

Toward Understanding Amines and Their Degradation Products from Postcombustion CO₂ Capture Processes with Aerosol Mass Spectrometry

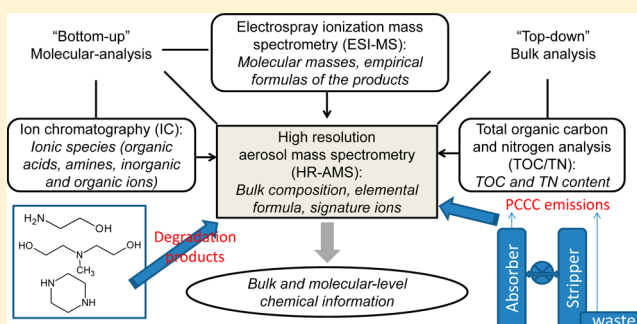
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S Supporting Information

ABSTRACT: Amine-based postcombustion CO₂ capture (PCCC) is a promising technique for reducing CO₂ emissions from fossil fuel burning plants. A concern of the technique, however, is the emission of amines and their degradation byproducts. To assess the environmental risk of this technique, standardized stack sampling and analytical methods are needed. Here we report on the development of an integrated approach that centers on the application of a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) for characterizing amines and PCCC-relevant species. Molecular characterization is achieved via ion chromatography (IC) and electrospray ionization high-resolution mass spectrometry (ESI-MS). The method has been optimized, particularly, by decreasing the AMS vaporizer temperature, to gain quantitative information on the elemental composition and major nitrogen-containing species in laboratory-degraded amine solvents commonly tested for PCCC applications, including ethanolamine (MEA), methyldiethanolamine (MDEA), and piperazine (PIP). The AMS-derived nitrogen-to-carbon (N/C) ratios for the degraded solvent and product mixtures agree well with the results from a total organic carbon and total nitrogen (TOC/TN) analyzer. In addition, marker ions identified in the AMS spectra are used to estimate the mass contributions of individual species. Overall, our results indicate that this new approach is suitable for characterizing PCCC-related mixtures as well as organic nitrogen species in other sample types. As an online instrument, AMS can be used for both real-time characterization of emissions from operating PCCC plants and ambient particles in the vicinity of the facilities.



1. INTRODUCTION

Carbon capture and storage has been recognized as a potentially effective strategy for abating anthropogenic CO₂ emissions.¹ A mature postcombustion CO₂ capture (PCCC) technology is based on chemical absorption using aqueous alkanolamines, such as ethanolamine (MEA), methyldiethanolamine (MDEA), piperazine (PIP), and various blends,² to scrub CO₂ from flue gas from coal-fired power plants.^{3,4} During an amine-based PCCC process, pretreated flue gas is counter-currently contacted with aqueous amine solution in the absorber to remove CO₂. The solution is then heated in the stripper/regenerator to release the captured CO₂, and the CO₂-lean solution is pumped back to the absorber for another cycle.⁵ Meanwhile, the treated flue gas is water-washed and discharged. Because of the high stripper temperature and the presence of O₂ and acidic species in flue gas,^{6–11} amines can undergo thermal and oxidative degradations over prolonged use.² These reactions reduce CO₂ absorption efficiency¹² and cause operational problems such as foaming, corrosion, and fouling.¹³ Moreover, the degradation products, along with amine solvents, can enter the environment via the discharge of treated gas,

reclaimer waste, and fugitive emissions.^{14,15} According to calculations conducted on a PCCC plant equipped with a well-designed water-wash section, an estimated 0.03 kg MEA/tonne CO₂ can be emitted.¹⁴ Also emitted are volatile species including ammonia and formaldehyde and submicrometer particles that contain amines and low-volatility degradation products.^{16,17} In addition, gaseous and particulate pollutants may be generated during the incineration of reclaimer wastes.¹⁴ Once present in the air, these discharged species may undergo further oxidation and form substances that are potentially of greater environmental risk.¹⁸ For instance, amines can react with nitrogen oxides in the atmosphere to form nitrosamines,^{19–21} some of which are carcinogens at sufficiently high doses.²² Amines are also precursors of secondary organic aerosols^{23–25} and play important roles in the formation and growth of new particles.^{26–28}

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The degradation of amines and release of pollutants from PCCC plants are complex and dynamic, influenced by flue gas flow rate and composition, reaction temperature, and a number of other factors which may change over the operational time of the facility.¹⁴ Analytical methods capable of characterizing a wide array of compounds are required to understand amine-based PCCC emissions and properly evaluate the environmental consequences of this technology. As summarized in Table 1, gas chromatography (GC), liquid chromatography (LC), and ion chromatography (IC) combined with mass spectrometry (MS) are commonly employed for PCCC-related analyses. Despite important roles they play in understanding PCCC applications, each method has limitations. For example, GC-MS detects mainly volatile species, leaving a large set of compounds, especially polar and thermolabile species, undetected.²⁹ IC can only characterize ionic species, while LC-MS provides limited structural and quantitative information of the products.

