**Atmospheric
Measurement
Techniques
Discussions**

Integrated method for the measurement of trace atmospheric bases

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Integrated method for the measurement of trace atmospheric bases

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Abstract

Nitrogenous atmospheric bases are thought to play a key role in the global nitrogen cycle, but their sources, transport, and sinks remain poorly understood. Of the many methods available to measure such compounds in ambient air, few meet the current
5   need of being applicable to the complete range of potential analytes and fewer still are convenient to implement using instrumentation that is standard to most laboratories. In this work, an integrated approach to measuring trace atmospheric nitrogenous bases has been developed and validated. The method uses a simple acid scrubbing step to capture and concentrate the bases as their phosphite salts, which then are
10   derivatized and analyzed using GC/MS and/or LC/MS. The advantages of both techniques in the context of the present measurements are discussed. The approach is sensitive, selective, reproducible, as well as convenient to implement and has been validated for different sampling strategies. The limits of detection for the families of tested compounds are suitable for ambient measurement applications, as supported
15   by field measurements in an urban park and in the exhaust of on-road vehicles.

1   Introduction

Nitrogenous atmospheric bases are thought to play a key role in the global nitrogen cycle, but their sources, transport, and sinks remain poorly understood. Few studies have addressed the chemistry and evolution of these compounds in the atmosphere,
20   and much uncertainty surrounds the range of atmospheric concentrations as a function of land use.

The U.S. Environmental Protection Agency (EPA) has recently shifted to a multi-pollutant approach to air quality management (2008, 2010), that will likely affect how nitrogenous bases are monitored and regulated in the future. Emerging tech-
25   nologies in the stationary and mobile source sectors will potentially constitute new sources of atmospheric nitrogenous bases, as illustrated by two examples below.

Carbon-dioxide-capture technologies from the emissions of fossil fuel power plants rely heavily on organic amino compounds (Choi et al., 2009). In 2010, the EPA's Tier 2 NO_x standard (2000) for on-road heavy duty diesel engines went into effect requiring the use of suitable NO_x reduction technologies such as urea injection or selective catalytic reduction (SCR).

Ammonia (NH_3), the predominant atmospheric base, plays a crucial role in determining the acid-neutralizing capacity of tropospheric air masses (Jacob et al., 1986a,b). Airborne sulfuric and nitric acid, which are produced by the atmospheric oxidation of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), respectively (Seinfeld and Pandis, 2006), react with gaseous NH_3 to afford fine particles (aerosol fraction with a mass median aerodynamic diameter of 2.5 μm or less, $PM_{2.5}$) of ammonium bisulfate (NH_4HSO_4), ammonium sulfate [$(NH_4)_2SO_4$], and ammonium nitrate (NH_4NO_3) (Russell et al., 1983; Russell and Cass, 1986; Brost et al., 1988; Russell et al., 1988a,b). Those secondary air pollution particles are well-known to degrade visibility via efficient light scattering (Larson and Cass, 1989; Horvath, 1991, 1993; Malm et al., 1994, 1996; Eldering et al., 1996; Barthelmie and Pryor, 1998), leading to the dense haze common to many polluted urban atmospheres. Atmospheric NH_3 emissions from anthropogenic sources are increasingly coming under scrutiny as associated environmental impacts are becoming better understood (Sutton et al., 1998). Evidence is mounting (Asman et al., 1998; Schjorring, 1998) that dry and wet deposition of NH_3 and its salts can adversely affect terrestrial (Friedland et al., 1991; Pearson and Stewart, 1993; Fangmeier et al., 1994; Sutton et al., 1994, 1995a,b; Hornung and Sutton, 1995; Bobbink et al., 1998; Pearson and Soares, 1998; Wyers and Erisman, 1998) and aquatic (Asman and Berkowicz, 1994; Lee et al., 1998; Spokes et al., 2000) ecosystems. Deposited NH_3 disturbs soil nutrient balance (Hornung and Sutton, 1995) and can contribute toward soil acidification following nitrification (Wyers and Erisman, 1998).

Studies on the significance and atmospheric composition of other nitrogenous bases aside from NH_3 are scarce. The sources, fluxes, and dynamics of atmospheric amines, including gas-phase reactions, gas-to-particle conversion and deposition have been

discussed in recent reviews (Ge et al., 2011a,b). Low-molecular-weight amines are emitted to the atmosphere by widespread and diverse sources (Ge et al., 2011a), including industrial emissions (Akyuz and Atu, 2006), vehicle exhaust (Cadle and Mulawa, 1980; Cadle et al., 1980), cattle feedlots (Mosier et al., 1973; Schade and Crutzen, 1995), waste incinerators (Leach et al., 1999), and sewage treatment plants (Pehlivanoglu-Mantas and Sedlak, 2006; Hwang et al., 1995). Once emitted into the atmosphere, amines are chemically transformed through reactions with oxidants such as hydroxyl radicals and ozone. Aromatic amines absorb radiation at wavelengths above 290 nm and, therefore, can be photolytically active in the troposphere. A major reason for the current interest in atmospheric amines is driven by their potential role in particle formation, as discussed by Ge et al. (2011a,b). Aliphatic amines have been detected in both urban and rural atmospheric aerosols (Murphy et al., 2007). Laboratory and field studies suggest that aminium salts contribute significantly to nanoparticle growth (Barsanti et al., 2009; Smith et al., 2010) and must be accounted for in climate models. Methanesulfonic acid (MSA) is present in significant quantities in air and has been used as a biogenic tracer. Salts of MSA and aliphatic amines are becoming recognized as important emissions in the marine environment and are implicated in aerosol formation.

