



Review

A review of sampling and pretreatment techniques for the collection of airborne amines



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ABSTRACT

This review critically assesses the methodologies available for sampling and pretreatment of amines in air and bound in airborne particulate matter. We emphasize the most common techniques reported to date for the collection of vapor-phase amines based on sorptive media [solution (e.g., with the aid of impinger), solid sorbents, solid-phase extraction (SPE), solid-phase microextraction (SPME), and denuder] or other approaches (e.g., derivatization). Moreover, we extend discussion to cover amines found in airborne particulate matter through membrane filters, impactors, or scrubbers. Finally, based on measurements made under laboratory and field conditions, we discuss the advantages and the disadvantages of each sampling and pretreatment technique for key amine species.

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1. Introduction

Atmospheric amine levels have increased significantly over the past 200 years due to anthropological causes (mainly biogenic from increased animal husbandry) now to exceed all natural (non-anthropological) sources combined (e.g., marine) leading to “nitrogen saturation” damage in forests and other environmental and ecological systems [1]. Although the database of atmospheric amines is smaller than other atmospheric volatile organic compounds (VOCs) [e.g., benzene, toluene and the xylenes (BTX) and carbonyl compounds], interest in their research has grown steadily in recent years. For example, Ge et al. [2] comprehensively reviewed up to 154 amines and 32 amino acids present in the atmosphere emitted from a range of sources. Cape et al. [3] also reviewed sources and fates of chemically complex atmospheric organic nitrogen compounds and the associated analytical issues. The atmospheric photochemistry and the fates of amines reacting with OH, O₃, and NO₃ have also been reviewed comprehensively [4].

Amine-emission sources include animal husbandry, automobiles, biomass burning, food processing and cooking, industrial activities, landfill, marine, sewage, and tobacco smoke. An emerging source of amine emissions has been reported to be carbon capture and storage (CCS) facilities [4]; amines are commonly used to reversibly capture CO₂ (e.g., ethanolamine – which can be thermally degraded to ethylamine and nitrosamines) [5]. Although the most common amines found in the atmosphere are methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA), the availability of data about them is still insufficient to estimate accurately their global emission fluxes (Gg N year⁻¹) [e.g., the sum of all three amines as (285 ± 78) with several major source components, such as animal husbandry (146 ± 45), marine (80, maximum), and biomass burning (60 ± 28)] [2].

As common atmospheric bases, amines can act as potential sinks for atmospheric inorganic acids (e.g., H₂SO₄) to yield particulate matter (PM) and aerosols [2]. Husbandry amines (MA, DMA, and TMA) undergoing photochemical reactions have been implicated to contribute ~10% to the annual N₂O budget; N₂O is an important atmospheric “greenhouse” gas, potentially influencing climate change [6]. DMA and ethylamine (EA) from inland biogenic sources are also important precursors of marine secondary organic aerosols (SOAs) [7]. The uptake of MA, DMA, and TMA (in the 15 ppb range) onto citric-acid and humic-acid substrates has been determined as $\sim 7 \times 10^{-3}$ and $\sim 5\text{--}12 \times 10^{-6}$ (mass ratio), respectively; as common components of fine particulate matter, these

acids are likely to be the potential sinks for airborne amines at the ppb level [8].

Atmospheric amines posed significant human-health risks directly or as more potent carcinogenic oxidation products (e.g., aminoxides and nitrosamines) [2]. For example, carcinogen dimethylnitrosamine [9], a chlorination disinfection byproduct of amines, has been detected in swimming pools well above the permissible regulatory level [10]. Mutagenic heterocyclic amines (present at low ppb or lower) have been detected in airborne particles, diesel-exhaust particles, cigarette smoke, cooking fumes, and other non-gaseous matrices [11]. Monocyclic aromatic amines were assessed as potential human carcinogens, and their environmental prevalence (e.g., indoor air) was discussed in detail [12].

In this review article, we present an overview to discuss and to evaluate a wide array of sampling and preconcentration methods needed for amine detection with the main emphasis on MA, DMA, and TMA. This study is a continuation of many efforts to review and to discuss the different sampling, preconcentration, and detection methods for the analysis of amines in the environment [e.g., [13]]. To this end, we expanded our review of field and laboratory studies, made 1980–2013, to cover most of the available approaches and to describe the basic characteristics of the most common techniques (e.g., the sorptive method). Through a comprehensive review of each technique and its field application, we address the fundamentals of amine-detection techniques and the associated quality assurance. Moreover, we extend discussion further with respect to basic quality assurance for their sampling and preconcentration (e.g., recovery) and to the presently available data measured under various conditions.

2. Sampling methods for amines in air

The quantitation of low-level amines (e.g., pptv in air) in environmental samples requires sufficient sample sizes and/or highly-sensitive detectors. Due to their low abundance in air, the determination of amines generally requires preconcentration or capture of large sample volumes (over 1 m³ in many cases) on sorptive media. The range of such media includes acidified water (in impingers), sorbents, acid-coated denuders, solid-phase extraction (SPE), solid-phase microextraction (SPME), and SPE/SPME coated with derivatization reagent. For amines on airborne particulate matter (PM), filters, membranes, and impactors have been used to capture PM independently of the gas-phase amines. Their preconcentration can also be made with the aid of derivatization.

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