



# On quantitative measurements of peroxy-carboxylic nitric anhydride mixing ratios by thermal dissociation chemical ionization mass spectrometry

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## ABSTRACT

Thermal dissociation chemical ionization mass spectrometry (TD-CIMS) has become an increasingly popular tool for rapid and sensitive quantification of peroxy-carboxylic nitric anhydrides (PANs), which are important trace gas constituents of the troposphere. In TD-CIMS, the PANs are thermally dissociated in a heated inlet to NO<sub>2</sub> and peroxyacyl radicals, which are converted in electron transfer reactions with iodide reagent ions to the corresponding carboxylate anions. Here, we evaluate the performance of the TD-CIMS method in the presence of interferences that occur in polluted air masses. Response factors of the TD-CIMS were determined using laboratory-generated air samples and parallel measurements of NO<sub>2</sub> and ΣPAN by blue diode laser thermal dissociation cavity ring-down spectroscopy (TD-CRDS) and of NO<sub>y</sub> by NO-O<sub>3</sub> chemiluminescence (CL). The TD-CIMS was less sensitive to peroxy-methacryloyl nitric anhydride (MPAN) than to other PANs tested, which was rationalized by differences in the temperature dependent loss rates of the peroxyacyl radicals in the heated inlet. To track matrix effects, photochemically generated <sup>13</sup>C-labeled PAN was continuously added as an internal standard. The presence of NO or NO<sub>2</sub> in the sample gas mixture resulted in signal suppression, which could be corrected using the internal standard. The presence of organic acids resulted in a redistribution of count intensity between carboxylate anions, impacting the instrument's ability to accurately quantify PANs other than peroxyacetic nitric anhydride under moderately polluted conditions.

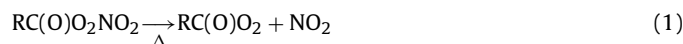
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## 1. Introduction

Peroxy-carboxylic nitric anhydrides (PANs, general structure RC(O)O<sub>2</sub>NO<sub>2</sub>, where R is typically an alkyl group) have long been recognized as important trace gas constituents of the troposphere (e.g., [1–4]). Commonly referred to by their non-IUPAC name peroxyacyl nitrates, the PANs are known as lachrymators and are phytotoxic to plants at high concentration [5]. The PANs are formed in the same photochemistry between NO<sub>x</sub> (≡NO + NO<sub>2</sub>) and volatile organic compounds (VOCs) that produces ozone (O<sub>3</sub>); thus, the relative PAN abundances contain information on the VOCs involved in the ozone-formation. For example, peroxypropanoic nitric anhydride (PPN, C<sub>2</sub>H<sub>5</sub>C(O)O<sub>2</sub>NO<sub>2</sub>) is a tracer of anthropogenic VOCs that react to form propanal, whereas peroxy-methacryloyl nitric anhydride (MPAN, H<sub>2</sub>C=C(CH<sub>3</sub>)C(O)O<sub>2</sub>NO<sub>2</sub>), produced by abstraction of the aldehydic hydrogen in methacrolein [6], is a tracer of isoprene oxidation chemistry [7,8]. PANs are susceptible to thermal dissociation, but are quite stable in the mid and upper

troposphere as the rates of thermal dissociation, photolysis and OH-initiated degradation reactions are slow [9]. As a consequence, PANs can act as NO<sub>x</sub> reservoir species and be transported over long distances, slowly releasing NO<sub>x</sub> in the form of NO<sub>2</sub> and affecting ozone production in many regions of the troposphere [10–15]. Of the more than 43 different PANs that have been detected in ambient air so far, peroxyacetic nitric anhydride (usually called peroxyacetyl nitrate or PAN, CH<sub>3</sub>C(O)O<sub>2</sub>NO<sub>2</sub>) is the most abundant PAN species and often also the most abundant odd nitrogen, or NO<sub>y</sub> (≡NO<sub>x</sub> + ΣPANs + ΣRONO<sub>2</sub> + HNO<sub>3</sub> + NO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub> + HONO + ClNO<sub>2</sub> + ...), species, in particular in the mid to upper troposphere [16].

