrene	PYR	202	24.15	202 → 202 (15)	202 → 200 (30)	2	
	Retene	RET	234	24.25	234 → 219 (15)	234 → 204 (30)	5	
	11H-Benzo[b]fluorene	B(b)FLU	216	25.60	216 → 215 (25)	216 → 216 (15)	10	
	11H-Benzo[a]fluorene	B(a)FLU	216	25.85	216 → 215 (25)	216 → 216 (15)	10	
	7H-Benzo[c]fluorene	B(c)FLU	216	25.95	216 → 215 (25)	216 → 216 (15)	5	
	1-Methylpyrene	1-MPYR	216	26.75	216 → 215 (25)	216 → 216 (10)	5	
	Benz[a]anthracene	B(a)ANT	228	30.05	228 → 228 (15)	228 → 226 (35)	5	
	Triphenylene	TPH	228	30.35	228 → 226 (35)	228 → 228 (15)	5	
	Chrysene	CHR	228	30.45	228 → 226 (35)	228 → 228 (15)	5	
	5-Methylchrysene	5-MCHR	242	32.45	242 → 241 (20)	242 → 242 (20)	5	
	Benzo[b]fluoranthene	B(b)FLT	252	35.30	252 → 252 (15)	252 → 250 (35)	2.5	
	Benzo[k]fluoranthene	B(k)FLT	252	35.40	252 → 252 (15)	252 → 250 (35)	2.5	
	Benzo[j]fluoranthene	B(j)FLT	252	35.50	252 → 252 (15)	252 → 250 (35)	2.5	
	Benzo[e]pyrene	B(e)PYR	252	37.10	252 → 252 (15)	252 → 250 (35)	2.5	
	Benzo[a]pyrene	B(a)PYR	252	37.40	252 → 252 (15)	252 → 250 (35)	2.5	
	Indeno[1,2,3-cd]pyrene	I(cd)PYR	276	43.30	276 → 276 (15)	276 → 274 (40)	10	
	Dibenzo[a,h]anthracene	DB(a,h)ANT	278	43.35	278 → 278 (15)	278 → 276 (35)	20	
	Benzo[ghi]perylene	B(ghi)PER	276	45.10	276 → 276 (15)	276 → 274 (40)	20	
	OPAHs <i>n</i> = 17	1,2-Naphthoquinone	1,2-NAPQ	158	7.35	130 → 102 (20)	102 → 76 (15)	200
		1-Indanone	INDO	132	8.50	132 → 104 (10)	132 → 78 (20)	4
		Phthalic anhydride	PHTLA	148	9.30	104 → 76 (10)	148 → 104 (10)	2
		1,4-Naphthoquinone	1,4-NAPQ	158	10.80	158 → 102 (20)	158 → 130 (15)	40
		1-Naphthaldehyde	NAPL	156	12.15	156 → 128 (20)	156 → 78 (35)	2
		Xanthone	XTO	196	19.10	196 → 139 (35)	196 → 168 (20)	2
		Phenalenone	PNO	180	20.90	180 → 152 (15)	152 → 151 (25)	10
9,10-Antraquinone		ANTQ	208	21.75	180 → 152 (15)	208 → 180 (15)	10	
2-Methyl-9,10-Antraquinone		2-MANTQ	222	24.05	222 → 165 (30)	165 → 164 (20)	10	
1,8-Naphthalic anhydride		1,8-NAPA	198	24.10	154 → 126 (15)	198 → 154 (10)	5	
11H-Benzo[a]fluoren-11-one		B(a)FLUO	230	28.60	230 → 202 (15)	230 → 201 (40)	2	
7H-Benzo[c]fluoren-7-one		B(c)FLUO	230	29.25	230 → 202 (15)	230 → 201 (40)	2	
11H-Benzo[b]fluoren-11-one		B(b)FLUO	230	29.75	230 → 202 (15)	230 → 201 (40)	2	
Benzanthrone		BANTO	230	31.70	230 → 202 (20)	230 → 200 (35)	5	
1,2-Benzanthraquinone		BANTQ	258	32.85	258 → 202 (30)	258 → 230 (20)	20	
5,12-Naphthacene quinone		NACEQ	258	34.40	258 → 202 (30)	258 → 230 (20)	10	
6H-Benzo[cd]pyrene-6-one		B(cd)PYRO	254	38.20	254 → 226 (30)	226 → 224 (15)	20	
NPAHs <i>n</i> = 14		1-Nitronaphthalene	1-NNAP	173	14.00	127 → 77 (20)	173 → 115 (25)	10
		2-Nitronaphthalene	2-NNAP	173	14.80	127 → 77 (20)	173 → 115 (25)	10
		5-Nitroacenaphthene	5-NACE	199	22.40	152 → 151 (15)	199 → 141 (20)	25
	2-Nitrofluorene	2-NFLU	211	24.30	211 → 165 (20)	165 → 163 (20)	100	
	9-Nitroanthracene	9-NANT	223	24.65	223 → 165 (35)	176 → 150 (30)	10	
	9-Nitrophenanthrene	9-NPHE	223	26.15	176 → 150 (30)	223 → 167 (25)	25	
	2-Nitrofluoranthene	2-NFLT	247	31.90	247 → 201 (25)	201 → 200 (25)	100	
	3-Nitrofluoranthene	3-NFLT	247	32.25	247 → 189 (30)	201 → 200 (25)	200	
	4-Nitropyrene	4-NPYR	247	32.60	201 → 200 (25)	247 → 189 (30)	100	
	1-Nitropyrene	1-NPYR	247	33.40	201 → 200 (25)	247 → 189 (30)	200	
	2-Nitropyrene	2-NPYR	247	33.70	247 → 201 (20)	201 → 200 (25)	200	
	7-Nitrobenz[a]anthracene	7-NBANT	273	36.00	273 → 215 (35)	215 → 189 (20)	200	
	6-Nitrochrysene	6-NCHR	273	37.90	273 → 215 (30)	226 → 224 (30)	1000	
	6-Nitrobenzo[a]pyrene	6-NBPYR	297	44.65	267 → 239 (25)	297 → 267 (20)	2000	
AZAs <i>n</i> = 17	Quinoline	QUI	129	7.90	129 → 129 (10)	129 → 102 (25)	5	
	Isoquinoline	isoQUI	129	8.15	129 → 129 (10)	129 → 102 (25)	5	
	Benzo[h]quinoline	B(h)QUI	179	17.70	179 → 179 (15)	179 → 151 (40)	5	
	Acridine	ACR	179	17.95	179 → 179 (15)	179 → 151 (40)	2.5	

(continued)

Table 1. Continued.

