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RESEARCH PAPER

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 μg mL^{-1} and 0.00026–0.0565 μg 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 μg 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. $PM_{2.5}$ 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 $PM_{2.5}$, 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 PM_{10} using isobutyl chloroformate (IBCF) as the derivatization reagent. Dong *et al*[11,12] determined six heterocyclic amines in PM_{10} 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 Ddigital 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.

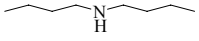
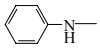
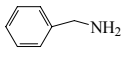
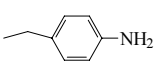
Ultrapure water (18.25 MΩ cm), dichloromethane (Pesticide Analysis Grade, Germany, CNW), methanol, *n*-hexane (LC, Germany Merck), anhydrous sodium sulfate (AR, Sinopharm Chemical Reagent Co., Ltd.), NaOH (AR, Guangzhou Chemical Reagent Factory), 36.5% HCl solution (AR, Guangzhou Chemical Reagent Factory) and Na_2CO_3 (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 m^3 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		31.06
2	Dimethylamine, DMA		45.08
3	Ethylamine, EA		45.08
4	Diethylamine, DEA		73.14
5	Propylamine, PA		59.11
6	Butylamine, BA		73.14
7	Dibutylamine, DBA		129.00
8	Pyrrolidine, PYR		71.12
9	Morpholine, MOR		87.12
10	*N*-methylaniline, NMA		107.16
11	Benzylamine, BMA		107.16
12	2-Ethylaniline, 2-ELA		121.18
13	4-Ethylaniline, 4-ELA		121.18