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Novel ionization reagent for the measurement of gas-phase ammonia and amines using a stand-alone atmospheric pressure gas chromatography (APGC) source

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Abstract

Rationale: Contaminants present in ambient air or in sampling lines can interfere with the target analysis through overlapping peaks or causing a high background. This study presents a positive outcome from the unexpected presence of *N*-methyl-2-pyrrolidone, released from a PALL HEPA filter, in the analysis of atmospherically relevant gas-phase amines using chemical ionization mass spectrometry.

Methods: Gas-phase measurements were performed using a triple quadrupole mass spectrometer equipped with a modified atmospheric pressure gas chromatography (APGC) source which allows sampling of the headspace above pure amine standards. Gas-phase *N*-methyl-2-pyrrolidone (NMP) emitted from a PALL HEPA filter located in the inlet stream served as the ionizing agent.

Results: This study demonstrates that some alkylamines efficiently form a $[\text{NMP} + \text{amine} + \text{H}]^+$ cluster with NMP upon chemical ionization at atmospheric pressure. The extent of cluster formation depends largely on the proton affinity of the amine compared with that of NMP. Aromatic amines (aniline, pyridine) and diamines (putrescine) were shown not to form cluster ions with NMP.

Conclusions: The use of NMP as an ionizing agent with stand-alone APGC provided high sensitivity for ammonia and the smaller amines. The main advantages, in addition to sensitivity, are direct sampling into the APGC source and avoiding uptake on sampling lines which can be a significant problem with ammonia and amines.

1 | INTRODUCTION

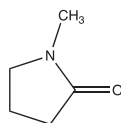
Amines are ubiquitous in the atmosphere, originating from many industrial and agricultural activities.^{1–5} They have been identified as key participants in numerous atmospheric processes, such as new particle formation and growth,^{6–12} and brown carbon formation.^{13,14} In addition, multifunctional amines such as monoethanolamine are currently used in carbon capture and storage (CCS) systems and their application will continue to increase with further developments in climate change mitigation processes.^{15–17}

A number of analytical techniques have been developed to identify and quantify gas-phase amines, including gas

chromatography/mass spectrometry (GC/MS) analysis coupled with derivatization^{5,18–21} and ion chromatography.^{22–25} Online chemical ionization mass spectrometry (CIMS) has also been successfully applied to the measurements of atmospherically relevant amines. CIMS includes gas-phase amine measurements by traditional proton transfer reaction mass spectrometry (PTR-MS) with protonated water clusters $(\text{H}_2\text{O})_n\text{H}^+$,^{4,17,26–29} or by charge transfer with O_2^+ ions^{29–31} or NO^+ ions.²⁹ Ethanol and acetone have also been used as the CIMS reagent.^{32–35} Simon and co-workers³⁶ showed that dimethylamine clusters with nitrate ions in a chemical ionization atmospheric pressure interface time-of-flight (CI-API-TOF) instrument. Several commercial APCI sources have been modified to allow direct air sampling

for the analysis of various amines including pyridine³⁷ and diamines from food via headspace extraction of the amines and direct injection into the APCI source.³⁸ Finally, particle-bound amines (aminium and ammonium ions) have been detected using thermal desorption chemical ionization mass spectrometry (TDCIMS), where the particles are collected onto the tip of a platinum wire followed by subsequent thermal desorption and ionization using water clusters formed using a ²¹⁰Po radioactive source.^{12,39,40}

Ambient ionization mass spectrometry methods have been exponentially growing over the past ten years due to their versatility, ease of use, reduced fragmentation due to 'soft' ionization mechanisms, and minimal sample preparation.⁴¹⁻⁵¹ A particularly difficult, but important, species to measure using these methods is ammonia (NH₃), which typically has high detection limits relative to the amines in part associated with a smaller proton affinity. Smaller amines can also be challenging due their intermediate volatility that makes wall effects in the ion source particularly problematic. During recent experiments measuring particle-phase NH₃ with TDCIMS, strong signals for clusters of NH₃ with an initially unknown ion were observed (on average the cluster ion was 15 times more intense than the corresponding NH₄⁺ ion). These new cluster ions provided much better sensitivity for the detection and measurement of NH₃ than the protonated precursor ion. Further investigation revealed the ionization agent was *N*-methyl-2-pyrrolidone (NMP),



released into the air flow from a HEPA filter (PALL Gelman; model 12144).

We report here studies of the use of NMP as a somewhat unconventional ambient ionization agent for ammonia and a series of amines. In addition, we show that of a commercial atmospheric pressure gas chromatography/mass spectrometry (APGC/MS) source can be used with this reagent ion to carry out ambient ionization MS. APGC/MS was first developed in the 1970s^{52,53} and has been

applied to the analysis of a number of toxic organic compounds,⁵⁴ including pesticides,⁵⁵⁻⁵⁷ polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs,⁵⁸⁻⁶⁰ dioxins⁶¹⁻⁶³ and brominated flame retardants.⁶⁴ We show here that the source can be used in stand-alone mode, i.e. without the GC interface, for ambient gas analysis.

2 | EXPERIMENTAL

2.1 | APGC/MS

Atmospheric pressure chemical ionization measurements of gas-phase amine standards were performed using an atmospheric pressure gas chromatography (APGC) source (Waters) connected to a triple quadrupole mass spectrometer (Xevo, TQ-S; Waters). The ambient pressure source was used as a stand-alone inlet without a GC interface (Figure 1). A 0.25-inch Teflon tube was centered on the APGC source door approximately 1 cm in front of the ionization chamber inlet. The corona discharge on the inside of the chamber provided the ionization source. A total flow rate of 7.9 L min⁻¹ was drawn from the room through the Teflon tubing, which was divided between a HEPA filter (1.5 L min⁻¹) and the branch opening of an Ultra-Torr[®] tee that was open to laboratory air and acts as the sample inlet (6.4 L min⁻¹). The flow rate was controlled by the combination of the rough pump connected to the source itself and the pressure differential existing at the sampling cone. Uncapped vials filled with nanopure water (18.2 MΩ cm; Thermo Scientific, Barnstead) were placed inside the APGC enclosure to facilitate protonation. Source settings were as follows: corona discharge current, 4.5 μA; cone size, 0.8 mm; cone voltage, 10 V; cone flow (headspace of liquid N₂, ultra-high quality; Airgas), 100 L h⁻¹; source temperature, 100°C; collision gas (argon; Oxygen Services), 0.10 mL min⁻¹. Data were acquired in the positive ion mode (mass range 15–300 amu) using the MassLynx software package. Full scan mass spectra were recorded with a collision energy of 2 eV and product ion scans were recorded with collision energy from 5 to 20 eV.

