

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/320857164>

Quantification of amine functional groups and their influence on OM/OC in the IMPROVE network

Article · October 2017

DOI: 10.1016/j.atmosenv.2017.10.053

CITATIONS

0

READS

69

3 authors:



Mohammed Kamruzzaman

Bangladesh Agricultural University

26 PUBLICATIONS 1,212 CITATIONS

SEE PROFILE



Satoshi Takahama

École Polytechnique Fédérale de Lausanne

83 PUBLICATIONS 1,456 CITATIONS

SEE PROFILE



Ann M. Dillner

University of California, Davis

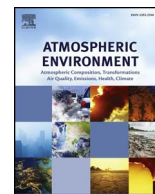
47 PUBLICATIONS 672 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



Southern Oxidant and Aerosol Study (SOAS) [View project](#)



Quantification of amine functional groups and their influence on OM/OC in the IMPROVE network



Mohammed Kamruzzaman^a, Satoshi Takahama^b, Ann M. Dillner^{a,*}

^a Air Quality Research Center, University of California, Davis, CA 95616, USA

^b Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland

ARTICLE INFO

Keywords:

Fourier transform-infrared spectroscopy
FTIR
Partial least squares regression
Particulate matter
Organic matter
Organic carbon

ABSTRACT

Recently, we developed a method using FT-IR spectroscopy coupled with partial least squares (PLS) regression to measure the four most abundant organic functional groups, aliphatic C-H, alcohol OH, carboxylic acid OH and carbonyl C=O, in atmospheric particulate matter. These functional groups are summed to estimate organic matter (OM) while the carbon from the functional groups is summed to estimate organic carbon (OC). With this method, OM and OM/OC can be estimated for each sample rather than relying on one assumed value to convert OC measurements to OM. This study continues the development of the FT-IR and PLS method for estimating OM and OM/OC by including the amine functional group. Amines are ubiquitous in the atmosphere and come from motor vehicle exhaust, animal husbandry, biomass burning, and vegetation among other sources. In this study, calibration standards for amines are produced by aerosolizing individual amine compounds and collecting them on PTFE filters using an IMPROVE sampler, thereby mimicking the filter media and collection geometry of ambient standards. The moles of amine functional group on each standard and a narrow range of amine-specific wavenumbers in the FT-IR spectra (wavenumber range 1550–1500 cm⁻¹) are used to develop a PLS calibration model. The PLS model is validated using three methods: prediction of a set of laboratory standards not included in the model, a peak height analysis and a PLS model with a broader wavenumber range. The model is then applied to the ambient samples collected throughout 2013 from 16 IMPROVE sites in the USA. Urban sites have higher amine concentrations than most rural sites, but amine functional groups account for a lower fraction of OM at urban sites. Amine concentrations, contributions to OM and seasonality vary by site and sample. Amine has a small impact on the annual average OM/OC for urban sites, but for some rural sites including amine in the OM/OC calculations increased OM/OC by 0.1 or more.

1. Introduction

Amines are organic molecules that contain nitrogen bonded to two or fewer hydrogen atoms. They are abundant in the atmosphere and present in both gas and particle phase. About 150 amines and about 30 amino acids, an amine that contains a carboxylate acid group, have been identified in the atmosphere (Ge et al., 2011). Gas-phase amines are emitted from both natural and anthropogenic sources. Examples of natural sources include vegetation, biomass burning, volcanoes, and the ocean; while anthropogenic sources include animal husbandry, waste incinerators, food industries, cooking, tobacco smoking, motor vehicles, and CO₂ sequestration (Ge et al., 2011; Cape et al., 2011). Although gas-phase amine (R-NH₂) concentrations are orders of magnitude lower than ammonia (NH₃), both compounds are ubiquitous in the atmosphere and participate in secondary formation of aerosols (You et al., 2014). The partitioning behavior of amines is strongly dependent on

aerosol composition such as the water content and acidity, which can change the form of amines into protonated aminium or aminium salts (e.g., Pratt et al., 2009; Pankow, 2015).

Like gas-phase amines, particle phase amines are ubiquitous in the atmosphere. They have been measured in various locations around the world, including urban and rural areas of the US using chromatography, mass spectrometry, ultraviolet, fluorescence, infrared and electrochemical detectors (Ge et al., 2011). Multi-hour filter-based sampling coupled with Fourier transform infrared spectroscopy (FT-IR) has shown that amines can contribute up to 10% of organic matter in various locations world-wide (Russell et al., 2011) and short-time scale aerosol mass spectrometry measurements (AMS) have shown they may contribute up to ~20% of the organic content of ambient particles during winter inversions (Silva et al., 2008). Therefore, the quantification of amine in ambient aerosol is important for understanding their role in atmospheric chemistry and their contribution to organic matter

* Corresponding author.

E-mail address: amdillner@ucdavis.edu (A.M. Dillner).

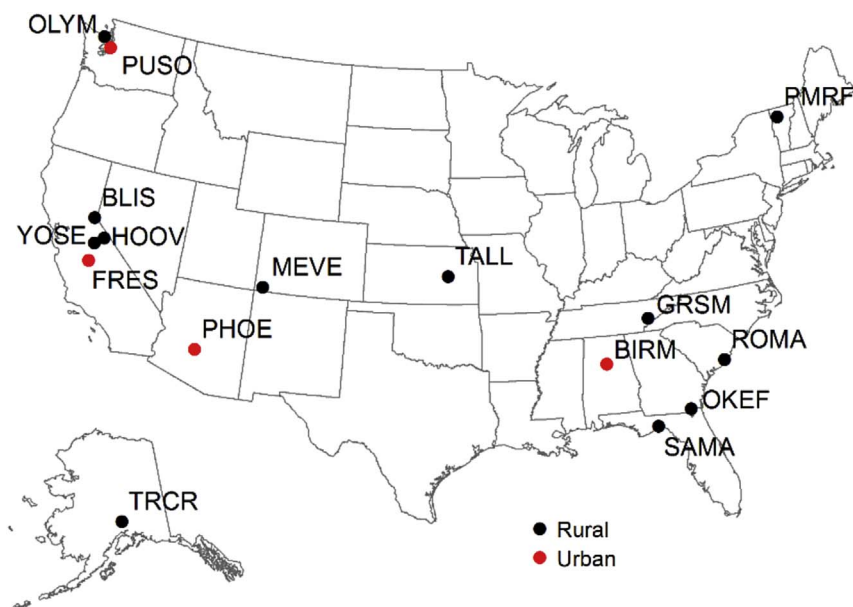


Fig. 1. Map of IMPROVE sites. Four letter site IDs are identified by full name in Table 1.

(OM), where OM is OC plus hydrogen, oxygen, nitrogen and sulfur heteroatoms.