Group	Compound Name	Abbrev.	MM (Da)	RT (min)	Quantitation transition (Q) (CE, V)	Qualification transition (q) (CE, V)	iLOQ (pg)
PASHs <i>n</i> = 6	Phenanthridine	PHI	179	18.50	179 → 179 (15)	179 → 178 (20)	5
	Benzo[f]quinoline	B(f)QUI	179	18.65	179 → 179 (15)	179 → 178 (20)	2.5
	Carbazole	CAR	167	19.00	167 → 167 (15)	167 → 166 (20)	1
	Benz[c]acridine	B(c)ACR	229	29.35	229 → 229 (15)	229 → 228 (30)	2.5
	Benz[a]acridine	B(a)ACR	229	30.30	229 → 229 (15)	229 → 228 (30)	2.5
	Benzo[a]carbazole	B(a)CAR	217	30.85	217 → 217 (15)	217 → 216 (30)	5
	Benzo[b]carbazole	B(b)CAR	217	32.05	217 → 217 (15)	217 → 216 (35)	5
	Benzo[c]carbazole	B(c)CAR	217	32.45	217 → 217 (15)	217 → 216 (35)	5
	Dibenz[c,h]acridine	DB(c,h)ACR	279	41.05	279 → 279 (15)	279 → 278 (25)	5
	Dibenz[a,c]acridine	DB(a,c)ACR	279	42.05	279 → 279 (15)	279 → 278 (25)	5
	Dibenz[a,h]acridine	DB(a,h)ACR	279	42.20	279 → 279 (15)	279 → 278 (25)	5
	Dibenz[a,j]acridine	DB(a,j)ACR	279	42.40	279 → 279 (15)	279 → 278 (25)	5
	Dibenzo[c,g]carbazole	DB(c,g)CAR	267	46.15	267 → 265 (30)	267 → 267 (15)	5
	Benzo[b]thiophene	B(b)T	134	7.25	134 → 134 (10)	134 → 139 (30)	10
	Benzo[thiazole]	BTH	135	7.85	135 → 135 (10)	135 → 108 (25)	2
	Dibenzothiophene	DBT	184	16.55	184 → 184 (15)	184 → 152 (25)	1
	Benzonaphtho(2,1-d) thiophene	BN(2,1)T	234	28.85	234 → 234 (15)	234 → 189 (40)	2
	Benzonaphtho(1,2-d) thiophene	BN(1,2)T	234	29.35	234 → 234 (15)	234 → 233 (25)	2
	Benzonaphtho(2,3-d) thiophene	BN(2,3)T	234	29.75	234 → 234 (15)	234 → 189 (40)	2
	ISTDs <i>n</i> = 7	Naphthalene-D8	NAP-D8	136	7.00	136 → 136 (10)	136 → 108 (20)
1-Nitronaphthalene-D7		1-NNAP-D7	180	13.95	180 → 122 (20)	134 → 82 (25)	
Phenanthrene-D10		PHE-D10	188	17.00	188 → 188 (15)	188 → 158 (35)	
Acridine-D9		ACR-D9	188	17.85	188 → 188 (15)	188 → 186 (20)	
9,10-Anthraquinone-D8		ANTQ-D8	216	21.65	188 → 160 (20)	188 → 188 (15)	
Pyrene-D10		PYR-D10	212	24.05	212 → 212 (15)	212 → 208 (25)	
	Chrysene-D12	CHR-D12	240	30.30	240 → 240 (15)	240 → 236 (35)	

QA/QC

The analytical method was validated against linearity of the calibration, intra-day and inter-day variability, limits of quantification (LOQ) and recoveries (see 'Results and Discussion - Method validation' section).

Calibration was performed by internal standardization. 7 deuterated analogs of PACs were selected (4 deuterated PAHs, 1 deuterated OPAH, 1 deuterated NPAH and 1 deuterated AZA) and used as internal standards for the 79 analytes (Table 1). For each analyte, the optimal internal standard was chosen to give the highest possible linearity of the calibration curve and a method recovery close to 100%. Calibration curves were built in quadratic mode with 1/X weighting. Dynamic calibration range was selected depending on each analyte's response intensity. Calibration curves were only validated if $R^2 > 0.99$. At each calibration point, it was verified that the deviation between theoretical and calculated concentrations did not exceed 20%, except for the instrumental LOQ (iLOQ) at which $\pm 60\%$ was tolerated.

For each injection series, accuracy of the method was checked by injecting a low-level and a high-level standard and calculating its recovery (in %). A $\pm 20\%$ deviation was considered as acceptable. If this criterion was not met, the series was reinjected. The same standard solutions were used to calculate intra-day repeatability over five replicates and inter-day repeatability for five replicates injected over five consecutive days.

LOQs were validated if all the following criteria were consistently met:

- signal-to-noise ratio (S/N) of the quantification transition higher than 10,
- S/N of the confirmation transition higher than 3,
- concentration higher than the average measured concentration in solvent blanks,

- LOQ validated as the lowest point of the calibration curve according to the rules previously presented for the validation of the calibration.

The instrumental LOQs presented in this article are thus not only based on S/N values, but rather on stronger criteria.

Method recoveries were calculated according to the following protocol. Three GFFs previously used for PM sampling were pre-washed by PLE according to the optimized protocol of this work and spiked with a given amount of PACs standards (from 0.1 to 2 μg depending on the analyte's response). All surrogates were also spiked on the filters at a level corresponding to their mid-range level used for the calibration. The sample preparation protocol was performed and after GC-MS/MS analysis, recoveries were computed as the ratio of measured vs. theoretical concentration by internal standardization.

To confirm the applicability of our method for the determination of PACs in particulate samples, we analyzed a Standard Reference Material from the NIST: Diesel Particulate Matter from an industrial forklift (SRM 2975).³⁴ The analysis of such materials is considered as the gold standard for the validation of new analytical methods.³⁵ We also took advantage of this experiment to assess the uncertainty of the analytical method. For this purpose, two preparations of the SRM were done with different weights (0.03 and 0.04 g) deposited on GFFs, spiked with isotope-labeled surrogates (Table 1) and extracted according to the optimized PLE protocol. These two samples were prepared separately. Each sample preparation was analyzed twice with the GC-MS/MS method, and then reprocessed twice with two different calibration curves. Therefore, when each of these analyses gave a positive quantification, up to eight different values were averaged for each compound and their standard deviation (SD) was determined.

Results and discussion

Selection of the target compounds

All 79 individual PACs studied in this article are summarized in Table 1 with their characteristics for this method. The choice of the compounds of interest was made according to commercial standards availability, occurrence reported in the literature and toxicological relevance. Our list of target PACs included 25 PAHs, 17 OPAHs, 14 NPAHs, 17 AZAs and 6 PASHs.

In particular, among the 9 PAHs which have been studied in this work even though they are outside the scope of the 16 EPA's PAHs, we analyzed 7H-benzo(c)fluorene, 1-methylpyrene and 5-methylchrysene which were reported as major contributors to the toxicity of PAHs mixtures.³⁶

OPAHs and NPAHs have often been described as very relevant to characterize photochemical aging of PAHs or typical emission sources such as diesel combustion, but also very important because of their toxicity which can be higher than the one of parent PAHs.³⁷⁻⁴¹ Although analytical methods for their determination have already been presented,^{20,42-44} it is very rare that these compounds are analyzed together with PAHs and heterocyclic derivatives in a single run. Quantifying OPAHs and NPAHs together with non-polar PACs was one of the main goals of this work.