Another class of alkaline, volatile compounds of concern are classified here as *activated primary amines* (X-NH$_2$, where $X = $ NR$^1R^2$, OR). Hydrazine ($X = $ NH$_2$), methylhydrazine ($X = $ NHCH$_3$), and hydroxylamine ($X = $ OH) are high-energy propellants used in large volumes for aerospace operations. These compounds also have a number of industrial applications, including in the synthesis of polymers, pesticides, pharmaceuticals, and chemotherapeutic agents (Schmidt, 2001), as etchants in microstructure fabrication (Mazzoni and Davis, 1991), and as additives to steam boiler water (Danielson and Conroy, 1982). Hydroxylamine also has been detected in emissions from a municipal incinerator, a waste collection center, and a sewage treatment plant (Leach et al., 1999). Little is known about the atmospheric fate of these activated primary amines, but it is expected to be dominated by the oxidative lability of the N-N

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and N-O bonds. The health effects associated with the inhalation of hydrazines have been studied in laboratory animals and include damage to internal organs, creation of blood abnormalities, irreversible deterioration of the nervous system, and documented teratogenic and mutagenic effects (Wald et al., 1984; Vernot et al., 1985; Choudhary and Hansen, 1998). These findings have led to the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limits (RELs) for hydrazine and methylhydrazine of 30 and 40 parts per billion (ppb), respectively (1995). Far less is known about the health effects of hydroxylamine and no REL has been published to date.

Numerous techniques have been described for the capture and analysis of a wide range of basic nitrogenous compounds. Most of these reports, however, are focused on a specific subset of this compound class, such as low-molecular weight aliphatic amines or methylhydrazines. An integrated approach is described here that is based on one method for capturing the gas-phase compounds and commonly used analytical instrumentation (GC/MS and LC/MS) for analyzing the derivatized compound mixtures. Much effort was dedicated to making the methods reliable and convenient to implement. The approach is sensitive, selective, and reproducible and has been validated for different sampling applications.

2 Experimental

2.1 Improved colorimetric NH_4^+ analysis

The literature indophenol blue (phenate) method (APHA, 2005) was adapted as described below. Briefly, the method involves the reaction of NH_3, hypochlorite, and phenol, catalyzed by sodium nitroprusside to form indophenol, an intensely blue dye. When the concentration of samples were expected to exceed the dynamic range of the method ($1.50\,\mathrm{mg\,l^{-1}}\ NH_4^+$), they were diluted with 0.04% phosphorous acid solution prior to color development. Aliquots (three replicates, $295\,\mu l$) from each

color-developed (2 h in the dark) sample were transferred to adjacent wells of a flat bottom 96-well plate (340 µl working volume). For each plate, aliquots (three replicates, 295 µl) from the following color-developed samples were also included: five standards (0.10–1.0 mg l^{-1} NH$_4^+$), deionized water, and appropriate controls. The absorbance of

5   the plates was measured at 631, 632, 633, 634, 635, and 800 nm using a Spectra Max PLUS 384 microplate spectrophotometer (Molecular Devices). For each sample, the reading at 800 nm was subtracted from the average of the readings in the 631–635 nm range to compensate for any baseline effects. The values from each triplicate group of samples then were averaged into a final absorbance value that was converted into

10 the concentration of NH$_4^+$ using the linear calibration curve generated with each set of samples.

2.2   Derivatization and analysis of amines

To a solution of H$_3$PO$_3$ (0.04 % w/v, pH 2.4, 2 ml) in a 10-mm test tube containing the amine sample was added borate buffer (aqueous sodium tetraborate decahy-

15 drate, 2.5 % w/v, pH 9.3, 1 ml) followed by the 2,4-dinitrofluorobenzene (DNFB) reagent (2 ml DNFB in 25 ml THF, 140 µl). The mixture was sonicated until a homogenous solution was obtained, mixed by vortex agitation for 20 s, heated at 60 °C for 60 min in a GC oven, and allowed to cool to room temperature over the course of 10 min. To the mixture was added sodium hydroxide (2 M, 350 µl) followed by further heating at 60 °C for

20 60 min. The mixture was cooled to room temperature and a 150 µl aliquot was added to a 250 µl glass insert in a standard 2-ml autosampler vial for analysis by LC/MS (see Supplement for conditions).

For GC/MS analysis, isopropyl acetate containing 1-fluoronaphthalene (20 µg l^{-1}, 2 ml) was added to the derivatized aqueous sample, followed by vortex agitation for

25 20 s. The organic (top) layer that formed on standing was transferred to a 15-ml conical tube followed by addition of sodium carbonate solution (1 M, 1 ml). The two components were mixed by vortex agitation for 20 s and centrifuged for 3 min to separate the two phases. The organic layer was transferred to a 15-ml conical tube and deionized

water (1 ml) was added. The two components were mixed by vortex agitation for 20 s and centrifuged for 3 min. The organic layer was removed, washed with deionized water a second time, and added to the top of a Pasteur pipette plugged with glass wool and a 3-cm column of anhydrous sodium sulfate. An aliquot (1.2 ml) of the dry isopropyl acetate solution was concentrated to ca. 120 µl (10 ×) using a Model SVC100H Speed-Vac system (Savant) and added to a 250 µl glass insert in a standard 2-ml autosampler vial for analysis by GC/MS (see Supplement for conditions).

