

We greatly value the careful reading and the detailed comments provided by the referees. The responses to the comments of the referees in our direct reply (shown below) and within the revised manuscript (see marked copy) are provided below. The pages and lines indicated below correspond to those in the marked copy.

5

Response to Referee 1 (Referees' comments are italicized)

General Comments

10 1. Referee comment: *“Since the major advantage of the low activity source is the ability to transport it without HazMat training, it would be helpful for the authors to be more clear on what (if any) limitations exist for transporting the sources. Or more specifically, at what activity can a source be sent without HazMat training?”*

15 **Author response:** We have added more details on the transport regulations for the sources. Namely, the maximum activity per package to be shipped without HazMat training is 9 mCi (369 MBq), but this still requires shipping documentation. The ionizer with the activity level below 5.41 mCi (200 MBq) can be shipped as excepted package that only requires the UN number on the package label. The package still needs to meet the general design requirements of radioactive materials. We have added the maximum
20 activity level for excepted package and referenced the code of federal regulations (CFR) in the revised manuscript.

2. Referee comment: *“Section 3.1 provides a nice discussion of sensitivity, but almost no discussion on backgrounds which drive LOD in many CIMS instruments. It would be helpful to include a discussion of
25 how the backgrounds changed between the standard source and the LAS and how that translates into LOD”*

Author response: As the referee suggested, we have reported the range of background signals and LOD in Section 3.1.

30

Author response:

Response to Referee 2 (Referees' comments are italicized)

General Comments

1. Referee comment: *“In several figures, the low activity source (1.5 mCi when new) was compared with the 'standard' source (20 mCi when new); however, these activities change over time due to the radioactive. In all figures, the age of the sources should be added”*

40

Author response: We have added the age of the sources to the caption of each figures.

2. Referee comment: *"As far as I know, ion sources with activity of <10 mCi only require white (NON-RQ) shipping papers, which a 20 mCi reaches after ~5 months. Would using a half-year old 'standard' source be a viable alternative to the LAS described here"*

Author response: The referee is correct in stating that an ionizer below 9 mCi can be shipped as "NON RQ" packaged of UN2911, which requires documentation and a UN label on the package. For excepted package, the activity level has to be below 5.41 mCi (200 MBq). However, it is very difficult for us to use an "old" standard due to the regulations at our Institute.

Minor Comments

line 9) *consider replacing "complications" with "regulatory burden"*

We have modified the texts as suggested.

line 11) *missing comma following (HCO₂H)*

60

We have added comma following (HCO₂H).

line 18) *consider replacing "some field applications" with "short-term field deployments" or similar.*

65 We have modified the texts as suggested.

line 60) *"49-CFR 173.410; 49CFR 173.425, Table 4" What does this mean? Where is table 4?*

70 The code in the parentheses represents federal regulation about shipping and handling of radioactive materials. Table 4 describes the activity limits for limited quantities and instruments and is included in the code of federal regulation (49CFR 173.425).

line 75-113) *Interference from peroxyacetic acid (and how it was minimized - see Phillips et al. Atmos. Chem. Phys., 13, 1129-1139, 10.5194/acp-13-1129-2013,2013) should be mentioned.*

75

The isotopically labelled PAN calibration standard was added to air drawn through a QF 40 nipple filled with heated stainless-steel wool, which limits potential interference from ambient PAA. In addition, the background measurement used for the ATom was performed by NO addition. We have added Phillips et al. 2013 to discuss possible interference from peroxyacetic acid.

80

line 82-84) *"PAN calibration standard" consider moving these 2 sentences to section 2.3.1 where the other calibration sources are described.*

85 We have modified the texts as suggested.

line 100) *remove comma following et al.*

We have modified the texts as suggested.

90

line 112) *replace "detected" with "quantified"*

We have modified the texts as suggested

95 line 119) *replace "as shown in Figure S2" with "and is shown in Figure S2"*

We have modified the texts as suggested.

100

line 121) *"effect from varying humidity". please state what is affected by RH (sensitivity?)*

We have modified the texts from "effect from varying humidity" to "variations in instrument sensitivity affected by ambient humidity".

105

line 140) *"In general, the sensitivity of the LAS is approximately 2 to 4 times lower than that of the standard source, whereas the activity ratio is roughly 13" Are the values obtained with the LAS consistent with a standard source aged to an activity of 1.5 mCi? This is partially discussed later on but perhaps worth mentioning here.*

110

We have added "Thus, it is likely that the initial activity of the LAS can result in higher sensitivity than the standard source aged to an equivalent activity level (~18 months), where the time dependence of sensitivity for both sources is discussed in section 3.4"

115

line 149) *"may be preferable in some applications." Another example would be in polluted areas, where a LAS may be preferred also as the signals at m/z 59 may get large ($>10^5$)*

As the referee mentioned, the LAS may be a preferable option in polluted areas that have elevated levels of ambient PAN (e.g., fire plumes).

120

line 137-151) *"Performance of LAS". The results shown in Figures 3c and 3d are not talked about at all.*

We have added more discussion on the experiments using a larger scroll pump (Figure 3c and 3d).

125

line 153) *What ions were used to monitor formic acid, chlorine, and nitryl chloride? (should be stated here). The sensitivities reported for chlorine and nitryl chloride are 2 orders of magnitude larger than*

reported by others (e.g., Mielke et al., 2011) who observed similar PAN sensitivity under conditions similar to panel (a).

130 We have added the ion signals monitored for formic acid (m/z 179), Cl₂ (m/z 197) and ClNO₂ (m/z 208). Absolute sensitivity presented in this work is specific to the experimental conditions and instrument parameters including transmission efficiency and declustering strength. For the configuration used for I adduct CIMS, the collision dissociation chamber (CDC) was operated at a relatively lower voltage (-10 V), resulting in electric field < ~22 V cm⁻¹ than that for TD-CIMS experiments (-25 V).

135 line 165) "Figure S4" is called out before "Figure S3"

We have renamed the figures from "Figure S4" to "Figure S3."

140 line 172) "less than the decay rate" Is this due to the generation of radioactive daughters?

We think that at 20 mCi you are not limited by the activity of the source due to space charge effects.

145 line 174) "Figure S2" should be Figure S3

We have renamed the figures from "Figure S2" to "Figure S4"

150 Figure 3b and 3 caption) correct typo in axis caption (ion source fow). Please specify the ions monitored in the caption

We have corrected typo in axis caption and added the ions monitored in Figure 3.

155 Figure 3) The difference between panels 3a and 3c isn't very clear. I suppose 3a was acquired at 2.7 slpm total flow and 3c at 6.5 slpm? Consider adding this information to textboxes to the figures (as was done in Figure 4).

As the referee suggested, we have added textboxes to Figure 3 to eliminate any confusion regarding the different total flows.

160 Figure 4 and 4 caption) consider increasing the contrast between squares and circles as they're challenging to tell apart (e.g., replace solid with open circles).

We have increased the contrast between squares and circles by using lighter colors for circles. The ions monitored has been added in the caption.