A thorough characterization of PCCC emissions may be achieved by combining different techniques and utilizing novel instruments with broader detection coverage and quantification capability. Additionally, instruments capable of online measurement are desirable for providing feedback by which the results of operational changes in the facilities can be monitored and optimized. For these reasons, we aim at developing an approach which centers on the application of a high-resolution time-of-flight aerosol mass spectrometer (thereafter AMS), which has been widely used for in situ and quantitative analysis of size-resolved chemical composition of submicrometer particles.^{30,31} Particles are thermally desorbed in the AMS and then subjected to 70 eV electron impact (EI) ionization – a universal ionization method with reproducible ion fragmentation,³² thus AMS can simultaneously measure the bulk properties of complex mixtures and, in favorable cases, identify individual species and functionally related compound classes based on matching reference spectra (e.g., from the NIST database, <http://www.nist.gov/srd/>). In addition, with a typical resolution of 5000–6000, the AMS also generates ion-specified mass spectra from which the average elemental composition of the analyte can be determined.³³

Because 70 eV EI induces extensive fragmentation, the AMS's ability to characterize molecular composition is limited. We therefore also develop IC and electrospray ionization mass spectrometry (ESI-MS) methods to characterize individual nitrogen-containing species. This integrated approach allows PCCC-related emissions to be comprehensively characterized via both top-down (i.e., bulk characterization using AMS and a total organic carbon and total nitrogen (TOC/TN) analyzer) and bottom-up analysis (i.e., molecular analyses using IC, ESI-MS, and AMS). Another advantage of this approach is that it can be used for both online and offline measurements. Indeed, AMS has been routinely used for online analysis, and both IC and TOC/TN have been coupled with particle-into-liquid-sampler (PILS)³⁴ or steam jet aerosol collector (SJAC)³⁵ for in situ analysis of particles. Here we report on the development and optimization of this integrated approach for degraded amines and demonstrate its application for characterizing samples generated from lab-degraded PCCC-relevant solvents including MEA (a benchmark primary amine), MDEA (a tertiary amine), and PIP (a cyclic secondary amine).

Table 1. Analytical Techniques for Characterizing Amines and Their Degradation Products Reported in Prior Studies

analytical techniques ^a	amines studied ^b and refs
Gas chromatography (GC)	
GC-MS	MEA, ^{8,12,29,54–59} MEA/MDEA blend, ^{56,60,61} 12 amines, ^{c,62,63} MDEA, ^{49,64–67} DEAOH, ^{68–70} MMEA, ⁷¹ AMP ⁷²
GC-FTIR	MEA ^{12,54}
GC-AED	MEA ⁵⁴
GC-FID	MDEA, ^{64,67} DEAOH, ^{69,70,73–76} MDEA/DEAOH/AMP blend ¹¹
GC-TCD	MDEA/DEAOH/AMP blend ¹¹
Liquid chromatography (LC)	
HPLC-RID	MEA, ^{7,10,29,56,57,77} MDEA, ⁷⁸ MEA/MDEA ⁵⁶
HPLC-ELSD	MEA ^{50,79}
HPLC-MS	MEA, ⁸ MDEA, ⁴⁹ PIP, ⁹ MMEA ⁷¹
HPLC	EDA, ⁸⁰ PIP ⁸¹
Ion chromatography (IC)	MEA, ^{6,8,54} 12 amines, ^{c,62,63} MDEA, ⁴⁹ MDEA/PIP blend, ⁸² PIP, ^{83–86} AMP ⁷²
IC-MS	PIP, ⁸¹ EDA ⁸⁰
Other techniques	
LVHRMS	MEA ^{12,54}
CE-DAD	MEA ^{29,58}
FTIR	MEA ^{8,50,87}
NMR	12 amines, ^{c,62,63} MDEA/PIP blend, ⁸⁸ PIP ^{89,81}
FTICR-MS	12 amines, ^{c,62,63}
TOC	MEA ^{6,50}
UV–vis	AMP ⁷²
ICP-AES	MEA ^{6,54}
PTR-ToF-MS	MEA ⁵²

^aThe acronyms are as follows: AED (atomic emission detector); CE-DAD (capillary electrophoresis-diode array detection); ELSD (evaporative light scattering detector); FID (flame ionization detector); FTIR (Fourier transform infrared absorption spectrophotometer); FTICR-MS (Fourier transform ion cyclotron resonance mass spectrometry); HPLC (high pressure liquid chromatography); ICP-AES (inductively coupled plasma-atomic emission spectrometry); LVHRMS (low-voltage high resolution mass spectrometry); MS (mass spectrometry); NMR (nuclear magnetic resonance); PTR-ToF-MS (proton transfer reaction time-of-flight mass spectrometry); RID (refractive index detector); TCD (thermal conductivity detector); TOC (total organic carbon); UV–vis (ultraviolet–visible spectrophotometer). ^bThe acronyms are as follows: AMP (2-amino-2-methyl-1-propanol); DEAOH (diethanolamine); EDA (ethylenediamine); MDEA (N-methyldiethanolamine); MEA (ethanolamine); MMEA (N-methylethanolamine); PIP (piperazine). ^cThe 12 amines include: N,N-dimethylethanolamine, N-methyldiethanolamine, N-methylethanolamine, diethanolamine, ethanolamine, 2-amino-2-methyl-1-propanol, N-(2-hydroxyethyl)ethylenediamine, N,N'-dimethylpiperazine, N,N,N',N'-tetramethylethylenediamine, N,N,N'-trimethylethylenediamine, N,N-dimethylethylenediamine, and N,N'-dimethylethylenediamine.