2.3 Derivatization and analysis of activated primary amines (X-NH$_2$)

To a solution of H$_3$PO$_3$ (0.04 % w/v, pH 2.4, 6 ml) of the X-NH$_2$ compound(s) in a 10-mm test tube was added 2-furaldehyde (50 µl). The mixture was mixed by vortex agitation for 20 s and heated for 2 h at 50 °C in a GC oven and a 150 µl aliquot was added to a 250 µl glass insert in a standard 2-ml autosampler vial for analysis by LC/MS (see Supplement for conditions).

For GC/MS analysis, the aqueous phase was extracted with a solution of 1-fluoronaphthalene (20 µg l^{-1}, 2 ml) in isopropyl acetate followed by vortex agitation for 20 s. The organic (top) layer that formed on standing was removed and added to the top of a Pasteur pipette plugged with glass wool and a 3-cm column of anhydrous sodium sulfate. An aliquot (1.2 ml) of the dry isopropyl acetate solution was concentrated to ca. 120 µl (10 ×), added to a 250-µl glass insert in a standard 2-ml autosampler vial, and analyzed by GC/MS (see Supplement for conditions).

2.4 Instrumentation methods

For LC/MS, an Agilent1100 LC system interfaced to an Agilent 1100 mass selective detector with an electrospray ionization (ESI) source was used in conjunction with a C8 100A Kinetex (Phenomenex, 2.1 × 100 mm, 2.6 µm particle size) column. Details of LC/MS methods are given in the Supplement.

For GC/MS, a 7890A gas chromatograph with 5975C Inert XL EI/CI mass selective detector (Agilent Technologies) was used in EI mode. Early method development was also carried out on a 5890 Series II GC with 5972 mass selective detector. A 5890 Series II GC (Agilent Technologies) with nitrogen-phosphorous detector (NPD) was used for determining detection limits using NPD. For all GC analyses, an Agilent DB-5ms (L, 30 m, ID, 0.25 mm, DF, 0.5 μm) was used. Details of GC/MS methods are given in the Supplement.

Experimental details on denuder and impinger efficiency tests are provided in the Supplement.

2.5 Safety considerations

All toxic materials were handled in fume hoods using standard safety protocols and were destroyed with appropriate chemical scrubbers prior to their release to the environment or were stored and collected by a hazardous materials contractor. Measurements of vehicle exhaust did not expose the instrument operator(s) to significant levels of emissions.

3 Results and discussion

The approach to the measurement of trace atmospheric bases discussed here is shown schematically in Fig. 1. All bases are collected as their aminium phosphite salts. Ammonium concentrations are determined colorimetrically using the indophenol blue method. Primary and secondary organic amines are converted to the corresponding 2,4-dinitroaniline derivatives by reaction with DNFB and activated primary amines are derivatized with 2-furaldehyde. The derivatized products are analyzed by LC/MS and/or GC/MS.

It should be noted that while the derivatization schemes are based on known chemistries, published methods did not afford sufficient reliability and sensitivity when

they were attempted in the context of the current report. Significant effort has been dedicated to maximizing the recovery efficiency, reproducibility, and sensitivity of these systems. The optimized methods presented here are designed to provide the research community with a validated, integrated, and sensitive system for routine measurement of trace amino compounds in ambient air and vehicle exhaust. The methods are easy to apply and use low-cost sampling devices and instrumentation that is available in most chemistry laboratories.

3.1 Improved colorimetric NH_4^+ analysis

Several iterations (USEPA, 1999; APHA, 2005) on the well-known Berthelot (indophenol) reaction (Searle, 1984) were compared to determine the most reliable system for atmospheric NH_3 measurements. It was found that the American Public Health Association standard method (APHA, 2005) afforded the most reliable results (data not shown). The 96-well plate format described here allows five standards, six samples, and six diluted samples to be measured with three replicates each in a single instrument read. Dilution is sometimes necessary when collecting atmospheric NH_3 using annular denuders and one hour integration times at $10\,l\,min^{-1}$ gas flow rates (USEPA, 1999). The standard deviation on the three replicates typically was below $2\,mAU$ and the slope of standard curves on successive days of measurements using fresh standards fell within a 5% ($1\,SD$) variance envelope. The method is convenient, allows a large number of samples to be processed in parallel with standards, and is ideally suited for atmospheric measurements, as discussed below. The limit of detection (LOD) for NH_4^+ obtained using this method was found to be $0.1\,mg\,l^{-1}$ ($3\,SD$, 6 replicates, $0.84\,mg\,l^{-1}$ standard).

3.2 Derivatization and analysis of amines

A broad palette of derivatization methods has become available to the analytical chemist specifically for amine analysis by GC (Kataoka, 1996). The best choice of

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method is highly dependent on the target amines and on the sample matrix. For the purposes of atmospheric measurements, it was desirable to carry out the derivatization reaction in an aqueous medium with the amines present as their protonated salts. This ensures compatibility with standard atmospheric collection methods, and allows the amines to be stored in a stable form for post-collection analysis. The two most attractive methods that meet these requirements are nucleophilic substitution reactions with either DNFB or benzenesulfonyl chloride. Both approaches have been reported for the analysis of amines in aqueous samples (Day et al., 1966; Hamano et al., 1980; Sacher et al., 1997). Amine trapping as substituted 2,4-dinitroanilines was chosen due to the reported simplicity of the reaction, the apparent ease of separation of products from other components of the reaction mixture, and the broad specificity of DNFB in its reaction with nucleophiles (Kataoka, 1996). In addition to NH_3, primary and secondary amines, thiols, imidazoles, and hydroxylated compounds (e.g. phenol) all form the corresponding DNFB derivative, enhancing the potential value of the method in the context of analyzing poorly characterized trace pollutants in air.