The new HEPA filter used in this study was purchased from PALL Corporation (PN 12144; hereafter referred to as the PALL HEPA

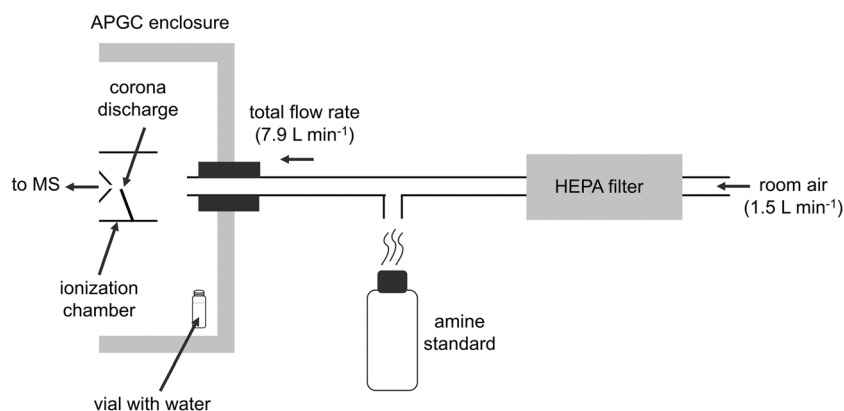


FIGURE 1 APGC/MS source configuration for ambient pressure chemical ionization sampling of the headspace above amine standards

filter) and is composed of a Versapor[®] membrane (acrylic copolymer) sealed with polyurethane and housed in a polypropylene case with a polyester filter support.⁶⁵ A second type of HEPA filter purchased from TSI Inc. (PN 1602051; hereafter referred to as the TSI HEPA filter) was also tested; this filter contains glass microfibers captured between polyester monofilament layers.

2.2 | Chemicals

All amine measurements were performed from the headspace of standards, including ammonium hydroxide (28–33% wt. in water, ACS grade; VWR), methylamine (40% wt. in water; Sigma Aldrich), dimethylamine (40% wt. in water; Aldrich), trimethylamine (45% wt. in water; Aldrich), ethylamine (66–72% wt. in water; Aldrich), propylamine ($\geq 99\%$; Aldrich), butylamine (99.5%; Sigma Aldrich), isopropylamine ($\geq 99.5\%$; Aldrich), sec-butylamine (99%; Aldrich), monoethanolamine ($\geq 99.5\%$; Aldrich), aniline ($>99\%$; Sigma), pyridine (ACS grade; EMD), putrescine (1,4-diaminobutane, 99%; Aldrich) and triethylamine ($>99.5\%$; EMD). *N*-Methyl-2-pyrrolidone (C_5H_9NO ; NMP) was purchased from Sigma-Aldrich (99.5%, anhydrous) and was used without purification. The chemical formulae and molecular masses of the amines and NMP are summarized in Table 1. In a separate set of experiments, gas cylinder mixtures in nitrogen of NH_3 (Airgas; 1.0 ± 0.05 ppm), MA (Airgas; 5.1 ± 0.1 ppm), DMA (Airgas; 0.35 ± 0.005 ppm) and TMA (Airgas; 0.86 ± 0.02 ppm) were also used as standards. The gas mixture concentrations were separately determined using collection of the gas-phase amines onto custom-build cation-exchange resin cartridges with subsequent analysis by ion chromatography.²² The resulting concentrations given above are the

TABLE 1 Chemical properties and proton affinities⁶⁶ of the compounds investigated in this study

Compounds	Chemical formula	Molecular mass ($g\ mol^{-1}$)	Proton affinity ($kJ\ mol^{-1}$)
<i>N</i> -Methyl-2-pyrrolidone	C_5H_9NO	99	923.5
Ammonia	NH_3	17	853.6
Methylamine	$(CH_3)NH_2$	31	899.0
Dimethylamine	$(CH_3)_2NH$	45	929.5
Trimethylamine	$(CH_3)_3N$	59	948.9
Ethylamine	$(CH_3CH_2)NH_2$	45	912.0
Propylamine	$CH_3(CH_2)_2NH_2$	59	917.8
Butylamine	$CH_3(CH_2)_3NH_2$	73	921.5
Isopropylamine	$(CH_3)_2CHNH_2$	59	923.8
sec-Butylamine	$CH_3CH_2CH(CH_3)NH_2$	73	929.7
Triethylamine	$(CH_3CH_2)_3N$	101	981.8
Aniline	$C_6H_5-NH_2$	93	882.5
Pyridine	C_5H_5N	79	930.0
Putrescine	$(NH_2)(CH_2)_4(NH_2)$	88	1005.6
Monoethanolamine	$(OH)CH_2CH_2(NH_2)$	61	930.3

averages over three replicate measurements, with one standard deviation. Calibrations were performed using dry clean air provided by an FTIR purge gas generator (Parker Balston, model 75-62).

3 | RESULTS AND DISCUSSION

3.1 | Unexpected cluster formation of alkylamine with NMP

Figure 2 shows the APGC/MS spectra from room air alone (Figure 2A), and with room air passing through the PALL HEPA filter (Figure 2B). While the water clusters $(H_2O)_2H^+$ at m/z 37 and $(H_2O)_3H^+$ at m/z 55 are visible in the room air sample, the APGC/MS spectrum of the HEPA filter exhibits one very intense peak at m/z 100 and a smaller one at m/z 199 attributed to a dimer ion. This was identified as protonated *N*-methyl-2-pyrrolidone (NMP; MW = $99.13\ g\ mol^{-1}$) by comparison with the APGC/MS spectrum of a pure standard (Figure 2C) which shows an intense precursor ion peak at m/z 100 $[NMP + H]^+$ and an additional dimer ion at m/z 199 $[2NMP + H]^+$.