In filter based particulate matter sampling, OM is typically estimated from organic carbon (OC) measurements using an OM/OC value of 1.8 for rural sites (Pitchford et al., 2007), and 1.4 for urban sites (White and Roberts, 1977). However, OM/OC has been shown to vary by site, season, and atmospheric conditions using various techniques, such as air quality models (Simon et al., 2011), linear regression on IMPROVE and CSN data (Malm et al., 2011), mass and light extinction reconstruction in IMPROVE (Lowenthal, and Kumar, 2003), and calculations from measured organic compounds (Turpin and Lim, 2001). The variability in OM/OC has also been measured by FT-IR on filter samples (Russell, 2003; Ruthenburg et al., 2014), using extractions of filter samples (El-Zanan et al., 2009) and by HR-AMS (Aiken et al., 2008). FT-IR techniques has shown promise in measuring OM/OC on each filter sample in a large sampling network, the Interagency Monitoring of Protected Visual Environments (IMPROVE, Ruthenburg et al., 2014), and can be applied to other monitoring networks such as the Southeastern Aerosol Research and Characterization (SEARCH) and EPA's Chemical Speciation Network (CSN) due to the low cost and non-destructive nature of the analysis on routinely collected filters. Recently we used FT-IR spectra of laboratory standards with known amounts of functional group mass and partial least squares (PLS) regression to measure four functional groups which make up a large portion of OM; alkane CH, alcohol OH, carbonyl and carboxylic acid OH (Ruthenburg et al., 2014). PLS is commonly used to calibrate spectral data that are highly collinear (i.e., have overlapping peaks) (Wold et al., 2001), as is the case for FT-IR spectra of aerosol samples (Dillner and Takahama, 2015; Weakley et al., 2016). The functional group measurements were used to estimate OM and OM/OC in IMPROVE samples collected at seven sites in 2011. In this work, we extend our method to include the amine functional group and apply it to samples collected at 16 IMPROVE sites in 2013. Amine measurements using FT-IR have several challenges including (1) some of the spectral bands of interest are obscured by large peaks from OH and the Teflon filter material, (2) uncertainty in the peak assignment of the amine functional group in the spectral region most useful for amine quantification, (3) other atmospherically relevant compounds absorb in the same region as amine, and (4) the position of the amine bands shift depending on the composition of the molecule to which it is attached (Kettle et al., 1989; Kumar et al., 2006; Venyaminov and Kalnin, 1990). To address these challenges, we evaluate multiple amine and amino acid compounds for

use as standards and select for our calibration a narrow spectral band which has been established as being due to amines and that has limited absorbance by other species. The calibration is evaluated in ambient samples using a peak height method, which is independent of PLS and a broad spectral range PLS calibration. Amine functional group concentrations were measured in 1795 samples, and site and seasonal variability in amine concentrations are reported. The impact that the measured amine concentrations have on OM/OC is highlighted.

2. Methods

To measure amine functional group in ambient samples, laboratory standards with known amounts of amine functional group are prepared. FT-IR spectra of all laboratory standards and ambient samples are collected. Spectra of about two-thirds of the amine laboratory standards along with the moles of amine functional group on the standards (based on mass measurements) are used to develop a partial least squares (PLS) regression calibration. The calibration is tested with the remaining laboratory standards. The calibration is applied to ambient samples and the results are compared to a simple peak height analysis to evaluate whether the PLS model results are based on observable differences in the spectra.

2.1. Description of the ambient samples

Ambient samples were obtained from January to December 2013 at 16 IMPROVE sites (1795 samples) as show in Fig. 1 and listed by name in Table 1. IMPROVE samples were collected every third day beginning at midnight local time and ending 24 h later. Samples were collected at a nominal flow rate of 22.4 L min^{-1} on PTFE filters (Pall Corporation, 25 mm diameter) with $\text{PM}_{2.5}$ sampling inlets as part of the routine operation of the IMPROVE network. A detailed description of the samples can be found elsewhere (Reggente et al., 2016).

2.2. Preparation of laboratory standards

A credible basis for calibrating a spectroscopic method (i.e., FT-IR, X-ray fluorescence) is to use standards with known amounts of analyte that mimic the physical characteristics (of the analyte and the substrate), the chemical nature and the sampling geometry of the samples to be measured (Indresand et al., 2013; Ruthenburg et al., 2014). For FT-IR measurements of functional groups in ambient particulate matter

Table 1

Description of IMPROVE sites used for this investigation. Abbreviations are: NP for National Park, NWR for National Wilderness Area, and R.F. for research facility.

Name/Site ID	Location, State	Site type	No. of samples
PUSO	Puget Sound, WA	Urban	121
FRES	Fresno, CA	Urban	114
PHOE	Phoenix, AZ	Urban	120
BIRM	Birmingham, AL	Urban	115
TRCR	Trapper Creek, AK	Rural	121
OLYM	Olympic NP, WA	Rural	118
YOSE	Yosemite NP, CA	Rural	113
BLIS	Bliss State Park, CA	Rural	85
HOOV	Hoover, CA	Rural	86
MEVE	Mesa Verde NP, CO	Rural	112
TALL	Tallgrass, KS	Rural	110
GRSM	Great Smoky Mountains, NP, TN	Rural	117
SAMA	St. Marks, FL	Rural	113
OKEF	Okefenokee NWR, GA	Rural	117
ROMA	Cape Romaine NWR, SC	Rural	113
PMRF	Proctor Maple R. F., VT	Rural	120

samples from the IMPROVE network, the sampling geometry and physical characteristics of the substrate are reproduced in the laboratory standards by collecting known amounts of dried laboratory generated particles on Teflon PTFE filters (IMPROVE filter type) using an IMPROVE sampler (Ruthenburg et al., 2014). The amount of analyte on each standard is accurately determined by the difference of the average of at least three weights before and after particle collection of dry particles using an ultra-microbalance (XP2U, Mettler-Toledo, Columbus, OH). A standard is considered for inclusion in the calibration if the pre and post weights standard deviation is less than 2 µg. To ensure that measured mass is due to the analyte only, chamber blanks, which are collected in the same manner as standards but with only deionized water, are weighed to determine that the particle generation, drying and collecting systems are clean prior to producing standards. The chemical nature of the sample is the most difficult to mimic in laboratory samples due to the large number of organic and inorganic species in atmospheric aerosol. The amine functional group compounds are selected using the following three criteria: the compound is soluble in water or ethanol so that the compound can be aerosolized and dried; the compound has low volatility so that the collected material remains on the filter during FT-IR and gravimetric analysis; and the compound is readily available at a high level of purity (> 98%) to minimize uncertainty in mass measurements. In addition, preference is given for compounds that have been measured in the atmosphere and have low toxicity. Amino acids are generally soluble in water (due to the carboxylic acid functional group) with low volatility and toxicity, and therefore ideal candidates for laboratory standards. Previous work (Liu et al., 2009; Russell et al., 2011) used the amino acid alanine, which has been measured in atmospheric particulate matter, fog, and rain, to calibrate primary amines (Ge et al., 2011). In this work, we use alanine along with three other atmospherically relevant amino acids: aspartic acid, valine, and glycine for laboratory standards. Multiple compounds are selected to account for the variability in peak location and infrared absorption per mass of compound. Using the solubility, volatility, toxicity, and purity criteria, we found an amine salt, N, N-diethyl-*p*-phenylenediamine sulfate salt (NND) to include in our suite of amine functional group standards. Amine compounds, such as NND, contain an amine functional group, but no carboxylic acid group. Only primary amines are included, since secondary and tertiary amines generally have weaker absorbances and are therefore more difficult to measure in complex mixtures such as ambient aerosol. All five compounds are used to create single compound standards over a range of amine functional group mass. Carboxylates are also known to absorb in the infrared above 1600 cm⁻¹. To evaluate the potential influence of carboxylates in the amine predictions, sodium oxalate standards are prepared. The chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and

had ≥ 98% purity.