The derivatization of amines using alkali-buffered DNFB, also known as Sanger's reagent in amino acid analysis (Sanger, 1949), has been carried out in the presence (Day et al., 1966; Kallinger and Niessner, 1999) and absence (Sacher et al., 1997) of organic co-solvents. The addition of a co-solvent is desirable to optimize reaction kinetics, as DNFB is poorly water soluble. On the other hand, the presence of an organic co-solvent means that only highly non-polar organic solvents (e.g. hexane or cyclohexane) can be used to extract the derivatized amine product from the aqueous phase without forming an intractable emulsion. This limitation seems to be overlooked frequently in the literature and leads to significant losses of 2,4-dinitroanilines derived from low-molecular-weight amines such as NH_3, methylamine, and ethylamine, common components of many environmental samples. The derivatization experiments in our laboratory using ammonium chloride as the test system resulted in no detectable derivatization product using either hexane or cyclohexane as the organic extraction solvent; methylamine yielded low quantities (<20 % recovery) of the desired product

under analogous conditions. The only extraction efficiency study in the literature was reported by Kallinger and Niessner (1999), who obtained extraction efficiencies of 33 % and 85 % for methylamine and ethylamine DNFB products, respectively, using cyclohexane. Other, less polar aliphatic amines afforded quantitative recovery with cyclohex-

5 ane extraction, although these estimates need to be tempered by observed recoveries exceeding 135 %, which is likely due to solvent evaporation. Clearly, these existing methods are unsatisfactory in the context of the present report, and alternative work-up procedures are required.

The approach initially under investigation in our laboratory made use of a mixed sol-

10 vent system for the derivatization reaction, followed by solvent evaporation in a Speed-Vac concentrator system. The residue then was re-dissolved in an immiscible aqueous-organic solvent system, allowing for extraction of the target analytes. This approach afforded mixed results related to poor recovery efficiencies and reproducibility for polar amines. A significant amount of effort was dedicated towards improving the conditions,

15 leading to the optimized method presented above. The most important modifications are described below.

Microwave irradiation has been shown to accelerate the rate of reaction of poorly nucleophilic amines with DNFB (Elder and Holtz, 1996). Three amines were compared using a heating block (20 min for the first step and 30 min for the second step) and

20 microwave heating (2 min for the first step and 3 min for the second step) of the re-action medium: methylamine, nucleophilic and polar; diethylamine, nucleophilic and non-polar; and aniline, non-nucleophilic and non-polar. The results of reproducibility and yield experiments using these heating approaches are shown in the Supplement. These data indicate that microwave irradiation does not have a significant impact on

25 the overall yield of the derivatized product, but affords less reproducible results than with the heating block method. While the microwave method is significantly faster than the heat block method, the latter affords more reliable data and is recommended. A programmable oven has been used subsequently to ensure more stable temperature control.

Experiments were carried out to minimize deterioration of GC performance in split-less mode due to column overload from repeated injection of excess DNFB and other non-volatile reaction components. The amount of nonvolatile material could be visualized by heating 10 µl of reaction mixture at 225 °C (injector temperature) for 3 min on a Pyrex microscope slide. Ethyl acetate solutions containing the derivatized amines were subjected to the following two sample clean-up approaches: (1) filtrations through columns of sodium carbonate (1 cm), silica (0.5 cm), and sodium sulfate (1 cm); and (2) extractions with 1 M sodium carbonate solution and deionized water followed by drying with sodium sulfate. A range of permutations was evaluated within each approach and was assessed for residual volatile material as described above. Purification of the DNFB by chromatography on silica gel prior to use also significantly reduced the non-volatile compounds, as well as the impurities in the organic extracts (by GC/MS and GC/NPD). The optimized combination is described in the experimental section. In separate experiments, a mixture of methylamine, diethylamine, and aniline in 0.04 % phosphorous acid was kept constant while the following four parameters were varied independently: the volume of DNFB solution (20–125 µl, 10 µl increments), volume of sodium hydroxide solution (50–200 µl, 25 µl increments), heating time (first and second stage, 20–60 min). The yield of all three 2,4-dinitroaniline products was maximized under the conditions described in the experimental section.

Having optimized the heating conditions and the relative amounts of reagents, p-dioxane, the commonly-used DNFB solvent in the Sanger reaction, and tetrahydrofuran (THF) were compared as co-solvents in the reaction. Both were freshly distilled. It was found that reactions with THF significantly reduced the number of extraneous peaks in chromatograms of the organic extracts. The nature of the organic solvent used to extract the derivatized amines from the reaction medium was also investigated. The motivation behind these experiments was to maximize extraction efficiency while using a solvent that could be concentrated by evaporation in a controlled fashion using a SpeedVac (*vide infra*). Ethyl acetate, *iso*-propyl acetate, and n-butyl acetate were compared, with the best results being obtained with *iso*-propyl acetate.

Reproducibility and yield data for the optimized derivatization method are presented in Table 2. These data clearly illustrate the reliability of the new method. The observed reaction yields are excellent for all amines, except ammonia, which affords the most polar product likely leading to extraction losses. These results compare favorably to those reported by Kallinger and Niessner (1999).

Chromatograms obtained from a complex mixture of low-molecular weight amines derivatized as their 2,4-dinitroaniline derivatives are shown in Fig. 2. These results suggest amines of atmospheric relevance will be resolvable, although ethylmethylamine and diethylamine separation may require additional chemometric treatment should they both be present in significant amounts (Fig. 2b).