Product ion scans of m/z 100 from the PALL HEPA filter sample (Figure S1A, supporting information) match perfectly with that from the pure NMP standard (Figure S1B), with two major ions observed at m/z 58 and 69 and two minor ions observed at m/z 41 and 82, confirming the identity of the chemical released by the HEPA filter as NMP. Our observations are also consistent with previously reported fragmentation of NMP using ambient ionization techniques that shows the formation of two major fragments at m/z 58 attributed to the loss of CH_3NH_2 and m/z 69 attributed to the loss of $CH_2-C=O$ from the parent NMP molecule.^{67,68} Additionally, product ion scans of m/z 199 for both the NMP standard and the HEPA filter samples (Figure S2, supporting information) show a unique peak at m/z 100 corresponding to a loss of a neutral NMP unit, confirming the identity of the m/z 199 as a dimer ion. This clearly shows that the PALL HEPA filter is releasing NMP into the air flow through the filter. To determine if the release of NMP is common to HEPA filters, another type manufactured by TSI Inc. was tested. As shown in Figure S3 (supporting information), no NMP was detected.

The degassing of NMP from the PALL HEPA filter was discovered in the course of studies involving amines where new, unexpected clusters were observed. Once NMP had been identified as the chemical ionization reagent, further studies were carried out to elucidate the factors that determine the nature of these NMP clusters for gas-phase amines having different structures. Figure 3 shows the APGC/MS spectra of the headspace of a standard aqueous solution of ammonium hydroxide (which releases gas-phase NH_3) as well as from the headspace of aqueous standard solutions of methylamine (MA), dimethylamine (DMA) and trimethylamine (TMA). Peaks corresponding to the NMP cluster adducts $[NMP + amine + H]^+$ are observed at m/z 117, 131, 145 and 159, respectively. The contributions of this cluster compared with that of the precursor $[amine + H]^+$ ion decreases along the series. The trend to increasing precursor $[amine + H]^+$ peaks follows the proton

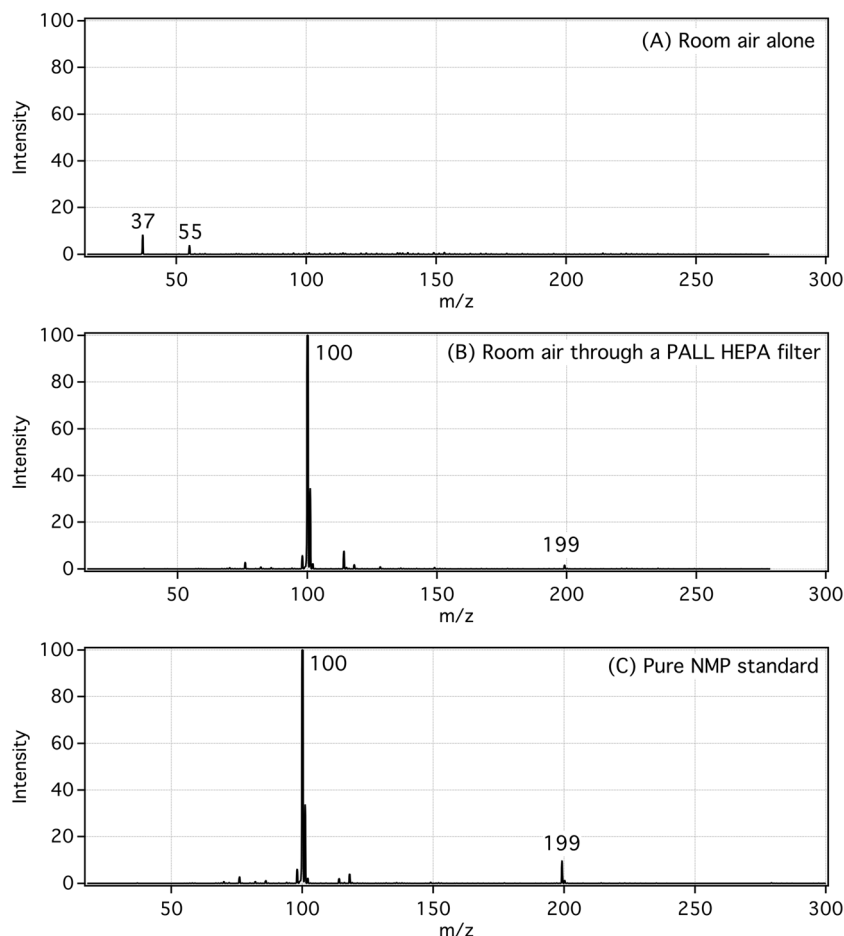


FIGURE 2 APGC/MS spectra of A, room air alone; B, room air drawn through a PALL HEPA filter; and C, a *N*-methyl-2-pyrrolidone (NMP) standard (in this case no HEPA filter was used at the APGC/MS source inlet). All spectra are normalized to 1.34×10^8 counts for ease of comparison

affinity⁶⁶ of the amines relative to NMP (Table 1): TMA ($948.9 \text{ kJ mol}^{-1}$) > DMA ($929.5 \text{ kJ mol}^{-1}$) > NMP ($923.5 \text{ kJ mol}^{-1}$) > MA ($899.0 \text{ kJ mol}^{-1}$) > NH_3 ($853.6 \text{ kJ mol}^{-1}$).