2. EXPERIMENTAL METHODS

2.1. Reagents and Samples. All chemicals used were reagent grade or better (see the Supporting Information for details), and all solutions were prepared using purified water (resistance >18.2 MΩ·cm) from a Milli-Q system (Millipore). Three filter samples were collected from a pulmonary toxicity study conducted at Lovelace Respiratory Research Institute.

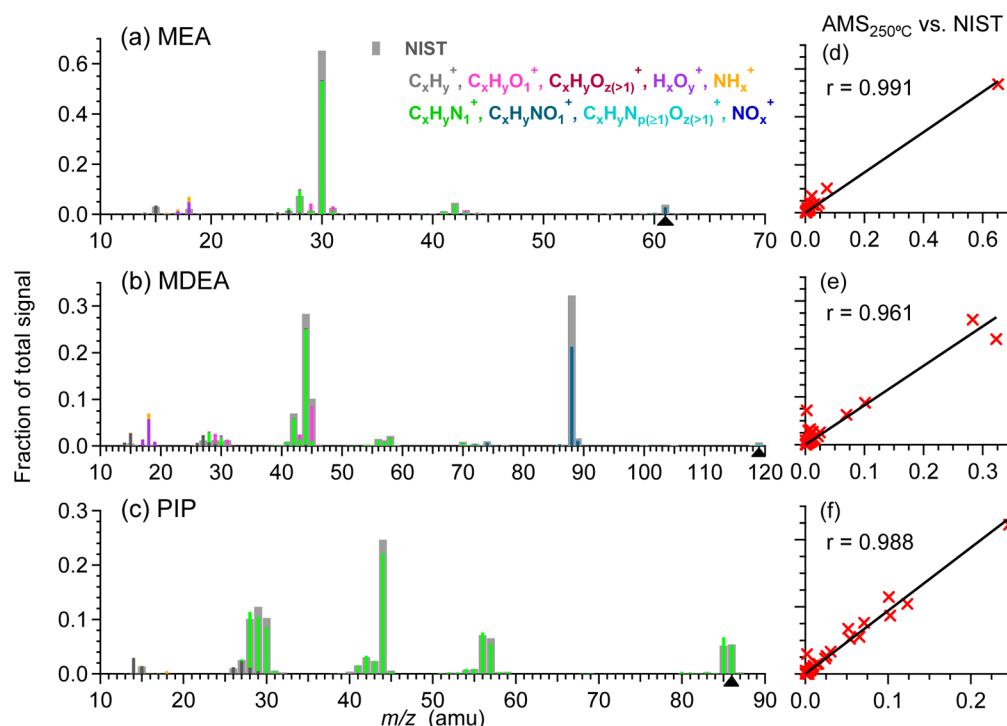


Figure 1. The AMS spectra acquired at vaporizer temperature of 250 °C and the NIST spectra of a) MEA, b) MDEA, and c) PIP. The scatter plots compare the 250 °C AMS spectra to the NIST spectra for d) MEA, e) MDEA, and f) PIP. The HR-ToF-AMS spectra are colored by 9 different ion categories listed in a). The solid triangles on the mass spectra indicate the molecular ions.

MEA, MDEA, and PIP were degraded separately for 2–3 months at ~150 °C under pure air and NO₂ inside a sealed stainless steel vessel pressurized to 12–15 psi. As discussed in the Supporting Information, these amine samples likely underwent both oxidative and thermal degradations similar to those during actual PCCC processes. The degraded solutions were atomized to create inhalation exposure atmospheres for mice. Simultaneously, particle filters were collected. Each filter was extracted by sonication in purified water at 0–4 °C for ~30 min. The extracts were then filtered (0.45 μm Acrodisc, Pall Life Science) and stored frozen (–20 °C) until analysis.

2.2. AMS Analysis. Detailed procedures for analyzing liquid samples using AMS were reported previously.^{36,37} Briefly, the solution was atomized using argon, dried by a diffusion drier, and analyzed by the AMS. Before every sample run, purified water was measured in the same manner as an analytical blank. In this study, we operated the AMS at two different vaporizer temperatures: 600 °C (typical for AMS measurements) and 250 °C (to reduce fragmentation). Since the AMS concentrates particles relative to the carrier gas by a very large factor (~10⁷) via aerodynamic particle focusing and differential vacuum pumping,³⁰ volatile PCCC products such as ammonia, CO, CH₄, formaldehyde, alkylamines, and nitrosamines are typically not measured. The mass spectra from replicate measurements show high agreement (Pearson's $r > 0.99$). Details about the AMS analyses are provided in the Supporting Information.

2.3. TOC and TN Analysis. A Shimadzu TOC-V_{CPH} analyzer with a TNM-1 unit was used to measure total carbon (TC), total inorganic carbon (TIC), and TN simultaneously. The instrument converts all carbon into CO₂ and all nitrogen into NO via combustion at 720 °C under ultrapure air. The resulting CO₂ was quantified by a nondispersive infrared (NDIR) analyzer and NO by a chemiluminescence analyzer. Prior to combustion, TIC (carbonates/bicarbonates and

dissolved CO₂) was transformed into CO₂ by 25% H₃PO₄ and determined by NDIR. TOC was calculated by subtracting TIC from TC, and TON (total organic nitrogen) was calculated by subtracting total inorganic nitrogen (= ammonium + nitrite + nitrate, from IC) from TN. The TOC/TN analyzer was calibrated using NaHCO₃, Na₂CO₃, potassium hydrogen phthalate, and KNO₃ standard solutions. Results from external TOC check standards (Aqua Solutions) were always within 10% of certified values.