A number of experiments were carried out to maximize the sensitivity of the method. Initially, 0.5 ml of acidic amine solution was derivatized and extracted with 1 ml of organic solvent, which was injected into the GC with no additional concentration. The reaction was scaled up by a factor of three and four (1.5 and 2.0 ml of acidic amine solution, respectively) with no statistically significant loss in efficiency (methylamine, diethylamine, aniline; four replicates each). The impact of the organic solvent volume on extraction efficiency also was studied for the reaction based on 2 ml of amine solution. It was found that 2 ml ethyl acetate gave a lower standard deviation on the mean than 4 ml (methylamine, diethylamine, aniline; four replicates each). When 2 ml of organic solvent was used in the extraction of the derivatized amines, ca. 1.5 ml remain after the washing and drying steps. A 1.2 ml aliquot of this solution was concentrated by factors of 3, 5, and 10 on a SpeedVac, and the reproducibility was determined to be statistically equivalent to the corresponding solution prior to evaporation (methylamine, diethylamine, aniline; four replicates each). When ethyl acetate, *iso*-propyl acetate, and n-butyl acetate were compared, the most reliable sample concentration was achieved with *iso*-propyl acetate. In summary, reaction scale up and sample concentration were used to increase the mass of amine derivatives injected into the GC/MS by a factor of 20 compared to the previous method. The LODs included in Table 1 correspond to this latest method. The LODs obtained by GC/NPD were either the same as by

GC/MS, or lower by a factor of 3, depending on the compound.

3.3 Derivatization and analysis of activated primary amines (X-NH$_2$)

Derivatization of X-NH$_2$ compounds is typically achieved via a condensation reaction with an electron-rich aldehyde such as 4-N,N-dimethylaminobenzaldehyde (Watt and Chrisp, 1952; McKennis and Yard, 1954; Gamble and Hoffman, 1967; Gamble, 1968; Amlathe and Gupta, 1988), salicylaldehyde (Abdou et al., 1977; Kester and Danielson, 1984), 4-hydroxybenzaldehyde (Kirchherr, 1993), 3,4-dimethoxybenzaldehyde (Kaveeshwar and Gupta, 1992), 2-hydroxy-1-naphthaldehyde (Manes et al., 1987), and 2,3-napthalene dicarboxaldehyde (Collins and Rosepehrsson, 1993). While the equilibrium in this system generally is strongly towards the right, high concentrations of water can favor the reverse reaction, leading to trapping inefficiencies. Four sets of conditions (see Supplement) were investigated in the derivatization of target X-NH$_2$ compounds. Given that derivatization involves a condensation reaction, it was unexpected that the best yield of both products was obtained in aqueous phosphorous acid solution. Chromatograms of the three X-NH$_2$ compounds of interest, derivatized with 2-furaldehyde, is given in Fig. 3.

As with the amine derivatization reactions with DNFB, efforts were dedicated towards minimizing the amount of low volatility compounds injected onto the column. The dependence of derivatization efficiency on the amount of 2-furaldehyde used in the reaction was investigated in the 25–125 µl range. A five-fold reduction (from 125 to 25 µl) was achieved without negatively impacting the yield of the corresponding condensation products.

The reproducibility of the method described above was investigated for all three X-NH$_2$ compounds and the results are presented in Table 3. During these tests it was suspected that methylhydrazine contained significant trace impurities, such as amines and hydrazines. The purity of commercial methylhydrazine is listed as 98 %. Methylhydrazine (1.37 mM, 63.3 mg l^{-1}, 72.3 µl l^{-1} in 0.04 % aqueous H$_3$PO$_3$) was derivatized with DNFB and 2-furaldehyde as described above ($n = 4$). Hydrazine, diethylamine,

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methylamine, aniline, and ammonia standards all were derivatized as one batch and analyzed by GC/MS. The methylhydrazine standard was found to contain ammonia (0.7 % mole fraction), methylamine (11.6 % mole fraction), and hydrazine (2.3 % mole fraction).

5 As with amine derivatization, the sensitivity of the method was maximized through a series of experiments. Initially, 3 ml of acidic amine solution was derivatized and extracted with 1 ml of organic solvent, which was injected into the GC with no additional concentration. The reaction was scaled up by a factor of two and three (6 and 9 ml of acidic solution, respectively) with no statistically significant loss in efficiency (hydrazine,

10 methylhydrazine, hydroxylamine; four replicates each). When 2 ml of organic solvent was used in the extraction of the derivatized X-NH$_2$ compounds, ca. 1.7 ml remain after the drying step. A 1.2 ml aliquot of this solution was concentrated by factor of 3, 5, and 10 on a SpeedVac, and the reproducibility was determined to be statistically equivalent to the corresponding solution prior to evaporation (hydrazine, methylhydrazine,

15 hydroxylamine; four replicates each). When ethyl acetate, iso-propyl acetate, and n-butyl acetate were compared, the most reliable sample concentration was achieved with iso-propyl acetate. In summary, reaction scale up and sample concentration were used to increase the amount of amine derivatives injected into the GC/MS by a factor of 10 compared to the previous method. The LODs included in Table 1 correspond to

20 this latest method.