Laboratory standards were prepared from aqueous solutions of each of the five amine compounds with concentrations between 0.002 and 0.01 M. Solutions were atomized using a custom atomizer (Ruthenburg et al., 2014). Atomized particles were passed through a diffusion dryer packed with silica desiccant into an aerosol chamber and mixed with an additional volume of dry, filtered air (Model 3074B Filtered Air Supply, TSI Inc., St. Paul, MN). Dry particles were collected on PTFE filters (the same filter used in the IMPROVE network) using an IMPROVE sampler with collection times ranging from 10 to 320 s. The mass range of amine functional group standards used in the calibration was initially estimated from previous measurements (Russell et al., 2011) and refined based on the mass of amine functional group predicted by the model. Individual compound standards were produced with mass concentration ranges of amine functional group up to 0.52 µg/m³ (assuming an IMPROVE volume of 32.8 m³) and were linear with respect to peak height over this range (Supplementary material section S1, Fig. S2).

2.3. Spectra collection

FT-IR spectra of laboratory standards and ambient samples are collected using a Tensor 27 FT-IR spectrometer (Bruker Optics, Billerica, MA) with a liquid nitrogen cooled cadmium telluride (MCT) detector over the spectral range of 4000–400 cm⁻¹. Measurements are made using 512 scans for each filter at 4 cm⁻¹ resolution and ratioed to the most recent (less than 1 h) background spectrum to obtain absorbance spectra using OPUS software (Bruker Optics, Billerica, MA). Filters are placed in a house-built sample chamber that is purged of water and CO₂ (PureGas) for 4 min prior to spectra acquisition to minimize spectral interference by these highly absorbing gases.

2.4. Spectral range and selection of standards for calibration

In FT-IR spectral interpretation compendia manuals, amines are reported to absorb in several spectral regions, 3500–3300 cm⁻¹, 1650–1590 cm⁻¹ and 1100–1000 cm⁻¹ (Dokmaijrjan et al., 2010; Coates, 2000; Ghenie and Garrigou-Lagrange, 1972; Shurvell, 2002). In ambient particulate matter samples, the absorption above 3300 cm⁻¹ is small compared to large C–OH peaks. The 1100–1000 cm⁻¹ region is obscured in filter samples by very large absorption due to PTFE. These bands were therefore not considered for developing the amine calibration.

The absorption peak centered at 1625 cm⁻¹, has been used to measure amine functional groups in particulate matter filter samples (Russell et al., 2011; Liu et al., 2009). For this work, we focus on the spectral region around 1600 cm⁻¹ for developing a PLS calibration for amine functional groups. Laboratory standard spectra are baseline corrected from 1750 cm⁻¹ to below 1400 cm⁻¹ to visualize peak locations in this region (Fig. 2). Alanine has peaks at 1625, 1595 cm⁻¹ and a smaller peak at 1520 cm⁻¹. The other amino acids, have peaks approximately in the same regions as alanine with absorption bands from 1660 to 1560 cm⁻¹ and another group of bands in the 1550–1500 cm⁻¹ region. The amine, NND, only has a strong peak in the lower range 1550–1500 cm⁻¹ and weaker peaks in the higher region. Note that the scale of absorbances vary by compound in Fig. 2.

Detailed peak assignments reported in the literature do not provide definitive identification for the peaks above 1560 cm⁻¹. FT-IR analysis of twenty amino acids (Wolpert and Hellwig, 2006), glycine (Rosado et al., 1998) and Raman analysis of alanine attribute the 1625 cm⁻¹ peak to amine and the 1590 cm⁻¹ peak to carboxyl groups (Wang and Storms, 1971; Susi and Byler, 1980). However, the absorption band at 1625 cm⁻¹ is attributed to carboxyl functional group and the 1590 cm⁻¹ peak to amine for alanine (Barthes et al., 2002; Garcia et al., 2008; Rosado et al., 1997; Rodriguez-Lazcano et al., 2012), and for aspartic acid (Alam and Ahmad, 2012; Lopez Navarrete et al., 1994, 1995). Sodium oxalate also has carboxyl group absorbances above

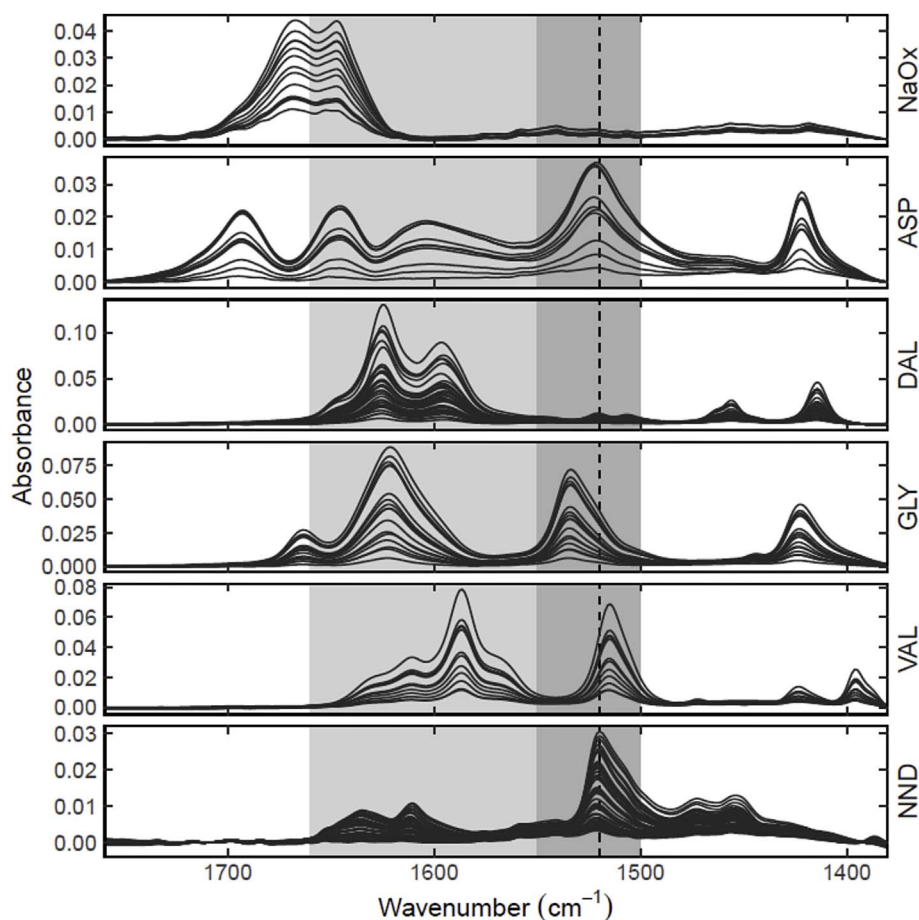


Fig. 2. Baseline corrected spectra of all of the laboratory standards developed in this work, segregated by compound. These include four amino acid compounds (ASP = Aspartic acid, DAL = D-alanine, GLY = Glycine, VAL = Valine), one amine compound (NND = N, N-Diethyl-*p*-phenylenediamine sulfate salt) and one carboxylate (NaOX = Sodium oxalate). Each spectrum was obtained from an individual standard. Standards with higher mass loadings have higher absorbances. Wavenumber 1520 cm^{-1} is indicated with a dashed vertical line. The shaded area indicated the extended wavenumber range (1660 cm^{-1} – 1500 cm^{-1}) and the dark gray shaded area indicates the narrow wavenumber range (1550 cm^{-1} – 1500 cm^{-1}).

1600 cm^{-1} (Fig. 2). However, peaks in the region 1550 – 1500 cm^{-1} are attributed to amine in all of these cited papers.