2.4. IC Analysis. Concentrations of ionic species were measured using two Metrohm ion chromatographs (881 Compact IC Pro) equipped with conductivity detectors, a shared autosampler, and a) for cation analysis, a Metrosep C4 guard/2.0 column and a Metrosep C4 250/2.0 column maintained at 30 °C, and b) for anion analysis, a Metrosep RP2 guard/3.6 column and a Metrosep A Supp15 250/4.0 column maintained at 45 °C. Cations were eluted at 0.3 mL·min^{–1} with 1.75 mM HNO₃ and 0.75 mM dipicolinic acid. Anions were eluted at 0.8 mL·min^{–1} using 5 mM Na₂CO₃ and 0.3 mM NaOH. In this study, 9 amines (ethanolamine, diethanolamine, triethanolamine, methyldiethanolamine, bis-2-hydroxypropylamine, methylamine, dimethylamine, trimethylamine and ethylamine), 6 inorganic cations (Li⁺, Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺), 7 inorganic anions (F[–], Cl[–], Br[–], NO₂[–], NO₃[–], SO₄^{2–}, and PO₄^{3–}), and 9 organic anions (glycolate, glyoxylate, formate, acetate, methanesulfonate, malate, malonate, oxalate, and maleate) can be separately determined (see examples in Figure S1). Since the IC method used in this study is not sensitive at detecting PIP, this compound was quantified by ESI-MS (Section 2.5).

Evaluation of the IC measurements are shown in Tables S1–S2. External check standards (6 cation and 7 anion standard mixtures; Dionex) and individual standards from Metrohm were analyzed, and the results were always within 10% of

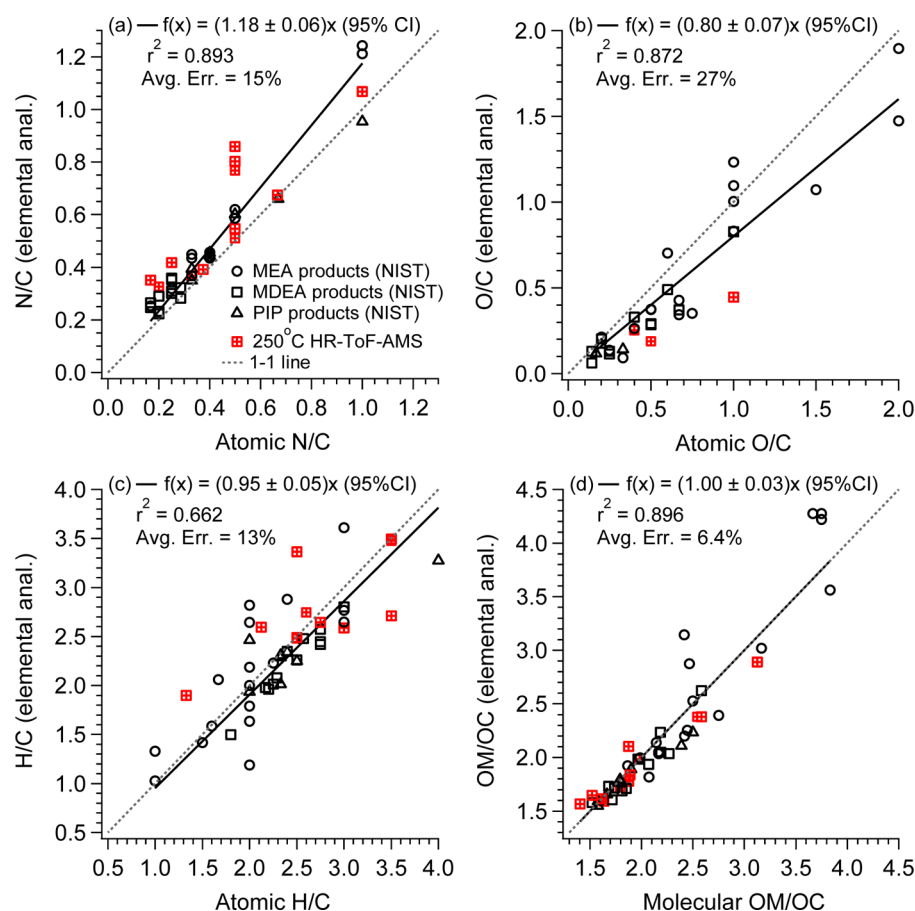


Figure 2. Atomic ratios of a) N/C, b) O/C, and c) H/C of organic species determined by analyzing the EI mass spectra versus the nominal values, and d) OM/OC ratios calculated from calibrated atomic ratios (CI: confidence interval). Details about the compounds are given in Table S3 in the Supporting Information. Red symbols correspond to compounds analyzed with a HR-ToF-AMS with vaporizer temperature of 250 °C; others are results from NIST spectra.

certified values. Method detection limits (MDL) for amines ranged from a few to $\sim 20 \mu\text{g}\cdot\text{L}^{-1}$ and for anions were $10\text{--}100 \mu\text{g}\cdot\text{L}^{-1}$. Recoveries of known additions in samples were within 80–115%. Relative percentage differences for replicate analyses of the degradation samples were within $\pm 10\%$.