3.4 Denuder efficiency tests

Annular denuders are used routinely to sample reactive gases in the atmosphere with high efficiency (Allegrini et al., 1987; Koutrakis et al., 1988; Williams et al., 1992; Perrino et al., 2001; Clemitshaw, 2004). These devices are inexpensive and can be coated

25 with acid or alkaline sorbents to efficiently concentrate reactive gases for subsequent characterization. Efficiency tests with citric acid-coated annular denuders as per EPA Compendium Method IO-4.2 (USEPA, 1999), however, failed to afford the high expected efficiencies. Perrino and Gherardi studied the performance of citric acid, oxalic

acid, and phosphorous acid as denuder coating layers for the determination of atmospheric NH_3 and found that phosphorous acid afforded the best performance (Perrino and Gherardi, 1999). These authors also reported that the citric acid coating did not efficiently retain collected NH_3. When 990 ppbv NH_3 was flowed (10 l min^{-1}, 30 min) directly through two phosphorous acid-coated denuders in series, a collection efficiency of 99.4 ± 0.7 % (1 SD, four replicates), determined by comparing the NH_3 collected in the second, overflow, denuder with the amount collected in the first (Eq. S1 in the Supplement) was obtained. The mass of NH_3 collected in the first denuder was quantitative (i.e. equivalent to the predicted mass).

3.5 Impinger efficiency tests

Midget impingers are commonly used in air quality studies to concentrate the target gas-phase analytes in a suitable liquid collection medium. In order to maintain consistent conditions with the above denuder tests it was important to determine the H_3PO_3 content and pH of the aqueous denuder rinse solutions and to maintain identical conditions in the impinger experiments. A H_3PO_3 solution (1 % w/v) was used to coat six denuders, which were found to retain 0.401 ± 0.056 g (mean ±1 SD) of the coating solution, or 4 mg of phosphorous acid, on the surface. When these denuders were dried and rinsed with DI-H_2O (2 × 5 ml), the pH of the six rinse solutions was found to be 2.60 ± 0.02 (mean ±1 SD). A 0.04 % solution of phosphorous acid in DI-H_2O was found to have a pH of 2.39, and this solution was used in the impinger efficiency evaluation. The collection efficiency of 0.04 % w/v aqueous H_3PO_3 for a range of volatile bases of atmospheric relevance was determined in two test matrices: N_2 and undiluted light duty vehicle exhaust. The experimental design (see Supplement) proved to be both simple and reliable. Locating two independent impingers in series allows their collection efficiency to be tested quantitatively (Dasgupta et al., 1988) without requiring the exact integrated mass of analyte passed through the scrubbers to be known. The results of these tests are presented in Table 4 and show quantitative collection efficiencies for all analytes tested.

Annular denuders and impingers were chosen as collection systems to concentrate nitrogenous bases from gas-phase sources due to their low cost, wide-scale adoption, and ease of use. For applications with air sampling flow rate restrictions, but with high analyte concentrations (e.g. undiluted vehicle exhaust), the impingers are more appropriate. Note that typically ten times more material is collected in an annular denuder than in a midget impinger as a result of the difference in air-flow rates ($10\,l\,min^{-1}$ versus $1\,l\,min^{-1}$) that can be used with these devices. The volume of two successive denuder rinses is the same as that used in an impinger: 10 ml. Liquid diffusion scrubbers (Frenzel, 1994; Chang et al., 2003; Takenaka et al., 2004) and wet effluent diffusion denuders (Simon and Dasgupta, 1993, 1995; Dasgupta et al., 1997; Boring et al., 1999; Zhang et al., 2003; Takeuchi et al., 2004) can also be used if semi-automated sample collection is desired. In cases where low concentrations of the target alkaline gases are anticipated and high sampling flow rates are possible (e.g. ambient air) the annular denuders are recommended.

3.6 Implications to atmospheric measurements

While the methods described here are also applicable to samples collected in water and soil, the primary focus of the present work is on measurements in a gaseous matrix. The $0.1\,mg\,l^{-1}$ LOD for NH_3 obtained with the colorimetric method (see Sect. 3.1) corresponds to an LOD_{air} of 0.8 ppbv with 3 h sampling at $10\,l\,min^{-1}$. This is sufficiently low for measurements in an urban setting, where ambient levels typically exceed 10 ppbv (*vide infra*). The LODs calculated for analytical samples, $LOD_{analyical}$ in Table 1, correspond to the minimum detectable concentration in the aqueous denuder rinse or impinger solution. The corresponding atmospheric concentrations, LOD_{air}, are shown in Table 1 and assume collection using an annular denuder ($10\,l\,min^{-1}$ sample flow rate, 3 h). The analytes in Table 1 have LOD_{air} values in the low pptv range, sufficiently low to detect ambient levels in an urban environment for some compounds, e.g. methylamine (Chang et al., 2003) and to monitor emission hot spots of the remaining bases

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(Ge et al., 2011a). Longer sampling times such as 24 h to afford daily averages lead to increased collected analyte masses and correspondingly lower LODs.

The results also offer a direct comparison of two common analytical techniques, LC/MS and GC/MS, both with inherent advantages. LC/MS afforded significantly higher sensitivity for the activated primary amines and provided a less labor intensive sample preparation, as the derivatized mixtures could be analyzed directly and did not require extraction with organic solvents followed by washing, drying, and concentration steps. GC/MS instrumentation still is more accessible in many laboratories than LC/MS, is easier to use, and allows mass spectra of unknown compounds to be matched to large databases.