Given the ambiguity in peak assignment above 1550 cm^{-1} , that the amine compound has its strongest peak around 1520 cm^{-1} , and that the amino acids all have peaks in this range (alanine, aspartic acid and NND peak between 1520 and 1525 cm^{-1} and valine peaks somewhat lower and glycine higher (Fig. 2 and supplemental material section S1)), we select the region around 1520 cm^{-1} for measuring the amine functional group. By using the region 1550 – 1500 cm^{-1} for calibrating and measuring amine functional groups, we are also minimizing the potential for over estimating amines by excluding other functional groups, particularly carbonyl functional groups which absorb above 1550 cm^{-1} and alkane CH functional group which absorbs below 1500 cm^{-1} (peak at 1440 cm^{-1}) in the measurement of amine (supplemental material section S4).

As mentioned in the Introduction, amine compounds also exist as ammonium ions or ammonium salts in the particle phase in the atmosphere. As both laboratory and ambient aerosols are measured under a dry environment, it is likely that the particles are dehydrated during analysis. While this has the potential to affect the interpretation of some peaks, past studies indicate that dried amine compounds can retain characteristic absorbances of their ionic form in solution (e.g., Rosado et al., 1998; Garcia et al., 2008). Furthermore, the RNH_2 and RNH_3^+ peak assignments in the vicinity of 1520 cm^{-1} appear to hold across its different forms (e.g., Barth, 2000; Machida et al., 1977; Wolpert and Hellwig, 2006); within variability observed across different amine compounds. Therefore, we expect that our reported amine concentrations encompass the sum of their abundances across their different forms in the particle phase.

2.5. Multivariate calibration

A partial least squares (PLS) regression was developed to calibrate the FT-IR spectra of laboratory standards to their corresponding moles of functional group. A detailed description of the PLS can be found in our previous studies (Kamruzzaman et al., 2016; Reggente et al., 2016; Takahama et al., 2016). Briefly, PLS is used to generate a regression model between the predictors (i.e. spectra, X) and the responses (moles of amine functional group, y). Generally, the PLS algorithm decomposes the spectral matrix into a series of latent variables (LVs), which consist of loadings and scores. LVs are statistically independent (uncorrelated) and ideally carry all the information within the spectra relevant to the response values (Wold et al., 2001). The scores are the predictors of y, while the loadings offer information about spectral characteristics that are correlated with the responses.

Moles of functional group on each standard are calculated from gravimetric mass and molecular structure of each compound. The moles of amine functional group on each standard and their respective spectrum are used as input to the PLS model. Model outputs are reported in mass of amine functional group (not amine compound). To avoid either over- or under-fitting the model, the minimum value of the root mean square error of cross-validation (RMSECV) using leave-one-out validation method was used during the calibration step to select the optimum number of LVs for PLS model.

Attempts to use all five amine compounds and various combinations of amine compounds were unsuccessful due to interferences in the PLS modeling within the narrow spectral range. For example, a model was made using the three compounds with the peaks closest to 1520 cm^{-1} , alanine, aspartic acid and NND. The resulting regression coefficients indicate that the measurements are very dependent on peak location and produced uninterpretable results, likely due to the inability of the

PLS model to resolve variations between compounds over such a small wavenumber window (supplemental material Fig. S7 in section S5). The narrow window model is therefore developed using standards made from aspartic acid only. Aspartic acid is chosen because its absorption coefficient is in the middle range for the five compounds (supplemental material, Fig. S2) and thus produces measurements that are an average of those from all the compounds. Thirteen aspartic acid standards ranging up to $0.29 \mu\text{g}/\text{m}^3$ were used, 8 in the calibration set and 5 in the test set. Eight blanks were used in the calibration model and 10 were used in the test set. The predicted amine masses on the blank filters in the test set were used to estimate the minimum detection limit (MDL) as three times the standard deviation of the blanks.

The PLS model using the aspartic acid standards over the narrow spectral window is the model used for ambient predictions. The model is applied to the ambient spectra collected from IMPROVE sites to predict the moles of amine functional groups for each sample. Mass of amine functional groups was then calculated from moles of functional groups determined by PLS model assuming a functional group structure of 0.5CNH_2 . All predicted amine concentrations in the IMPROVE samples except the highest point ($0.6 \mu\text{g}/\text{m}^3$) are known to be within the linear range of the FT-IR measurement based on standards which were linear up to $0.52 \mu\text{g}/\text{m}^3$, Fig. S2 in the supplemental material.

2.6. Evaluation of the calibration model

The predictive capabilities of the calibration model were evaluated by applying the model to spectra in the test set and using the known moles of functional group on each test set standard to calculate the coefficient of determination for calibration (R_c^2), and prediction (R_p^2) and the root mean square errors for calibration (RMSEC) and prediction (RMSEP). A good model should have a high R^2 value and low errors and small difference between RMSEC and RMSEP.

To evaluate the physical basis of the amine narrow window model, a peak height analysis was performed within the same spectral region ($1550\text{--}1500 \text{ cm}^{-1}$). In this analysis, ambient spectra are baseline corrected and the peak location and height are determined. Differences in the baseline correction method and the magnitude of interferences from neighboring bands between laboratory and ambient sample spectra prevented the development of a quantitative peak height calibration to predict amine functional group mass, so the peak heights are compared to the amine PLS predictions. Further description of the method and plots of the baselined ambient spectra are in the supplemental material, section S1 and S3, respectively.

To estimate the potential for overestimating amine functional groups concentrations in ambient samples due to possible amino acid carboxyl absorbances (section 2.4) and carboxylate absorbances (Fig. 2), another PLS model was developed using the same standards but with a broader wavenumber range $1660\text{--}1500 \text{ cm}^{-1}$, which includes the carboxyl and carboxylate region. This model is called the extended wavenumber model and is discussed in section 3.1 but is not used to report amine functional group concentrations in the IMPROVE network because it over estimates amine functional group mass.

3. Results and discussion

3.1. Evaluation of the amine functional group calibration model

The prediction capabilities of the PLS calibration model using the aspartic acid standards in the narrow spectral window are shown in Fig. 3. FT-IR spectroscopy and gravimetric analysis show good agreement for amine functional group in both the aspartic acid standards used for the calibration (calibration set) and an independent set of aspartic acid laboratory standards (test set). As expected, the blanks are predicted at approximately zero (data is jittered on the graphs) in both the calibration and test set. This shows that the calibration produces accurate predictions of amine functional group in laboratory standards

(high R^2 and low error). The MDL is small ($0.008 \mu\text{g}/\text{m}^3$) and no ambient samples are below MDL.

The physical plausibility of the ambient sample measurements are evaluated by comparing the peak height to the amine predictions from the calibration. Strong correlation ($r = 0.88$) of the peak height in the neighborhood of 1520 cm^{-1} and the amine prediction from the PLS model was found (Supplemental Material Section S3), confirming the physical underpinnings of the PLS model in the ambient samples. In addition to providing quantitative estimates of amine functional group abundances, the PLS predictions resolve variations at lower concentrations which are not detected by the peak height analysis (Supplemental Material Section S3).

An estimate of the potential for over prediction of amine functional groups when using the spectral range of $1600 \pm 50 \text{ cm}^{-1}$, is made by correlating the wide window model (section 2.6) with narrow window model that is used throughout this paper (section 2.4). The models are highly correlated ($R^2 = 0.88$, Supplemental Material Section S4), suggesting the models are predicting variations in the amine concentrations similarly. The wide window model predicts amine concentrations that are on average 29% higher than the narrow window model (Supplemental Material Section S4), suggesting that some of the predicted amine mass in the wide window model is due to amino acid carboxyl or possibly carboxylates that are fairly correlated to amine groups being incorrectly measured as amine.