165 Figure S1c) ¹³C-PAN - is this m/z 61? Please clarify in the caption. "showing no obvious interference". The signal is plotted on a logarithmic scale, so changes in intensity are difficult to spot to begin with. It

170 *appears that there may some effect (factor of 2 perhaps) but it's difficult to see. Please show these data on a linear scale. To claim "no obvious interference" there would have to be some change in [NO] and [NO2]. Consider adding a scatter plot of the internal standard against [NO].*

175 We have added the ion monitored for ^{13}C -PAN (m/z 61) in the caption. We have illustrated the data on a linear scale, and modified the texts from "showing no obvious interference" to "showing a minimal interference." Figure S4d has been added to exemplify relative sensitivity of PAN as a function of NO concentrations, showing less than 20% reduction in the detected ion signal for PAN by NO mixing ratios below 100 ppbv.

Response to Referee 3 (Referees' comments are italicized)

180 **General Comments**

185 1. Referee comment: *"Since 2U500 can be shipped and received without radiation source licenses, this improvement simplifies logistics in field campaigns. So this is a necessary step towards reducing the activity level of radiation in aircraft and field experiments. However, the authors should also mention that even this low activities (e.g., 0.5 mCi) are not exempted and in many states, they still require a radiation source license (even when used in the lab on the academic campus)"*

190 **Author response:** The 500 μCi static eliminator cartridges are a generally licensed device so don't necessarily require a site license. The degree of regulation varies by institution and state. s. For example, the LAS cartridge are exempted in the state of Georgia, but Georgia Tech requires them to be listed on their license as well. We have added " The 500 μCi static eliminator cartridges are a generally licensed device. However, the degree of regulation is specific to the institutions and states in which they are deployed." to the revised manuscript.

195 line 50) *Please elaborate "For example, we have found that a significant fraction of the 20 mCi ionizers have leaks on the body of the device."*

200 **Author response:** In our experience, we have found that about half of the 20 mCi ionizers have vacuum leaks on the body of the device. They generally leak on the screws under the product label. In addition, we have found that leaks are possible near the ends of the ionizers where the central tube is mated to the pipe threads on the ends.

A low activity ion source for measurement of atmospheric gases by CIMS

Young Ro Lee¹, Yi Ji¹, David J. Tanner¹, L. Gregory Huey¹

¹School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, 30332, USA

5 Correspondence to: L. Gregory Huey (greg.huey@eas.gatech.edu)

Abstract. Most I-CIMS (iodide-chemical ionization mass spectrometers) for measurement of atmospheric trace gases utilize a radioactive ion source with an initial activity of 10 or 20 mCi of ²¹⁰Po. In this work, we characterize a ²¹⁰Po ion source with an initial activity of 1.5 mCi that can be easily constructed from commercially available components. The low level of radioactive activity of this source significantly reduces regulatory burden with storage and shipping relative to higher activity
10 sources. We compare the sensitivity of the low activity source (LAS) to a standard 20 mCi source, as a function of carrier gas flow and flow tube pressure, for peroxyacetyl nitrate (PAN), formic acid (HCO₂H), molecular chlorine (Cl₂), and nitryl chloride (ClNO₂) using an I-CIMS. The LAS provides 2 to 5 times less sensitivity than that of the standard source even though the ratio of activity is approximately 13. However, detection limits of less than 2 pptv for the tested compounds are achieved for integration times of the order of a minute. The sensitivity of the LAS is less dependent on the magnitude of the carrier gas than
15 a standard source. In addition, the LAS provides maximum sensitivity at relatively low carrier gas flows. Finally, we demonstrate that the LAS can be used to measure PAN in the remote atmosphere from an aircraft by showing data obtained on the NASA DC-8 during the Atmospheric Tomography (ATom) mission. In summary, the LAS may be an excellent substitute for a standard ion source in short-term field deployments.

Deleted: complications

Deleted: some field applications

1 Introduction

20 Chemical ionization mass spectrometry (CIMS) is a versatile method for the measurement of atmospheric trace gases (Huey et al., 2007). CIMS has excellent sensitivity and rapid time response ($t < 1$ s) which allows the observation of atmosphere compounds with high temporal resolution which is particularly important for airborne measurements. There are a variety of different CIMS methods used to measure atmospheric species such as: PTR-MS (Proton-Transfer Mass Spectrometry), atmospheric pressure CIMS commonly utilizing NO₃⁻ as a reagent ion, reduced pressure CIMS utilizing I⁻ as well as other
25 reagent ions such as CF₃O⁻, acetate, and SF₆⁻ (Lindinger et al., 1998; de Gouw and Warneke, 2006; Eisele and Tanner, 1993; Huey et al., 1995, 1996; Crounse et al., 2006; Veres et al., 2008; Bertram et al., 2011; Slusher et al., 2001).

The defining characteristic of CIMS is ionization of a compound by a chemical reaction with a reagent ion. Reagent ions are produced by flowing precursor gases through an ion source. Typically, most I-CIMS flow dilute methyl iodide in

nitrogen through a tube containing a ^{210}Po metal foil which emits alpha particles. The alpha particles ionize the nitrogen producing secondary electrons that can be thermalized and dissociatively attached by methyl iodide to form I. PTR-MS instruments typically use a hollow cathode electrical discharge to produce H_3O^+ ions that can be introduced into a drift tube reactor (de Gouw et al., 2003b; Inomata et al., 2006). Other common ion sources include X-ray, Americium (alpha emitter),
35 and corona discharges (Jost et al., 2003; Kürten et al., 2011; Zheng et al., 2015). The choice of an ion source for a specific application is influenced by many factors that include: operating pressure, ion current, background contamination, and regulatory environment. For example, radioactive ion sources are generally not used at operating pressures below 10 torr as the path length of the emitted alpha particles is too large to generate sufficient ion current. In contrast, PTR-MS typically operate at ionization pressures below 1 torr which is more compatible with a discharge source (Yuan et al., 2017).

40 The use of radioactive ion sources for CIMS has several significant advantages. These include stability, ease of use, and reliability. Perhaps the most important feature is the efficiency of ion generation. A 20 mCi ^{210}Po ion source produces 7.4×10^8 disintegrations per second. This dissipates less than 1 mW of power, and can produce more than 10^7 reagent ions per second impacting an ion detector (Nah et al., 2018). Thus, high ion count rates are achieved while limiting the production of radicals that can react and produce molecules that interfere with measurement of atmospheric species.

45 There are significant disadvantages to radioactive ion sources as well. Polonium sources need to be replaced regularly, due to a half-life of 138 days, at some expense. More importantly polonium is highly toxic and most ^{210}Po sources require HAZMAT shipping and a significant degree of institutional oversight. For example, standard radioactive sources used in CIMS are commercial anti-static devices, P-2021 (10 mCi) and P-2031 (20 mCi), manufactured by NRD. Both of these sources require HAZMAT shipping if returned to the manufacturer on the time scale of months. The activity level of these sources
50 may constrain their use in field locations for which permissions to transport or use radioactive source may not be feasible (49CFR 173.425, Table 4). In addition, while these commercially available devices are designed to be used in evacuated systems, they may require additional preparation to ensure a good vacuum seal. For example, we have found that a significant fraction of the 20 mCi ionizers have vacuum leaks (e.g., leaks on the screws under the label are common).