Polycyclic Aromatic Heterocycles are also atmospheric contaminants of great interest. Their health effects need to be addressed, but environmental occurrence data are missing for this purpose.^{13,15,27,45} The choice of the azaarenes and thiaarenes studied here was based on the priority semi-polar PACs defined by Schwarz et al. and available occurrence data.^{12,13,15}

The exception to this careful selection is the absence of 9-Fluorenone (FLUO) and 9,10-Phenanthrenequinone (PHEQ) in our method. These two OPAHs are of real interest in the context of PACs environmental analysis, but we observed complete degradation of PHEQ to FLUO

in the injector, so that precise quantification of both molecules was made impossible. Therefore, we advise that future works targeting the analysis of one of these two molecules by GC-MS with classical high temperature split/splitless injection involve a prior verification of the existence of any conversion from PHEQ to FLUO with commercial standards, because this could seriously hinder an accurate quantification of both molecules.

GC separation method

A good separation of PACs was successfully achieved thanks to the Rxi-PAH stationary phase. This stationary phase was specially designed to resolve groups of isobaric PACs which are not separated on the more usual 5% phenyl and 50% phenyl stationary phases.¹⁵ The low film thickness of this column also enabled a lower retention of the high molecular weight (HMW) PACs and a lower peak width. A Total Ion Chromatogram of a standard solution gathering the 79 PACs and 7 deuterated analogs is shown in Figure 1. All PACs of interest are eluted between 7.05 minutes (NAP) and 46.15 minutes (DB(c,g)CAR) (Table 1).

A satisfying resolution was particularly obtained for critical pairs of PAH isomers such as phenanthrene and anthracene ($R = 2.79$), triphenylene and chrysene ($R = 1.13$), and benzofluoranthene isomers b, j and k ($R_{b/k} = 1.27$ and $R_{k/j} = 1.16$) (Figure 1). According to the literature, these isomers are usually difficult to resolve on other stationary phases.^{15,46–48} Similar results were obtained for critical azaarenes isomers: phenanthridine and benzo(f)quinoline ($R = 1.84$), and dibenzacridines isomers (a,c), (a,h) and (a,j) ($R_{(a,c)/(a,h)} = 1.11$ and $R_{(a,h)/(a,j)} = 1.35$) (Figure 1).

For the particular case of benzofluoranthene and benzopyrene isomers, a good improvement of separation was obtained thanks to the addition of an isothermal step at 300 °C from 34 to

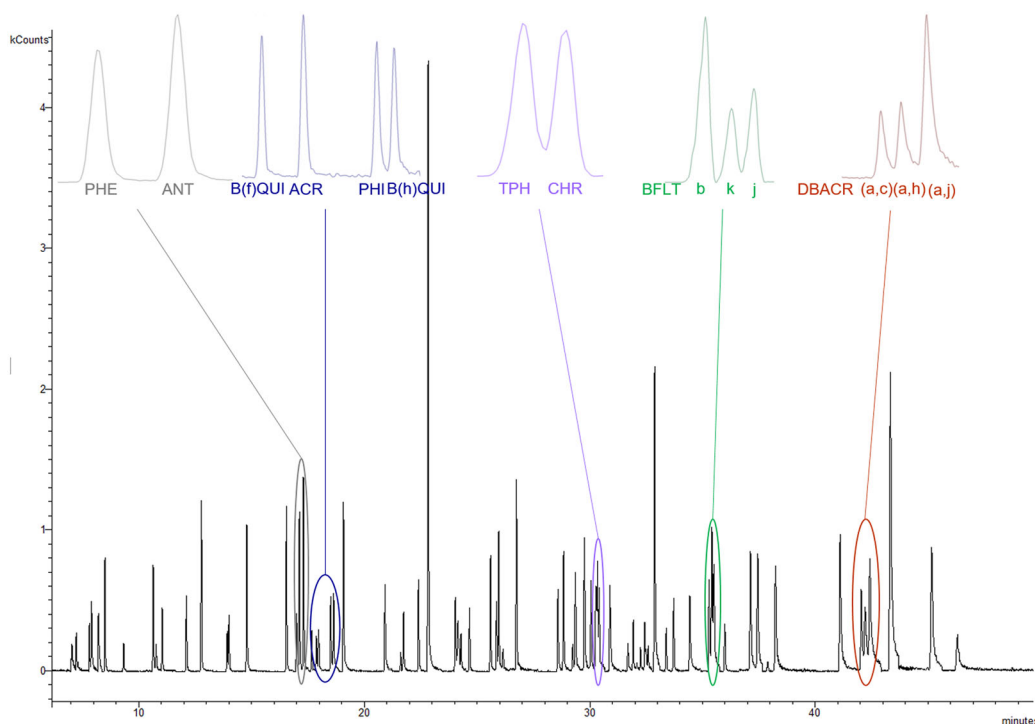


Figure 1. Total ion chromatogram of the 79 targeted polycyclic aromatic compounds and 7 internal standards of this study (t_R from 6 to 50 minutes), with a focus on the most critical pairs of isomers (see Table 1).

39 minutes. Additionally, an improvement of sensitivity for the heaviest compounds ($M > 216$ Da) was obtained when a pressure pulse was added at the injection (pressure of 50 psi, i.e. He flow rate 4.0 mL/min, during 1 minute). A similar improvement was previously described by Cochran et al.⁴⁹

MS detection: MRM and pseudo-MRM

The MS/MS detection of the PACs was also optimized. The major finding of this development was the high improvement of sensitivity for PAHs, AZAs and PASHs when pseudo-MRM mode was used instead of MRM, i.e. MS/MS transitions with no mass loss were monitored.³³

This is shown in Figure 2 with two examples per PAC group. In this figure are reported the peak areas measured for two classic MRM transitions and the pseudo-MRM transition, at various collision energies.

For BN(2,1)T for example, there was a five-fold signal increase when measuring the transition $234 \rightarrow 234$ instead of classic MRM transitions $234 \rightarrow 189$ and $234 \rightarrow 233$ (Figure 2(f)). When such transitions were used for quantification or confirmation of PACs, non-zero collision voltages were applied, so that the selectivity of MRM was preserved in pseudo-MRM.³³ The application of voltages from 10 to 20 volts also gave considerably higher signal intensities and S/N than voltages below 10 volts (Figure 2).

On the other hand, pseudo-MRM was not favored for polar PACs such as OPAHs and NPAHs which possess labile chemical groups cleaved by collision-induced dissociation (CID): all OPAHs and NPAHs studied in this work exhibited a loss of signal intensity when pseudo-MRM was used instead of MRM (Figure 2(g-j)).

Pressurized liquid extraction (PLE)

The selected extraction method of this work was PLE, due to its known benefits for PACs determination in atmospheric particulates samples.¹⁴

The main parameter optimized here was the nature of the solvent. Indeed, eight solvents were compared in terms of extraction efficiency: acetonitrile (ACN), dichloromethane (DCM), toluene (TOL), ethyl acetate (EtOAc), and the following solvent mixtures in 1:1, v/v proportions: TOL/ACN, TOL/DCM, n-hexane (n-HEX)/DCM and n-HEX/acetone (ACO). These were selected according to the most common solvents presented in the literature for such applications.¹⁴

Pre-washed GFFs which had been previously used for PM sampling, and therefore still presented particulates sorbed onto them, were spiked with levels of PACs varying from 0.4 to 10 μ g depending on the compounds' sensitivity. For this optimization, 15 PACs were selected to cover the broadest possible range of volatility and polarity: 4 PAHs (FLU, PYR, 1-MPYR, B(ghi)PER), 3 OPAHs (PNO, ANTQ, B(b)FLUO), 3 NPAHs (1-NNAP, 1-NPYR, 7-NBANT), 3 AZAs (QUI, PHI, DB(a,c)ACR) and 2 PASHs (DBT, BN(1,2)T). The measured extraction yields relative to the highest extraction yield obtained for each compound are described in Figure 3. These data enabled us to identify the most efficient solvent for each compound.