Further analysis of the product ion scans of the $[\text{NMP} + \text{amine} + \text{H}]^+$ cluster ions were carried out at a collision energy of 5 eV (Figure S4, supporting information). For ammonia (Figure S4A, supporting information), the cluster observed at m/z 117 loses a neutral NH_3 molecule, suggesting that NMP is the species that retains the proton and the cluster is of the form of $[\text{NH}_3 + (\text{NMP} + \text{H})]^+$. This is consistent with the larger proton affinity of NMP ($923.5 \text{ kJ mol}^{-1}$)⁶⁶ compared with NH_3 ($853.6 \text{ kJ mol}^{-1}$). On the other hand, both TMA and DMA have a higher proton affinity than that of NMP, and the clusters show preferential loss of a neutral NMP molecule (Figures S4C and S4D, supporting information), suggesting that the cluster is instead of the form of $[\text{NMP} + (\text{amine} + \text{H})]^+$. For MA (Figure S4B, supporting information), although the proton affinity of MA is lower than that of NMP, the product ion spectra show both the loss of MA and NMP, suggesting that the cluster formed is a

combination of $[\text{NMP} + (\text{MA} + \text{H})]^+$ and $[\text{MA} + (\text{NMP} + \text{H})]^+$, with the loss of MA favored. It is interesting to note that, although the concentration of gas-phase NH_3 above the ammonium hydroxide solution is extremely high ($\sim 3 \times 10^5$ ppm; using $K_{\text{H}} = 0.54 \text{ mol m}^{-3} \text{ Pa}^{-1}$ from Sander),⁶⁹ no $[\text{NH}_3 + \text{H}]^+$ precursor ion is observed, and NH_3 would not be detected in APGC/MS if it was not for its cluster with NMP.

The sensitivity of this technique was tested using gas mixtures for NH_3 , MA, DMA and TMA in nitrogen and a dilution system that was connected to the inlet of the APGC source (branch of the tee; Figure S5A, supporting information). For those measurements, the instrument was operated in multiple reaction monitoring (MRM) mode, following the specific transitions for the respective $[\text{amine} + \text{NMP} + \text{H}]^+$ clusters as follows: $117 \rightarrow 100$ for NH_3 ; $131 \rightarrow 32$ for MA (note: a contaminant peak at m/z 131 interfered with the $131 \rightarrow 100$ transition); $145 \rightarrow 46$ for DMA; $159 \rightarrow 60$ for TMA. A typical trace as a function of concentration is shown in Figure S5B (supporting information). Using successive dilution of the gas

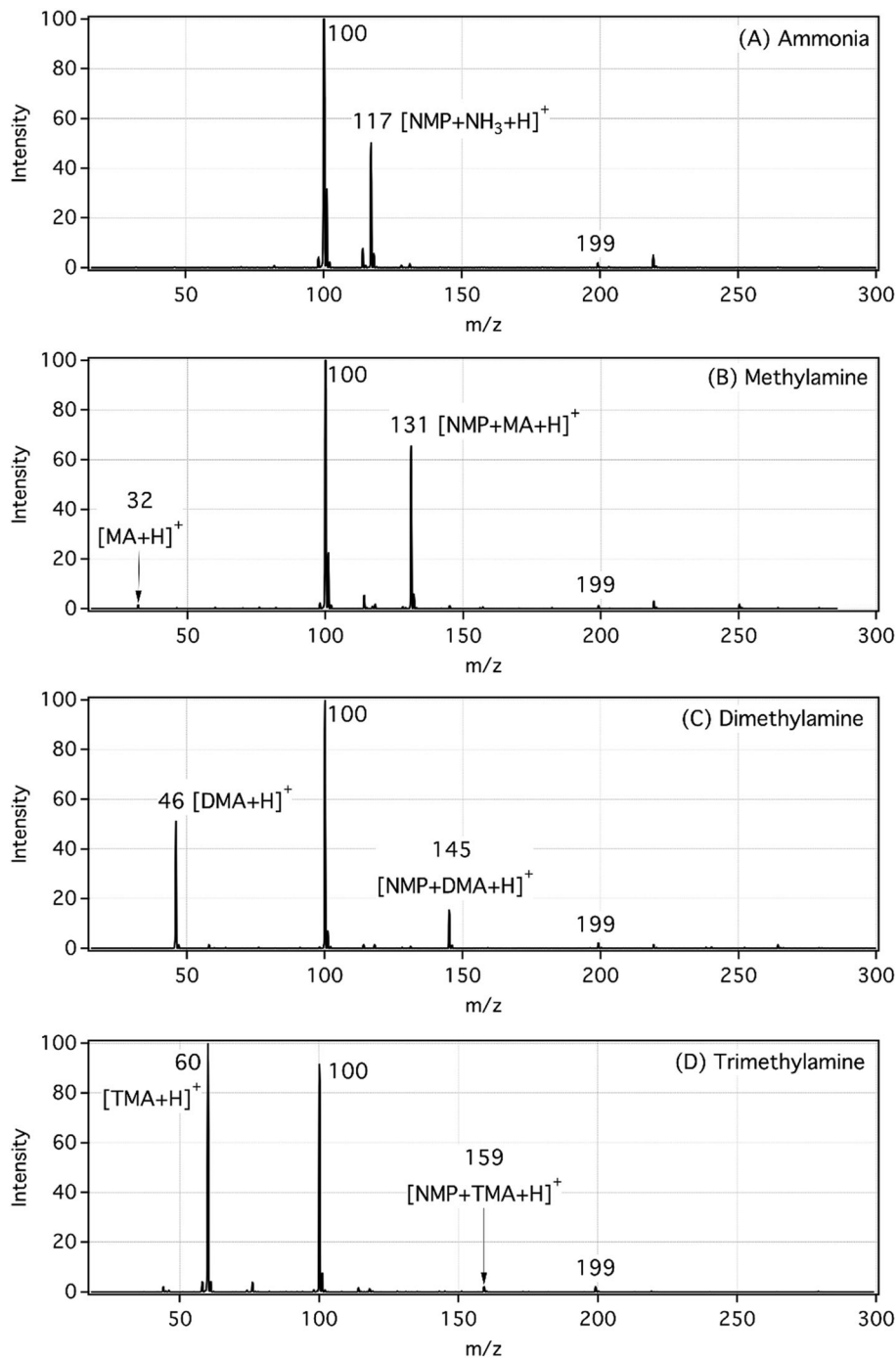


FIGURE 3 APGC/MS spectra from headspace measurements of A, ammonia (NH_3) from the headspace of ammonium hydroxide; B, methylamine (MA); C, dimethylamine (DMA); and D, trimethylamine (TMA) performed with room air that had passed through a PALL HEPA filter. All spectra are normalized to the highest peak intensity. The precursor NH_4^+ ion for NH_3 was not observed

mixtures, calibration curves were established and the limits of detection (LODs) were determined to be 1.6 ppb for NH_3 , 1.7 ppb for MA, 55 ppt for DMA and 89 ppt for TMA. The LODs were determined based on the signal intensity corresponding to 3σ of the baseline noise for clean air, with the peak-to-peak baseline variation taken as 5σ .⁷⁰ While the three amines have insignificant signal

intensities in laboratory air, the NH_3 background level was typically 9 ppb in laboratory air. This is not surprising as NH_3 is a common species associated with the presence of humans.^{71,72} It can also be present as an impurity in nitrogen gas.⁷³ This LOD for NH_3 is smaller than that reported using traditional PTR-MS or SIFT-MS analysis.^{31,74}

