

Determination of Amines Associated with Particles by Gas Chromatography-mass Spectrometry



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Abstract: A method was developed for the simultaneous determination of thirteen amines including seven aliphatic amines, two heterocyclic amines and four aromatic amines associated with atmospheric particulate matter (PM) by gas chromatography-mass spectrometry (GC-MS). PM samples were ultrasonically extracted with ultrapure water, and derivatized by benzenesulfonyl chloride (BSC) under alkaline condition. The derivatives were extracted with dichloromethane and then detected by GC-MS with DB-5MS chromatographic column. The method detection limits ($S/N = 3$) and quantitative limits ($S/N = 10$) for thirteen amines were between 0.00008–0.01695 $\mu\text{g mL}^{-1}$ and 0.00026–0.0565 $\mu\text{g mL}^{-1}$, respectively. Good linear correlations were obtained for all the thirteen amines with the linear relative coefficients between 0.9903–0.9996. The recoveries of thirteen amines were in the range of 54.4%–159.7% except for methylamine and benzylamine at spiked level of 1.0 $\mu\text{g mL}^{-1}$, and the reproducibility expressed as relative standard deviations (RSDs) of thirteen amines were less than 30%, which indicated that the method had high precision and good reliability. $\text{PM}_{2.5}$ samples were collected in Guangzhou city, China, and nine amines were detected by our established method. Methylamine, dimethylamine and butylamine accounted for 90% of the total nine amines which suggested that they were main amine components in $\text{PM}_{2.5}$, while propylamine exhibited the lowest level with the concentration less than 1.0 ng m^{-3} .

Key Words: Atmospheric particulates; Amines; Gas chromatography-mass spectrometry

1 Introduction

Amines are organic derivatives of ammonia with one or more hydrogen atoms replaced by substituent groups such as alkyl or aryl groups, and they are divided into aliphatic amines, alcohols amines, amides, aromatic amines and heterocyclic amines according to the different substituent groups. Amines in atmosphere are emitted as gases from a wide range of sources, including natural sources (such as ocean, forest fire and vegetation) and anthropogenic sources (such as animal husbandry operations, industry, composting operations and vehicular exhaust)^[1–6]. Most amines are toxic, allergic and irritate to the eyes, nose, skin, respiratory tract, liver and

kidneys, and even some can react with nitrites to generate nitrosamines which are carcinogenic^[1,7]. The atmospheric reaction mechanisms of amines include the acid-base reaction with nitric acids, sulfuric acids and organic acids, the reaction with carbonyl compounds to form imines, enamines and amine polymers, and the reaction with oxidants such as OH, and O_3 ^[8]. Amines participate in the formation of secondary organic aerosol, promote the formation of new particles and the growth of submicron particles, and then affect ambient air quality and regional climatic change directly or indirectly. For instance, amines could comprise up to 20% of the organic matter in fine particulate matter (PM) during some wintertime periods in the State of Utah, USA^[9].

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Nowadays, the research of amines in aerosols has become a hot topic, and the most commonly used techniques include gas chromatography (GC) coupled with different detectors, high-performance liquid chromatography (HPLC), and ion chromatography (IC). Typically, Akyuz *et al.*^[10] determined thirty-four amines in PM_{2.5} and PM₁₀ using isobutyl chloroformate (IBCF) as the derivatization reagent. Dong *et al.*^[11,12] determined six heterocyclic amines in PM₁₀ using HPLC. Tao *et al.*^[13] determined six amines during new particles formation events using IC. Generally, amines are firstly derivatized before analysis by GC-MS. The derivatization methods include acylation, silylation, dinitrophenylation and permethylation, etc.^[14,15], which are time-consuming and tend to side reactions. In addition, HPLC is prone to "out of column effect"^[16]. For IC analysis, the pretreatment process is simple and does not require derivatization, however, only a few low molecular weight aliphatic amines and alcohol amines can be analyzed, and it is difficult to separate diethylamine and trimethylamine.