For all PACs, EtOAc and n-HEX/DCM were generally among the solvents giving the lowest yields. Therefore, the possibility of using them as extraction solvents was quickly ruled out.

For PAHs, DCM and TOL/ACN were the most powerful solvents for all compounds, followed by TOL/DCM, ACN and TOL (Figure 3(a)).

Yields obtained with TOL/DCM were high for all three OPAHs presented in Figure 3(b). TOL/ACN was very efficient for PNO and ANTQ but less for B(b)FLUO. ACN and DCM were efficient only for PNO, and TOL only for ANTQ (Figure 3(b)).

Results were more ambivalent for NPAHs. Depending on the compound studied, ACN, DCM, TOL/ACN, TOL/DCM and n-HEX/ACO could be considered as relatively efficient solvents.

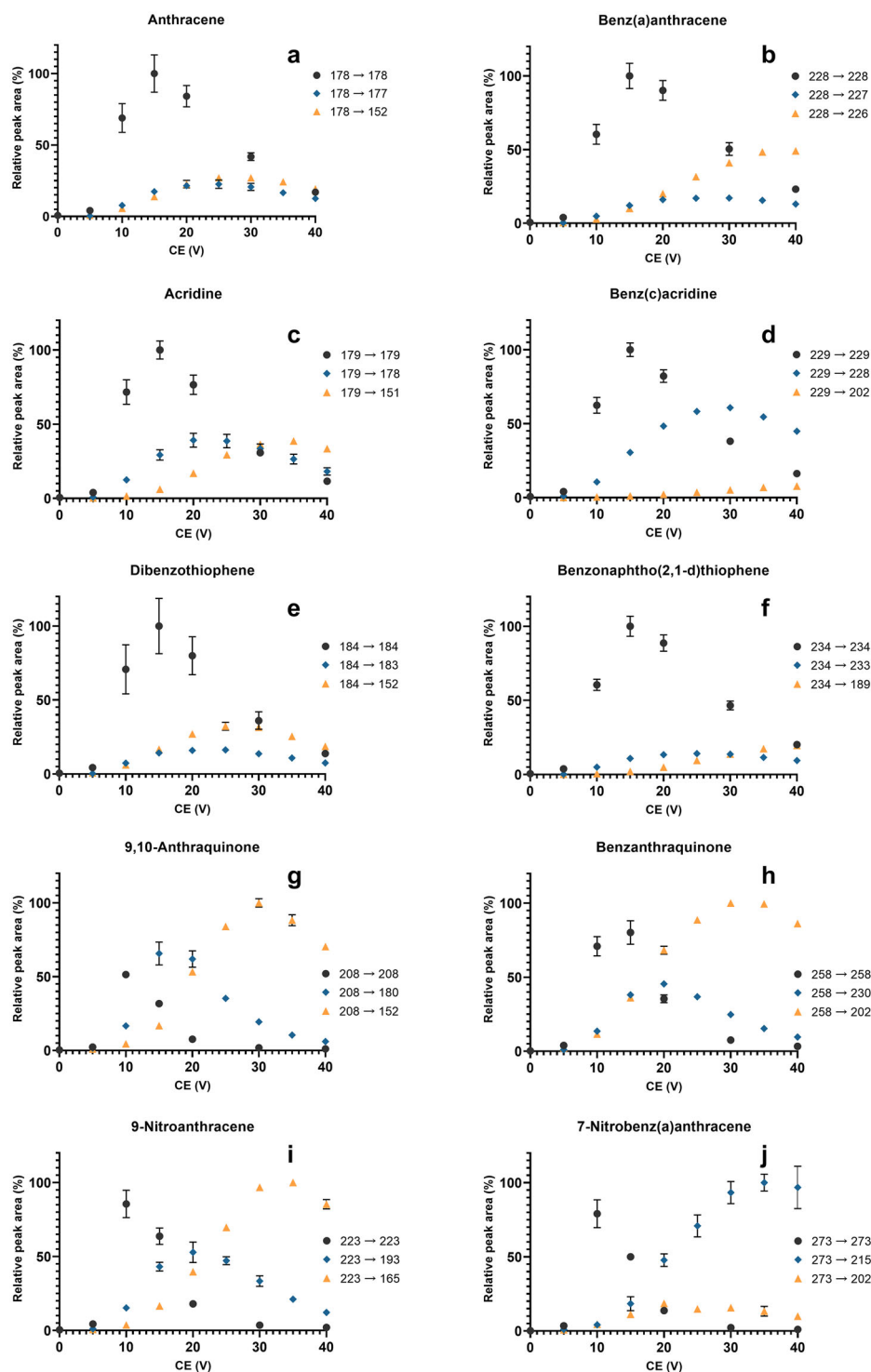


Figure 2. For eight different PACs (2 PAHs, 2 AZAs, 2 PASHs, 2 OPAHs and 2 NPAHs), peak areas of the three main MS/MS transitions relative to the highest peak area obtained for a given compound, depending on the collision energy applied. The dark grey circles correspond to the pseudo-MRM transition, the blue diamonds to the MRM transition with the smaller mass loss, the orange triangles to the MRM transition with the higher mass loss. The error bars express standard deviations on triplicate analyses. Reproduced from Galniche et al.³³

