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Determination of atmospheric alkylamines by ion chromatography using 18-crown-6 as mobile phase additive

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ABSTRACT

An improved ion chromatographic method including two elution procedures was proposed for the quantitative determination of atmospheric alkylamines in field atmospheric samples involving high levels of inorganic cations by using 18-crown-6 as mobile phase additive. When 18-crown-6 was added to the mobile phase, the retention times increased significantly for Na⁺, NH₄⁺, K⁺ and primary alkylamines but decreased for secondary and tertiary alkylamines due to the complexation with certain cations and interaction with both stationary and mobile phases of 18-crown-6. As a result, the separation of the cations was greatly promoted, which reduced the interference of peak distortion of overloaded inorganic cations on the quantitation of adjacent alkylamines. By using the presented method, five inorganic cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) and six alkylamines (dimethylamine (DMAH⁺), trimethylamine + diethylamine (TMAH⁺ + DEA⁺), propylamine (MPAH⁺), triethylamine (TEAH⁺), ethanolamine (MEOAH⁺) and triethanolamine (TEOAH⁺)) were effectively separated and determined, and the relative standard derivations (RSDs) of objective cations were all less than 1% for retention time and 3.1% for peak area (n=9), respectively. The linearity was excellent for each cation (R² > 0.993) except for NH₄⁺ and TEOAH⁺ showing a non-linear response (R² > 0.998 for theoretical non-linear fitting), and the detection limit of these cations were 0.03–1.19 ng. The proposed method was successfully used in the determination of both alkylamines and inorganic cations in ambient particulate matters and gaseous alkylamines in ceiling duct exhaust. The annual average concentrations of DMAH⁺, TMAH⁺ + DEA⁺ and TEAH⁺ were 15.56, 4.35 and 16.00 ng m⁻³ in PM_{2.5} over Shanghai in 2013. The concentrations of gaseous DMA and TMA + DEA in ceiling duct exhaust reached a maximum of 940.0 and 112.7 μg m⁻³, and were positively correlated with the human activity intensity, suggesting that human excreta emissions was a potential important source of atmospheric alkylamines in urban area of Shanghai.

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1. Introduction

Amines are ubiquitous organic compounds in ambient atmosphere worldwide, and have a wide variety of both natural and anthropogenic sources [1,2]. Short-chain alkylamines are the most abundant species of amines in the environment and have attracted increasing attention because of their potential roles in the formation of secondary aerosols by enhancing nucleation and growth of new particles, which has been revealed by both theoretical calculation and field observation [3–8]. However, there still lacks extensive field concentration measurements and source emission inventories, which is largely attributed to the fact that simple and effective determination methods for atmospheric alkylamines have been

rarely developed. Therefore, reliable, simple and low-cost determination methods for alkylamines in observation work in ambient atmospheric environment and source regions are necessary.

Atmospheric alkylamines can be detected on line through MS techniques, such as high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) [9,10], ambient pressure proton transfer mass spectrometer (AmPMS) [11], proton transfer reaction-time-of-flight mass spectrometer (PTR-TOFMS) [12], aerosol time-of-flight mass spectrometer (ATOFMS) [13,14], which have high time resolution but are usually costly and difficult-to-maintain. As for off-line measurements, chromatographic methods, including gas chromatography (GC), high performance liquid chromatography (HPLC), and ion chromatography (IC) in tandem with various detectors, are the most commonly used methods. The derivatization procedures are usually required to avoid peak tailing and reach good separation for GC analysis, or to be converted to detectable compounds for HPLC analysis with ultraviolet (UV) or

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fluorescence detectors [15–17]. Unfortunately, the derivatization procedures are time-consuming and labor-intensive and usually result in decrease of method recovery, reproducibility and accuracy. On-line derivatization of alkylamines with *o*-phthalaldehyde (OPA) has been developed to simplify the manual operation procedures, but only primary amines can react with OPA and then to be detected [16]. In contrast, alkylamines can be detected conveniently without any derivatization operation by conductivity detection in IC methods. However, due to the extremely low levels of alkylamines in ambient atmosphere, together with the similar retention behaviors between alkylamines and inorganic cations, some alkylamines would coelute with each other or with inorganic cations. Moreover, the overloading of inorganic cations in field samples would lead to peak broadening and distortion and further limit the separation of adjacent alkylamines. In order to address the above problems, following measures have been proposed: using MS as a detector to identify different ions through *m/z* [17,18], pre-treatment using SPE to remove inorganic cations [19], re-separation with column switching technique [20], or significantly changing the retention behaviors of relevant analytes.

18-crown-6 can form stable complexes with some specific cations, such as K^+ , NH_4^+ , Sr^{2+} , Ba^{2+} [21], which will greatly change the distribution of these cations between the mobile and stationary phases [22,23]. Therefore, 18-crown-6 has been used in ion chromatography to improve the separation of inorganic cations and solve the problem of quantitative analysis for samples with cations in disproportionate concentration ratios (e.g., high Na^+ and low NH_4^+) by combining the 18-crown-6 groups into the stationary phase [24–27] or adding 18-crown-6 into the mobile phase [23,28–30]. Similar to NH_4^+ , primary amines can also complex with 18-crown-6 through hydrogen bonds [30,31], which enables the systematic investigation of the influence of mobile phase 18-crown-6 on the retention behaviors of alkylamines and inorganic cations in this study. Nine alkylamines (methylamine ($MMAH^+$), dimethylamine ($DMAH^+$), trimethylamine ($TMAH^+$), ethylamine (MEA^+), diethylamine ($DEAH^+$), triethylamine ($TEAH^+$), propylamine ($MPAH^+$), ethanolamine ($MEOAH^+$), and triethanolamine ($TEOAH^+$)) and five inorganic cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) are taken in to consideration. By adjusting the concentration of 18-crown-6 and the elution procedure, an improved method including two single elution procedures was developed to accurately determine low levels of atmospheric alkylamines in the presence of high concentrations of inorganic cations using ion chromatography. The present method was successfully applied to atmospheric $PM_{2.5}$ samples and exhaust gasses of ceiling ducts in Shanghai.

