



Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma



Determination of atmospheric amines by on-fiber derivatization solid-phase microextraction with 2,3,4,5,6-pentafluorobenzyl chloroformate and 9-fluorenylmethoxycarbonyl chloride

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ARTICLE INFO

Article history:

Received 1 October 2014
Received in revised form
27 November 2014
Accepted 11 December 2014
Available online xxx

Keywords:

Dimethylamine
Alkylamines
2,3,4,5,6-pentafluorobenzyl chloroformate
9-fluorenylmethoxycarbonyl chloride
On-fiber derivatization
SPME

ABSTRACT

Alkylamines play an important role in atmospheric chemistry and are of concern for human health. Determining them from the vapor phase is challenging owing to their high polarity and volatility, water solubility, low concentrations, and poor chromatographic properties. We propose on-fiber derivatization solid-phase microextraction (SPME) to increase sensitivity and selectivity for the determination of alkylamines in air samples. SPME fibers coated in head-space with 2,3,4,5,6-pentafluorobenzyl chloroformate (PFBCF, 10 min) or 9-fluorenylmethoxycarbonyl (FMOC) chloride (5 min) were exposed to the sample for 5–120 min, after which the derivatized alkylamines were thermally desorbed in the GC injection port and analyzed by GC-MS. The specific focus of the research was dimethylamine (DMA) but, as well as secondary amines, both coating agents readily react with primary and tertiary amines and with ammonia at ambient temperatures. The fiber coating procedures, sampling times, and analytical conditions were optimized, and methods were tested with natural samples. PFBCF was more selective and almost an order of magnitude more sensitive than FMOC chloride. Both reagents are applicable, however, depending on the requirements. With scan mode and use of molecular ion for quantification, the limit of quantification for DMA was $0.17 \mu\text{g L}^{-1}$ when derivatized with PFBCF and $3.4 \mu\text{g L}^{-1}$ when derivatized with FMOC chloride. When selected ion monitoring was used with the most abundant ion, the limit of quantification for DMA was 2.8 ng L^{-1} . Intermediate reproducibility expressed as relative standard deviation was around 30% with PFBCF and less than 20% with FMOC chloride. Fibers coated with PFBCF could be used at least up to 24 h when stored at 4°C and for 5 to 7 h when stored at room temperature. After sampling/derivatization, storage time before analysis should not exceed 48 h at 4°C or 24 h at room temperature. At maximum, the PFBCF-coated fiber can be used in 100 coating/sampling/analysis cycles.

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1. Introduction

Amines are ubiquitous atmospheric organic bases originated from a wide range of sources in the environment [1]. They have high acid-neutralizing properties and may play an important role in atmospheric aerosol formation through enhancing nucleation [2,3]. Alkylamines form aerosols in chamber experiments and they have been determined in ambient aerosols at various geographical locations. Vapor-phase amines are still poorly characterized [4–6]. In addition to their importance in atmospheric chemistry, some amines are hazardous to health, either directly or through formation of N-nitrosamines [7–9].

Today, quantitative analysis of atmospheric amines (aerosol or vapor phase) relies mainly on off-line chromatographic techniques after filter, adsorbent or denuder sampling. Because of their high volatility (vapor pressures over 100 kPa at 20°C for the most volatile ones), and their reactivity, adsorption, and thermal decomposition, amines pose a problem for the most frequently used non-polar columns in GC. Liquid chromatography, and especially ion chromatography (IC), is suitable for the analysis of small alkylamines, but sensitivity is low with most detectors. Derivatization is often used to increase the chromatographic retention and detection sensitivity [10,11].

On-line methods are reported for determinations of alkylamines in aerosol or gas phase by mass spectrometry, but individual amines are not accurately determined, mainly because of the small molecular weights and trace level atmospheric concentrations [12–14]. Despite the significance of alkylamines in atmospheric chemistry and for human health, there are still only

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a few methods available for their determination in gas samples [15,16].

Solid-phase microextraction (SPME) is a simple, fast, economical, and solvent-free sample preparation technique, in which a fiber is coated with a stationary phase and exposed to an aqueous or gaseous sample during a certain period of time. Analytes are then desorbed from the fiber in a hot GC injector, and analyzed by GC or dissolved in a suitable solvent for LC or CE analysis [17,18]. Derivatization is frequently used together with SPME to improve sampling efficiency or the analytical properties of analytes [19]. Derivatization can be done before sampling, on-fiber during the sampling, or after sampling before the analysis.

Chloroformates are common derivatization reagents for the determination of amines [10]. 9-Fluorenylmethoxycarbonyl chloride (Fmoc chloride) has frequently been used for the derivatization of methylamine, dimethylamine, and trimethylamine before LC analysis [20]. It has been used in combination with SPME before LC analysis, with derivatization carried out in a solution, followed by SPME of the derivatives. Moreover, sampling can be done from a liquid followed by immersion of the fiber in the derivatization solution or extraction/derivatization of analytes was done with fibers previously coated with reagent [21,22]. Isobutyl chloroformate has been used for the determination of amines extracted from atmospheric aerosols and gas-phase samples by GC-MS [23,24]. However, the procedures are time-consuming, laborious, and costly, including extraction, derivatization with a large volume of solvent and derivatization reagent and, finally, clean-up before the GC-MS analysis. In addition, the several sample preparation steps required result in high measurement uncertainty. 4-Nitrophenyl trifluoroacetate has been successfully used for derivatization of gaseous amines before SPME sampling [25], but this approach is not applicable for trace concentrations of amines in the atmosphere. The on-fiber derivatization of primary amines with pentafluorobenzaldehyde (PFBA) before GC-MS analysis has recently been reported, but is not suitable for secondary amines, which play a more important role in atmospheric chemistry [26].