One problem that we have repeatedly encountered at remote field sites or at aircraft facilities is a lack of ability to
55 store the radioactive sources which necessitates shipping the source back to the manufacturer immediately after the field observations are completed. However, most field campaigns are of the order of a month or two in duration which necessitates HAZMAT shipping of the standard sources. The goal of this work is to develop a source with lower activity that we can easily ship back to the manufacturer after field use. In this manuscript, we describe a ^{210}Po ion source with an initial activity of 1.5 mCi using standard anti-static products, commonly employed in mass balances, mounted in commercially available vacuum
60 fittings, which can be easily interchanged with traditional radioactive ion sources. This initial level of activity for the LAS, below the maximum activity limit for excepted package of 200MBq, does not require specific packaging, labelling, and documentations except for the UN identification number (i.e., UN2911) marked on the outside of the package and included in

the packing list (49CFR 173.410; 49CFR 173.425, Table 4). [The 500 \$\mu\$ Ci static eliminator cartridges are a generally licensed device. However, the degree of regulation is specific to the institutions and states in which they are deployed.](#) We compare the sensitivity of this source to a standard 20 mCi source for CIMS measurements of peroxyacetyl nitrate (PAN), molecular chlorine (Cl_2), nitril chloride (ClNO_2), and formic acid (HCO_2H). We also show the performance of the LAS for airborne measurement of PAN from the NASA DC-8 research aircraft during the Atmospheric Tomography (ATom) mission.

2 Method

2.1 Low activity ion source

A drawing and photograph of the LAS are shown in Figure 1. The LAS contains three commercial anti-static ionizing cartridges (2U500, NRD), housed in a standard QF-40 nipple. Each cartridge has an initial activity of 500 μ Ci equivalent to 1.85×10^7 disintegration per second and is equipped with a protective grid to prevent physically touching of the polonium foil (Figure 1b). The cartridges, with a total activity of 1.5 mCi (55.5 MBq), were mounted on a thin (~ 0.1 mm) stainless-steel foil that is 6 cm wide and 10 cm height as shown in the left of Figure 1. The foil with the cartridges were folded to fit in a QF-40 nipple. The QF-40 stainless steel nipple containing ionizing cartridges was connected to a flow tube reactor (QF-40 stainless steel tee). The opposite opening of the nipple was connected to a manifold that enables delivery of a flow of dilute methyl iodide (CH_3I) in nitrogen.

2.2 Laboratory configuration for TD-CIMS PAN measurement technique

Characterization of the LAS is performed using the TD-CIMS technique for PAN measurement (Slusher et al., 2004; Zheng et al., 2011). The CIMS instrument used herein is very similar to that described by Kim et al., (2007) and Chen et al., (2016). As shown in Figure 2, the CIMS consists of the following differently pumped regions: a flow tube, a collisional dissociation chamber (CDC), an octopole ion guide and a quadrupole mass filter with an ion detector. Ambient air is sampled through an inlet constructed from 1.27 cm outer diameter and 0.95 cm inner diameter FEP Teflon tubing at a constant flow rate of approximately 2.7 standard liters per minute (slpm). Background measurements were performed regularly by drawing ambient air through a QF 40 nipple filled with stainless steel wool heated to 150 C, which effectively destroys the thermally generated radicals (Flocke et al., 2005; Zheng et al., 2011). A 29.6 cm section of the Teflon tubing in front of the flow tube orifice is heated to an external temperature of approximately 180°C to thermally dissociate PAN (R1). It should be noted that longer length and higher temperature than typical operation conditions for PAN measurements are used to achieve full thermal dissociation of PAN within the residence time in the heated inlet. Additional details are provided in Figure S1.



~~PAN calibration standard was generated from a photolytic source similar to that described by Warneck and Zerbach (1992). The output of the photolytic source was periodically added to PAN free air, downstream of the heated metal tubing...~~



The thermal dissociation (TD) region is evacuated into the CIMS and a small scroll pump (Varian IDP3; 60 L min⁻¹). The TD region was maintained at a constant pressure of 100 torr by the combination of an upstream metering valve and a commercial pressure controller (MKS 640) mounted downstream of the TD before the small scroll pump. Reduced pressure in the thermal dissociation region minimizes negative interferences (e.g. loss of sensitivity) due to NO, NO₂ and radical-radical reactions. The impact of ambient NO and NO₂ on sensitivity was minimal in these experiments as shown in SI Figure S1b. The flow rate before the pressure controller was held constant at 2.7 slpm so a constant dilution of the calibration standard and thermal dissociation conditions were maintained. The sample mass flow into the low-pressure flow tube is controlled by an automatic variable orifice (AVO). The area of a triangular opening in the AVO varies by a microprocessor controlled stepping motor. The AVO is used in these experiments to maintain a constant total mass flow into the flow tube as the ion source flow is varied. This feature has been utilized in Chen et al. (2016) to maintain a constant flow tube pressure over the vertical range of aircraft sampling. An example of the gas flows at a flow tube pressure of 40 torr is shown in Figure S1c.

The experiments were carried out using two different scroll pumps (Edwards nxDS 6i or Varian Triscroll™ 300) with corresponding pumping speeds of 105 L min⁻¹ and 240 L min⁻¹. This allowed us to evaluate the use of the LAS under conditions typical of both airborne and ground based operation. We commonly use a large scroll pump for ground-based measurements but are often required to use a smaller scroll pump due to power and weight limitations encountered on aircraft. Flow tube pressures higher than 20 torr were achieved by placing a restrictive orifice between the flow tube and the scroll pump. The total flows sampled into the scroll pumps were 2.7 and 6.5 slpm, respectively. Iodide reagent ions (I⁻) are produced by passing dilute methyl iodide in nitrogen through a tube containing ²¹⁰Po (1.5 mCi or 20 mCi). Ion-molecule reactions occur over the length of the flow tube (R2-R3), and the resulting product ions are transmitted into a collisional dissociation chamber (CDC) evacuated by a molecular drag pump (Alcatel MDP 3011). Weakly bound cluster ions are dissociated into core ions in the CDC (e.g., RC(O)O⁻(H₂O)_n dissociates into RC(O)O⁻). The ions are guided by octopole to the quadrupole filter for mass selection and then detected by an electron multiplier. PAN is quantified as acetate anion (59 m/z ¹²CH₃¹²C(O)O⁻ or 61 m/z ¹³CH₃¹³C(O)O⁻) in the TD-CIMS.

2.3 Laboratory configuration for Iodide-Adduct CIMS

In addition to the characterization of the LAS using the TD-CIMS technique, similar experiments are performed to demonstrate the capabilities of the LAS using iodide-adduct formation for the detection of formic acid, Cl₂ and ClNO₂. This tests the LAS for a more generally used chemical ionization method (e.g. Le Breton et al., 2012; Lee et al., 2014; Osthoff et al., 2008; Thornton et al., 2010; Mielke et al., 2011). The configuration of the CIMS system used in this work is very similar to that described in the previous section and is shown in Figure S2. For this experiment, the flow tube was humidified by a constant amount of water vapor by passing a flow of 10 ccm of pure N₂ through a water bubbler kept in an ice bath in order to mitigate variations in instrument sensitivity affected by ambient humidity.