3.2 | Effects of the amine chain length on cluster formation with NMP

Similar measurements (Figure 4) were carried out on primary amines with increasing chain length from C₁ (methylamine) to C₄ (butylamine). As the chain length increases, the ratio of the [NMP + amine + H]⁺ cluster ion to the precursor [amine + H]⁺ ion decreases. The ratio is 42 for methylamine (MA), 2.9 for ethylamine (EA), 0.52 for propylamine (PA) and 0.23 for butylamine (BA). This is consistent with the increase

in proton affinities along the series (Table 1).⁶⁶ For EA, two additional minor ions are observed in the APGC/MS spectra at *m/z* 74 and 72, corresponding to [2EA + H - NH₃]⁺ and [2EA + H - 19]⁺, respectively, as described below. For BA, an additional intense ion is observed at *m/z* 128, and is attributed to the [2BA + H - 19]⁺ ion. Formation of a protonated imine ion at [2amine + H - 19]⁺ by nucleophilic substitution at the α-carbon to form an [RCH₂NH₂⁺CH₂R] intermediate and ammonia, followed by decomposition to the protonated imine and H₂,

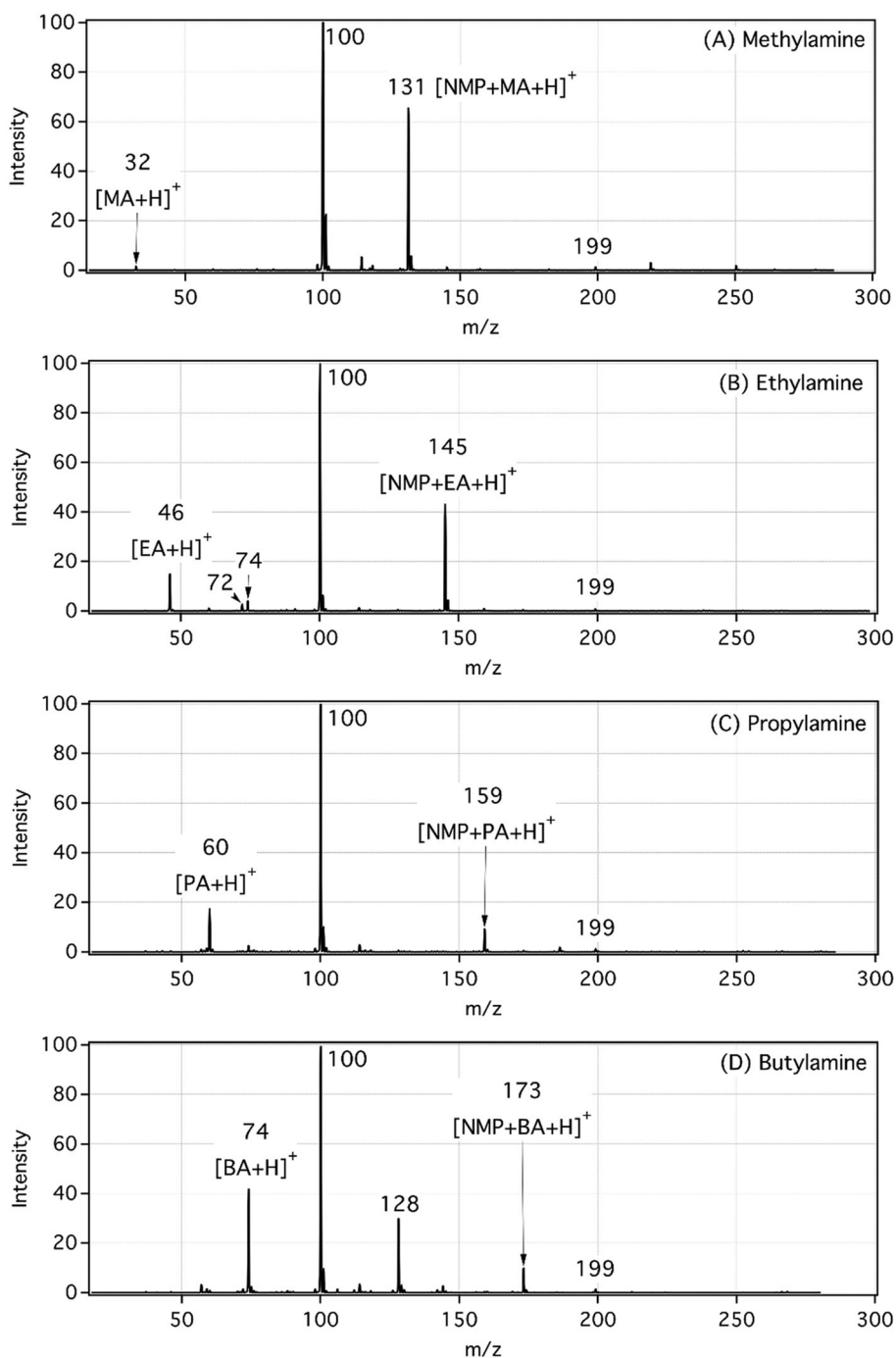
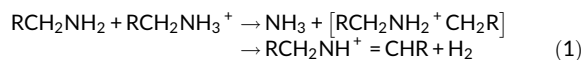


FIGURE 4 APGC/MS spectra from headspace measurements of A, methylamine (MA); B, ethylamine (EA); C, propylamine (PA); and D, butylamine (BA) performed with room air through the PALL HEPA filter. All spectra are normalized to the highest peak intensity

has been reported previously in APCI-MS for butylamine and propylamine (Equation 1)⁷⁵:



The product ion mass spectrum of m/z 128 (Figure S6A, supporting information) from *n*-butylamine is in good agreement with the fragmentation reported by Zhang et al.,⁷⁵ with m/z 86 and 72 as the two major ions. These arise from the loss of alkenes from either side of the aminium site in the ion.⁷⁵ A similar [2amine + H]⁺ ion at m/z 100 is expected for propylamine, but an intense precursor [NMP + H]⁺ ion at that mass-to-charge ratio masks it. As seen in Figure S6C (supporting information), the fragmentation of m/z 100 when PA is present is different than that on the NMP precursor [NMP + H]⁺ (Figure S1, supporting information), confirming the presence of this ion for PA.