3.2. Prediction of amine functional groups in ambient samples by site

The narrow window PLS calibration model is applied to the ambient samples from the IMPROVE network. The annual functional group concentrations by site, Fig. 4, demonstrates the ubiquity and variability in amine composition in ambient aerosols at urban and rural locations throughout the US. Amine functional group is detected in all samples measured in this work. The amine functional group concentrations are typically less than $0.1 \mu\text{g}/\text{m}^3$ except for some Fresno, CA samples. In general, the highest concentrations are observed in urban sites whereas the lowest concentrations are observed at the rural sites. The annual median amine functional groups concentration ranges from $0.044 \mu\text{g}/\text{m}^3$ at Trapper Creek, AK (rural site) to approximately $0.075 \mu\text{g}/\text{m}^3$ at Birmingham, AL and Fresno, CA (urban sites). The median amine concentrations are similar across the rural sites. High concentrations are observed on a few days at the rural prescribed fire sites and the rural wildfire sites and at urban sites in the winter (particularly Fresno and Phoenix). However, these high amine samples also have high OM and amine is not shown to be a unique tracer for smoke or for winter urban samples (Fig. 6).

3.3. Composition of organic aerosols at the IMPROVE sites

Although the amine functional groups concentrations are higher in urban sites than rural, the percent of amine functional groups in total OM as determined from (Ruthenburg et al., 2014) measurements of CH, CO and OH, is higher in some rural sites than in the urban sites (Fig. 5). The annual median amine functional group concentration at all four urban sites and five of the 12 rural sites is less than 5% of OM concentration, while it is 5%–10% of OM at the other rural sites. Ninety five percent of all samples have less than 11% amine functional groups in OM. The annual median is 4.2%. Russell et al. (2011) reported amine functional group concentrations of less than 10% for sampling campaigns around the world.

The seasonality of aerosol composition is different for urban and rural sites. For Fresno (Fig. 6, top), and for the other urban sites (supplemental material, Fig. S7a), the amine fraction in OM does not vary by season. Fresno's amine concentrations are high in the winter as is the total OM. Although Fresno experiences wood burning in the winter and biogenic emissions in the summer, the constant percentage of amine in OM suggests that the higher winter amine concentrations are due to

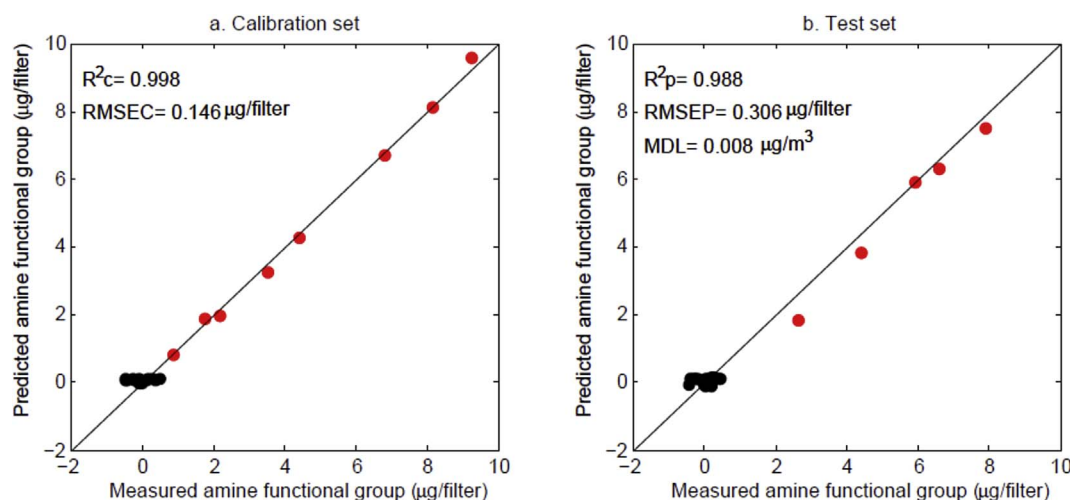


Fig. 3. Prediction of amine functional group mass in laboratory standards (red markers are the aspartic acid amine standards and black markers are blank filters) using PLS: (a) Measured versus predicted functional group mass for the laboratory standards used in the calibration, (b) measured versus predicted functional group mass for laboratory standards not included in the calibration (test set). Predicted values of blank filters are jittered to better show the near-zero values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lower boundary layer and stagnation events that occur during the winter (Zhao et al., 2011) not to changes in sources. The strong seasonal nature of more oxygenated, likely secondary, compounds in the summer, is also clearly observed in Fresno. Some rural sites, including Great Smoky Mountains National Park and St. Marks, are similar to the urban sites in that the amine concentration does not vary seasonally (supplemental material, Fig. S7c). Yosemite (Fig. 6, bottom) and other rural sites in the west (supplemental material, Fig. S7b), except Olympic National Park, show increased % amine in OM in the winter. At Yosemite National Park, the concentration of amine is fairly constant across the year but other functional groups, especially oxygenated groups, increase during the summer due to increased production of secondary organic aerosol (SOA). Even while amine SOA can be formed during the same summer months, the decrease in the percentage of amine functional group during these periods is likely due to increases in non-amine-containing SOA which increases the overall OM concentrations relative to amine compounds.

3.4. Contribution of amine to OM/OC

OM/OC is calculated for each sample and the site-averaged contribution from each functional group is shown in Fig. 7. The average annual OM/OC has considerable variability, from 1.47 at an urban site in Fresno, CA, to almost 2.1, at Olympic National Park, WA, a rural site. OM/OC is generally lower at urban sites than rural sites. OM/OC is lowest at three (Birmingham, Fresno and Phoenix) of the four urban sites, but the annual value between 1.47 and 1.55 for those sites, was higher than the 1.4 often used at urban sites (White and Roberts, 1977). Five rural sites (Yosemite NP, CA, Bliss State Park, CA, Olympic NP, WA, Proctor Maple Research Facility, VT and Trapper Creek, AK) are well above the value of 1.8 used by IMPROVE while Okefenokee, Cape Romain, Tallgrass and Great Smoky Mountains NP have annual average OM/OC of 1.65 or less, well below the 1.8 used for rural sites. The observed variability is similar to previous FT-IR work (Gilardoni et al., 2009; Ruthenburg et al., 2014) and work by researchers using other analytical and modeling methodologies referenced above.

Amine contributions to OM/OC also vary by site. For the three urban sites with low OM/OC, the amine functional group contributes