Deleted: detected

Deleted: as shown

Deleted: from varying humidity in ambient air

2.3.1 Calibration sources

The isotopically labelled PAN calibration standard was generated from a photolytic source similar to that described by Warneck and Zerbach (1992). The output of the photolytic source was periodically added to PAN free air, downstream of the heated metal tubing, which limits potential interference from ambient peroxy acetic acid (Phillips et al., 2013).

A permeation tube (KIN-TEK Laboratories, Inc.) was used as a calibration standard for formic acid. The permeation rate of the formic acid permeation tube was quantified by passing the output of the permeation tube in a flow of 50 sccm of N₂ through DI water. The resulting water solution of formic acid was analyzed using ion chromatography (Metrohm 761 Compact ICs). A permeation tube (KIN-TEK Laboratories, Inc.) was used as a calibration standard for Cl₂. To determine the emission rate of the Cl₂ permeation tube, the output was measured using a method described in detail by Kazantseva et al. 2002 and Chen et al. 2016.

The ClNO₂ standard was generated by passing a humidified flow of Cl₂ in N₂ through a bed of sodium nitrite (NaNO₂) via the following reaction:



The resulting ClNO₂ was quantified by passing it through a heated quartz tube (150-230°C). NO₂ was generated via thermal dissociation of ClNO₂ and measured by a CAPS (Cavity Attenuated Phase Sift) NO₂ monitor (Thaler et al., 2011; Kebabian et al., 2008). The sensitivity for ClNO₂ was acquired by measuring the increase in the NO₂ concentration simultaneously with the decrease in ClNO₂ signal in CIMS.

3 Results

3.1 Performance of LAS for the CIMS measurement of PAN

Performance of the LAS is compared to a standard 20 mCi radioactivity source by examining the detection sensitivity and the background signal level. Figure 3a and 3b show the sensitivity of both sources to ¹³C-PAN as a function of ion source flow at total flow of roughly 2.7 slpm and 6.5 slpm respectively. In general, the sensitivity of the LAS is approximately 2 to 4 times lower than that of the standard source, whereas the activity ratio is roughly 13. Thus, it is likely that the initial activity of the LAS can result in higher sensitivity than the standard source aged to an equivalent activity level (~18 months), where the time dependence of sensitivity for both sources is discussed in section 3.4. Both sources at two different total flows give sensitivities of the order of tens of Hz pptv⁻¹. The ion signals during background measurements (i.e. air through the heated stainless steel wool) ranges from tens to thousands hertz for both sources, where the LAS shows generally lower levels by a factor of ~ 2. The detection limits (LOD) for PAN using the LAS were comparable to that of the standard source, resulted in less than 2 pptv for a 2 minute integration (for a 23% duty cycle at m/z 59), where LOD were estimated as 3 times the standard deviation values (3σ) of the background level. Maximum sensitivity was observed at flow tube pressures of 40 torr for both sources and total flows. We could undoubtedly gain more sensitivity at flow tube pressures higher than 40 torr. However, we

165 have found that higher pressures significantly enhance the risks of interference from unwanted secondary chemistry (Chen et al., 2016). For experiments at higher total flow, the sensitivities of both sources were similar to those at lower total flow but less sensitive to changes in ion source flow (Figure 3c and 3d). The tests do show that the LAS is more sensitive to pressure than the standard source. In contrast, the sensitivity of the LAS for PAN is significantly less dependent on the ion source carrier gas flow compared to the standard source (Figure 3a). In particular, the LAS provides near maximum sensitivity at ion source flows a little greater than 1 slpm as illustrated in Fig. 3a. Thus, a low activity source may be preferable in some applications, where reaching maximum sensitivity is not necessary (e.g., high ambient mixing ratios of targeting species), and the availability of carrier gas is limited.

3.2 Performance of LAS for the CIMS measurement of Formic Acid, Cl₂ and ClNO₂

175 Figure 4 presents the sensitivity comparison for the detection of formic acid, Cl₂ and ClNO₂, where ion signals are monitored at m/z 179, m/z 197 and m/z 208, respectively. The trends presented were generally consistent with the PAN measurements. LODs were 1pptv, 1pptv and 0.5pptv, respectively, with an integration time of 1 minute. The sensitivity of the LAS is approximately 3 to 5 times lower than that of the standard source. Maximum sensitivity for both sources was observed at a flow tube pressure of 40 torr for all three species. Similar to the measurements of PAN, the ratio of the LAS sensitivity to that of the standard source is greater at lower flows.

3.3 Application to Studies of the Ambient Atmosphere

180 The performance of the LAS source is illustrated in airborne observations of PAN during the Atmospheric Tomography (ATom) field mission shown in Figure 5. Global-scale sampling of the atmosphere, profiling continuously over a span of altitudes, was conducted by an extensive gas and aerosol payload on board of the NASA DC-8 research aircraft. Figure 5a illustrates the performance of the low radioactivity source for the ATom instrument conditions along with the sensitivity values using a standard source. Figure 5b demonstrates flight data collected within a southern hemisphere biomass burning plume near New Zealand on Oct. 8th, 2017 (ATom-3 science flight #5), where gaseous reactive nitrogen (NO_x) is 185 dominated by PAN. Figure S3 shows the flight path coloured by the mixing ratio of PAN. Inside the plume intersects, the clear variation of PAN signal (CH₃C(O)O[•]; 59 amu) is observed with a good signal to background noise ratio. Outside of the plume, PAN signal decreased simultaneously with the observed NO_x mixing ratios. Clearly, the LAS can provide sensitive, fast time response detection of PAN from an aircraft platform.

3.4 Time dependence of sensitivity

190 As ²¹⁰Po ion sources age and lose activity the reagent signal decreases as well. In our experience, with a 20 mCi source you lose sensitivity at less than the decay rate of the ²¹⁰Po. We typically observe a loss of sensitivity of about a factor of 2 in sensitivity after approximately one year. In order to estimate the time response of the sensitivity of the LAS we compared a fresh LAS to that of one that was decayed by approximately one ²¹⁰Po half-life ($\tau_{1/2}$ ~138 days). The sensitivity of

Deleted: S4

195 the LAS (Figure S4) was found to decay about a factor of two after one half-life. This indicates that the sensitivity of the LAS
will decay faster than that of a standard source.

Deleted: S2

4 Discussion

200 The relative sensitivity of the LAS and the standard 20 mCi source is not in proportion to their activity ratios. The
ratio of LAS sensitivity to activity is clearly higher than for a standard source. A likely explanation for much of this difference
is the geometry of the sources. The LAS contains three cartridges mounted on a stainless-steel foil plate in a QF40 nipple.
This gives an effective inner diameter of the ion source of ~3 cm. The standard source, NRD P-2031, has a more compact
geometry with 1/4" NPT fittings on each end and an effective inner diameter of ~1 cm. The different inner diameters impact
ion source flow characteristics such as residence time and ion loss rates to the wall. For a given flow rate the larger ID LAS is
205 expected to have a lower wall loss than the standard source. In addition, the larger ID of the LAS provides a longer path length
for the emitted alpha particles. In short, the more open geometry of the LAS likely provides for more efficient transport of the
generated ions. This is also in accord with the observation that the LAS signal decays at approximately the same rate as the
activity of the ^{210}Po .