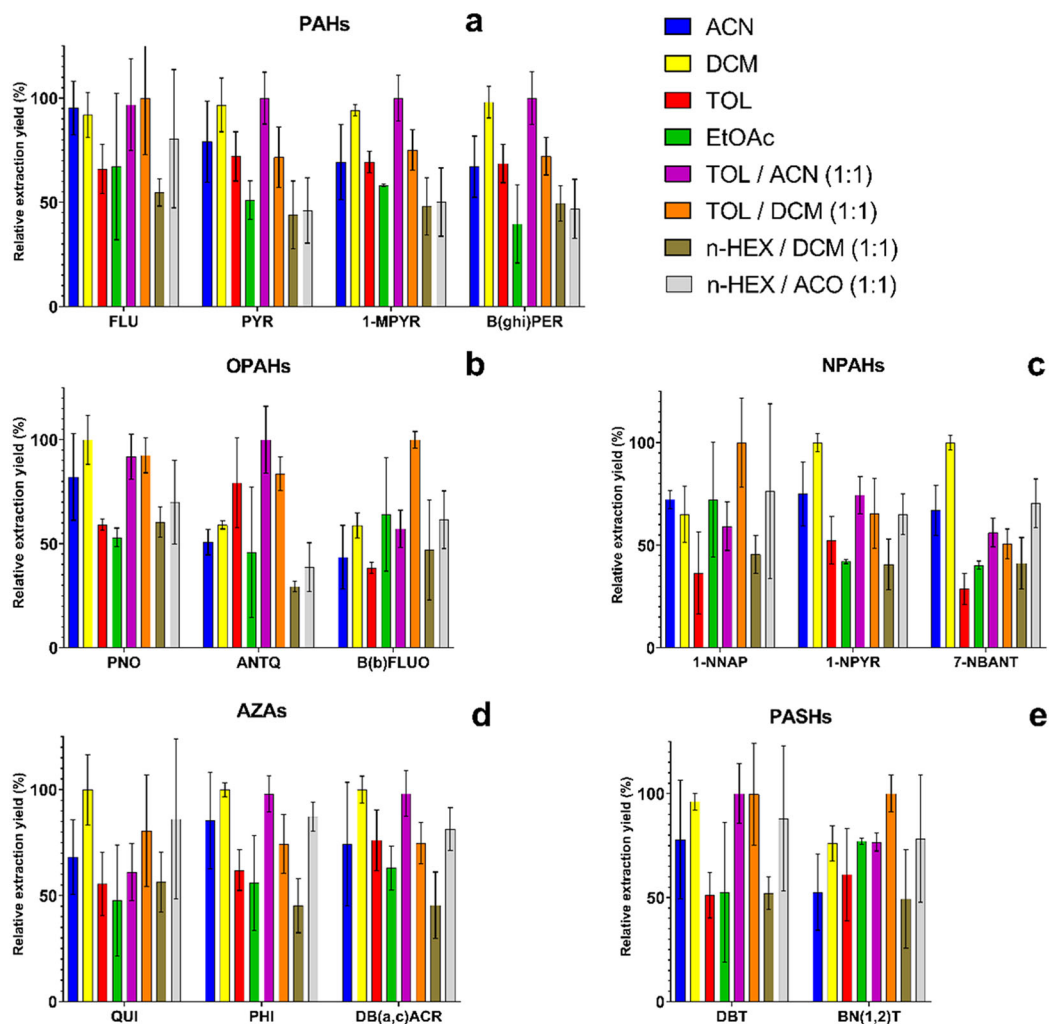


Figure 3. Pressurized liquid extraction yields with eight different solvent or solvent mixtures, for 15 PACs (4 PAHs, 3 OPAHs, 3 NPAHs, 3 AZAs and 2 PASHs), relative to the highest yield obtained for each compound. The error bars express standard deviations on triplicate analyses.

DCM was particularly more powerful than the other solvents for 1-NPYR and 7-NBANT (Figure 3(c)).

DCM was the most efficient solvent for all AZAs presented in Figure 3(d). TOL/ACN and n-HEX/ACO also gave satisfying results for these compounds.

For the two PASHs presented in Figure 3(e), TOL/DCM, TOL/ACN and DCM were the most efficient extraction solvents.

Considering all those results and the existing differences between each category of PACs and even between different compounds inside their category, a broad selection was first made including DCM, TOL/ACN and TOL/DCM.

Finally, due to the little average deviation between the efficiency of these solvents, we chose to avoid using dichloromethane according to the 2nd principle of Green Sample Preparation: ‘use safer solvents and reagents.’⁵⁰ The choice of the toluene/acetonitrile mixture (1:1, v/v) gave very satisfying extraction yields and also enabled us to perform the simultaneous extraction of other

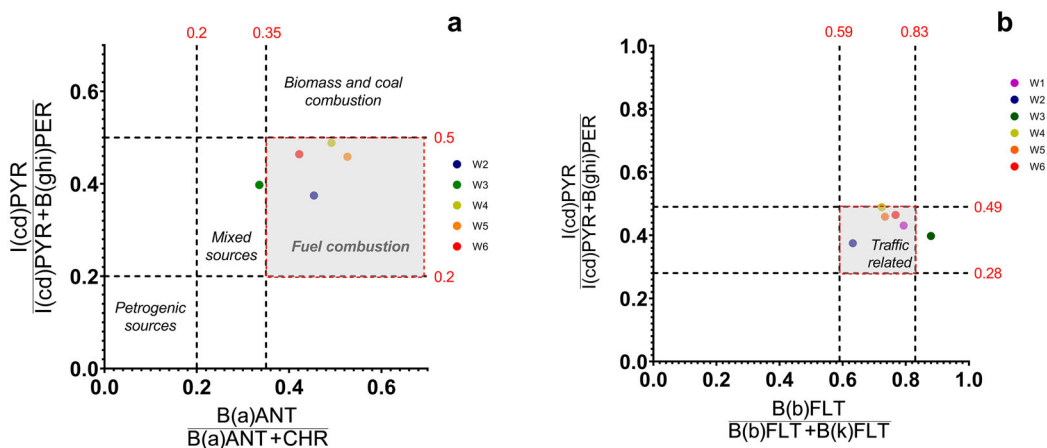


Figure 4. Diagnostic ratios of individual PAHs to assess the main emission sources of the PM₁₀ samples from this work: (a) $I(cd)Pyr / (I(cd)Pyr + B(ghi)PER)$ versus $B(a)ANT / (B(a)ANT + CHR)$ to identify the main combustion source and (b) $I(cd)Pyr / (I(cd)Pyr + B(ghi)PER)$ versus $B(b)FLT / (B(b)FLT + B(k)FLT)$ to search for traffic-related samples.

organic compounds. To the best of our knowledge, this is the first time that the application of such a solvent is presented for PACs extraction.

Method validation

Examples of calibration curves for one compound per PAC group are shown in Figure S1. All compounds could be validated in terms of linearity of the calibration by internal standardization, with six to ten calibration points depending on the analyte's response. In Table S1 are reported method validation data for each compound: R^2 values (calibration curves were all obtained with $R^2 > 0.99$), dynamic calibration ranges, accuracy of the method at a low-range and a high-range level, as well as intra-day and inter-day precision of the method at a low-range and a high-range level.

Instrumental LOQ (iLOQ) were estimated according to the criteria described in the 'QA/QC' section. The values expressed as an injected mass (in pg) are presented in Table 1. The corresponding concentration (in $\mu\text{g/L}$) is reported in Table S1. iLOQ ranged from 1 pg for CAR and DBT to 2 ng for 6-NBPYR (Table 1). Generally, iLOQ were higher for NPAHs due to the lesser efficiency of EI for these compounds compared to other groups of PACs.

Method recoveries are presented for 15 compounds in Figure S2. These are the same compounds which were already studied for the optimization of the extraction method. Method recoveries for these compounds ranged from $96 \pm 26\%$ for 1-NNAP to $185 \pm 68\%$ for DB(a,c)ACR. As all mean recoveries of spikes on GFFs were higher than 96%, no recovery action was specified.

A further and decisive method validation was obtained thanks to the analysis of the Standard Reference Material 2975.

Analysis of a standard reference material: SRM 2975

Up to eight different concentrations were measured for each compound in SRM 2975. The average and SD of these concentrations are presented in Table 2. A concentration was reported in Table 2 when a compound showed at least four positive quantifications.