2. Experimental

2.1. Chemicals

18-crown-6 and alkylamines, including methylamine hydrochloride, dimethylamine hydrochloride, trimethylamine hydrochloride, ethylamine hydrochloride, diethylamine hydrochloride, triethylamine hydrochloride, ethanolamine hydrochloride, triethanolamine hydrochloride, and propylamine, were all purchased from Aladdin Industrial Corp. (97–99.5%, Shanghai, China). Methanesulfonic acid (MSA) (HPLC grade) was purchased from ANPEL (Shanghai, China), and ultrapure deionized water (18.25 $M\Omega$ cm) was produced with Molelement 1805A water purifier system (Molecular, Shanghai, China).

2.2. Instrumentation

The analysis of alkylamines was carried out by Dionex ICS-3000 system (Thermo Fisher Scientific Inc.) with IonPac[®] CS17 analytical column (2 × 250 mm) and CG17 guard column (2 × 50 mm) (Thermo Fisher Scientific Inc.), which have extremely

low hydrophobicity and moderate column capacity (0.363 and 0.073 meq/column for CS17 and CG17 respectively) [32]. Samples were injected via an AS40 autosampler with an injection volume of 100 μ L and detected by conductivity detector after passing through the columns and a CERS 500 suppressor. The suppressor was operated in AutoSuppression Recycle Mode and the baseline noise was always below 0.01 μ S. MSA, 18-crown-6, and deionized water were mixed online using a quaternary gradient pump. The column temperature, cell temperature and flow rate of mobile phase was set as 35 °C, 40 °C and 0.25 mL/min respectively unless specified otherwise. Two standard solutions named Sample-a and Sample-b were prepared to investigate the influence of variable proportion of inorganic cations to alkylamines on the elution procedure performance and the analytical accuracy. The concentrations of alkylamines and inorganic cations were close for Sample-a, while for sample-b, the concentrations of inorganic cations were two orders of magnitude higher than those of alkylamines, which was similar to the actual atmospheric samples with high I/A (concentration ratio of inorganic cations to alkylamines). The mass loadings ($massloading = concentration \times injectionvolume$) of each cation for Sample-a and Sample-b in this study are shown as follows: sample-a: $Na^+/NH_4^+/K^+$ (50 ng), $Mg^{2+}/Ca^{2+}/MMAH^+/DMAH^+/MEA^+$ (100 ng), $TMAH^+/DEAH^+/MPAH^+/MEOAH^+$ (150 ng), $TEAH^+$ (200 ng), $TEOAH^+$ (400 ng); sample-b: Na^+/NH_4^+ (1000 ng), K^+ (500 ng), Mg^{2+}/Ca^{2+} (250 ng), $MMAH^+/DMAH^+/MEA^+$ (5 ng), $TMAH^+/DEAH^+/MPAH^+/MEOAH^+$ (7.5 ng), $TEAH^+/TEOAH^+$ (20 ng). All data acquisition and chromatographic analysis were carried out using Chromeleon[®] 6.8 software.

2.3. Sample collection and pretreatment

2.3.1. Particulate sample

Totally 131 $PM_{2.5}$ samples were collected on the roof of No. 4 teaching building of Fudan University in Shanghai during Mar. 25–Apr. 27, 2013 (spring), Jul. 16–Aug. 17, 2013 (summer), Oct. 30–Nov. 20, 2013 (autumn), and Dec. 1, 2013–Jan. 23, 2014 (winter). The sampling duration of each sample filter was generally 24 h and the detail information of the sampling site and sampling procedure was given elsewhere [16]. After sampling, one-fourth of each filter was extracted ultrasonically with 15 mL deionized water for 40 min and the extract was then filtered through microporous membranes (0.45 μ m, Shanghai Xinya Purification Equipment Co., Ltd). The filtrate was stored at 4 °C and should be determined as soon as possible.

2.3.2. Gaseous sample

NH_3 and alkylamines in the ceiling duct connected to a septic tank were also collected on the roof of the teaching building in January 2016, and the detail information about the ceiling duct was presented previously [33]. Gas samples were collected with two fritted bubblers (containing 10 mL 0.005 M H_2SO_4 as absorbing solution in each bubbler) in series linked to a gas sampler (GS-IIIC, Shanghai Hongyu Environmental Application Research Institute) at a flow rate of 0.4 L/min, and the sampling duration was 50 min for each sample. A Teflon membrane (PALL Life Science, 2 μ m) was placed in front of the bubblers to exclude the interference of the corresponding species in particles. After sampling, the absorbing solution was filtered through microporous membranes and stored at 4 °C for IC analysis. The absorption efficiency was proved to be higher than 95% for NH_3 and 80% (81.0%–97.4%) for alkylamines.

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