5 Conclusions

210 A low activity ^{210}Po ion source with an initial activity of 1.5 mCi is a viable alternative to the larger activity sources
typically used for I-CIMS. The sensitivity and detection limits of low activity ion source presented in this work are more than
adequate to measure PAN, Cl_2 , ClNO_2 and formic acid in most environments. In applications that require maximum sensitivity,
and the availability of carrier gas for the ion source flow is not limiting, a standard source is probably preferable. In field
experiments that have limited or no radioactive storage the LAS may be a preferable option. The LAS may also be extended
to other CIMS methods and reagent ions and will be a focus of our future ion source development.

215 6 Acknowledgements

This work was supported by NASA grant NNX15AT90G. This publication was also partially supported by an EPA
STAR Grant R835882 awarded to Georgia Institute of Technology. It has not been formally reviewed by the EPA. The views
expressed in this document are solely those of the authors and do not necessarily reflect those of the EPA. EPA does not
endorse any products or commercial services mentioned in this publication and EPA Grant. The NO_y data was provided by
220 Thomas Ryerson, Chelsea Thompson, and Jeff Peischl. We thank the ATom science team and the NASA DC-8 flight crew for
their support.

References

- Bertram, T. H., Kimmel, J. R., Crisp, T. A., Ryder, O. S., Yatavelli, R. L. N., Thornton, J. A., Cubison, M. J., Gonin, M., and
225 Worsnop, D. R.: A field-deployable, chemical ionization time-of-flight mass spectrometer, *Atmos. Meas. Tech.*, **4**, 1471–1479,
<https://doi.org/10.5194/amt-4-1471-2011>, 2011.
- Chen, D., Huey, L. G., Tanner, D. J., Salawitch, R. J., Anderson, D. C., Wales, P. A., Pan, L. L., Atlas, E. L., Hornbrook, R.
S., Apel, E. C., Blake, N. J., Campos, T. L., Donets, V., Flocke, F. M., Hall, S. R., Hanisco, T. F., Hills, A. J., Honomichl, S.
B., Jensen, J. B., Kaser, L., Montzka, D. D., Nicely, J. M., Reeves, J. M., Riemer, D. D., Schaubfler, S. M., Ullmann, K.,
230 Weinheimer, A. J., and Wolfe, G. M.: Airborne measurements of BrO and the sum of HOBr and Br₂ over the Tropical West
Pacific from 1 to 15 km during the CONvective TRansport of Active Species in the Tropics (CONTRAST) experiment, *J.
Geophys. Res.-Atmos.*, **121**, 12560–12578, <https://doi.org/10.1002/2016JD025561>, 2016.
- Crounse, J. D., McKinney, K. A., Kwan, A. J., and Wennberg, P. O.: Measurement of Gas-Phase Hydroperoxides by Chemical
Ionization Mass Spectrometry, *Anal. Chem.*, **78**, 6726–6732, <https://doi.org/10.1021/ac0604234>, 2006.
- 235 de Gouw, J., Warneke, C., Karl, T., Eerdeken, G., van der Veen, C., and Fall, R.: Sensitivity and specificity of atmospheric
trace gas detection by proton-transfer-reaction mass spectrometry, *Int. J. Mass Spectrom.*, **223**, 365–382, 2003.
- de Gouw, J. A. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-
reaction mass spectrometry, *Mass Spectrom. Rev.*, **26**, 223–257, <https://doi.org/10.1002/mas.20119>, 2007.
- Eisele, F. L., and Tanner, D. J.: Measurement of the gas phase concentration of H₂SO₄ and methane sulfonic acid and estimates
240 of H₂SO₄ production and loss in the atmosphere, *J. Geophys. Res.-Atmos.*, **98** (D5), 9001–9010,
<https://doi.org/10.1029/93JD00031>, 1993.
- [Excepted packages for limited quantities of Class 7 \(radioactive\) materials, 49 CFR 172.421, 2010.](#)
- Flocke, F. M., Weinheimer, A. J., Swanson, A. L., Roberts, J. M., Schmitt, R., and Shertz, S.: On the measurement of PANs
245 by gas chromatography and electron capture detection, *J. Atmos. Chem.*, **52**, 19–43, doi:10.1007/s10874-005-6772-0, 2005.
- Huey, L. G., Hanson, D. R., and Howard, C. J.: Reactions of SF₆⁻ and I⁻ with Atmospheric Trace Gases, *J. Phys. Chem.*, **99**,
5001–5008, 1995.
- Huey, L. G., Villalta, P. W., Dunlea, E. J., Hanson, D. R., and Howard, C. J.: Reactions of CF₃O⁻ with Atmospheric Trace
Gases, *J. Phys. Chem.*, **100**, 190–194, 1996.

- 250 Huey, L. G.: Measurement of trace atmospheric species by chemical ionization mass spectrometry: Speciation of reactive nitrogen and future directions, *Mass Spectrom. Rev.*, 26, 166–184, <https://doi.org/10.1002/mas.20118>, 2007.
- Inomata, S., Tanimoto, H., Aoki, N., Hirokawa, J., and Sadanaga, Y.: A novel discharge source of hydronium ions for proton transfer reaction ionization: design, characterization, and performance, *Rapid Commun. Mass Spectrom.*, 20, 1025–1029, <https://doi.org/10.1002/rcm.2405>, 2006.
- 255 Jost, C., Sprung, D., Kenntner, T., and Reiner, T.: Atmospheric pressure chemical ionization mass spectrometry for the detection of tropospheric trace gases: the influence of clustering on sensitivity and precision, *Int. J. Mass Spectrom.*, 223, 771–782, [https://doi.org/10.1016/S1387-3806\(02\)00963-6](https://doi.org/10.1016/S1387-3806(02)00963-6), 2003.
- Kazantseva, N. N., Ernepesova, A., Khodjamamedov, A., Geldyev, O. A., and Krungal, B. S.: Spectrophotometric analysis of iodide oxidation by chlorine in highly mineralized solutions, *Anal. Chim. Acta.*, 456 (1), 105–119, 2002.
- 260 Kebabian, P. L., Wood, E. C., Herndon, S. C., and Freedman, A.: A Practical Alternative to Chemiluminescence-Based Detection of Nitrogen Dioxide: Cavity Attenuated Phase Shift Spectroscopy, *Environ. Sci. Technol.*, 42 (16), 6040–6045, <https://doi.org/10.1021/ac048715y>, 2008.
- Kim, S., Huey, L. G., Stickel, R. E., Tanner, D. J., Crawford, J. H., Olson, J. R., Chen, G., Brune, W. H., Ren, X., Leshner, R., Wooldridge, P. J., Bertram, T. H., Perring, A., Cohen, R. C., Lefer, B. L., Shetter, R. E., Avery, M., Diskin, G., and Sokolik, I.: Measurement of HO₂NO₂ in the free troposphere during the intercontinental chemical transport experiment – North America 2004, *J. Geophys. Res.-Atmos.*, 112, D12S01, <https://doi.org/10.1029/2006jd007676>, 2007.
- Kürten, A., Rondo, L., Ehrhart, S., and Curtius, J.: Performance of a corona ion source for measurement of sulfuric acid by chemical ionization mass spectrometry, *Atmos. Meas. Tech.*, 4, 437–443, <https://doi.org/10.5194/amt-4-437-2011>, 2011.
- Le Breton, M., McGillen, M. R., Muller, J. B. A., Bacak, A., Shallcross, D. E., Xiao, P., Huey, L. G., Tanner, D., Coe, H., and 270 Percival, C. J.: Airborne observations of formic acid using a chemical ionization mass spectrometer, *Atmos. Meas. Tech.*, 5, 3029–3039, <https://doi.org/10.5194/amt-5-3029-2012>, 2012.
- Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurten, T., Worsnop, D. R., and Thornton, J. A.: An Iodide-Adduct High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer: Application to Atmospheric Inorganic and Organic Compounds, *Environ. Sci. Technol.*, 48, 6309–6317, <https://doi.org/10.1021/es500362a>, 2014.

