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Determination of Nitro Polycyclic aromatic hydrocarbons in PM2.5 using GC-MS/MS

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives, such as nitrated, oxygenated, and hydroxylated derivatives (NPAHs, OPAHs, and OHPAHs), are ubiquitous atmospheric pollutants with toxic, mutagenic, and carcinogenic properties. These compounds are predominantly produced from a wide variety of anthropogenic sources such as the incomplete combustion of fossil fuels for industrial plants, heating, as well as diesel powered vehicles. NPAHs, which generally exhibit higher mutagenicity and carcinogenicity than the parent PAHs, are also generated from atmospheric reactions of PAHs released into the gas-phase with radical species such as OH and NO3 radicals and nitrogen oxides. Concentrations of NPAHs adhering to air particulate matter are generally 10 to 100 times lower than concentration of PAH and the complex matrix of atmospheric particles, it's difficult to detect the content of NPAHs in the total suspended particulates. It had be published that the detection of NPAHs using HPLC-FLD, GC-ECD, GCMS-NCI, etc, but have not be reported using GC-MS/MS to detect the content of NPAHs.
In this study, we try to detect the content of NPAHs in the total suspended particulates using gas chromatography Tandem mass spectrometry (GC-MS/MS). For the high selectivity of GC-MS/MS, it can significantly reduce the affect of the matrix and system detection limits to enhance the detect accuracy of NPAHs in the total suspended particulates.

Experimental

Sample pretreatment

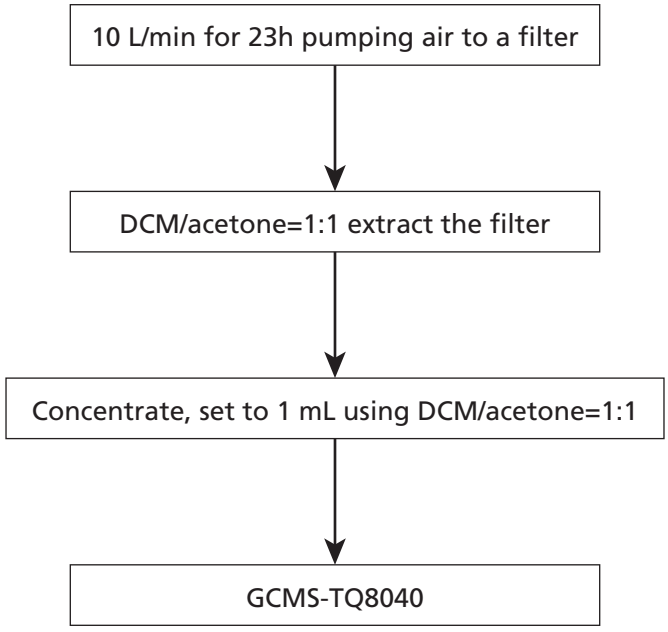

Figure 1. Scheme of Sample preparation

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Instrument

A triple quadruple mass spectrometer (Shimadzu GCMS-TQ 8040, Kyoto, Japan) was used to analyze the NPAHs in PM2.5 samples.

GC	
analysis column	: Rxi-5 Sil MS, 30m×0.25mmid ×0.25µm
Carrier gas	: Helium
Inlet temp	: 280°C
Col oven temp program	: 60°C(1min)_10°C/min_300°C(10 min)
Col flow	: 1.69 mL/min
Injection mode	: Splitless (1 min)
High pressure injection	: 250 kPa (1 min)
MS	
Ionization mode	: EI
Ion source temp	: 300°C
IF temp	: 280°C
CID gas	: Argon
Injection volume	: 2µL
The MRM parameter of NPAHs is showed in table 1.	