2.5. ESI-MS Analysis. A linear ion trap Orbitrap MS (Thermo Electron Corp.) with a mass resolution of $\sim 30,000$ and mass accuracy of 1–2 ppm was employed. Samples were delivered to a capillary (275 °C) at $10 \mu\text{L}\cdot\text{min}^{-1}$ and electrosprayed (5 kV) to form positive ions (e.g., MH^+ or MNa^+).³⁸ A standard mixture of caffeine, Met-Arg-Phe-Ala acetate salt, and Ultramark 1621 (Thermo Scientific) was used for m/z calibration. The instrument was operated in a full scan mode ranging from m/z 50 to 500. Before each run, methanol was used to rinse the lines and analyzed in the same manner to generate a background spectrum. PIP was quantified by the ESI-MS using a standard addition method (MDL $\sim 18 \mu\text{g}\cdot\text{L}^{-1}$). All ESI-MS spectra were processed using the Decon2LS program (<http://omics.pnl.gov/software/DeconTools.php>).³⁹ Elemental formulas were assigned for peaks with signal-to-noise (S/N) ratios larger than 3 and intensities higher than 10 times the corresponding signals in the background spectrum using the MIDAS Molecular Formula Calculator v1.1.

3. RESULTS AND DISCUSSIONS

3.1. Determination of Elemental and Bulk Composition. Knowing the average elemental composition of a complex

mixture is important for probing its chemical properties. This information can be obtained from the composition of the ions generated when the mixture is subjected to 70 eV EI – a universal ionization method that simultaneously ionizes all vaporized species in a sample.⁴⁰ However, due to the losses of neutral fragments (e.g., H_2O , H_2 , etc.)³² and the lack of detection of some ions (e.g., H^+), calibration factors are needed to scale the elemental ratios (e.g., nitrogen-to-carbon (N/C), oxygen-to-carbon (O/C), and hydrogen-to-carbon (H/C) atomic ratios) computed directly from mass spectra.³²

For AMS analysis, the calibration factors may also be influenced by the vaporizer temperature – higher temperature adds extra thermal energy and generally leads to smaller ion fragments. The AMS vaporizer is typically set at ~ 600 °C for ambient measurements to ensure fast evaporation, thus quantitative determination of the size distributions of non-refractory aerosol components (i.e., organics and ammonium salts of nitrate, sulfate, and chloride).^{41,42} Using lower vaporizer temperature may reduce fragmentation and produce spectra more similar to the standard NIST spectra.³⁰ As shown in Figures 1 and S3a, the AMS spectra of amino-compounds acquired at 250 °C indeed agree well with the NIST spectra. The 250 °C spectra also contain richer chemical information than the 600 °C spectra, showing more prominent molecular ions (i.e., $\text{C}_2\text{H}_7\text{NO}^+$ at m/z 61 for MEA, $\text{C}_5\text{H}_{13}\text{NO}_2^+$ at m/z 119 for MDEA, and $\text{C}_4\text{H}_{10}\text{N}_2^+$ at m/z 86 for PIP) and signature

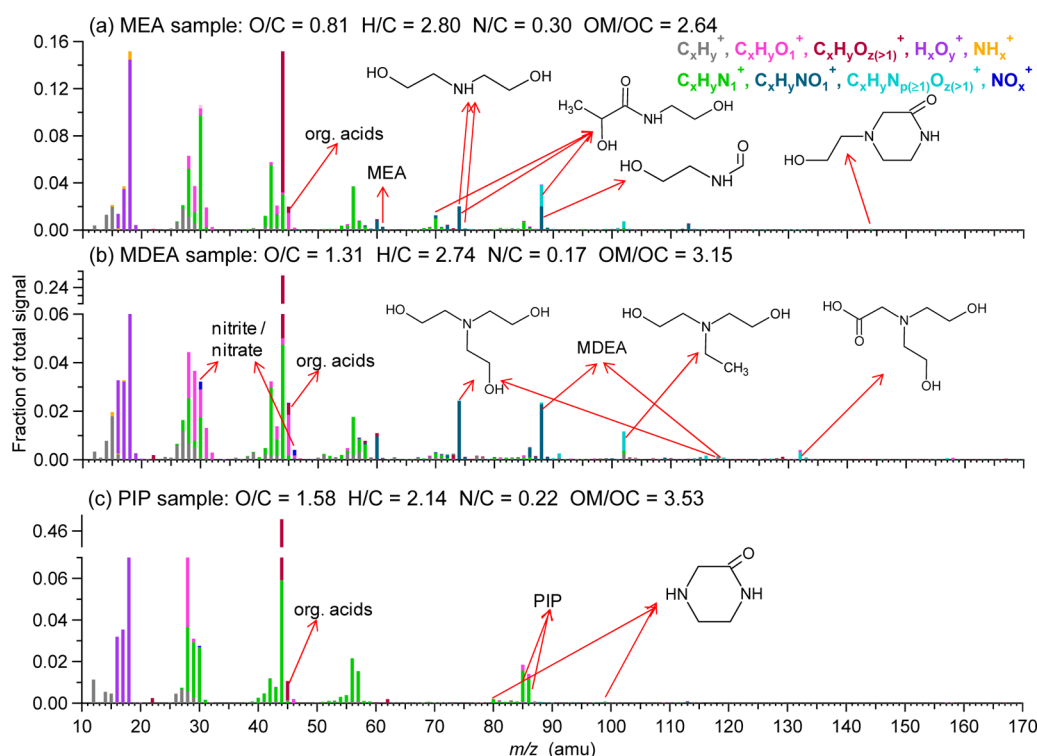


Figure 3. The HR-ToF-AMS spectra (vaporizer temperature = 250 °C) of three amine degradation samples from lab-simulated PCCC processes: a) ethanolamine (MEA), b) methyldiethanolamine (MDEA), and c) piperazine (PIP). Ions in the spectra are color coded according to 9 different ion categories listed in panel a). Elemental ratios were calculated using the calibration factors determined in Figure 2. The molecular structures of a few identified degradation products and their AMS signatures are also marked.