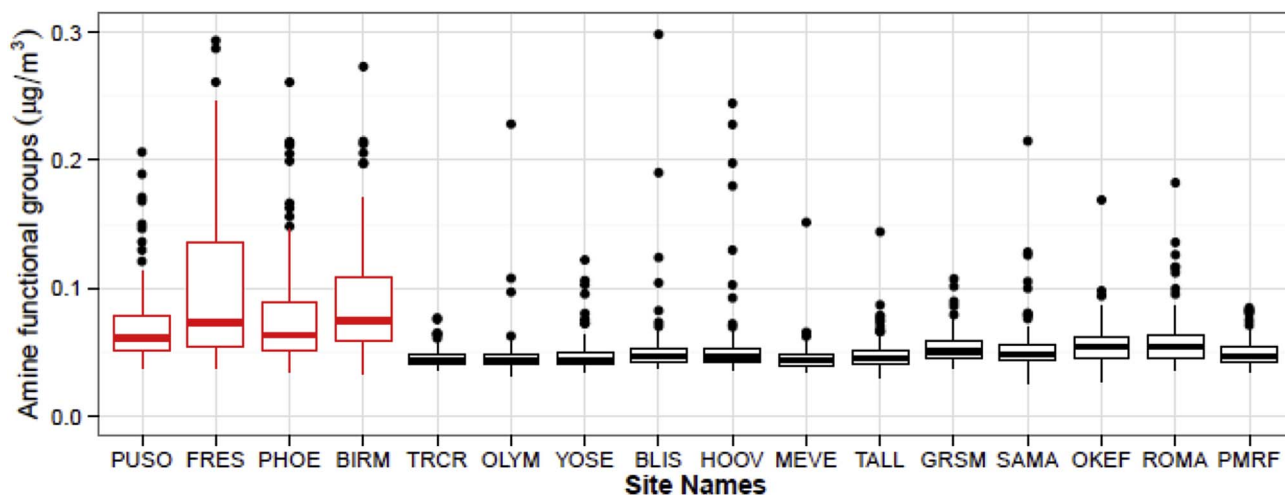


Fig. 4. Annual ambient amine functional group concentration at 16 IMPROVE sites. Sites in red are urban and sites in black are rural. The box shows the 25th and 75th percentile of the data and the bar within the box is the median. The whiskers are 1.5 * (interquartile range) and the outliers are identified with data points. For clarity, 3 high data points are not shown (YOSE on September 1, BLIS on August 26 and SAMA on January 22). See Table 1 for full site names that correspond to the site IDs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

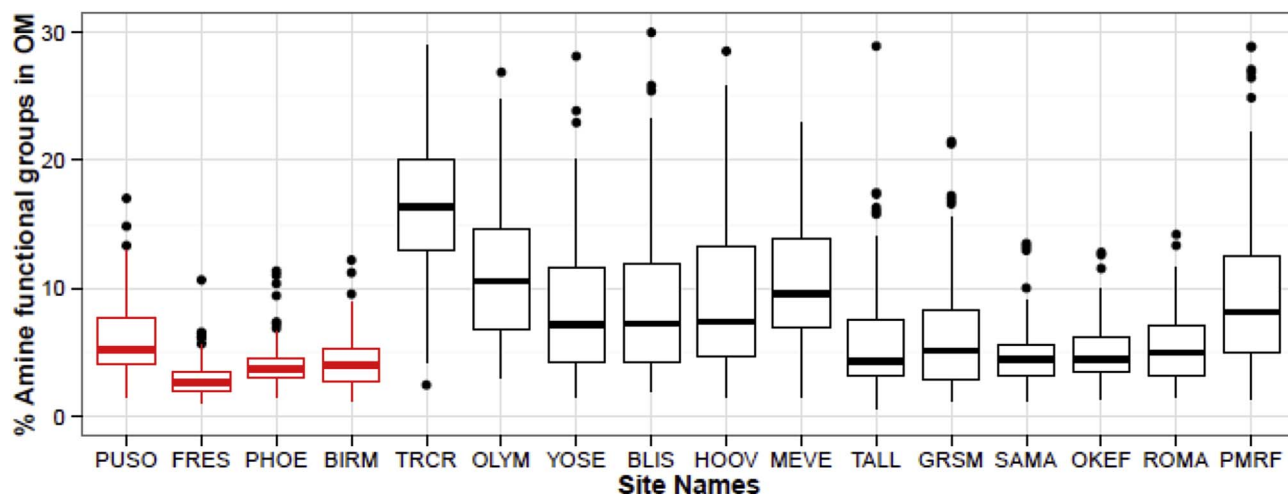


Fig. 5. Percent of amine functional groups in OM. The box and whiskers represent the same percentiles as in Fig. 4.

0.04 or less to the OM/OC ratio. For example, the OM/OC in Phoenix based on four main functional groups is 1.52 but increases by 0.04–1.56 when amine is included. For the rural sites in the Southeast (OKEF, GRSM, ROMA and SAMA) and in the Midwest (TALL), amine contributes about 0.05 to OM/OC. The rural sites in the northeast (PMRF) and in the west, have OM/OC of 1.74 or higher and the amine functional group contributes considerably more (0.08 and 0.22) to the OM/OC ratio. Seasonal and individual sample OM/OC ratios vary even more indicating the value in measuring OM or OM/OC by sample.

4. Conclusions

In this study, a multivariate calibration was developed using FT-IR spectra for the quantification of amine functional groups in the ambient

samples collected throughout 2013 from 16 IMPROVE sites. A narrow window of the FT-IR spectra was selected for the calibration to minimize errors due to the large OH and PTFE peaks and from carboxylate functional groups and carboxyl groups from amino acids. The wave-number region proved too limited to accommodate variability in absorbances from multiple compounds containing amine, so one amino acid, aspartic acid, which was shown to mid-range absorption efficiency, was used. The PLS model had good prediction capabilities when applied to standards not included in the calibration. The physical underpinnings of the model in ambient samples were highlighted via a comparison to peak heights in the ambient sample spectra.

Amines were ubiquitous in the ambient particle matter samples tested in this study. Annual median amine concentrations vary by site and are higher at urban sites than rural sites. Individual samples during

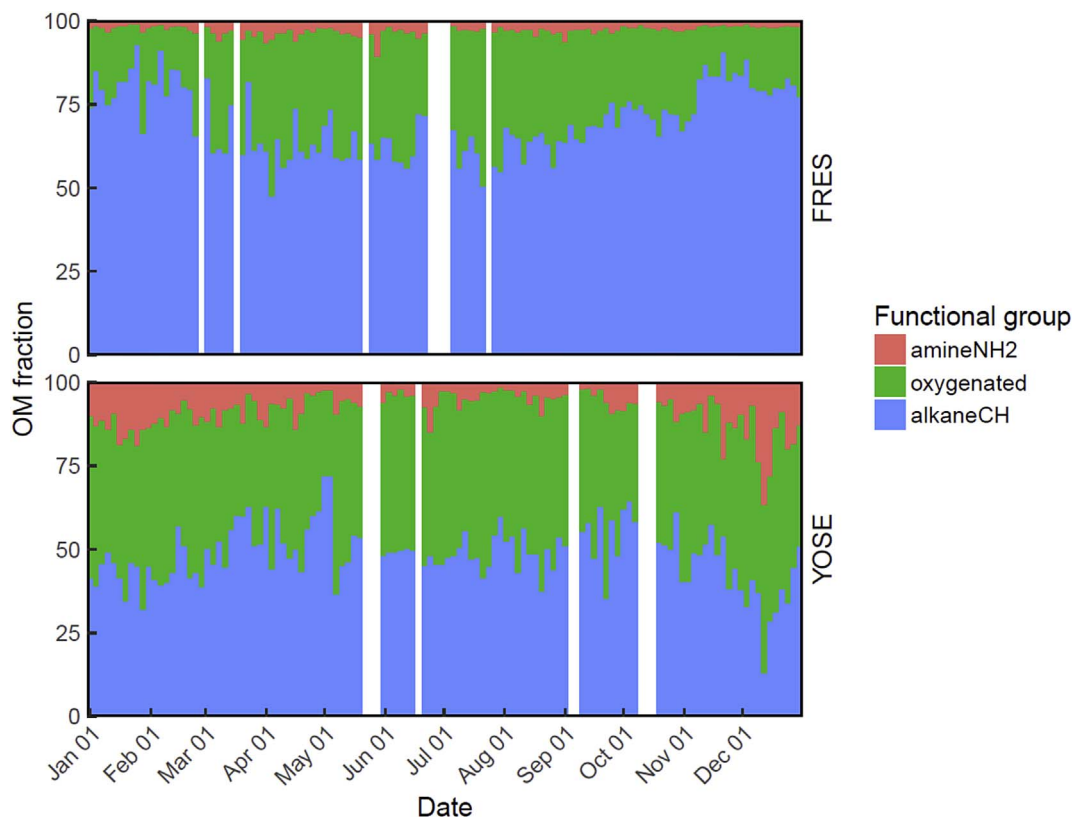


Fig. 6. Composition of a year of samples at Fresno, CA (top) and Yosemite NP, CA (bottom).