The methods were evaluated in the field under two scenarios: ambient air and undiluted vehicle exhaust. Ambient air in Hermon Park (Los Angeles, CA, USA) was sampled ($10 \, \text{l min}^{-1}$) for three-hour periods between 04:00 and 07:00 p.m. over the course of five days in September 2009 through a phosphorous acid coated denuders and the denuder extracts were analyzed as described above. A range of primary amines were detected over the following concentration ranges: NH_3, 9–16 ppbv; methylamine, 25–40 pptv; ethylamine, 43–84 pptv; n-propylamine, 1.6–4.6 pptv; n-butylamine, 0–6 pptv; methylethylamine, 5–9 pptv; and diethylamine, 0–28 pptv. Undiluted, on-road tailpipe emission measurements on a fleet of 10 vehicles were carried out in April 2011. The vehicles were tested for 5 min at idle followed by an 19.5 km on-road circuit chosen to mimic a range of common driving conditions. A range of bases were detected over the following concentration ranges: NH_3, 0.1–80 ppmv; methylamine, 1.9–166 ppbv; ethylamine, 1.2–7.0 ppbv; and n-propylamine, 0.4–2.2 ppbv. Control scrubbers, prepared as above, that were capped and not exposed to flowing air showed no detectable levels of these compounds. These results not only illustrate the usefulness of the technique described here, but also show that the measurements could be carried out without interferences from other components of the complex ambient air and raw vehicle exhaust mixtures.

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An integrated approach to measuring trace atmospheric nitrogenous bases has been developed and validated. The method uses a simple acid scrubbing step to capture and concentrate the bases as their phosphite salts, which then are derivatized and analyzed using GC/MS and LC/MS. The approach is sensitive, selective, reproducible, as well as convenient to implement and has been validated for different sampling strategies. The limits of detection for the families of tested compounds are suitable for ambient measurement applications, as supported by field measurements.

Supplementary material related to this article is available online at:
http://www.atmos-meas-tech-discuss.net/4/6007/2011/amtd-4-6007-2011-supplement.pdf.

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Table 1. Sensitivity of Analytical Methods to Compounds of Trace Atmospheric Amino Compounds; $LOD_{analytical}$, analytical sensitivity (3 SD); LOD_{air}, corresponding sensitivity in a sampled air stream assuming 3 h of sampling at $10\,l\,min^{-1}$.

Analyte	GC/MS		LC/MS	
	$LOD_{analytical}$ $(\mu g\,l^{-1})$	LOD_{air} (pptv)	$LOD_{analytical}$ $(\mu g\,l^{-1})$	LOD_{air} (pptv)
hydrazine	0.3	1.5	3.0×10^{-2}	0.1
methylhydrazine	25	74	0.6	2.0
hydroxylamine	0.15×10^{3}	0.6×10^{3}	5.0	20
methylamine	0.3	1.5	0.3	1.0
ethylamine	0.5	2.0	0.7	2.0
n-propylamine	0.7	1.5	0.4	1.0
n-butylamine	0.6	1.0	0.3	0.5
methylethylamine	0.5	1.0	0.2	0.5
dimethylamine	0.4	1.0	0.4	1.0
diethylamine	0.6	1.0	1.0	2.0
morpholine	0.7	1.0	2.0	4.0
aniline	0.7	1.0	0.3×10^{2}	0.4×10^{2}

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Table 2. Reproducibility and Yield of the Optimized DNFB Amine Derivatization Method. Yields are calculated based on recovery of derivatized products relative to standards of authentic samples of known concentration.

Amine	Variability (%)[a]	Yield (%)[b]
ammonia	2.8	60
methylamine	1.6	98
diethylamine	1.9	115[c]
aniline	2.6	99

[a] Calculated as the standard deviation from five replicates divided by the mean;

[b] mean of five replicates;

[c] exceeds 100 % due to solvent evaporation.

Table 3. Reproducibility of the Activated Primary Amine Derivatization Method.

Compound	Peak area reproducibility (%)[*]
hydrazine	1.3
methylhydrazine	1.0
hydroxylamine	0.7

[*] Calculated as the standard deviation from five replicates divided by the mean.

Table 4. Collection Efficiencies, Measured in N_2 ($CE_{ambient}$) and in Undiluted Vehicle Exhaust ($CE_{exhaust}$), for Volatile Bases by Midget Impingers.

Amine	Collection efficiencies ($n = 3$)	
	$CE_{ambient}$ (%)	$CE_{exhaust}$ (%)
ammonia	100 ± 0	95.0 ± 2.4
methylamine	99.7 ± 0.5	100 ± 0.0
diethylamine	99.5 ± 0.7	99.0 ± 1.0
aniline	99.9 ± 0.1	92.5 ± 13
hydrazine	99.1 ± 2.1	98.7 ± 0.7
methylhydrazine	99.4 ± 1.0	N/A[*]
hydroxylamine	99.0 ± 1.8	100 ± 0.0

[*] Unstable under the conditions used.