ions (e.g., CH_4N^+ at m/z 30 for MEA, $\text{C}_4\text{H}_{10}\text{NO}^+$ at m/z 88 for MDEA, and $\text{C}_4\text{H}_9\text{N}_2^+$ at m/z 85 for PIP).

These results indicate that 250 °C is more suitable for characterizing amine-based emissions. Since the calibration factors reported in Aiken et al.³³ were determined at ~600 °C, we refine the factors for the lower temperature condition based on the AMS spectra of 12 amino compounds acquired at 250 °C and the NIST spectra of 37 compounds identified as degradation products from MEA, MDEA, and PIP in previous studies² (see Table S3 for details). For the NIST spectra, which are all unit mass resolution (UMR), we estimated the ion composition at each m/z based on the major ion formation mechanisms and the chemical structure and connectivities of substructures of the parent compound.³² If more than one explainable composition exists for a particular m/z (e.g., CH_2N^+ and C_2H_4^+ at m/z 28), we assume equal contributions from all possible ions. The average elemental ratio was subsequently calculated from all ions in a signal-weighted way.⁴⁰

Figure 2 compares the elemental ratios calculated from the EI spectra to the nominal values of the compounds. The calibration factors for O/C (0.80) and H/C (0.95) are very similar to those reported in Aiken et al. (O/C: 0.75; H/C: 0.91), whereas that of N/C is significantly higher (1.18 vs 0.96).³³ The positive bias is partly because α -cleavage is an important reaction of amines under EI that favors the loss of alkyl group and formation of N-containing ions.³² For example, α -cleavage of the C–C bond in MEA favors the formation of CH_4N^+ (m/z 30)³² (Figure 1a). Similarly, α -cleavage favors the formation of $\text{CH}_3\text{–NH=CH}_2^+$ (m/z 44) and the loss of $\text{C}_2\text{H}_3\text{OH}$ and CH_3 moieties from MDEA (Figure 1b). In contrast, the bias is smaller for PIP due to its symmetrical ring

structure and α -cleavage generates $\text{C}_2\text{H}_6\text{N}^+$ (base peak at m/z 44, Figure 1c) which has the same N/C as the parent molecule. However, the positive bias of N/C appears to be dependent more on the AMS response to the vaporizer temperature than on the usage of compounds that differ from those used by Aiken et al.³³ For example, as shown in Figure S3c and S3d, for the same 12 substances analyzed by the AMS, the average ($\pm 95\%$ confidence interval) bias in the N/C ratios calculated from the 250 °C spectra is 1.22 (± 0.08) whereas that from the 600 °C spectra is 1.07 (± 0.06), which is statistically more similar to the value (0.96 ± 0.05) reported in Aiken et al.³³

The bias varies from molecule to molecule and can be fairly large for individual compounds (Figure 2). However, for complex mixtures such as emissions from amine-based PCCC processes, the uncertainty is expected to be smaller because of compensating effects from different compounds, which is verified by the analyses of lab-generated degradation samples (details in Section 3.3). The average uncertainty for the new N/C calibration factor, defined as the average absolute value of the relative error of each data point with respect to the regression line,³³ is 15% (Figure 2a). The organic mass-to-carbon (OM/OC) ratios calculated using the new calibration factors agree well with the actual values (slope = 1; $r^2 = 0.90$; Figure 2d), indicating that this method permits good mass quantification of organic nitrogen mixtures. The calibration factors reported here are applicable to elemental analysis of AMS data acquired at low vaporizer temperatures.

3.2. Determination of Organic Nitrogen Species and Compound Classes. 70 eV EI mass spectrometry is a widely accepted technique for molecular structure determination.³² The reproducible EI fragmentation pattern may allow individual molecules or compound classes to be identified in

mixtures. For example, several previous studies demonstrated the capability of using AMS mass spectral fingerprints to determine methanesulfonic acid (MSA),^{43,44} amino compounds,^{45,46} polycyclic aromatic hydrocarbons (PAHs),⁴⁷ and organosulfates and organonitrates⁴⁸ in ambient particles.

In this study, we examine the EI spectra of PCCC-relevant amines and degradation products for prominent ions that may be used as chemical fingerprints. For amines, the candidates include the molecular ions, e.g., $C_2H_7NO^+$ (m/z 61) for MEA, $C_5H_{13}NO_2^+$ (m/z 119) for MDEA, and $C_4H_{10}N_2^+$ (m/z 86) for PIP and major N-containing ions at even masses, e.g., CH_4N^+ for MEA, $C_4H_{10}NO^+$ for MDEA, and $C_2H_6N^+$ for PIP. As shown in Figure 1, these ions are abundant and conspicuous in the corresponding AMS mass spectra. More signature ions representative of amine degradation products were identified via examining the NIST spectra of product species reported in previous studies as well as compounds determined in lab-generated degradation samples based on IC and ESI-MS analyses. A detailed list of the signature ions useful for screening for MEA, MDEA, and PIP degradation species is shown in Tables S4–S6.