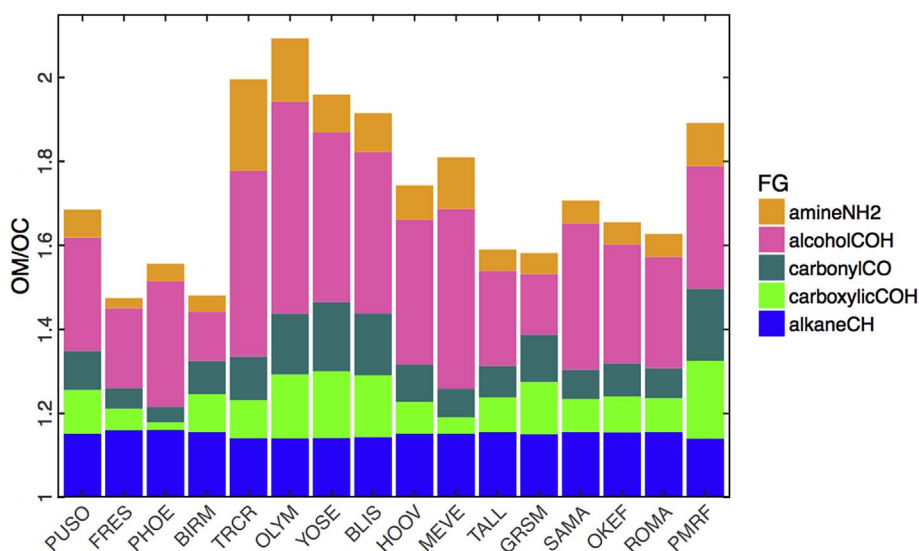


Fig. 7. Annual average OM/OC ratios calculated based on amine, alkane, alcohol, carboxylic acid OH, and carbonyl functional groups by site.

wildfire events and winters in urban areas have highest amine functional group concentrations. The percentage of organic matter due to amine is lower in most urban sites than rural. Urban sites show little seasonality in the amine fraction of organic aerosol even though the concentrations were higher in the winter; this is likely due to lower inversion heights in the winter based on the concurrent rise of OM; not seasonal changes to source strength of amines. At some rural sites, the amine fraction was higher in the winter than in the summer due to increased SOA in the summer. Organic matter to organic carbon ratios were calculated based on functional group predictions of aliphatic CH, alcohol OH, carbonyl, carboxylic acid OH and amine. The annual average OM/OC varies by site, with the lowest values at urban sites as expected. Rural sites ranged in OM/OC from 1.6 to 2.1. Amine contributions to OM/OC were smallest urban sites, approximate 0.04 and highest at rural sites, up to 0.22.

FT-IR spectroscopy in tandem with multivariate calibration using an amine-specific region of the spectra produces ambient amine predictions that are based in the variability of the spectra, are sensitive to small differences at low concentrations and vary by site, season and atmospheric conditions. By adding the amine functional group to our previously reported functional group measurements, the OM/OC is increased at all sites and for many samples and several sites, it is increased by almost 0.1 or more, indicating the value of including amine functional groups in OM/OC measurements.

Acknowledgements

The authors would like to gratefully acknowledge the EPRI agreement 10003745. Additional support was provided by NPS Cooperative Agreement P11AC91045 and EPFL. We would also like to thank our technical editor, Steph Spada.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2017.10.053>.

References

Aiken, A.C., DeCarlo, P.F., Kroll, J.H., Worsnop, D.R., Huffman, J.A., Docherty, K.S., Uibrich, I.M., Mohr, C., Kimmel, J.R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P.J., Canagarta, M.R., Onasch, T.B., Alfarra, M.R., Prevot, A.S.H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., Jimenez, J.L., 2008. O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. *Environ. Sci. Technol.* 42, 4478–4485.

Alam, M.J., Ahmad, S., 2012. Anharmonic vibrational studies of L-aspartic acid using HF and DFT calculations. *Spectrochimica Acta Part A Mol. Biomol. Spectrosc.* 96, 992–1004.

Barth, A., 2000. The infrared absorption of amino acid side chains-review. *Prog. Biophysics Mol. Biol.* 74, 141–173.

Barthes, M., Vik, A.F., Spire, A., Bordallo, H.N., Eckert, J., 2002. Breathers or structural instability in solid L-alanine: a new IR and inelastic neutron scattering vibrational spectroscopic study. *J. Phys. Chem. A* 106, 5230–5241.

Cape, J.N., Cornell, S.E., Jickells, T.D., Nemitz, E., 2011. Organic nitrogen in the atmosphere- where does it come from? A review of sources and methods. *Atmos. Res.* 102, 30–48.

Coates, J., 2000. Interpretation of Infrared Spectra, a Practical Approach. Interpretation of infrared spectra, a practical approach.

Dillner, A.M., Takahama, S., 2015. Predicting ambient aerosol thermal-optical reflectance (TOR) measurements from infrared spectra: organic carbon. *Atmos. Meas. Tech.* 8, 1097–1109.

Dokmaïrijan, S., Sanghiran, V., Nimmanpipug, P., 2010. The gas phase conformers and vibrational spectra of valine, leucine and isoleucine: an ab initio study. *J. Mol. Struct. THEOCHEM* 953, 28–38.

El-Zanan, H.S., Zielinska, B., Mazzoleni, L.R., Hansen, D.A., 2009. Analytical determination of the aerosol organic mass-to-organic carbon ratio. *J. Air Waste Manag. Assoc.* 59, 58–69.

Garcia, A.R., De Barros, R.B., Lourenco, J.P., Ilharco, L.M., 2008. The infrared spectrum of solid L-alanine: influence of pH-induced structural changes. *J. Phys. Chem. A* 112, 8280–8287.

Ge, X., Wexler, S., Clegg, S., 2011. Atmospheric amines-Part I. *A Rev. Atmos. Environ.* 45, 524–546.

Ghenie, Y., Garrigou-Lagrange, C., 1972. Infrared spectra of glycine isotopic species isolated in an argon or nitrogen matrix. *J. Mol. Spectrosc.* 41, 240–248.

Gilardoni, S., Liu, S., Takahama, S., Russell, L.M., Allan, J.D., Steinbrecher, R., Jimenez, J.L., De Carlo, P.F., Dunlea, E.J., Baumgardner, D., 2009. Characterization of organic ambient aerosol during MIRAGE 2006 on three platforms. *Atmos. Chem. Phys.* 9, 5417–5432.

Indresand, H., White, W.H., Trzepla, K., Dillner, A.M., 2013. Preparation of sulfur reference materials that reproduce atmospheric particulate matter sample characteristics for XRF calibration. *X-Ray Spectrom.* 42, 359–357.

Kamruzzaman, M., Makino, Y., Oshita, S., 2016. Rapid and non-destructive detection of chicken adulteration in minced beef using visible near-infrared hyperspectral imaging and machine learning. *J. Food Eng.* 170, 8–15.