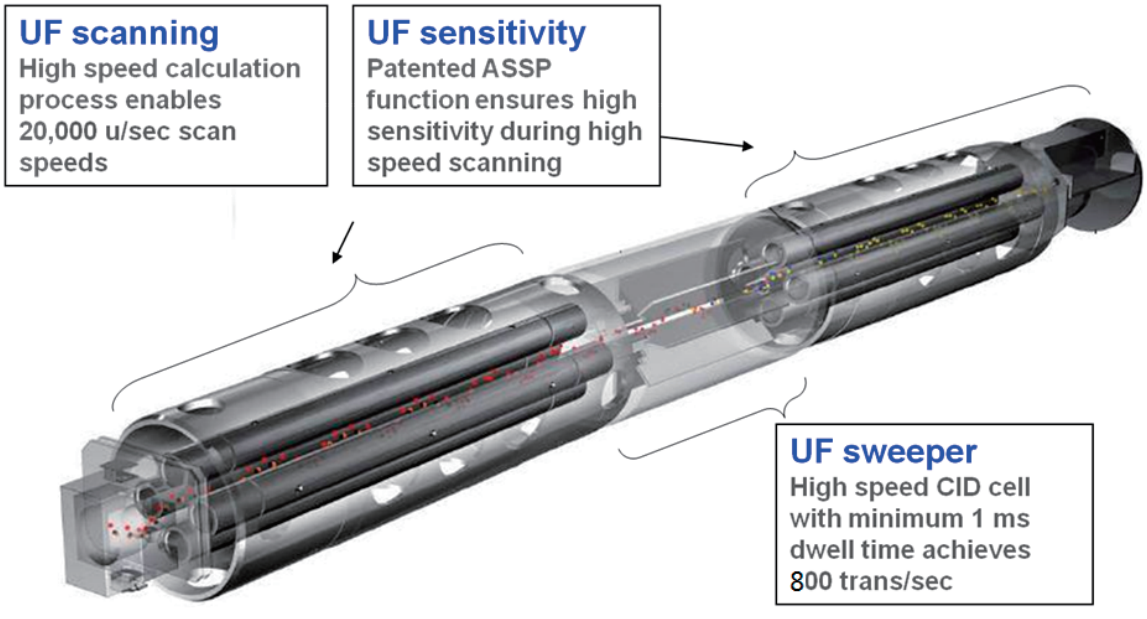

Figure 2. Key features of GCMS-TQ 8040

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Talbe1. MRM parameter for NPAHs

No.	Compound name	Retention Time (min)	CAS Number	Target Ion	Ref.Ion1	Ref.Ion2
1	1-Nitronaphthalene	8.658	86-57-7	127>77.1(15)	115>89.1(15)	173>115.1(18)
2	9-nitroanthracene	11.516	602-60-8	176>150.1(24)	193>165.1(21)	223>165.1(24)
3	4- nitropyrene	13.339	57835-92-4	247>189(30)	217>189.1(27)	189>187(36)
4	1- nitropyrene	13.612	5522-43-0	247>189.2(30)	217>189.1(24)	189>187.1(30)
5	7-Nitrobenz(a)anthracene	14.558	20268-51-3	226>224(30)	215>213(30)	215>189.1(21)
6	6-Nitrobenz(a)pyrene	17.747	63041-90-7	267>239(30)	239>237(30)	250>247.9(30)