275 Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer reaction mass spectrometry (PTR-MS) - Medical applications, food control and environmental research, *Int. J. Mass Spectrom. Ion Processes*, 173, 191–241, [https://doi.org/10.1016/S0168-1176\(97\)00281-4](https://doi.org/10.1016/S0168-1176(97)00281-4), 1998.

Mielke, L. H., Furgeson, A., and Osthoff, H. D.: Observation of ClNO₂ in a mid-continental urban environment, *Environ. Sci. Technol.*, 45, 8889–8896, <https://doi.org/10.1021/es201955u>, 2011.

280 Nah, T., Ji, Y., Tanner, D. J., Guo, H., Sullivan, A. P., Ng, N. L., Weber, R. J., and Huey, L. G.: Real-time measurements of gas-phase organic acids using SF₆⁻ chemical ionization mass spectrometry, *Atmos. Meas. Tech.*, 11, 5087–5104, <https://doi.org/10.5194/amt-11-5087-2018>, 2018.

Osthoff, H. D., Roberts, J. M., Ravishankara, A. R., Williams, E. J., Lerner, B. M., Sommariva, R., Bates, T. S., Coffman, D., Quinn, P. K., Dibb, J. E., Stark, H., Burkholder, J. B., Talukdar, R. K., Meagher, J., Fehsenfeld, F. C., and Brown, S. S.: High

285 levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nat. Geosci.*, 1, 324–328, 2008.

Slusher, D. L., Pitteri, S. J., Haman, B. J., Tanner, D. J., and Huey, L. G.: A chemical ionization technique for measurement of pernitric acid in the upper troposphere and the polar boundary layer, *Geophys. Res. Lett.*, 28, 3875–3878, <https://doi.org/10.1029/2001gl013443>, 2001.

290 Slusher, D. L., Huey, L. G., Tanner, D. J., Flocke, F. M., and Roberts, J. M.: A thermal dissociation-chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide, *J. Geophys. Res.-Atmos.*, 109, D19315, <https://doi.org/10.1029/2004JD004670>, 2004.

[Table of activity limits - excepted quantities and articles, 49 CFR 172.425, 2011.](#)

Thaler, R. D., Mielke, L. H., and Osthoff, H. D.: Quantification of nitryl chloride at part per trillion mixing ratios by thermal dissociation cavity ring-down spectroscopy, *Anal. Chem.*, 83 (7), 2761–2766, <https://doi.org/10.1021/ac200055z>, 2011.

295 Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dube, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., and Brown, S. S.: A large atomic chlorine source inferred from midcontinental reactive nitrogen chemistry, *Nature*, 464, 271–274, <https://doi.org/10.1038/nature08905>, 2010.

300 Veres, P., Roberts, J. M., Warneke, C., Welsh-Bon, D., Zahniser, M., Herndon, S., Fall, R., and de Gouw, J.: Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere, *Int. J. Mass Spectrom.*, 274, 48–55, <https://doi.org/10.1016/j.ijms.2008.04.032>, 2008.

Warneck, P. and Zerbach, T.: Synthesis of peroxyacetyl nitrate in air by acetone photolysis, *Environ. Sci. Technol.*, 26, 74–79, 1992.

305 [Phillips, G. J., Pouvesle, N., Thieser, J., Schuster, G., Axinte, R., Fischer, H., Williams, J., Lelieveld, J., and Crowley, J. N.: Peroxyacetyl nitrate \(PAN\) and peroxyacetic acid \(PAA\) measurements by iodide chemical ionisation mass spectrometry: first analysis of results in the boreal forest and implications for the measurement of PAN fluxes, *Atmos. Chem. Phys.*, 13, 1129–1139, doi:10.5194/acp-13-1129-2013, 2013.](#)

310 Yuan, B., Koss, A. R., Warneke, C., Coggon, M., Sekimoto, K., and de Gouw, J. A.: Proton-Transfer-Reaction Mass Spectrometry, Applications in Atmospheric Sciences, *Chem. Rev.*, 117, 13187– 13229, doi:10.1021/acs.chemrev.7b00325, 2017.

Zheng, W., Flocke, F. M., Tyndall, G. S., Swanson, A. L., Orlando, J. J., Roberts, J. M., Huey, L. G., and Tanner, D. J.: Characterization of a thermal decomposition chemical ionization mass spectrometer for the measurement of peroxy acyl nitrates (PANs) in the atmosphere, *Atmos. Chem. Phys.*, 11, 6529–6547, <https://doi.org/10.5194/acp-11-6529-2011>, 2011.

315 Zheng, J., Yang, D. S., Ma, Y., Chen, M. D., Cheng, J., Li, S. Z., and Wang, M.: Development of a new corona discharge based ion source for high resolution time-of-flight chemical ionization mass spectrometer to measure gaseous H₂SO₄ and aerosol sulfate, *Atmos. Environ.*, 119, 167–173, <https://doi.org/10.1016/j.atmosenv.2015.08.028>, 2015.

320

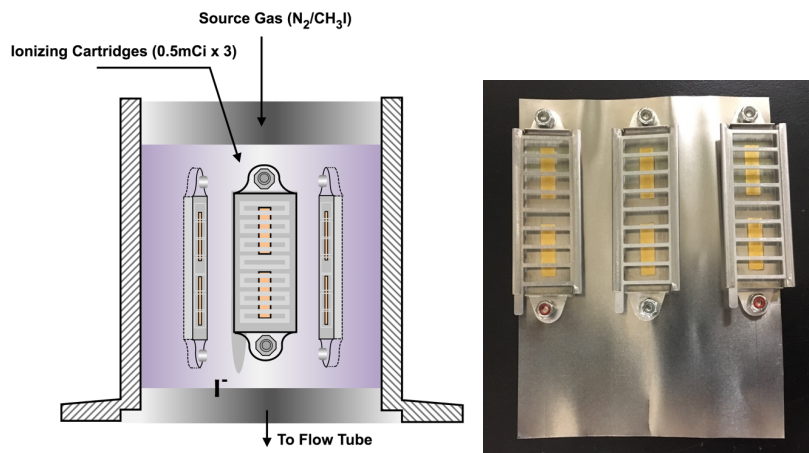


Figure 1. (a) Schematic of the LAS with three anti-static ionizing cartridges are placed in a standard QF-40 nipple. (b) Photograph of the ^{210}Po cartridges mounted on a stainless steel foil.