The AMS spectra of three filter samples collected from lab-simulated amine degradation experiments clearly indicate the presence of various products (Figure 3), such as $C_3H_8NO^+$ and $C_5H_{12}NO_2^+$ for triethanolamine – a MDEA product (Table S5) and $C_4H_8N_2O^+$ and $C_3H_7N_2^+$ for piperazine – a PIP product (Table S6). Based on the signal intensities of the signature ions, we estimate the mass contributions of major species in a sample by solving the following linear equation using multilinear regression

$$ms_{\text{mix}} = \sum_{i=1}^n ms_i * c_i \quad (1)$$

where ms_{mix} and ms_i are the mass spectra of the mixture and compound i , respectively. c_i is the mass fraction of i in the mixture if the total signal in each mass spectrum is normalized to 1. This approach works well for deconvolving three binary mixtures: MEA/sucrose, MDEA/sucrose, and PIP/sucrose (see details in Figures S4–S5).

3.3. Characterization of Lab-Generated PCCC Amine Samples. Three amine degradation samples from lab-simulated PCCC processes were characterized using the approach described above. Figure 3 shows the AMS spectra measured at vaporizer temperature of 250 °C. Elemental analyses of the spectra indicate that the average N/C ratios of the MEA, MDEA, and PIP degradation samples are 0.3, 0.17, and 0.22, respectively. These values are all lower than the N/C ratios of the original amines, consistent with the fact that the amines underwent oxidation and carbamation during PCCC processes. The N/C ratios determined by the combustion-based TOC/TN analyzer agree well with the AMS results, especially for measurements conducted at 250 °C (Figure 4). The significantly higher N/C ratio of the PIP sample measured at 600 °C was mainly due to much lower CO_2^+ signal compared to that in the 250 °C spectrum (Figures S6c and S6f), for which one possible explanation is that the vaporizer temperature affects the relative amounts of gaseous CO_2 produced from pyrolysis compared to vaporized oxygenated organics and carbamates prior to ionization.

The large CO_2^+ and H_2O^+ peaks in the AMS spectra are primarily contributed by aminium bicarbonate or carbamate formed from the reactions of CO_2 with amines.¹⁴ The amide

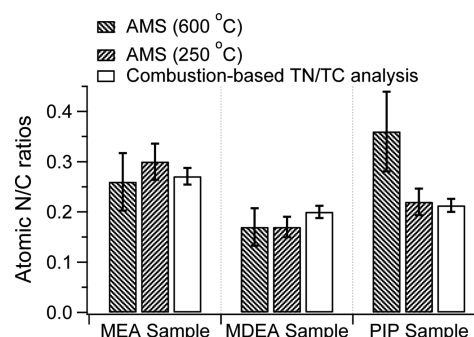


Figure 4. Comparisons of the N/C ratios determined by the HR-ToF-AMS with the values determined by TOC/TN analyzer for the degraded samples. The N/C ratios from the 250 °C spectra were calculated using the new calibration factor of 1.18, while those from the 600 °C spectra were calculated using the factor of 0.96 reported in Aiken et al.³³ The error bars represent the uncertainties in the N/C values (22% in Aiken et al.,³³ 15% in this study, and 6.1% for TN/TC analysis).

bonds in carbamates are weak, and the reactions are reversible, meaning that these species, although being emitted in particulate form, can act as a reservoir of gaseous amines in the atmosphere. Another key spectral feature of these samples is the dominance of even-mass $C_xH_yN_p^+$ and $C_xH_yN_pO_z^+$ ions ($x \geq 1, y \geq 0, p \geq 1, z \geq 1$), indicating the presence of various organic nitrogen species. Using ESI-MS, we screened for main species and determined their molecular formulas (Figure S10, Tables S4–S6). For compounds that match the molecular formulas of PCCC-related chemicals reported previously, we confirm the presence of these compounds by comparing their NIST mass spectra to the AMS spectra of the degraded samples. For species that were not reported in the literature, we propose the structures and validate them by examining the presences of fingerprint ions in the AMS spectra.

As detailed in Tables S4–S6, most of the species identified in this study were reported previously, but a few, such as N-(2-hydroxyethyl)lactamide from MEA degradation (Figure 3a), ethyldiethanolamine from MDEA degradation (Figure 3b), and piperazine from PIP degradation (Figure 3c), are new. This is an example of improving analytical capability via a combination of AMS and ESI-MS. Moreover, the AMS spectra of these samples indicate the formation of organic acids (because of CHO_2^+) and nitrates (e.g., NO^+ and NO_2^+) from the degradation of amines during a simulated PCCC process and the IC analysis indeed detected glycolate, formate, oxalate, nitrite, and nitrate.