Table 2. Quantification of PACs in SRM 2975 (diesel particulate matter), in $\mu\text{g/g}$, with the certified and reference values from the NIST.³⁴

Compound name	Abbrev.	Concentration (this study, $\mu\text{g/g}$)	NIST Certified value ($\mu\text{g/g}$)	NIST Reference value ($\mu\text{g/g}$)	
				100 °C	200 °C
Naphthalene	NAP	3.59 ± 1.15		1.78 ± 0.48	4.00 ± 0.13
Acenaphthene	ACE	0.19 ± 0.05		0.548 ± 0.029 ^b	
Fluorene	FLU	0.39 ± 0.14		0.440 ± 0.071	2.88 ± 0.19
Phenanthrene	PHE	10.6 ± 1.5		17.3 ± 1.0	20.7 ± 0.3
Anthracene	ANT	0.14 ± 0.07		0.039 ± 0.003	0.049 ± 0.002
Fluoranthene	FLT	15.5 ± 3.6		26.9 ± 1.1	30.9 ± 0.5
Pyrene	PYR	1.03 ± 0.06		0.94 ± 0.11	1.52 ± 0.20
1-Methylpyrene	1-MPYR	0.12 ± 0.05			
Benz[a]anthracene	B(a)ANT	1.10 ± 0.37		0.330 ± 0.037	0.966 ± 0.043
Triphenylene	TPH	4.77 ± 0.27	5.32 ± 0.24		
Chrysene	CHR	4.56 ± 1.54		4.58 ± 0.17	5.73 ± 0.11
5-Methylchrysene	5-MCHR	0.68 ± 0.33			
Benzo[b]fluoranthene	B(b)FLT	>12 ^a		11.5 ± 2.8 ^b	
Benzo[k]fluoranthene	B(k)FLT	0.91 ± 0.54		0.699 ± 0.058	1.75 ± 0.09
Benzo[j]fluoranthene	B(j)FLT	1.02 ± 0.45	0.819 ± 0.093		
Benzo[e]pyrene	B(e)PYR	1.09 ± 0.49		1.14 ± 0.06	2.28 ± 0.18
Benzo[a]pyrene	B(a)PYR	1.41 ± 0.77		0.053 ± 0.003	0.766 ± 0.039
Indeno[1,2,3-cd]pyrene	I(cd)PYR	1.12 ± 0.27		1.37 ± 0.16	2.13 ± 0.12
Dibenz[a,h]anthracene	DB(a,h)ANT	1.67 ± 0.56	0.523 ± 0.047 ^c		
Benzo[ghi]perylene	B(ghi)PER	1.58 ± 0.38		0.489 ± 0.032	1.59 ± 0.09
1-Indanone	INDO	0.30 ± 0.20			
Phthalic Anhydride	PHTLA	31.6 ± 7.7			
1-Naphthaldehyde	NAPL	1.05 ± 0.21			
Xanthone	XTO	0.31 ± 0.06			
Phenalenone	PNO	24.8 ± 4.5			
9,10-Anthraquinone	ANTQ	25.2 ± 3.8			
2-Methyl-9,10-Anthraquinone	2-MANTQ	3.41 ± 0.64			
1,8-Naphthalic anhydride	NAPA	>50 ^a			
11H-Benzo[a]fluoren-11-one	B(a)FLUO	6.24 ± 1.63			
7H-Benzo[c]fluoren-7-one	B(c)FLUO	5.17 ± 0.94			
11H-Benzo[b]fluoren-11-one	B(b)FLUO	4.94 ± 2.00			
Benzanthrone	BANTO	13.9 ± 5.5			
1,2-Benzanthraquinone	BANTQ	13.2 ± 5.9			
5,12-Naphthacene quinone	NACEQ	1.77 ± 0.59			
6H-Benzo[cd]pyrene-6-one	B(cd)PYRO	18.1 ± 7.6			
9-Nitroanthracene	9-NANT	4.01 ± 0.84		3.07 ± 0.28	3.94 ± 0.19
3-Nitrofluoranthene	3-NFLT	8.10 ± 1.38	3.80 ± 0.24		
1-Nitropyrene	1-NPYR	38.2 ± 8.0	35.2 ± 2.2		
7-Nitrobenz[a]anthracene	7-NBANT	4.96 ± 0.60	3.57 ± 0.32		
Quinoline	QUI	0.46 ± 0.13			
Isoquinoline	isoQUI	0.45 ± 0.09			
Carbazole	CAR	1.02 ± 0.43			
Benz[c]acridine	B(c)ACR	0.08 ± 0.05			
Benz[a]acridine	B(a)ACR	1.29 ± 0.53			
Benzo[a]carbazole	B(a)CAR	0.55 ± 0.18			
Benzo[b]carbazole	B(b)CAR	1.08 ± 0.84			
Benzo[c]carbazole	B(c)CAR	0.40 ± 0.09			
Dibenz[c,h]acridine	DB(c,h)ACR	0.95 ± 0.38			
Dibenz[a,c]acridine	DB(a,c)ACR	0.80 ± 0.37			
Dibenz[a,h]acridine	DB(a,h)ACR	0.76 ± 0.55			
Dibenz[a,j]acridine	DB(a,j)ACR	0.72 ± 0.46			
Dibenzo[c,g]carbazole	DB(c,g)CAR	1.12 ± 0.64			
Benzothiazole	BTH	2.07 ± 0.56			
Dibenzothiophene	DBT	0.57 ± 0.17			
Benzonaphtho(2,1-d) thiophene	BN(2,1)T	0.30 ± 0.09			
Benzonaphtho(1,2-d) thiophene	BN(1,2)T	0.15 ± 0.05			
Benzonaphtho(2,3-d) thiophene	BN(2,3)T	0.16 ± 0.04			

^aB(b)FLT and NAPA concentrations were reported as '> X' because the measured concentrations exceeded the highest calibration level.

^bFor these compounds, the reference values were obtained from extraction temperatures between 100 and 200 °C

^cThe certified concentration of dibenz(a,h)anthracene is given as a sum of dibenz(a,h + a,c)anthracene.

Bold values signifies the value obtained in the study in comparison to those from the literature.

Overall results

Finally, 57 PACs (out of 79) were detected and quantified in SRM 2975. Among them were 20 PAHs (out of 25), 15 OPAHs (out of 17), 4 NPAHs (out of 14), 13 AZAs (out of 17) and 5 PASHs (out of 6). The high amount of detected and quantified PACs in SRM 2975 highlights the relevance of this material for our method validation.

Comparison with NIST certificate of analysis

Among the 57 quantified PACs, 22 had either a certified or a reference value reported by the NIST (18 PAHs + 4 NPAHs) (Table 2).³⁴ When considering their average \pm SD range, 16 of these 22 compounds were validated with a quantification consistent with the reference (Table 2). This was a very satisfying result and enabled us to firmly validate the analytical method presented in this work.

On the other hand, 8 certified NPAHs could not be detected because of an insufficient LOQ.