Result

The standard chromatography of NPAHS

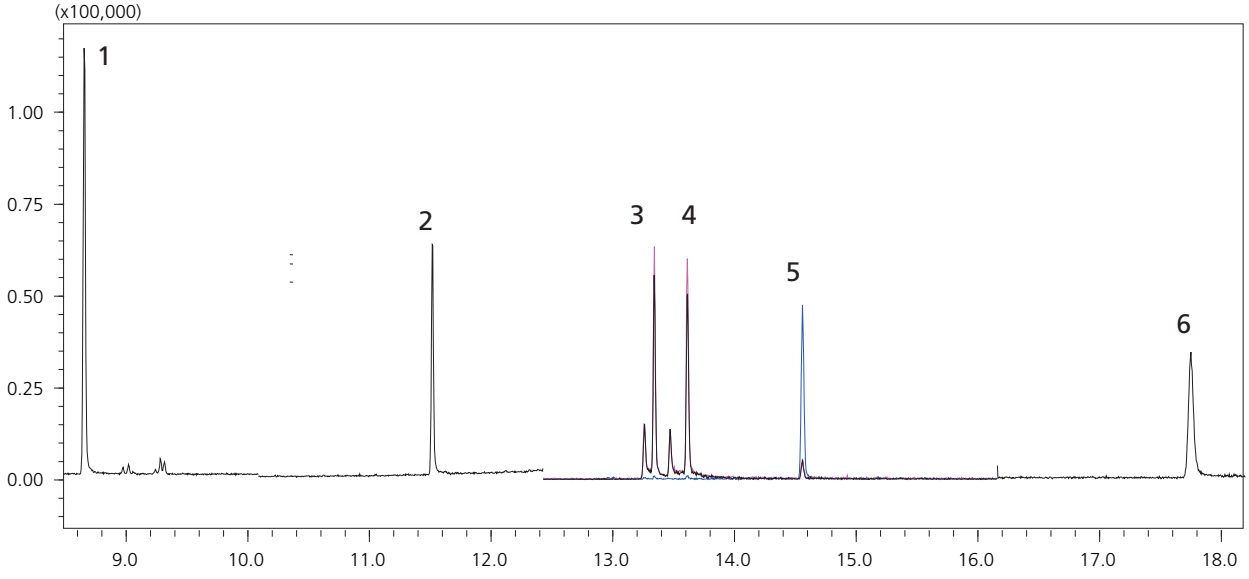

Figure 3. The MRM chromatogram of NPAHs (concentration of each compound : 10ppb)

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The calibration curve of NPAHs

The standard sample was diluted by hexane to the content of 0.5, 1, 2, 5, 10, 20, 50, 100 μg/L, the calibration curve and the Relative coefficients (r) were showed in Fig.2.The Limit of Detection (LOD) were calculated by the 3 S/N (Peak to Peak).