Based on the method developed and used by Zhang *et al.*^[17] for water samples, a rapid and simple method for the determination of amines associated with PM was established in this study. The derivatization process did not need to add other reagents as catalyst and could be completed at ambient temperature under alkaline condition. The column heating program of GC was optimized. The qualitative and quantitative ions of seven aliphatic amines, two heterocyclic amines and four aromatic amines were determined in the study. The established method will provide technical support for the further study of particulate amines.

2 Experimental

2.1 Instruments and reagents

Numerical Control Ultrasonic Cleaner (KQ-500DE, Kunshan Ultrasonic Instrument Co., Ltd.), Multi Head Digital Display Constant Temperature Magnetic Stirrer (HJ-6A, Changzhou Aohua Instrument Co. Ltd.), Rotary Evaporator (R-300, Switzerland, Buchi) and Nitrogen Blowing Instrument (BF-2000, Beijing Bafang Century science and Technology Co Ltd.) were used for the samples pretreatment. Agilent 7890A gas chromatograph equipped with a 5975C mass detector (GC/MSD, Agilent 7890A/5975C, USA) was used to analyze the amines.

Ultrapure water (18.25 MΩ cm), dichloromethane (Pesticide Analysis Grade, Germany, CNW), methanol, *n*-hexane (LC, Germany Merck), anhydrous sodium sulfate (AR, Sinopharm Chemical Reagent Co., Ltd.), NaOH (AR, Guangzhou Chemical Reagent Factory), 36.5% HCl solution (AR, Guangzhou Chemical Reagent Factory) and Na₂CO₃ (AR, Tianjin Noke Technology Development Co. Ltd.) solution were used for the samples pretreatment.

Benzenesulfonyl chloride (BSC, 99%, J&K Scientific Ltd.) was used as derivatization reagent. Hexamethylbenzene (99%, Germany, Dr. Ehrenstorfer) was used as internal standard. Dimethylamine-d₆ (99%, Canada, Toronto Research Chemicals) was used as recovery standard.

The following reagents were used in this study: thirteen amines standard solution consists of seven aliphatic amines, including methylamine (2500 μg mL⁻¹ in water, USA, Accustandard), dimethylamine, ethylamine (both were 10000 μg mL⁻¹ in methanol, Canada, Toronto Research Chemicals), propylamine (1000 μg mL⁻¹ in methanol, USA, Accustandard), diethylamine, butylamine and dibutylamine (all were high purity reagent, Germany, Dr. Ehrenstorfer), two heterocyclic amines including pyrrolidine (high purity reagent, Germany, Dr. Ehrenstorfer) and morpholine (high purity reagent, China, J&K Scientific Ltd), and four aromatic amines, including *N*-methylaniline, benzylamine (both were 99%, Germany, Dr. Ehrenstorfer), 2-ethylaniline (99%, China, J&K Scientific Ltd.) and 4-ethylaniline (99%, Japan, TCI). The structure and molecular weight of thirteen amines are shown in Table 1.

2.2 Sample collection

A PM_{2.5} high volume sampler (Andersen Instruments Inc., flow rate of 1.13 m³ min⁻¹. Quartz fiber filters were used to

Table 1 The structure and molecular weight of thirteen amines

No.	Compounds	Structure	Molecular weight
1	Methylamine, MA	<chem>N</chem>	31.06
2	Dimethylamine, DMA	<chem>CN(C)</chem>	45.08
3	Ethylamine, EA	<chem>CCN</chem>	45.08
4	Diethylamine, DEA	<chem>CCN(CC)</chem>	73.14
5	Propylamine, PA	<chem>CCCN</chem>	59.11
6	Butylamine, BA	<chem>CCCCN</chem>	73.14
7	Dibutylamine, DBA	<chem>CCCCN(CCCC)</chem>	129.00
8	Pyrrolidine, PYR	<chem>C1CCNC1</chem>	71.12
9	Morpholine, MOR	<chem>C1CCNOC1</chem>	87.12
10	<i>N</i> -methylaniline, NMA	<chem>CNc1ccccc1</chem>	107.16
11	Benzylamine, BMA	<chem>Nc1ccccc1C</chem>	107.16
12	2-Ethylaniline, 2-ELA	<chem>Nc1ccccc1CC</chem>	121.18
13	4-Ethylaniline, 4-ELA	<chem>Nc1ccc(CC)cc1</chem>	121.18