Among the few values which were significantly different from their standard, it is worth noting that the concentration of FLT was in line with the work of Cochran et al.⁴⁹ and the concentration of 7-NBANT was in accordance with the one reported by Bamford et al.,⁵¹ even though the extraction method used in these studies were different from ours.^{49,51} The amount of DB(a,h)ANT had the highest deviation with the standard value (around + 200%), which could possibly be explained by interfering isomers not targeted in this work, and by the potential contribution of co-eluted I(cd)PYR (MM = 276 Da) on the quantification transition of DB(a,h)ANT (m/z 278 \rightarrow 278). However, this 'outlier' concentration of DB(a,h)ANT was still consistent with the value reported by Cochran and Kubátová.⁵²

Uncertified compounds

35 of the 57 PACs quantified in this analysis of SRM 2975 had no certified or reference value.³⁴ They mostly belonged to the categories of oxygenated PAHs, azaarenes and thiaarenes, except the two methylated PAHs of interest in this study. Among these, 23 compounds were even quantified for the first time ever in SRM 2975. A comparison of the concentrations measured in this study for uncertified PACs with those of previous works from the literature is presented in Table S2.

Notably, all 13 azaarenes measured in this work were never reported before. This result highlights the importance of performing multi-class analysis of PACs including the broadest possible range of PACs. Even though the individual concentrations of AZAs measured here do not exceed 1.3 $\mu\text{g/g}$, the estimated total concentration of azaarenes in SRM 2975 would be around 10 $\mu\text{g/g}$. Thus, azaarenes seem to be relevant compounds to study if one wants to address the topic of combustion-related particles.

Similarly, most targeted PASHs were detected and quantified in SRM 2975, with the highest individual concentration for BTH (2.1 $\mu\text{g/g}$) and a sum of all PASHs concentrations around 3.3 $\mu\text{g/g}$. The amount of DBT measured in this work is slightly lower than the value of Schantz et al.,⁵³ while the reported amount of BN(1,2)T is perfectly in line with the results of Christensen et al.⁵⁴ (Table S2).

More occurrence data were available for OPAHs in SRM 2975. However, the discrepancies between the results of various studies made it difficult to conclude on the agreement with our results.^{42,49,52,55} For instance, the concentration of ANTQ was about the same as the one reported by Nocun and Schantz,⁴² about three times the values of Cochran et al. and Cochran and Kubátová,^{49,52} and inferior to the value of Ahmed et al.⁵⁵ The same tendency was also observed for BANTO and BANTQ (Table S2).

A major finding of this work is the very high total concentration and detection frequency of OPAHs in SRM 2975. 15 OPAHs out of 17 could be quantified, for a total concentration of 200 $\mu\text{g/g}$, largely exceeding the total concentration of the 20 PAHs which would be around 65 $\mu\text{g/g}$.

g. In particular, PHTLA (32 $\mu\text{g/g}$) and NAPA ($>50 \mu\text{g/g}$) were two of the three most concentrated PACs in SRM 2975, the third one being the well-known 1-NPYR (38.2 $\mu\text{g/g}$) (Table 2). These compounds can be classified as highly oxygenated organic molecules (HOM) and were reported as typical of photochemical aging of soot.⁵⁶ Therefore, our observation is plausible. However, it would be interesting to explore the formation of these compounds in the course of diesel PM generation and analysis: Do they occur immediately when the particles are released? During the sampling? In the course of the storage period of the material? During the sample preparation? More studies would be necessary to further study this question.

Environmental application: PM₁₀ samples from a parking lot

General trends in PACs content of the PM₁₀ samples

To confirm the application of this analytical method on real-world samples, PM₁₀ was collected in a residential parking lot from an urban area for one week during six consecutive weeks.

In these samples, 19 PAHs, 10 OPAHs, 5 AZAs, 4 PASHs and not any NPAHs were detected in at least one sample, i.e. 38 compounds out of 79 target analytes overall. 16 of them were even detected in all six samples.

All measured concentrations of PACs are reported in Table 3.

PAHs total concentrations ranged from 1.2 to 7.7 ng/m^3 . PAHs was always the most abundant class of compounds, with the exception of Week 6, when OPAHs were more concentrated.

OPAHs total concentration varied from 0.63 to 6.5 ng/m^3 . AZAs total amount was from no AZA detected to 0.23 ng/m^3 . PASHs concentration was comprised between 0.15 and 0.32 ng/m^3 and BTH accounted for most of the PASHs amount.

There was a high increase in PACs concentration after the first two weeks of sampling (2.3 and 2.8 ng/m^3 vs. from 11 to 14 ng/m^3). This could be because these first two weeks corresponded to winter holidays. One could expect less everyday traffic inside the parking lot during this period, and thus less generation of particulate-phase PACs. Additionally, due to spatial constraints of the parking lot, the ground-level sampling could not be performed at the entrance and exit access of the parking lot, where everyday vehicular traffic was the most constant. Our ground-level samples (Week 1 to 3) were therefore more affected by individual passages of cars directly nearby the sampling device, whereas at the underground level (Week 4 to Week 6), the PM₁₀ sampler could be positioned close to entrance and exit access.

Individual compounds of particular interest

The most abundant individual PACs on average from Week 3 to Week 6 were PHTLA ($\approx 1.5 \text{ ng/m}^3$), NAPA ($\approx 1.5 \text{ ng/m}^3$) and B(b)FLT ($\approx 1.1 \text{ ng/m}^3$). These three compounds were also among the most concentrated in the Diesel Particulate Matter SRM. This is coherent with the sampling location described here, which should be mostly affected by vehicular exhausts emissions.

On the other hand, 1-NPYR, which was the second most abundant compound in SRM 2975, was not detected. The method LOQ for this compound was about 1 ng/m^3 for ground-level samples and 0.5 ng/m^3 for underground-level samples. This LOQ was too high to be able to quantify 1-NPYR in ambient particles of the parking lot.

Among the 16 PACs detected in all six PM₁₀ samples were 13 PAHs, 2 OPAHs and 1 PASH. This latter was BTH, a 2-ring Polycyclic Aromatic Heterocycle containing a nitrogen and a sulfur atom. This compound was previously described as a potential marker of traffic pollution, partly because of its release from rubber and tires in which it is used as a vulcanizing agent.^{45,57} The continual presence of BTH in PM₁₀ from the parking lot studied in this work reinforces the interest of monitoring Polycyclic Aromatic Heterocycles besides PAHs to assess traffic-related atmospheric pollution.

Table 3. Concentration of PACs measured in PM₁₀ samples from a parking lot over six consecutive weeks in February and March 2022.