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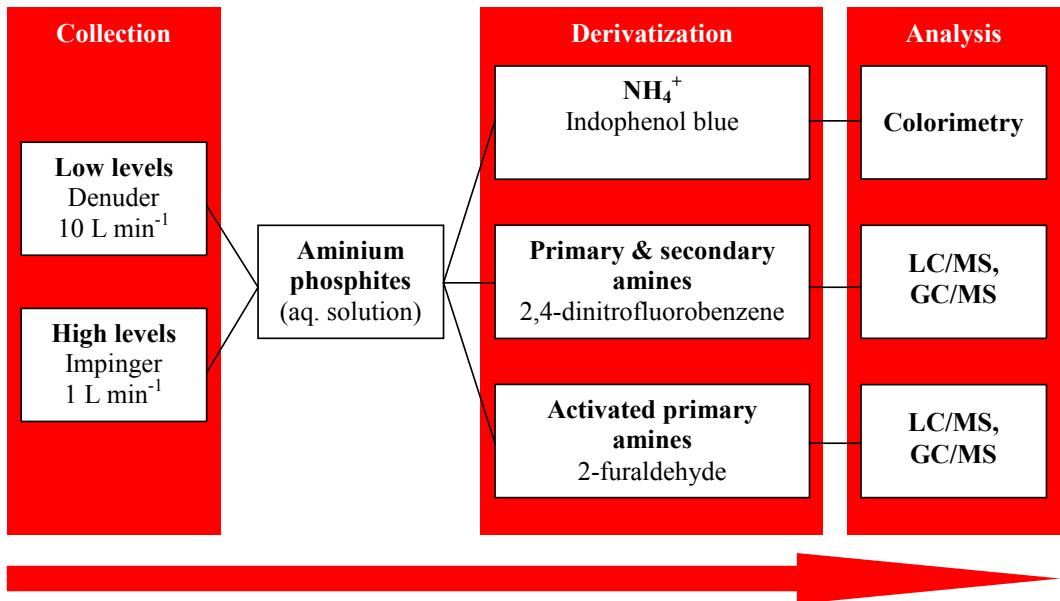
Fig. 1. Schematic Representation of the Measurement Strategy for Trace Atmospheric Bases.
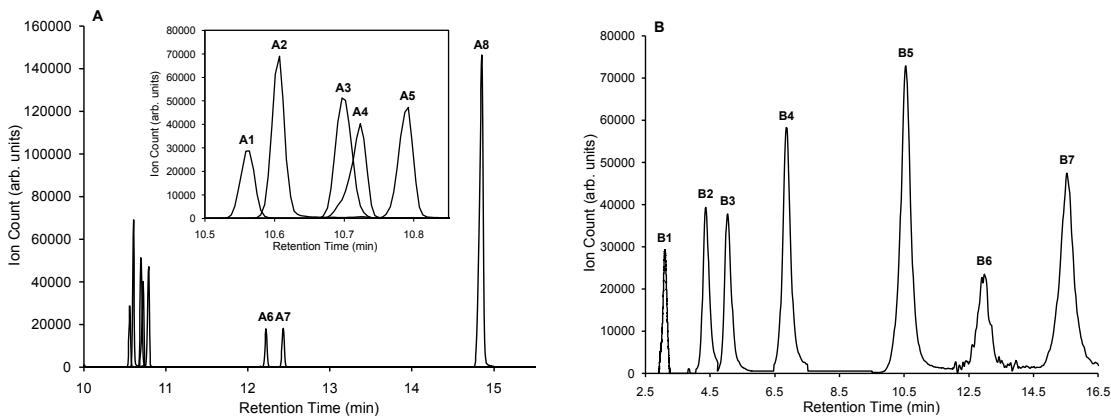
Fig. 2. (A) Chromatogram from a derivatized mixture of amines analyzed by GC/MS. Inset: Expanded view of the peaks in the 10.5–11.0 min range. A1, *m/z* 211, dimethylamine; A2, *m/z* 183, ammonia; A3, *m/z* 239, diethylamine; A4, *m/z* 225, ethylmethylamine; A5, *m/z* 197, methylamine; A6, *m/z* 239, n-butylamine; A7, *m/z* 253, morpholine; A8, *m/z* 259, aniline. **(B)** Chromatogram from a derivatized mixture of amines analyzed by LC/MS. B1, methylamine (*m/z* 98); B2, morpholine (*m/z* 254); B3, dimethylamine (*m/z* 212); B4, ethylmethylamine (*m/z* 226); B5, diethylamine (*m/z* 240); B6, aniline (*m/z* 260); B7, n-butylamine (*m/z* 240).

Integrated method for the measurement of trace atmospheric bases

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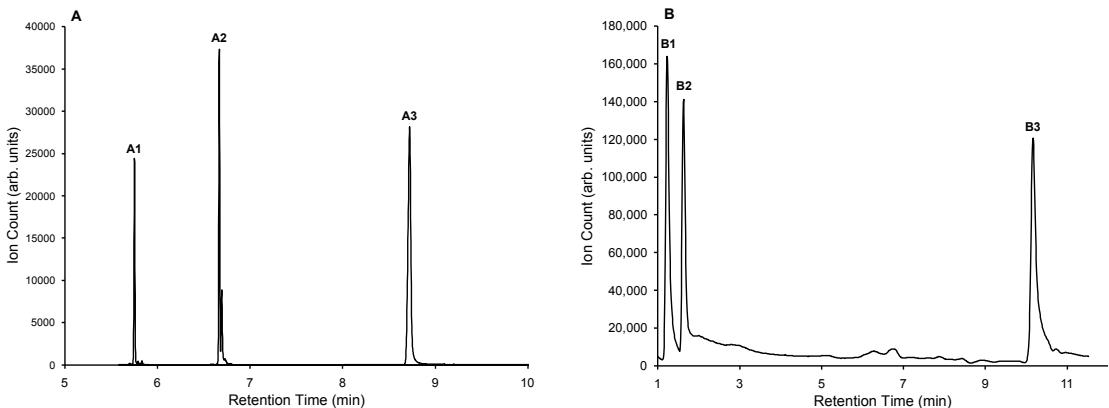
Fig. 3. **(A)** Chromatogram of X-NH$_2$ compound mixture in H$_3$PO$_3$ derivatized with 2-furaldehyde analyzed by GC/MS. A1, hydroxylamine (m/z 111, oxime); A2, methylhydrazine (m/z 124, N-methylhydrazone); A3, hydrazine (m/z 188, azine). **(B)** Chromatogram of X-NH$_2$ compound mixture in H$_3$PO$_3$ derivatized with 2-furaldehyde analyzed by LC/MS. B1, methyl-hydrazine (m/z 125, N-methylhydrazone); B2, hydroxylamine (m/z 112, oxime); B3, hydrazine (m/z 189, azine).