Figure S7 (supporting information) shows the product ion mass spectra for each [NMP + amine + H]⁺ cluster ion (m/z 131 for MA, m/z 145 for EA, m/z 159 for PA and m/z 173 for BA). All clusters shown in Figure S7 (supporting information) exhibit the loss of both NMP and the amine, suggesting that the initial [NMP + amine + H]⁺ ion is a mixed cluster of [NMP + (amine + H)]⁺ and [amine + (NMP + H)]⁺. It is interesting to note that, as the chain length increases, the cluster changes from a preference for [(NMP + H) + amine]⁺ which loses the amine, to a preference for [NMP + (amine + H)]⁺ which loses NMP. The observations are again consistent with the increase in proton affinity along the series.

3.3 | Study of other more complex amines

Additional alkylamines were tested with regard to the potential of formation of a cluster with NMP. Figure 5 displays the APGC/MS spectra for isopropylamine (isoPA), sec-butylamine (secBA) and triethylamine (TEA). Both isoPA and secBA spectra (Figures 5A and 5B) show the

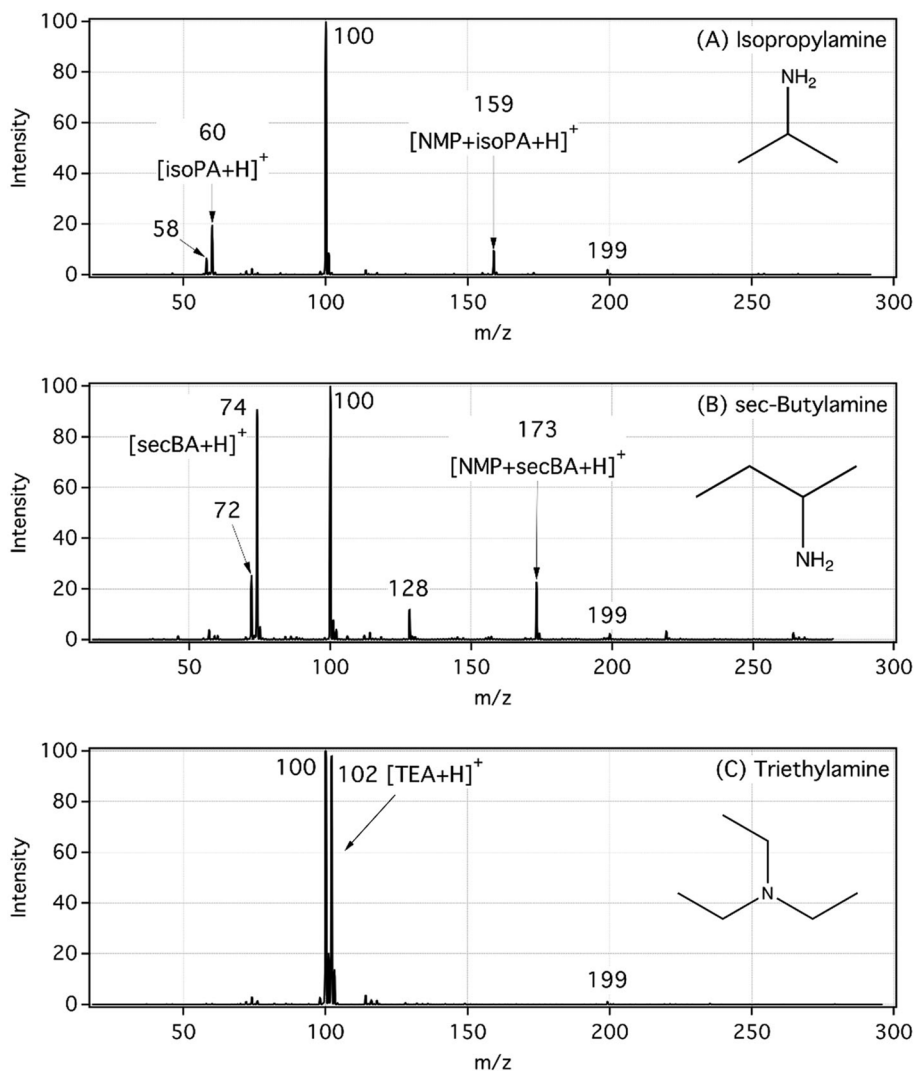


FIGURE 5 APGC/MS spectra from headspace measurements of A, isopropylamine (isoPA); B, sec-butylamine (secBA); and C, triethylamine (TEA) performed with room air through the PALL HEPA filter. All spectra are normalized to the highest peak intensity

presence of a $[\text{NMP} + \text{amine} + \text{H}]^+$ cluster at m/z 159 and 173, respectively, in addition to their $[\text{amine} + \text{H}]^+$ precursor ions at m/z 60 and 74. On the other hand, TEA, having a much higher proton affinity than NMP, does not form an NPM cluster, and only an intense $[\text{TEA} + \text{H}]^+$ precursor ion is observed at m/z 102 (Figure 5C).

A peak at $[2\text{amine} + \text{H} - 19]^+$ is observed for sec-butylamine at m/z 128 (Figure 5B), but the corresponding ion at m/z 100 for isopropylamine (Figure 5A) is masked by the intense $[\text{NMP} + \text{H}]^+$ precursor ion, as was the case for BA and PA, respectively. Product ions of

m/z 100 (Figure S6D, supporting information) show a different fragmentation than that of the $[\text{NMP} + \text{H}]^+$ precursor ion, confirming that $[2\text{isoPA} + \text{H} - 19]^+$ ion is contributing to the m/z 100 peak.