Figure 5 shows the average compositions of the amine degradation samples determined by analyzing the 250 °C AMS. A comparison to the spectra acquired at 600 °C are shown in Figure S7. In each sample, the mass fraction of the undegraded amine was estimated based on the relative intensity of its most representative signature ion, e.g., $C_2H_7NO^+$ for MEA, $C_4H_{10}NO^+$ for MDEA, and $C_4H_{10}N_2^+$ for PIP. Because the NIST spectra are available for all MDEA degradation products (Table S5), we estimated the mass distributions of those products via multivariate linear regression analysis discussed in Section 3.2. The fitting diagnostics are presented in Figure S11. The signals of a majority of signature ions are well reconstructed, and the correlation between the reconstructed spectrum and the sample spectrum is tight ($r^2 = 0.90$; Figure S11b). However, approximately 17% of the AMS spectral signal

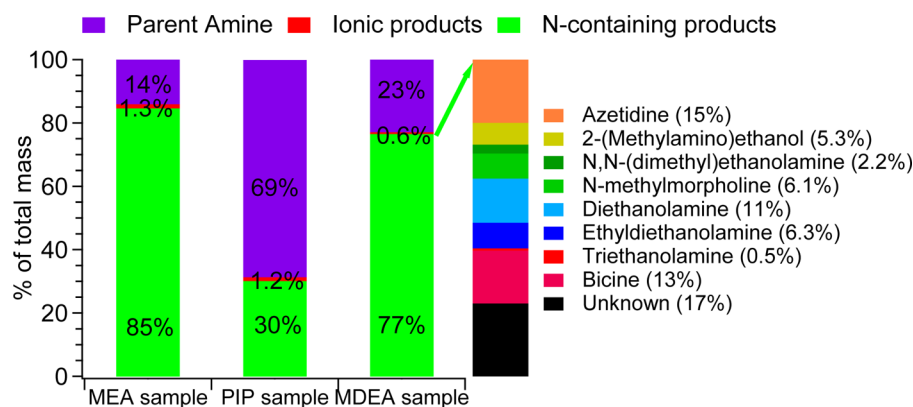


Figure 5. Average compositions of the degradation samples of MEA, PIP, and MDEA.

is left unaccounted for, indicating the lack of detections of other species. Note that this analysis could be improved if we use the ion-specified AMS spectra of the product species in the multilinear regression. In addition, a thorough evaluation of the accuracy of results should be conducted, e.g., via comparing results obtained with independent analytical methods such as LC-MS. In this study, we found that azetidine, bicine, and diethanolamine were the top three MDEA degradation products (Figure 5) where diethanolamine and bicine were found to be major MDEA degradation products as reported previously.⁴⁹

4. PERSPECTIVE

The integrated approach described here focuses on the application of an Aerodyne AMS and additional methods for characterizing emissions from amine-based PCCC processes. Particularly, as the importance of particulate matter (PM) emissions from PCCC applications has emerged recently,¹⁶ this approach allows us to probe the bulk characteristics as well as the molecular compositions of the particle-bound species, which are important for health risk assessments since fine particles can be inhaled deep into the lung. In addition, coupled with proper atomization techniques, this approach is applicable for characterizing the liquid waste from PCCC processes as well. Future investigations of real-world PCCC plant samples, especially those taken from different stages of degradation, would be valuable for evaluating and improving this analytical approach and for better understanding the chemistry of PCCC processes and emissions. Although the approach reported here is not designed for analyzing gaseous chemicals, emission factors for PCCC processes could be applied to estimate the emission rates of important gaseous species, such as formaldehyde. For example, Sexton and Rochelle⁵⁰ estimated that a $5.8 \text{ mM}\cdot\text{h}^{-1}$ loss of MEA corresponds to $\sim 0.09 \text{ mM}\cdot\text{h}^{-1}$ formation of formaldehyde. Since our approach can quantify amine degradation rate, the formation rate of formaldehyde could be estimated.

In addition to offline analyses of PCCC-relevant emissions, AMS is capable of monitoring emissions in real-time from operating PCCC facilities, at pilot or other scales. AMS has been routinely used to quantify sulfate, nitrate, ammonium, chloride, and organic matter and determine the elemental composition of organics in fine particles. In this study, we further show that using lower vaporizer temperature (e.g., 250°C) can improve the determination of individual species with AMS. For future field deployment aiming to characterize

PCCC in-stack emissions, the AMS can be programmed to alternate between 600 and 250°C :⁵¹ using 250°C to minimize fragmentation and thus gain more information about compound speciation; and using the “conventional” 600°C to gain more quantitative information about the bulk chemical properties and size distributions of the samples. Information acquired at 600°C can also be compared to other ambient AMS studies where key signature ions are detected. Another issue relevant to this application is that since PM concentrations in the treated flue gas can be very high, proper dilution prior to sampling by AMS and other online instruments might be necessary. Indeed, this has been demonstrated with the deployment of a PTR-ToF-MS for measuring gaseous species.⁵² However, dilution may cause loss of semivolatile species, thus changes in aerosol composition. Simultaneous measurements of particulate composition and trace gases (e.g., using PTR-MS) could help quantify losses of semivolatile species during dilution. In addition, acquiring volatility profiles of PCCC particles, e.g., through coupling the AMS with a thermodenuder,⁵³ could help constrain gas-to-particle partitioning behaviors of semivolatile species in the undiluted flue gas.

Being a field deployable instrument, AMS can be used to characterize the affected ambient PM in the vicinity of a PCCC unit and evaluate its impacts on local and regional air quality. In addition, the techniques developed in this study may be applied broadly for characterizing organic nitrogen species in environmental samples such as ambient aerosols, fog/rain waters, snow/ice, sewage water, and soil extracts.

■ ASSOCIATED CONTENT

● Supporting Information

Additional text, Tables S1–S7, and Figures S1–S11. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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