USA) was used to collect the PM_{2.5} samples at the sampling collect particles and baked for 4 h in muffle furnace under the temperature of 500 °C before use. The filters were balanced in the temperature and humidity chamber (at 25 °C, RH = 50%) for 24 h before weighing, then transported to the laboratory and stored at -40 °C until analysis. The PM_{2.5} samples were collected on the roof of Specimen Building in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences from 1 to 3 October, 2014, and each sample was collected 24 h continuously.

2.3 Sample pretreatment

Quarter of each sample was ultrasonically extracted with ultrapure water (3 × 20 mL) for 15 min. The extract was collected in a 250 mL flat bottom flask, and basified with 4 mL of 10 M NaOH solution. Then 1 mL BSC was added. The flask was closed and agitated using a magnetic stirrer for 30 min at room temperature. Another 5 mL of 10 M NaOH solution was added and the mixture was agitated for 30 min at 80 °C. Subsequently, the solution was cooled down and acidified to pH 5.5 with 36.5% HCl solution. The mixture was extracted with dichloromethane (3 × 10 mL). The aqueous solution was discarded while the organic phase was washed once with 10 mL 0.05 M NaCO₃ solution and dried with anhydrous sodium sulfate. The solvent was evaporated to specific volume for GC-MS analysis.

2.4 Preparation of standard solution

Mixed standard solution was dissolved or diluted in methanol to 100 µg mL⁻¹ for each amine, and 1 mL of the solution was used to react with BSC for derivatization. Then each amine derivative was diluted to the following concentration 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 8.0, 10.0, 15.0, 20.0 and 25.0 µg mL⁻¹ for the establishment of calibration curve.

2.5 Chromatographic condition

Samples were analyzed for thirteen amines using an Agilent GC-MS. The chromatographic column was a 30 m DB-5MS column (i.d. 0.25 mm, 0.25 µm film thickness, Agilent, USA). The GC temperature program showed as follows: temperature was initiated at 80 °C, held for 1 min, and then continuously programmed to 180 °C at 5 °C min⁻¹, 240 °C at 10 °C min⁻¹, 290 °C at 25 °C min⁻¹ and finally held for 10 min. The injector and transfer line temperatures were maintained at 290 °C. Helium was used as carrier gas and the flow rate was 1.56 mL min⁻¹. Splitless injection of a 1-µL sample was performed. Electron energy was 70 eV and scan range was *m/z* 50–450.

2.6 Quality control and quality assurance

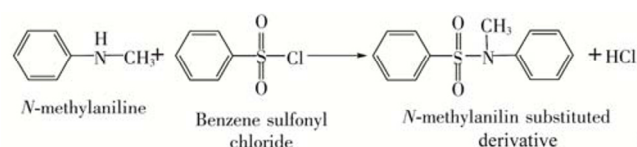
Hexamethylbenzene was added as internal standard. All samples were spiked with DMA-d6 served as recovery standard. Laboratory blanks consisting of ultrapure water and matrix blanks consisting of blank filters were treated and analyzed as regular samples to detect the impact of solvent and matrix on the method, and control the pollution in the whole experiment process in which human errors or environmental factors could bring. The results showed that the concentration of amines in blank filters was less than 1% of the actual samples, being similar with that in the laboratory blanks. Thus the data was not corrected by the blank concentrations.

