Simultaneous determination of PAHs, nitro-PAHs and quinones in aerosol samples

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Abstract

The study focuses in 20 PAHs, 27 nitro-PAHs and 5 quinones associated particulate-phase, collected inside a bus station and in Baia de Todos os Santos area.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of environmental pollutants that might be present in both vapor and particulate phases. As products of incomplete combustion processes, PAHs and their derivatives are present not only in ambient particles but also in urban dust[1]. PAHs and their nitrated and oxygenated derivatives deserve attention due to their well known toxicities and harmful effects on health. Certain PAHs are carcinogenic and/or mutagenic, and nitro-PAHs and quinones have proved to be more potentially mutagenic and/or carcinogenic than the parent PAHs[2]. The main goal of this study was to develop a comprehensive, simple and green analytical method for simultaneous determination of PAHs, nitro-PAHs and quinones in atmospheric particulate matter using GC–MS[3]. Was employed the Doehlert matrix and response surface methodology for optimizing simultaneous extraction of the studied substances in one single step. In this latter, a very simple and fast sample preparation was sought, requiring a very low extraction volume and bypassing pre-concentration, sample fractionation and clean-up prior to analysis.The method was validated by using the IUPAC criteria and urban dust particulate matter SRM 1649b (NIST).The methodology was applied to real samples collected at a bus terminal in Salvador, BA, Brazil.

Results and Discussion

This method employs a miniaturized micro-extraction step that uses 500 µL of an acetonitrile–dichloromethane mix and instrumental analysis by high-resolution GC–MS. The results are in good agreement with the certified values and show recoveries between 75% and 145%. Limit of detection (LOD) values for PAHs were found to be between 0.5 pg (benzo[a]pyrene) to 2.1 pg (dibenzo[a,h]anthracene), for nitro-PAHs ranged between 3.2 pg (1-nitrobenzo[e]pyrene) and 22.2 pg (3-nitrophenanthrene), and for quinones ranged between 11.5 pg (1,4-naphthoquinone) and 458 pg (9,10-phenanthraquinone). The validated method

was applied to real PM_{10} samples (n=5) collected on quartz fiber filters. The results are shown in Table 1.

Table 1. Absolute mass units (pg) and concentration ranges (ng m^{-3}) for PAHs, nitro-PAHs and quinones in particulate matter samples PM_{10} (n = 5).

Compounds*	Mass (pg)	Concentration range	Compounds*	Mass(pg)	Concentration range
1,4-benzoquinone	68,8	3.25 - 9.45	9,10-phenanthraquinone	LOD > 25,7	1.50 - 4.55
naphthalene	13,9	0.74 - 1.80	3-nitrophenanthrene	125	5.03 - 22.3
1,4-naphthoquinone	47,5	7.87 - 7.25	9-nitrophenanthrene	155	6.21 - 28.3
acenaphthylene	2,37	0.13 -0.30	2-nitroanthracene	218	9.11 - 39.5
acenaphthene	4,78	0.25 - 0.69	9-nitroanthracene	485	15.3 – 31.6
fluorene d10*	-	-	Benzo[a]anthracene	88,1	4.66 - 15.0
fluorene	19,4	1.13 - 2.72	chrysene	66,9	3.54 - 11.1
1-nitronaphthalene	102	7.06 - 12.7	2-nitrofluoranthene	369	13.4 - 69.4
1.2 - naphthoquinone	LOD > 3,93	0.27 – 0.58	3-nitrofluoranthene	445	15.4 – 29.9
1-methyl-4-nitronaphthalene	n.d	n.d	1-nitropyrene	288	4.93 - 26.5
2-nitronaphthalene	158	11.1 - 21.9	2-nitropyrene	114	4.15 - 19.5
2-nitrobiphenyl	49,8	1.72 – 4.00	4-nitropyrene	133	4.71 - 24.1
1-methyl-5-nitronaphthalene	n.d	n.d	Benzo[b]fluoranthene	65,3	3.48 - 11.2
1-methyl-6-nitronaphthalene	n.d	n.d	Benzo[k]fluoranthene	58,8	3.16 - 10.1
2-methyl-4-nitronaphthalene	n.d	n.d	7-nitrobenz[a]anthracene	166	9.95 - 28.6
phenantrene	100,7	5.59 - 14.4	Benzo[a]pyrene	26,6	1.42 - 4.49
anthracene	18,5	0.98 - 2.84	peryleno	20,3	1.03 - 3.43
3-nitrobiphenyl	20,4	1.47 - 2.49	6-nitrochrysene	98,0	3.38 - 17.8
4-nitrobiphenyl	10,0	0.44 - 1.32	3-nitrobenzanthrone	64,7	3.89 - 10.8
9,10-anthraquinone	644	25.1 - 115	Indeno[1.2.3 c.d]pyrene	7,60	0.40 - 1.27
5-nitroacenaphthene	19,9	0.57 - 3.69	Dibenzo[a.h]anthracene	14,4	0.76 - 2.53
fluoranthene	25,6	1.28 - 3.78	6-nitrobenzo[a]pyrene	146	4.62 - 26.7
pyrene d10*	-	-	1-nitrobenzo[e]pyrene	54,9	2.05 - 11.8
2-nitrofluorene	51,8	2.06 - 10.0	Benzo[ghi]perylene	6,84	0.35 - 1.16
pyrene	34,0	1.66 - 4.63	3-nitrobenzo[e]pyrene	21,3	0.89 - 3.00
2-nitrophenanthrene	173	9.92 - 30.3	coronene	1,1	0.06 - 0.18

Concentrations in the PM10 samples ranged from 0.06 to 15 ng m^{-3} for PAHs, from < LOD to 69.4 ng m^{-3} for nitro-PAHs, and from 0.27 to 115 ng m^{-3} for quinones. The quantification of such compounds as benzo[a]pyrene, 1-nitropyrene, 3-nitrofluoranthene and 9,10-anthraquinone at elevated concentrations indicates the impact of emission sources and incomplete combustion processes, primarily diesel engines and diesel exhaust gases[4].

Conclusions

The use of a GC-MS method and a simple micro-extraction device was proposed for the extraction of 52 organics compounds. The method allowed simultaneous characterization of PAHs, nitro-PAHs and quinones at low concentrations in atmospheric particulate matter. The concentrations of PAHs, nitro-PAHs and quinones found in real samples collected from a bus station showed concentration levels comparable with the data in the literature.

Acknowledgements

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