Compound	Individual PAC concentrations (pg/m ³)					
	Ground level (daytime only)			Underground level (day and night)		
	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
NAP	106	274	87	91	111	135
FLU		51	60	46	53	66
PHE	57	79	286	302	173	259
FLT	45	43	415	306	218	161
PYR	98	122	1005	705	439	372
B(b)FLU			266	116	137	83
B(a)FLU			138		171	93
1-MPYR				73	54	
B(a)ANT		113	360	601	458	241
TPH	35	37	111	141	108	102
CHR	95	136	713	621	412	330
B(b)FLT	190	228	1138	> 1000 ^a	> 1000 ^a	871
B(k)FLT	49	133	156	476	435	264
B(j)FLT	91	108	368	547	550	366
B(e)PYR	106	120	454	645	684	380
B(a)PYR	61	172	665	961	989	597
I(cd)PYR	93	124	295	470	575	284
DB(a,h)ANT			113	126	133	55
B(ghi)PER	123	207	447	492	679	328
∑ PAHs	1.2·10³	1.9·10³	7.1·10³	7.7·10³	7.4·10³	5.0·10³
PHTLA	143	352	1138	1484	1025	2231
PNO			507	272	276	247
ANTQ			238	213	198	198
NAPA	616	276	1684	1987	933	1239
B(a)FLUO			227	182	92	134
B(c)FLUO			249	242	113	114
B(b)FLUO			192	177	154	82
BANTO			506	1106	517	1136
BANTQ				152	258	209
B(cd)PYRO				660	665	571
∑ OPAHs	0.76·10³	0.63·10³	4.7·10³	6.5·10³	4.2·10³	6.2·10³
QUI				37		48
isoQUI				33	45	33
CAR	82		64	51	111	64
B(a)ACR						83
DB(a,j)ACR	82					
∑ AZAs	0.16·10³		0.06·10³	0.12·10³	0.16·10³	0.23·10³
BTH	153	244	211	259	174	246
DBT				9		
BN(2,1)T				49		18
BN(1,2)T						23
∑ PASHs	0.15·10³	0.24·10³	0.21·10³	0.32·10³	0.17·10³	0.29·10³
∑ PACs	2.3·10³	2.8·10³	12·10³	14·10³	11·10³	12·10³

^asome B(b)FLT concentrations were reported as "> X" because the measured concentrations exceeded the highest calibration level

Bold value are used to visualize sum of concentrations instead of individual concentrations of compounds.

PAHs diagnostic ratios for source apportionment

Diagnostic ratios of several PAHs individual concentrations have been described as an interesting tool for source apportionment of these compounds.¹⁵ However, their use as a sole indicator to firmly identify emission sources of PAHs has also been questioned, notably due to the fact that PAHs concentrations are generally not conservative in the environment.⁵⁸ Therefore, the implementation of cross-plots of two PAHs diagnostic ratios has been presented in recent times as an improvement to increase the reliability of source apportionment.^{15,59,60}

We decided to use two examples of PAHs diagnostic ratios cross-plots to assess the main emission sources of PAHs in our samples. First, the association of I(cd)PYR/

(I(cd)Pyr + B(ghi)PER) and B(a)ANT/(B(a)ANT + CHR) enables to define regions of the cross-plot characteristic of petrogenic sources, fuel combustion, and biomass or coal combustion.^{59,61} Second, the plotting of I(cd)Pyr/(I(cd)Pyr + B(ghi)PER) versus B(b)FLT/(B(b)FLT + B(k)FLT) defines values which are typical of traffic-related emissions. This latter cross-plot of two diagnostic ratios was recently described as more accurate because it should not be affected by spatial and temporal distributions.^{60,62}

Results obtained with the PM₁₀ samples of this study are presented in Figure 4. In Figure 4(a), samples from weeks 2, 4, 5 and 6 are all in the region of the cross-plot typical of fuel combustion, i.e. B(a)ANT/(B(a)ANT + CHR) > 0.35 and I(cd)Pyr/(I(cd)Pyr + B(ghi)PER) between 0.2 and 0.5. Week 1 could not be plotted in Figure 3(a) because B(a)ANT could not be detected at this time point. Week 3 is the only sample outside the 'fuel combustion' area, suggesting a contribution from other sources during this period, but it is still very close to this area (B(a)ANT/(B(a)ANT + CHR) = 0.34). The identification of fuel combustion as the main PAH source is very consistent with the fact that PM₁₀ samples were collected in a parking lot.

This assumption of fuel combustion prevalence for PAHs release in our samples was further investigated in Figure 3(b). The corresponding cross-plot was studied for a particular region of interest previously utilized by Xing et al. and Wang et al.^{60,62} for I(cd)Pyr/(I(cd)Pyr + B(ghi)PER) from 0.28 to 0.49 and B(b)FLT/(B(b)FLT + B(k)FLT) from 0.59 to 0.83, the PACs content of the samples was described as traffic-related. The criteria were met for all PM₁₀ samples, except Week 3 which exhibited a slightly higher B(b)FLT/(B(b)FLT + B(k)FLT) value (0.88) and is again a slight outlier for which other sources may have contributed to PACs emission. Therefore, results obtained with both cross-plots are consistent with each other, and both suggest the importance of vehicular exhaust as the major source of PACs. These results are a further confirmation of the applicability of the analytical method presented in this paper, since it is in line with the sampling location, a parking lot.

Comparison with PACs concentrations from the literature

In this section, the results of this study on PM₁₀ of a parking lot are compared with previous works from the literature on similar environments.

The sum of the concentrations of 19 PAHs monitored by Villanueva et al. in an underground parking in Spain reached 6.7 ng/m³.⁶³ This level is in good agreement with our range of total PAHs concentrations from 1.2 to 7.7 ng/m³, also obtained with 19 individual PAHs.

Similarly, Kim et al. reported a mean level of the sum of 24 PAHs of 4.1 ng/m³ over eight indoor parking lots in Korea.⁶⁴ This corresponds to our range of values as well. In their work, highest individual PAHs concentrations were observed for FLT (0.54 ± 0.24 ng/m³) and Pyr (0.54 ± 0.29 ng/m³), which were also quite abundant in our samples (0.27 ± 0.11 ng/m³ and 0.63 ± 0.29 ng/m³, respectively, from Week 3 to 6). However, B(b)FLT and B(a)Pyr were even more concentrated in our study.

Overall, the PAHs concentrations reported here are coherent with typical levels from the literature.

Conclusion

In this article, the development of a new analytical method aiming at the simultaneous determination of 79 PACs was presented. Much attention was paid to including as many important target compounds as possible in the method, for the purpose of screening a broad range of pollutants in a single method.

Important method parameters were optimized, such as the extraction solvent, the separation gradient, the injection conditions, and most of all the MS/MS transitions for which pseudo-MRM gave a major sensitivity improvement in the case of PAHs, AZAs and PASHs.

The method was firmly validated thanks to the analysis of a Standard Reference Material which gave a quantification of 57 different PACs. 16 of the 22 certified compounds were in their certified range, and 35 additional compounds were reported. It would be interesting that future works also search for these compounds in SRM 2975.

Finally, the method was applied to environmental PM₁₀ samples collected in an urban parking lot. 38 different PACs were found in these samples and the maximal total concentration was 14 ng/m³. In the environmental samples as well as in the SRM, phthalic anhydride and naphthalic anhydride were among the most concentrated compounds, highlighting the interest of more monitoring of these PACs in combustion-related particles. Cross-plots of diagnostic ratios finally confirmed that fuel combustion and vehicular traffic was the main emission source of PACs in the parking lot.

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ORCID

Mathieu Galmiche  <http://orcid.org/0000-0001-5840-4786>

Olivier Delhomme  <http://orcid.org/0000-0001-5312-8858>

Yannis-Nicolas François  <http://orcid.org/0000-0002-8776-071X>

Maurice Millet  <http://orcid.org/0000-0001-7542-2636>

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