In this research, the suitability of three derivatization reagents was tested for the on-fiber SPME derivatization and GC-MS analysis of amines in atmospheric gas-phase samples. One of the reagents, pentafluorobenzaldehyde (PFBA), has previously been used in on-fiber SPME of primary amines [27], and Fmoc chloride was used in on-fiber derivatization of aliphatic amines before HPLC analysis [21]. 2,3,4,5,6-Pentafluorobenzyl chloroformate (PFBCF) have been used in the off-line derivatization of amines and amino acids before HPLC analysis but not for on-fiber derivatization SPME GC analysis [27]. We clarify the applicability of these derivatization reagents for the determination of primary, secondary, and tertiary amines and ammonia in gas-phase samples. Methods for simultaneous sampling/derivatization were optimized especially for the highly volatile analyte dimethylamine, which was the main target of the study. Ethylamine and trimethylamine were included as well, so that primary, secondary, and tertiary amines would all be represented. The methods developed were applied to the determination of amines in natural atmospheric air samples. The suitability of the method was also tested for the determination of ammonia and methylamine.

2. Materials and methods

2.1. Materials and reagents

Polydimethylsiloxane/divinylbenzene SPME fibers (65 μm) (Supelco, Bellefonte, USA) installed to CUSTODION™ manual SPME syringes (Torion Technologies, American Fork, USA) were used throughout the study. Fiber coating material was chosen due to

higher affinity towards aromatic derivatization reagents. Before first use and between uses the fibers were conditioned according to the manufacturer's instructions.

A 33% solution of dimethylamine (DMA) in ethanol and a 40% solution of methylamine (MA) in water from Sigma-Aldrich (St. Louis, USA) were diluted in ultrapure water (DirectQ-UV, Millipore, USA) to give 214.5 mg L^{-1} and 2176 mg L^{-1} primary standards. In addition, solid ethylamine HCl (Sigma-Aldrich, St. Louis, USA) was used to prepare ethylamine (EA) primary standard (263.2 mg L^{-1}) by weighing it and diluting it with ultrapure water. A 25% aqueous solution of trimethylamine (TMA; Sigma-Aldrich, St. Louis, USA) was diluted with ultrapure water to obtain a 157.5 mg L^{-1} primary standard. These primary standards were further diluted with ultrapure water to obtain the other standards. Ammonia solution (min. 25%) was from VWR International (Fontenay-sous-Bois, France), and the stock solution of 2620 mg L^{-1} was prepared in water. Potassium hydroxide (5 M) (J.T. Baker, Sweden) was used for pH adjustment, to keep amines in the head space.

2,3,4,5,6-Pentafluorobenzaldehyde (PFBA, 98%), 2,3,4,5,6-Pentafluorobenzyl chloroformate (PFBCF, purity not available) and 9-fluorenylmethoxycarbonyl chloride (Fmoc chloride, >99% pure) were purchased from Sigma-Aldrich (St. Louis, USA). Note that Fmoc chloride is corrosive and can cause skin burns and eye damage. When not in use, all standards and reagents were stored in dark in a refrigerator. For coating procedures, derivatization reagents were used in pure form or diluted with acetonitrile (VWR International, 99.9%).

2.2. Gas chromatography–mass spectrometry

An Agilent 6890N GC coupled with an Agilent 5793N quadrupole mass selective detector (Agilent Technologies, Palo Alto, USA) was used for the analysis. Injections were made in splitless mode using a Merlin Microseal in a split/splitless injection port (Merlin Instrument Company, Half Moon Bay, USA). Injector temperatures and injection/desorption times were optimized with solutions of derivatization reagents and coated fibers. For these first experiments, parameters for coating and sampling were generic, since parameters were optimized later. The following trials were made to optimize injection temperature and desorption time for pure reagents: PFBCF 200, 250 °C and 10, 20, 30 s; Fmoc chloride 180, 200, 220, 250 °C and 10, 20, 30, 35, 40 s. For the preliminary studies with PFBA, the injector temperature was kept at 250 °C and desorption times were 10, 20, and 30 s.

The analytical column was a ZB-5MS (30 m \times 0.25 mm \times 0.25 μm , Phenomenex, Torrance, USA) with a 5% diphenyl, 95% dimethylpolysiloxane stationary phase. A 1 m \times 0.53 mm deactivated guard column was used in front of the analytical column, coupled to it with a deactivated press-fit connector (BGB Analytik, Boeckten, Switzerland). The carrier gas was helium (99.996%, AGA, Espoo, Finland) fed with a constant pressure of 90 kPa. All injections were made manually in splitless mode and in the case of liquid standards, one microliter was injected.

GC temperature programs optimized for the different derivatization reagents (optimization data not shown) were as follows: for PFBA and its derivatives 50 °C (2 min), then 15 °C/min to 135 °C, and then 20 °C/min to 280 °C; for PFBCF and its derivatives 50 °C (0 min), then ramp to 130 °C at 10 °C/min and to 280 °C at 100 °C/min and keep for 2 min; for Fmoc chloride and its derivatives 90 °C (2 min), then 5 °C/min to 130 °C, and then 50 °C/min to 280 °C (5 min). With all programs, the MS transfer line was maintained at 300 °C, the ion source temperature at 230 °C and the quadrupole temperature at 150 °C. The mass spectrometer was operated in scan mode with mass range from 40–450 amu for PFBA, 30–300 amu for PFBCF, and 50–400 amu for Fmoc chloride and their derivatives. Ions m/z 196 for PFBA, m/z

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