3 Results and discussion

3.1 Optimization of method

3.1.1 Determination of qualitative and quantitative ions of amines

The qualitative and quantitative ions of the first nine amines in Table 2 were determined based on the previous study^[17], and the ions of latter four amines were confirmed by the derivatization reactions and authentic standard verification in this study. *N*-methylaniline was taken as an example as follows:



The substituted derivative of *N*-methylaniline was (C₆H₅)OSON(CH₃)(C₆H₅) (molecular weight 247). The ions observed at *m/z* 77, 106 and 141 could be formed by the loss of (C₆H₅)(CH₃)NOSO, (C₆H₅)OSO and (C₆H₅)N(CH₃) groups from the molecular ion observed at *m/z* 247, respectively. Therefore, ion fragments should include C₆H₅, C₇H₈N, C₆H₅O₂S as well as the molecular ion, and they were further confirmed by the authentic standard. Finally, the *m/z* of 77, 106 and 247 were chose for qualitative and quantitative analysis. Qualitative and quantitative ions of the other three anilines were determined in the similar way. The results of thirteen amines are shown in Table 2.

3.1.2 Selection of extractant and optimization of chromatographic conditions

In previous studies^[10], HCl solution was used to extract amines in particles. Amines are polar organic compounds, easily soluble in water and exist in particles mainly in the form of aminium salts. In addition, water was already applied in the extraction of other water soluble ions in particles. Therefore, in view of the safety and operation convenience, ultrapure water, instead of HCl solution, was chose to be extractant in this study. The GC temperature procedure used

Table 2 Parameters of the calibration curves

No.	Compound	Qualitative ion and quantitative ion (<i>m/z</i>)	Regression equation	Correlation coefficient (R^2)	Linear range ($\mu\text{g mL}^{-1}$)
1	MA	77, <u>171</u> *, 141, 106	$y = 0.0895x + 0.0042$	0.9929	1.0–25.0
2	DMA	77, 120, 141, <u>185</u>	$y = 0.3743x - 0.0012$	0.9996	0.5–15.0
3	EA	77, 141, 170, <u>185</u>	$y = 0.0837x - 0.0034$	0.9994	0.2–10.0
4	DEA	77, 141, <u>198</u> , 213	$y = 0.5162x - 0.0115$	0.9992	0.5–20.0
5	PA	77, 141, <u>170</u> , 199	$y = 0.5112x - 0.0158$	0.9993	0.1–10.0
6	BA	77, 141, <u>170</u> , 213	$y = 0.3209x - 0.0148$	0.9982	0.2–10.0
7	DBA	77, 141, 184, <u>226</u>	$y = 0.4226x - 0.0154$	0.9993	0.2–10.0
8	PYR	70, 141, 210, <u>211</u>	$y = 0.1230x - 0.0039$	0.9993	0.2–10.0
9	MOR	86, 141, 184, <u>227</u>	$y = 0.0830x - 0.0020$	0.9995	0.1–10.0
10	NMA	106, 77, 182, <u>247</u>	$y = 0.1660x - 0.0033$	0.9994	0.2–10.0
11	BMA	77, <u>106</u> , 125, 143	$y = 0.2171x - 0.0233$	0.9907	0.2–10.0
12	2-ELA	77, 91, 120, <u>261</u>	$y = 0.1281x - 0.0161$	0.9903	0.2–10.0
13	4-ELA	77, 93, 120, <u>261</u>	$y = 0.1744x - 0.0645$	0.9907	1.0–20.0

*: Bold and underlined words represent the quantitative ion.

in the previous study^[17] was 120 °C (3 min), 5 °C min⁻¹ to 220 °C, 10 °C min⁻¹ to 290 °C (5 min), however, it was difficult to separate the peaks of DMA and an impurity. Herein, the heating process was constantly adjusted and the optimum heating condition was shown in Section 2.5, where the peaks of DMA and the impurity were completely separated. The total ion current is shown in Fig. 1.

3.2 Method validation

3.2.1 Calibration curve

Calibration curves were carried out for the thirteen amines concentration ranged from 0.05 $\mu\text{g mL}^{-1}$ to 25 $\mu\text{g mL}^{-1}$, and high linearity of calibration curves for thirteen amines was observed with coefficients of determination (R^2) in the range of 0.9903–0.9996. Table 2 summarizes the parameters of the calibration curves.