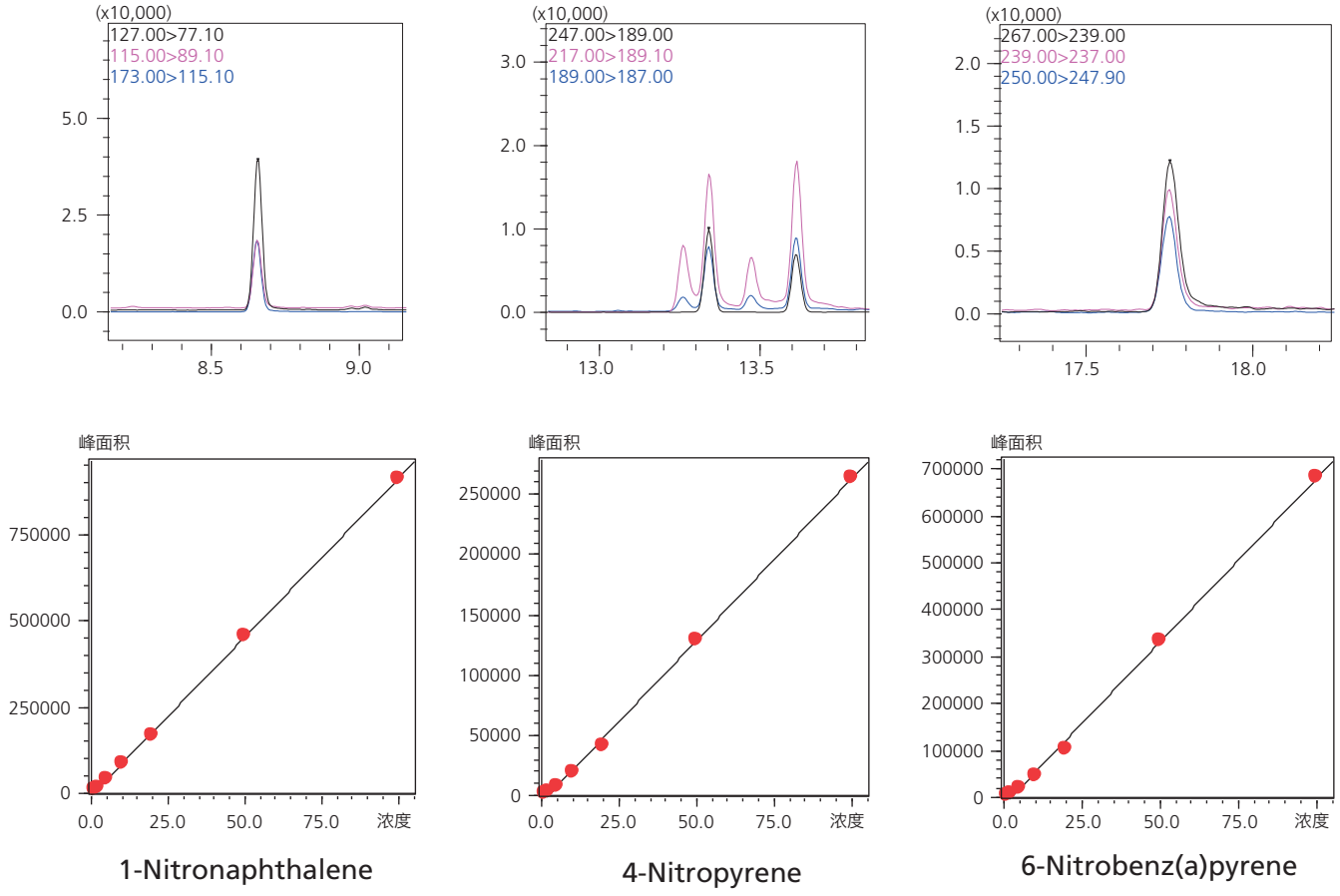

Figure 4. calibration curve of NPAHs (10ppb)

Talbe2. The relative coefficients (r), limits of detection (LOD, μg/L) and the repeatability (n=8)

No.	Compound name	R	LOD (μg/L)	1μg/L RSD%
1	1-Nitronaphthalene	0.9998	0.064	6.39
2	9-nitroanthracene	0.9997	0.073	6.42
3	4- nitropyrene	0.9992	0.031	8.83
4	1- nitropyrene	0.999	0.046	5.49
5	7-Nitrobenz(a)anthracene	0.999	0.082	5.79
6	6-Nitrobenz(a)pyrene	0.999	0.248	7.03

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Recovery test

Add the amount of 1ng NPAHs standard samples in the blank filter was analyzed under the same conditions. Three replicates were analyzed for the spike level. Table 3 lists the recoveries and precision values obtained in the validation portion of the study.

Talbe3. The recovery results of NPAHs

No.	Compound name	Spiked amount of 1 ng NPAHs (n=3)	
		Average recovery (%)	RSD (%)
1	1-Nitronaphthalene	0.9998	0.064
2	9-nitroanthracene	0.9997	0.073
3	4- nitropyrene	0.9992	0.031
4	1- nitropyrene	0.999	0.046
5	7-Nitrobenz(a)anthracene	0.999	0.082
6	6-Nitrobenz(a)pyrene	0.999	0.248

Conclusions

A quick, easy, reliable and robust analytical method using GC-MS/MS for determining the amount of 6 kinds of NPAHs in the total suspended particulates was developed. Using DCM:actone=1;1 directly extracted the atmospheric sampling filter can largely reduced the sample pretreatment time, and the MRM mode in GC-MS/MS can provide much better selectivity thus significantly lower system detection limits. This GC-MS/MS method yields excellent precision, sensitivity and respectable selectivity for NPAHs.

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