Kettle, S.F., Lugwisha, E., Eckert, J., McGuire, N.K., 1989. Intermolecular vibrational coupling in glycine. *Spectrochim. Acta* 45A, 533–539.

Kumar, S., Rai, A.K., Rai, S.B., Rai, D.K., Singh, A.N., Singh, V.B., 2006. Infrared, Raman and electronic spectra of alanine: a comparison with ab initio calculation. *J. Mol. Struct.* 791, 23–29.

Liu, S., Takahama, S., Russell, L.M., Gilardoni, S., Baumgardner, D., 2009. Oxygenated organic functional groups and their sources in single and submicron organic particles in MILAGRO 2006 campaign. *Atmos. Chem. Phys.* 9, 6849–6863.

Lopez Navarrete, J.T., Hernandez, V., Ramirez, F.J., 1994. IR and Raman spectra of L-aspartic acid and isotopic derivatives. *Biopolymers* 34, 1065–1077.

Lopez Navarrete, J.T., Hernandez, V., Ramirez, F.J., 1995. Vibrational study of aspartic acid and glutamic acid dipeptides. *J. Mol. Struct.* 348, 249–252.

Lowenthal, D.H., Kumar, N., 2003. PM2.5 mass and light extinction reconstruction in IMPROVE. *J. Air & Waste Manag. Assoc.* 53 (9), 1109–1120.

Machida, K., Kagayama, A., Saito, Y., Urado, C., Uno, T., 1977. Vibrational spectra and intermolecular potential of the a-form crystal of glycine. *Spectrochim. Acta.* 33A, 569–574.

Malm, W.C., Schichtel, B.A., Pitchford, M.L., 2011. Uncertainties in PM2.5 gravimetric and speciation measurements and what we can learn from them. *J. Air Waste Manag.*

- Assoc. 61, 1131–1149.
- Pankow, J.F., 2015. Phase considerations in the gas/particle partitioning of organic amines in the atmosphere. *Atmos. Environ.* 122, 448–453.
- Pitchford, M., Malm, W., Schichtel, B., Kumar, N., Lowenthal, D., Hand, J., 2007. Revised algorithm for estimating light extinction from IMPROVE particle speciation data. *J. Air Waste Manag. Assoc.* 57, 1326–1336.
- Pratt, K.A., Hatch, L.E., Prather, K.A., 2009. Seasonal volatility dependence of ambient particle phase amines. *Environ. Sci. Technol.* 43, 5276–5281.
- Reggente, M., Dillner, A.M., Takahama, S., 2016. Predicting ambient aerosol thermal-optical reflectance (TOR) measurements from infrared spectra: extending the predictions to different years and different sites. *Atmos. Meas. Tech.* 9, 441–454.
- Rodriguez-Lazcano, Y., Maté, B., Gálvez, O., Herrero, V.J., Tanarro, I., Escribano, R., 2012. Solid L-alanine: Spectroscopic properties and theoretical calculations. *J. Quantitative Spectrosc. Radiat. Transf.* 113, 1266–1275.
- Rosado, M.T., Duarte, M.L.T.S., Fausto, R., 1997. Vibrational spectra (FT-IR, Raman and MI-IR) of cy- and D-alanine. *J. Mol. Struct.* 410–411, 343–348.
- Rosado, M.T., Duarte, M.L.T.S., Fausto, R., 1998. Vibrational spectra of acid and alkaline glycine salts. *Vib. Spectrosc.* 16, 35–54.
- Russell, L.M., 2003. Aerosol organic mass-to-organic carbon ratio measurements. *Environ. Sci. Technol.* 37, 2982–2987.
- Russell, L.M., Bahadur, R., Ziemann, P.J., 2011. Identifying organic aerosol sources by comparing functional group composition in chamber and atmospheric particles. *PNAS* 108, 3516–3521.
- Ruthenburg, T.C., Perlin, P.C., Liu, V., McDade, C.E., Dillner, A.M., 2014. Determination of organic matter and organic matter to organic carbon ratios by infrared spectroscopy with application to selected sites in the IMPROVE network. *Atmos. Environ.* 86, 47–57.
- Shurvell, H.F., 2002. *Spectra–Structure Correlations in the Mid- and Far-infrared*. John Wiley & Sons Ltd.
- Silva, P.J., Erupe, M.E., Price, D.E., Elias, J., Malloy, Q.G.J., Li, Q., Warren, B., Crocker III, D.R., 2008. Trimethylamine as precursor to secondary organic aerosol formation via nitrate radical reaction in the atmosphere. *Environ. Sci. Technol.* 42, 4689–4696.
- Simon, H., Bhawe, P.V., Swall, J.L., Frank, N.H., Malm, W.C., 2011. Determining the spatial and seasonal variability in OM/OC ratios across the US using multiple regression. *Atmos. Chem. Phys.* 11, 2933–2949.
- Susi, H., Byler, D.M., 1980. Vibrational analysis of L-alanine and deuterated analogs. *J. Mol. Struct.* 63, 1–11.
- Takahama, S., Ruggeri, G., Dillner, A.M., 2016. Analysis of functional groups in atmospheric aerosols by infrared spectroscopy: sparse methods for statistical selection of relevant absorption bands. *Atmos. Meas. Tech.* 9, 3429–3454.
- Turpin, B.J., Lim, H.-J., 2001. Species contributions to PM_{2.5} mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Sci. Technol.* 35, 602–610.
- Veniaminov, S.Y., Kalnin, N.N., 1990. Quantitative IR spectrophotometry of peptide compounds in water (H₂O) solutions. 1. Spectral parameters of amino acid residue absorption bands. *Biopolymers* 30, 1243–1257.
- Wang, C.H., Storms, D.R., 1971. Temperature-dependent raman study and molecular motion in L-alanine single crystal. *J. Chem. Phys.* 5, 3291–3299.
- Weakley, A.T., Takahama, S., Dillner, A.M., 2016. Ambient aerosol composition by infrared spectroscopy and partial least-squares in the chemical speciation network: organic carbon with functional group identification. *Aerosol Sci. Technol.* 1096–1114.
- White, W.H., Roberts, P.T., 1977. On the nature and origin of visibility-reducing aerosols in the Los Angeles air basin. *Atmos. Environ.* 11, 803–812.
- Wold, S., Sjöström, M., Eriksson, L., 2001. PLS-regression: a basic tool of chemometrics. *Chemom. Intelligent Laboratory Syst.* 58, 109–130.
- Wolpert, M., Hellwig, P., 2006. Infrared spectra and molar absorption coefficients of the 20 alpha amino acids in aqueous solutions in the spectral range from 1800 to 500 cm⁻¹. *Spectrochim. Acta Part A* 64, 987–1001.
- You, Y., Kanawade, V.P., de Gouw, J.A., Guenther, A.B., Madronich, S., Sierra-Hernández, M.R., Lawler, M., Smith, J.N., Takahama, S., Ruggeri, G., Koss, A., Olson, K., Baumann, K., Weber, R.J., Nenes, A., Guo, H., Edgerton, E.S., Porcelli, L., Brune, W.H., Goldstein, A.H., Lee, S.-H., 2014. Atmospheric amines and ammonia measured with a chemical ionization mass spectrometer (CIMS). *Atmos. Chem. Phys.* 14, 12181–12194.
- Zhao, Z., Chen, S.-H., Kleeman, M.J., Mahmud, A., 2011. The impact of climate change on air quality-related meteorological conditions in California. Part I: present time simulation analysis. *J. Clim.* 24, 3344–3361.