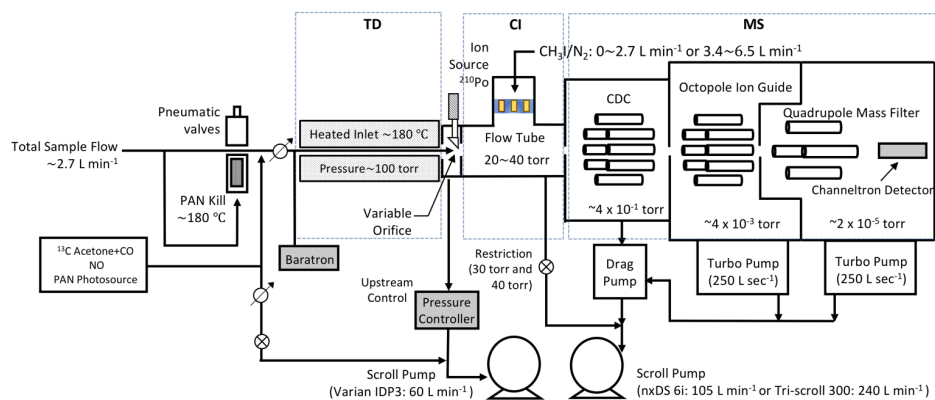
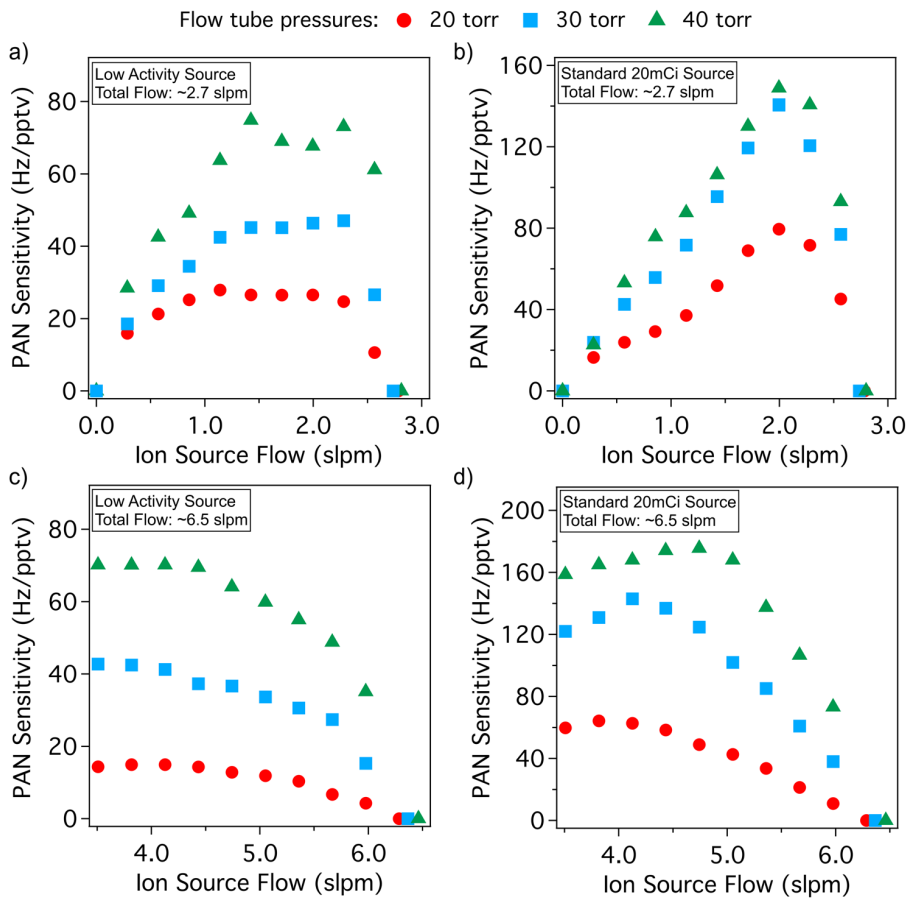
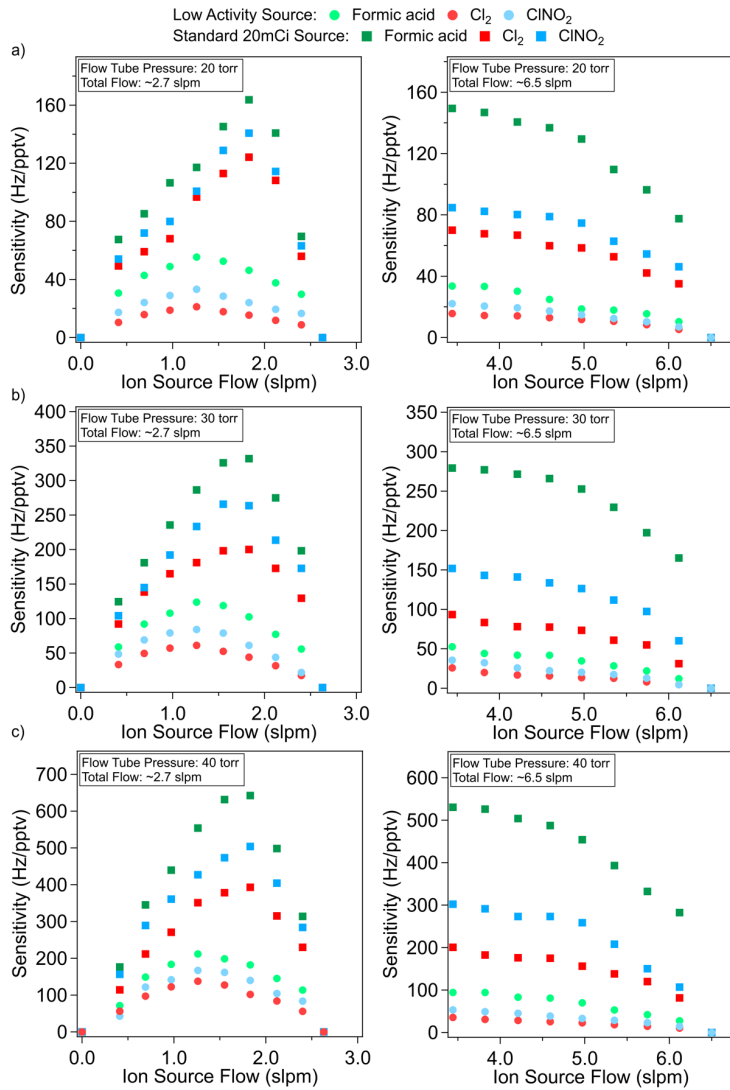


Figure 2. Schematic diagram of the TD-CIMS. The air is sampled through the TD (thermal dissociation) region and enters the flow tube through the AVO (automatic variable orifice).