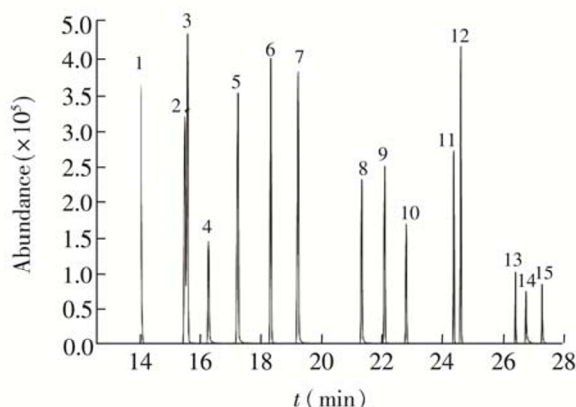


Fig. 1 Total ion chromatography of amines (SIM mode)

1, Hexamethyl benzene; 2, Dimethylamine-d6; 3, Dimethylamine; 4, Methylamine; 5, Ethylamine; 6, Diethylamine; 7, 1-Propylamine; 8, 1-Butylamine; 9, Pyrrolidine; 10, Morpholine; 11, Dibutylamine; 12, *N*-methylaliline; 13, 2-Ethylaniline; 14, Benzylamine; 15, 4-Ethylaniline

3.2.2 Recovery and precision

The 1.0, 5.0 and 10.0 $\mu\text{g mL}^{-1}$ standard solutions for each amine were spiked on blank filters, and then pretreated as regular samples. The relative standard deviations (RSDs) of the measurement results were the ratio of standard deviation to arithmetic mean of measured results and calculated to reflect the precision and reproducibility of the results. The limit of detection (LOD) and limit of quantification (LOQ) of each amine were defined as three and ten times of the signal-to-noise ratio (S/N), respectively. All the recoveries, LODs, LOQs and RSDs are listed in Table 3.

The recoveries of thirteen amines in the concentration of 1.0 $\mu\text{g mL}^{-1}$ ranged from 75.2% to 237.9%, which was interpreted by the high deviation of calibration curve in low concentration. The corresponding RSDs ranged from 0.07% to 28.9%. In contrast, the recoveries of thirteen amines in the concentration of 5.0 $\mu\text{g mL}^{-1}$ and in the concentration of 10.0 $\mu\text{g mL}^{-1}$ ranged from 70.2% to 114.4% and from 54.4% to 98.4%, respectively. The corresponding RSDs ranged from 3.3% to 22.7% and from 0.02% to 22.9%, respectively, indicating that the method had good reproducibility. To sum up, it showed that the pretreatment method was reliable.

3.3 PM_{2.5} sample analysis

The PM_{2.5} samples were pretreated and analyzed by using the methods shown in Section 2.2 and 2.5, respectively. Nine amines including MA, DMA, EA, DEA, PA, BA, DBA, PYR and MOR were determined in the PM_{2.5} samples. The results are showed in Table 4. Among them, MA was the maximum amines in PM_{2.5}, the sum of the predominant components (MA, DMA and DBA) contributed approximately 90% of the total nine amines, and PA was the minimum one with the concentration less than 1 ng m^{-3} (Fig. 2).

Table 3 Recoveries, LODs, LOQs and RSDs of thirteen amines ($n = 3$)