The most commonly used technique to quantify PANs in ambient air has been gas chromatography with electron capture detection (GC-ECD). In state-of-the-art GC-ECD instruments, run times of less than one minute and limits of detection of a few parts-per trillion by volume (pptv, 10<sup>–12</sup>, v/v) have been achieved [17]. However, ECD detectors are prone to interference from halogenated species and oxygen and exhibit different response factors for different PANs. Alternatively, PANs have been detected post-column by thermal dissociation (TD) to, and quantification of, NO<sub>2</sub> by luminol chemiluminescence (CL) [18] or luminol CL coupled to peroxy radical chemical amplification [19]:



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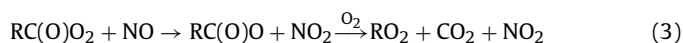
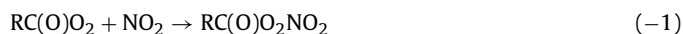
In a variant of the TD technique, the time-consuming separation step is bypassed, and the PANs are quantified as  $\Sigma$ PAN by selective TD and detection (of the generated  $\text{NO}_2$ ) using laser-induced fluorescence (TD-LIF) [20,21] or cavity ring-down spectroscopy (TD-CRDS) [22,23].

In recent years, mass spectrometric techniques to quantify mixing ratio of PANs in ambient air have become popular, offering the advantages of fast measurement speeds, high sensitivity, and high selectivity. For example, mixing ratios of PAN, PPN and MPAN have been quantified by proton transfer reaction mass spectrometry (PTR-MS) utilizing  $\text{H}_3\text{O}^+$  reagent ion with limits of detection of <70 pptv (15 s) [24]. However, detection of PAN using its protonated organic peroxy product ion at  $m/z$  77 ( $\text{CH}_3\text{C}(\text{O})\text{OOHH}^+$ ) suffers from interference by acetone–water clusters and protonated peracetic acid [25]. More recently, selected ion flow tube mass spectrometry (SIFT-MS) using  $\text{H}_3\text{O}^+$  reagent ion has been used to quantify PAN at  $m/z$  122 ( $\text{CH}_3\text{C}(\text{O})\text{OONO}_2\text{H}^+$ ) with limits of detection of 20 pptv (10 s) [26].

An alternative mass spectrometric method that has been gaining in popularity is iodide ion thermal dissociation chemical ionization mass spectrometry (TD-CIMS) [27–33]. In iodide ion TD-CIMS, the PANs are dissociated in a heated inlet via reaction (1), and the generated peroxyacyl (PA) radicals react with  $\text{I}^-$  to form the corresponding carboxylate anions:

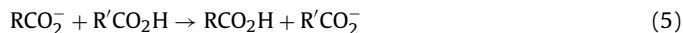


The carboxylate anions are usually mass-selected using a quadrupole mass filter, but an ion trap has also been recently used [32]. The detection limits (<10 pptv) and response times (<1 s) of iodide ion TD-CIMS instruments are superb – even allowing for measurements of PAN deposition rates by eddy covariance [30,33]. However, the TD-CIMS response factors vary between PAN species [31,34]. Further, interference from  $\text{NO}_2$ ,  $\text{NO}$  and other peroxy radicals which remove peroxy radicals generated in the heated inlet must be considered.



Usually, an isotopically labeled PAN ( $^{13}\text{CH}_3^{13}\text{C}(\text{O})\text{O}_2\text{NO}_2$ , hereafter referred to as  $^{13}\text{C}$ -PAN) is added to the TD-CIMS inlet as an internal standard [17,31].

An added complication is that carboxylate anions proton-exchange with acids, for example carboxylic acids:

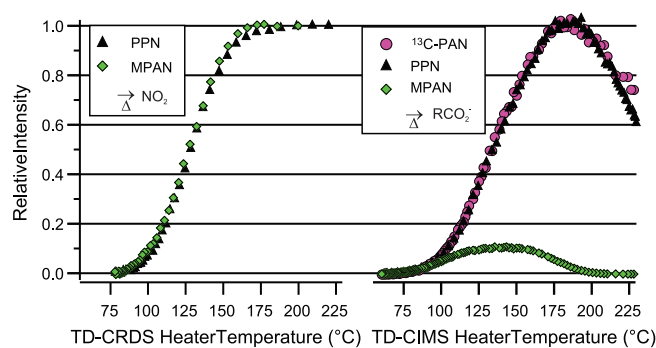


Reaction (5) has recently been utilized to monitor organic and inorganic acids with acetate reagent ion [35,36]. Furthermore, iodide ion TD-CIMS suffers from interference from peroxy-carboxylic acids [34]:



The peroxy-carboxylic acids are usually less abundant than PANs in ambient air [37] but can nevertheless be a significant interference, for example in photochemical PAN sources [34].