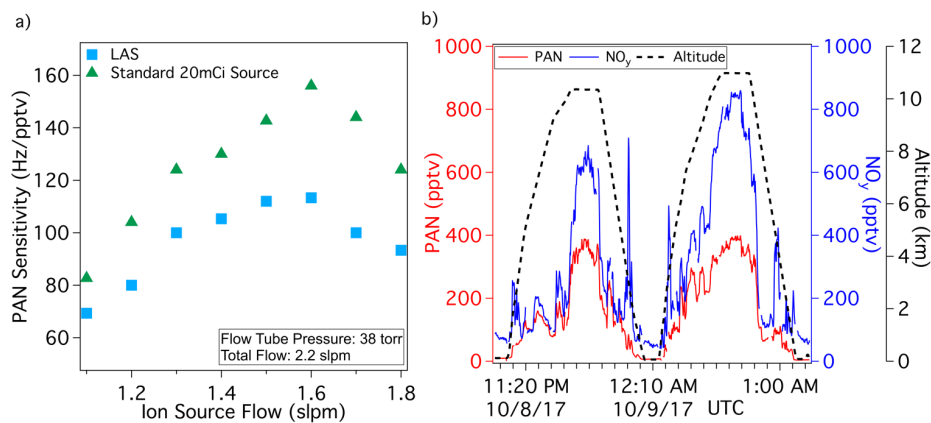


330 **Figure 3.** The sensitivity (Hz pptv^{-1}) of the LAS and a standard source for PAN (m/z 61) at different flow tube pressures and total flows, plotted as a function of ion source flow. The age of the LAS and the standard source used here is approximately two and four months old, respectively. (a) PAN sensitivity using the LAS, and (b) the standard source at total flow of ~2.7 slpm. (c) PAN sensitivity using the LAS, and (d) the standard source at total flow of ~6.5 slpm. Red circles, cyan squares and green triangles correspond to flow tube pressures of 20, 30, and 40 torr, respectively.



340

Figure 4. Comparison of the sensitivity (Hz pptv^{-1}) of the LAS and a standard source for formic acid (m/z 179, green), Cl_2 (m/z 197, red) and ClNO_2 (m/z 208, cyan) plotted as a function of ion source flow (slpm). The age of the LAS and the standard source used here is approximately two and four months old, respectively. Panels a-c show the sensitivity at flow tube pressures of 20, 30 and 40 torr at a total flow of 2.7 slpm (left) and 6.5 slpm (right).



345

Figure 5. The performance of the LAS for PAN measurement during the ATom field mission. Both sources are less than one month old. (a) The sensitivity comparison of the LAS and a standard source for the ATom instrument conditions. (b) DC-8 flight data obtained during intersects of a southern hemisphere plume. PAN (red trace) and NO_y (blue trace) are plotted along with the pressure altitudes (black trace).

350

Supplement Information for:

**A low activity ion source for measurement of atmospheric gases by
CIMS**

Young Ro Lee¹, Yi Ji¹, David J. Tanner¹, L. Gregory Huey¹

5 ¹School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, 30332, USA

Correspondence to: L. Gregory Huey (greg.huey@eas.gatech.edu)

10

This document contains four figures, totaling 4 pages.

15

20

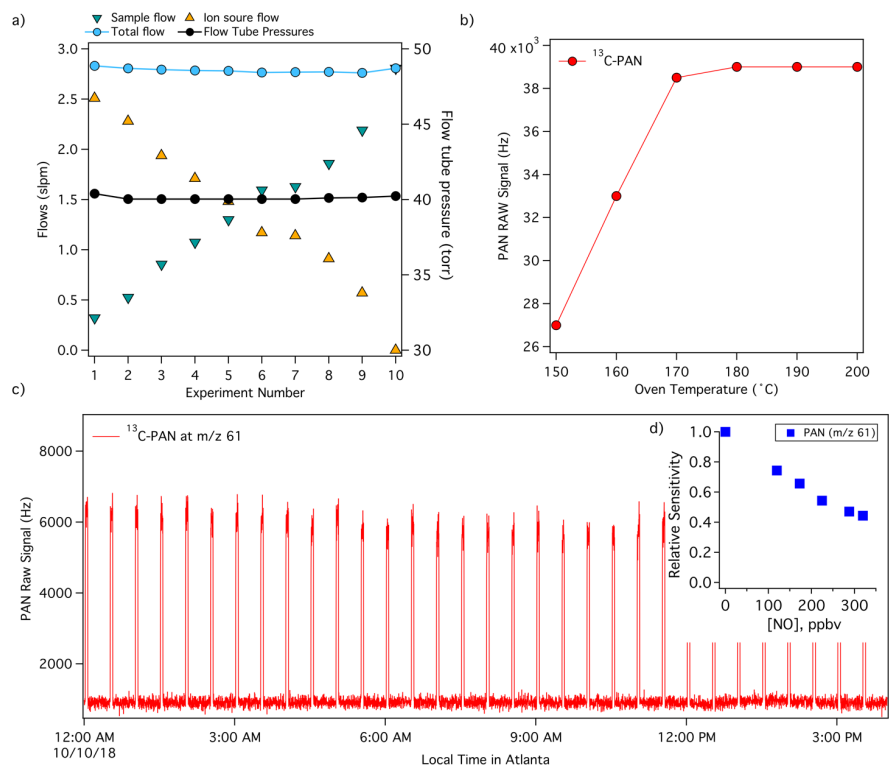


Figure S1. (a) An example of flows controlled by the AVO (automatic variable orifice) at 40 torr flow tube pressure. (b) PAN calibration signal as a function of temperature. The rate coefficient for the thermal decomposition of PAN (at 453 K and 100 torr) is $\approx 790 \text{ s}^{-1}$ (Atkinson et al., 2006; IUPAC, 2018), so that PAN calibration standard should be fully thermally dissociated within the residence time of $\sim 40 \text{ ms}$. This is confirmed by measurement of the calibration signal as the inlet temperature varies. (c) Time series of PAN calibration signal while sampling ambient air in Atlanta, showing a minimal interference by ambient species such as NO and NO_2 . (d) Example of relative sensitivity of PAN as a function of NO concentration.

25

30

Figure S3. Flight map of the ATom-3 science flight #5 from Fiji to New Zealand. Orange box highlights the location of the southern hemisphere plume presented in Figure 5b.

40

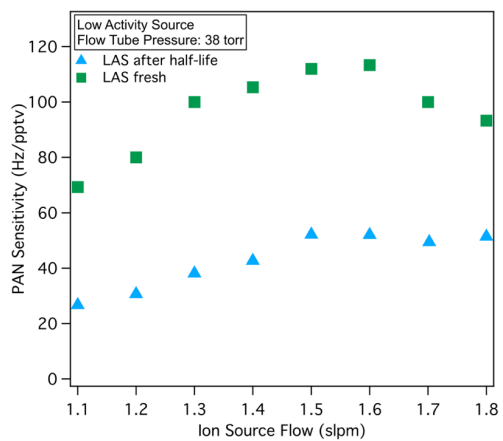


Figure S4. Time dependence of the sensitivity of the LAS. The sensitivity of a fresh (green square) and one half-life aged (cyan triangle) LAS for PAN.

45