Peaks in the APGC/MS spectra for secBA and isoPA are also observed at m/z 72 and 58, respectively, that are attributed to $[\text{amine} - \text{H}]^+$ ions. The product ion scan of m/z 128 for secBA at a collision energy of 10 eV shows a major fragment at m/z 72 (Figure S6B, supporting information). However, at much lower collision energy (5 eV), this ion disappears from the product ion spectra, suggesting

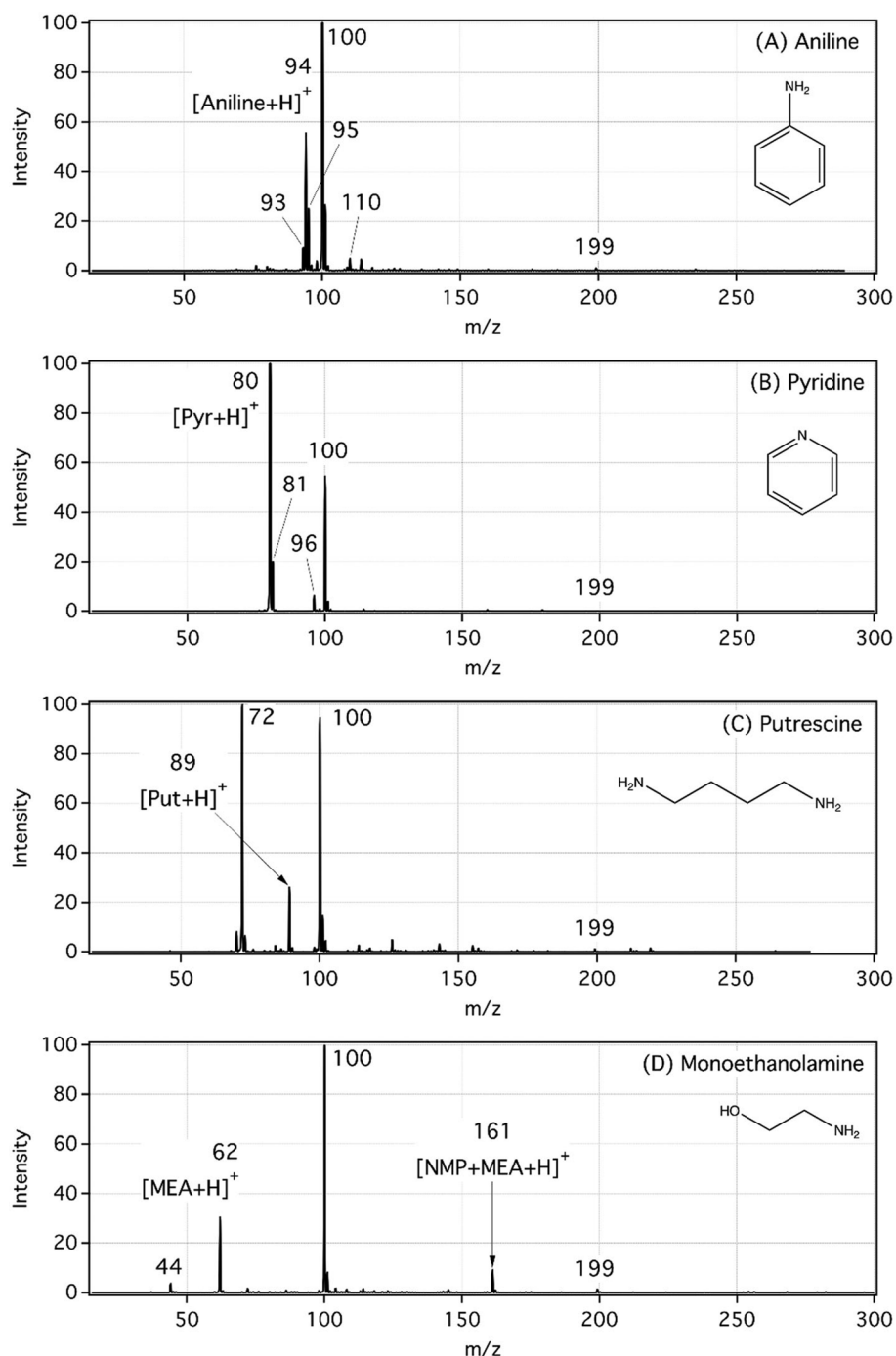


FIGURE 6 APGC/MS spectra from headspace measurements of more complex amines: A, aniline; (B) pyridine (Pyr), (C) putrescine (Put), and (D) monoethanolamine (MEA) performed with room air through the PALL HEPA filter. All spectra are normalized to the highest peak intensity

that its presence in the full scan mass spectra may come from an isolated molecular ion. It is interesting that this [amine - H]⁺ ion is not present in the corresponding linear alkylamine spectra (Figures 4C and 4D), but a small peak is visible for TMA in Figure 3D at *m/z* 58. The formation of an [amine - H]⁺ ion has been previously thought to originate from an hydride ion abstraction by the protonation reagent in the chemical ionization (CI) process. For example, an abundant ion signal corresponding to an [amine - H]⁺ ion was observed for cyclohexylamine⁷⁶ and trimethylamine⁷⁷ using CH₅⁺ as the protonating reagent (methane CI). Using HCO⁺ as the protonating reagent (CO/H₂ CI process), others have shown that *sec*-butylamine (and other C₄H₉NH₂ isomers) can also produce this ion,⁷⁸ consistent with our observations. Lastly, [amine - H]⁺ ions have also been measured in photoionization of amines^{79,80} and in matrix-assisted laser desorption ionization (MALDI).⁸¹ Following similar pathways, we attribute the formation of the [amine - H]⁺ ion in our present study to the hydride abstraction by the [NMP + H]⁺ protonating reagent.

Product ion mass spectra for the [NMP + amine + H]⁺ peaks at *m/z* 159 (isoPA) and 173 (secBA) are shown in Figure S8 (supporting information). The cluster ion for isopropylamine is a mixed cluster with a preference for the [NMP + (isoPA + H)]⁺ form, whereas, for *sec*-BA, the cluster is mainly attributed to the [NMP + (secBA + H)]⁺ ion. This is again consistent with their proton affinities relative to NMP, which are 0.3 kJ mol⁻¹ and 6.2 kJ mol⁻¹ higher than NMP for isoPA and secBA, respectively.