Our research group has recently acquired a commercial TD-CIMS and has described its design and application (with iodide reagent ion) to measurement of nitryl chloride ( $\text{ClNO}_2$ ) [38]. In this paper, we focus on the application of iodide ion TD-CIMS to measurements of PAN abundances in ambient air. We investigated why TD-CIMS is considerably less sensitive to MPAN compared to PAN and PPN [27]. Matrix effects and the response to interferences (including  $\text{NO}$ ,  $\text{NO}_2$ , and organic acids) were characterized using laboratory-generated



**Fig. 1.** Thermal dissociation profiles for PPN and MPAN using TD-CRDS (left-hand side) and for  $^{13}\text{C}$ -PAN, PPN, and MPAN using the TD-CIMS (right-hand side). The yield of  $\text{NO}_2$  exhibits the same temperature dependence for PPN and MPAN, whereas the yield of methacrylate is considerably different from that of  $^{13}\text{C}$  acetate or propionate.

air samples containing PAN, PPN, or MPAN and parallel measurements of  $\text{NO}_2$  and  $\Sigma$ PAN by blue diode laser TD-CRDS and of  $\text{NO}_y$  by  $\text{NO}-\text{O}_3$  CL. To track matrix effects, the TD-CIMS was equipped with a photochemical source of  $^{13}\text{C}$ -PAN as internal standard. Advantages and limitations of applying iodide ion TD-CIMS to measure PAN abundances and challenges associated with measurements of less abundant PANs in ambient air are discussed.

## 2. Experimental

### 2.1. Chemical ionization mass spectrometry of peroxy-carboxylic nitric anhydrides

The CIMS was purchased from THS Instruments (Atlanta, GA) and is a compact version of the one described by Slusher et al. [27]. A schematic of the instrument is shown in Fig. 1 of Mielke et al. [38]. Briefly, the CIMS is comprised of three differentially pumped regions that house an ion-molecule reaction chamber (IMR) operated at 21 Torr, a collisional dissociation chamber (CDC) to break up water clusters which is evacuated by a molecular drag pump (Alcatel MDP 3011) to a pressure of 0.5 Torr, an octopole ion guide ( $\sim 10^{-3}$  Torr), and a 3/4 in. quadrupole mass analyzer ( $<10^{-5}$  Torr) with channeltron detector (Ceramax 7550M). The ion guide and mass analyzer regions are evacuated by a pair of 250 L/s turbo pumps (Varian, model Turbo-V 81-M). Sample gas entered the CIMS via a pinhole and was diluted with a flow of 400 standard cubic centimeters per minute (sccm) of humidified nitrogen to ensure that formation of carboxylate anions via reaction (2) was independent of the humidity of the sample air [38]. Iodide reagent ions were generated by passing 1 sccm of 150 parts-per-billion by volume (ppbv)  $\text{CH}_3\text{I}$  in  $\text{N}_2$  diluted with a flow of 1.2 standard-liters per minute (slpm) of  $\text{N}_2$  gas past a  $^{210}\text{Po}$  radioactive ion source (NRD P-2031, 20 mCi activity) and were added to the IMR via a side arm. The mass analyzer is controlled using a modified RF unit (Extrel U72) and was operated in selective ion mode. A typical list of masses monitored and dwell times are given in Table S1 of [38]. Mass counts were normalized to  $10^6$  counts of  $\text{I}^-$  before presentation.

For the experiments in this manuscript, the CIMS sampled from an inlet constructed from 1/2 in. outer diameter (o.d.) and 3/8 in. inner diameter (i.d.) FEP Teflon tubing. Approximately 50 sccm of  $^{13}\text{C}$ -PAN internal standard (approximate mixing ratio 7.5 ppbv) were added to the sampled air via a PFA Teflon Tee. The  $^{13}\text{C}$ -PAN was generated photochemically using the source described in [34] and was monitored at  $m/z$  61. A 11.5 cm section of the inlet was heated to (typically) 180–190 °C to dissociate the PANs to PA radicals and  $\text{NO}_2$  as per reaction (1). This heated section of the TD inlet could be bypassed with a 3-way valve, if desired, and was followed by a 14 cm long section of unheated Teflon tubing. One end of this

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