No.	Compound	Spiked ($\mu\text{g mL}^{-1}$)	Recovery (%)	RSD (% , $n = 3$)	LOD ($\mu\text{g mL}^{-1}$)	LOQ ($\mu\text{g mL}^{-1}$)
1	DMA	1.0	143.1	5.2	0.00024	0.00081
		5.0	89.5	3.3		
		10.0	94.4	3.7		
2	MA	1.0	237.9	1.0	0.01136	0.03788
		5.0	94.6	21.4		
		10.0	92.1	5.1		
3	EA	1.0	148.9	13.1	0.01695	0.05650
		5.0	98.3	11.7		
		10.0	84.5	3.9		
4	DEA	1.07	147.9	5.0	0.00008	0.00026
		5.38	100.0	6.7		
		10.76	88.7	3.1		
5	PA	1.0	157.8	13.7	0.00101	0.00335
		5.0	101.4	8.4		
		10.0	87.8	2.5		
6	BA	0.83	152.4	2.8	0.00213	0.00710
		4.14	98.7	9.0		
		8.29	81.5	2.5		
7	PYR	1.58	159.7	0.6	0.00046	0.00153
		7.93	110.1	9.3		
		15.87	96.3	0.02		
8	MOR	1.21	155.4	0.07	0.00048	0.00160
		6.08	114.4	12.1		
		12.16	98.4	2.9		
9	DBA	1.06	75.2	9.0	0.00008	0.00027
		5.31	70.2	13.5		
		10.62	54.4	22.9		
10	NMA	1.10	100.4	6.9	0.00019	0.00064
		5.50	84.4	8.5		
		11.01	92.7	5.8		
11	2-ELA	1.17	148.5	0.9	0.00119	0.00395
		5.84	77.0	11.1		
		11.68	60.4	2.5		
12	BMA	1.0	189.7	2.2	0.00011	0.00037
		5.0	104.0	22.7		
		10.0	84.5	0.4		
13	4-ELA	1.08	109.5	28.9	0.00673	0.02242
		5.38	87.0	19.3		
		10.76	85.8	5.6		

Table 4 Analysis results of amines in $\text{PM}_{2.5}$

Sample No.	Concentration(ng m^{-3})								
	DMA	MA	EA	DEA	PA	BA	PYR	MOR	DBA
1	51.6	131.7	6.61	6.92	0.88	5.67	2.04	2.04	26.4
2	55.9	127.2	6.78	6.74	0.94	5.35	2.85	2.19	30.0
3	42.6	109.7	5.41	6.39	0.80	4.97	1.77	2.38	25.2

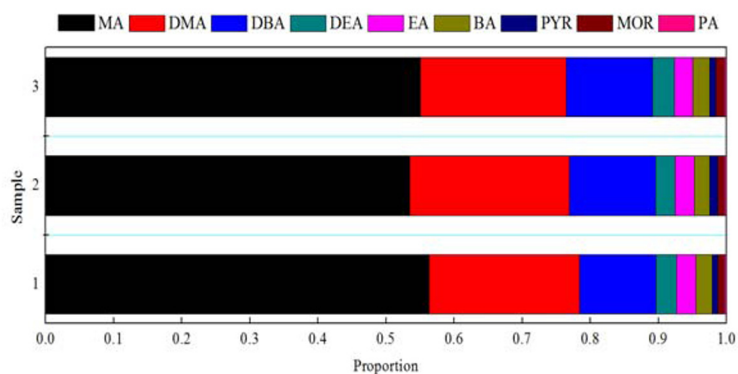


Fig.2 The proportion of nine amines in $\text{PM}_{2.5}$

4 Conclusions

Based on the pretreatment process of amines in water samples described in the previous study^[17], a method for the determination of amines associated with PM was established in this study. Ultrapure water was used as extractant in the pretreatment process, and it only cost about 45 min for ultrasonic extraction, which was time-saving compared with the traditional Soxhlet extraction (48 h). Moreover, the derivatization reaction was completed in 1 h at room temperature under alkaline conditions and did not need other reagents as catalyst. In addition to the nine amines reported in previous studies, four anilines were determined by the theoretical analysis and authentic standards verification. The GC temperature program was optimized to make sure that the thirteen amines, internal standard and recovery standard could be well separated. The whole process was simple and time-saving. The established method was well applied in the PM samples. Nine amines including MA, DMA, EA, DEA, PA, BA, DBA, PYR and MOR were determined in PM_{2.5}. MA, DMA and DBA accounted for 90% of the total nine amines which indicated that they were predominated amines in PM_{2.5} while PA exhibited the lowest level in PM_{2.5} with the concentration less than 1.0 ng m⁻³.

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