Figure 6 shows the APGC/MS spectra of more complex amines, including two aromatic amines (aniline and pyridine), one diamine (putrescine), and one multifunctional amine (monoethanolamine). Aniline, pyridine and putrescine have intense [amine + H]⁺ precursor ion peaks at *m/z* 94, 80 and 89, respectively, and do not show evidence of clusters with NMP. Both pyridine and putrescine have proton affinities much higher than that of NMP (930.0 kJ mol⁻¹ and 1005.6 kJ mol⁻¹ respectively),⁶⁶ which explains the absence of the cluster; however, the proton affinity of aniline (882.9 kJ mol⁻¹)⁶⁶ is lower than that of NMP. Other properties must play a role, such as a steric effect due to the presence of the aromatic ring. Aniline APGC/MS spectra show additional ions at *m/z* 93, 95 and 110, and pyridine at *m/z* 81 and 96, respectively. Aromatic compounds have been shown to give M⁺, [M + H]⁺ and [M + 2H]⁺ ions under APCI conditions⁸²; thus peaks at *m/z* 93 and 95 are attributed to aniline⁺ and [aniline + 2H]⁺ ions, and that at *m/z* 81 to [pyridine + 2H]⁺. Peaks at *m/z* 110 for aniline and *m/z* 96 for pyridine correspond to a generic [M + OH]⁺ ion; the product ion mass spectra for *m/z* 110 and 96 (Figure S9, supporting information) both exhibit loss of a neutral water molecule, suggesting those compounds are likely alcohols, which are known to lose water.⁸³ Hydroxyl radicals are known to form in APCI sources,⁸⁴ and can react with aniline ($k^{\text{OH}} = 1.1 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K) and pyridine ($k^{\text{OH}} = 4.9 \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 296 K).⁸⁵ Formation of an alcohol is a likely outcome of this in-source reaction, as was observed for benzene reaction with OH radicals.⁸⁶

The product ion mass spectra for *m/z* 89 from putrescine standard at a collision energy of 5 eV (Figure S10, supporting information) shows a very intense fragment ion at *m/z* 72 corresponding to

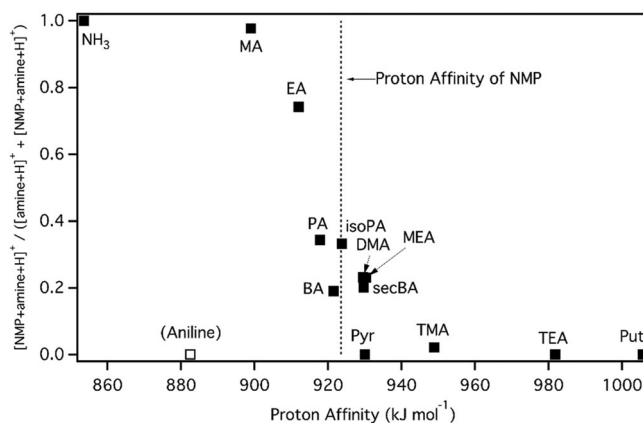


FIGURE 7 Ratio of the [NMP + amine + H]⁺ ion intensity to the sum of the ion intensities {[amine + H]⁺ and [NMP + amine + H]⁺} as a function of the proton affinities of the amines

the [amine + H - NH₃]⁺ ion, consistent with previously reported fragmentation for putrescine.^{87,88} As a consequence, the ion at *m/z* 72 observed in the full scan putrescine APGC/MS spectrum (Figure 6C) is attributed to this fragment.

Interestingly, although monoethanolamine (MEA) has a higher proton affinity than that of NMP by 6.8 kJ mol⁻¹, this amine forms a cluster with NMP at *m/z* 161 in addition to its [amine + H]⁺ precursor ion (Figure 6D). The product ion of *m/z* 161 (Figure S11A, supporting information) shows that it is preferentially in the [NMP + (MEA + H)]⁺ form. An additional ion is observed in the APGC/MS spectra of monoethanolamine at *m/z* 44. The tandem mass (MS/MS) spectrum of the [amine + H]⁺ precursor ion of MEA (Figure S11B, supporting information) shows the loss of water, forming an ion at *m/z* 44 [MEA + H - H₂O]⁺.

In summary, shown in Figure 7, the contribution of the NMP clusters to the mass spectra depends almost entirely on the proton affinities of the amines, with aniline being the one exception.

There are several implications with regard to the use of such filters for air purification. Amines are known to greatly enhance particle formation in air from acids such as sulfuric⁸⁹⁻⁹¹ and methanesulfonic acids.^{6,7} The unexpected addition of a compound such as NMP to an airflow containing such acids could lead to artifacts in the formation of particles. In addition, given that inhalation of NMP has been reported to have negative effects on reproduction and development,⁹²⁻⁹⁵ the application of such filters to air to which humans will be exposed should be approached with caution.

4 | CONCLUSIONS

We report for the first time the use of an APGC source as a stand-alone APCI source, i.e. without the GC interface, for the detection of gas-phase amines. We demonstrate that *N*-methyl-2-pyrrolidone (NMP) degassing from a PALL HEPA filter can be used as an ionization agent for ammonia and amines with smaller proton affinities than NMP. As the proton affinity of an amine decreases, clusters with

NMP are formed. Moving from primary to tertiary amines, the increasing proton affinity competes with that of NMP to form [amine + H]⁺ clusters and the formation of the [NMP + amine + H]⁺ cluster decreases. A similar trend is observed with chain length for primary alkyl amines, where the potential for forming NMP clusters decreases from methylamine (C₁) to butylamine (C₄). More complex amines such as aromatic amines do not cluster with NMP.

This novel ionization method is a simple and cost-effective approach for the selective detection of ammonia and some amines in air. This is particularly true for NH₃, where it is often difficult to detect as mass spectrometry is typically not very sensitive for this molecule. While we used NMP released from a PALL HEPA filter as the ionization agent in these studies, the pure standard can obviously be used directly as the ionization reagent.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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