Quantitative analysis of nitro-polycyclic aromatic hydrocarbons in $PM_{2.5}$ samples with graphene as a matrix by MALDI-TOF MS

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Supplementary Information

Synthesis of 9-nitroanthracene-d_9

0.9411 g of powered anthracene-d_{10} and 5mL of glacial acid were added into a 50 mL three-necked round-bottomed flask with a 25 mL dropping funnel and an electromagnetic stirrer. The flask was immersed in a water bath at 20-25°C, and 0.45 mL of concentrated nitric acid (70 % by weight) was added slowly from the dropping funnel with stirring vigorously. The rate of addition was controlled and the reaction temperature did not exceed 30 °C. After all of nitric acid has been added, the mixture was stirred until a clear solution was obtained, then stirring was continued for 1 h. The solution was filtered to remove unreacted anthracene-d_{10}, and a mixture of 3 mL of concentrated hydrochloric acid (37 % by weight) and 3 mL of glacial acetic acid was added dropwise to the filtrate with vigorous stirring. The pale-yellow precipitate which forms was separated by suction filtration on a sintered-glass funnel and was washed with a small amount of glacial acetic acid. The obtained orange compound was removed from the funnel and triturated thoroughly with 20 mL of warm (>60 °C) 10 % sodium hydroxide solution. The product was separated from the warm slurry by suction filtration and was finally washed thoroughly with warm water (>60 °C) until the washings were neutral The crude 9-nitroanthracene-d_9 was dried and recrystallized from glacial acetic acid.

Characterization of 9-nitroanthracene-d_9

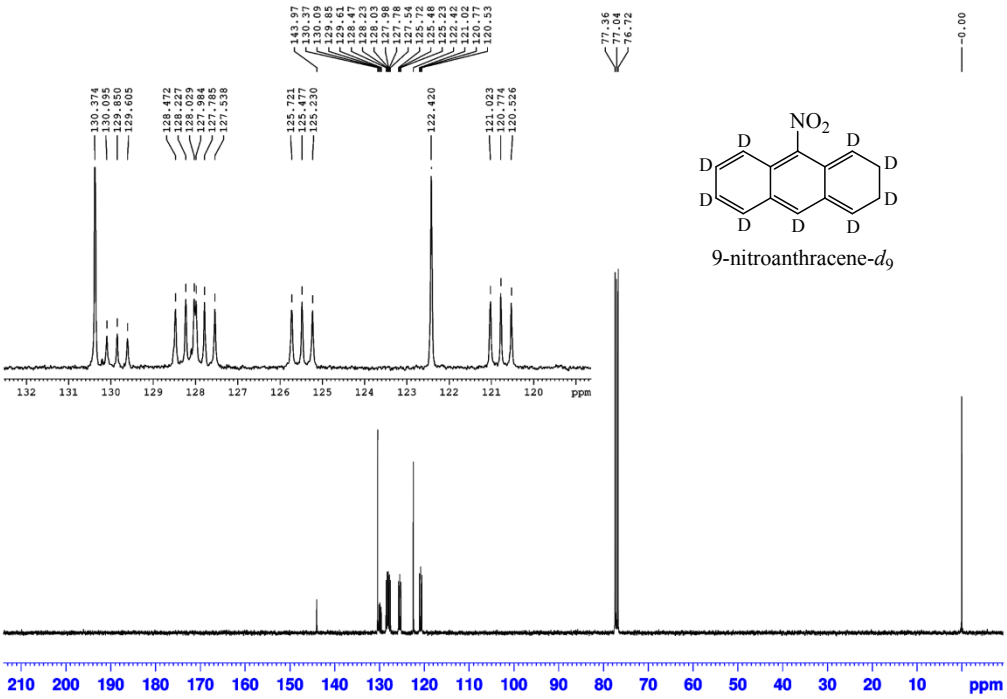

Fig. 1 ^{13}CNMR chart of 9-nitroanthracene-d_9($CDCl_3$,400 MHz)

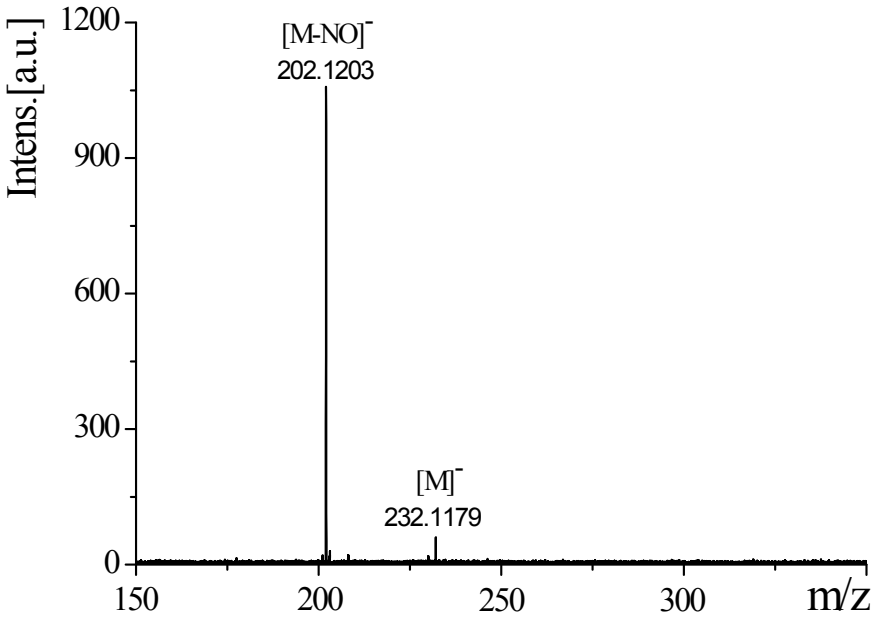

Fig. 2 MALDI-TOF MS chart of 9-nitroanthracene-d_9

Table S1. The linear response ranges and detection limits of 1-NP from different analytical methods.

Quantified compound name	Detection method	Linear ranges	LOD	Reference
1-NP	HPLC-FL	0.01-7μg/mL	2.20pg	49
1-NP	HPLC-MS	0.01-10ng/mL	0.001ng	67
1-NP	GC-EI/MS	200-1000ng/mL	200pg	68
1-NP	GC-NCI/MS	1-50ng/mL	0.1pg	16
1-NP	MALDI-TOFMS	0.005-0.5μg/μL	0.74ng/μL	This work*

* MALDI-TOF MS instrument detection limit.