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Laboratory evaluation of a novel thermal dissociation chemiluminescence method for in situ detection of nitrous acid

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Abstract

We describe a new laboratory-based method for in situ detection of nitrous acid (HONO) using a combination of thermal dissociation (TD) and chemiluminescent (CL) detection of nitric oxide. A prototype was built using a commercial NO sensor. Laboratory tests for possible chemical interferences show that measurements are affected in predictable ways by NO_2, peroxy nitrates, alkyl nitrates, HNO_3, O_3 and H_2O.

Keywords: Nitrous acid; Instrument; Nitrogen oxides; HONO

1. Introduction

Nitrous acid, HONO, has been recognized as an important contributor to atmospheric HO_x production (Alicke et al., 2002, 2003; Aumont et al., 2003; Ren et al., 2003; Kleffmann et al., 2005) and may represent as much as 13% of the atmospheric reactive nitrogen reservoir (Zhou et al., 2002a). Although the mechanism for HONO production remains elusive and controversial (e.g. Finlayson-Pitts et al., 2003), field measurements are providing evidence for the presence of HONO in a range of urban, rural and remote locations (e.g. Honrath et al., 2002; Zhou et al., 2002a; Stutz et al., 2004). An improved understanding of the mechanisms controlling HONO concentrations will require measurements of HONO in concert with a full suite of other HO_x and NO_y species, measurements of HONO fluxes and measurements of vertical gradients in HONO concentration.

Most prior measurements of HONO in the atmosphere have been based on wet chemical methods or on long path absorption spectroscopy. Wet chemical sampling with derivatization followed by HPLC separation (e.g. Zhou et al., 1999) and UV detection (e.g. Heland et al., 2001) and direct sampling with denuders or filters followed either by ion chromatography (e.g. Ferm and Sjödin, 1985; Večeřa and Dasgupta, 1991; Simon and Dasgupta, 1995; Oms et al., 1996; Zellweger et al., 1999; Genfa et al., 2003; Bytnerowicz et al., 2005) or

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by derivatization and fluorescent detection (Takenaka et al., 2004) have been used extensively. The integration time for wet sampling or filter sampling techniques spans from a few minutes up to weeks. Heland et al. (2001) report detection limits of 3–6 ppt with a 4 min integration time and Beine et al. (2005) report detection limits of 0.5 ppt with an integration time of 5 min. Bytnerowicz et al. (2005) describe a passive sampling method for measuring HONO that is intended for integrating over extended periods of time, usually 1–4 weeks. HONO has also been detected directly using differential optical absorption spectroscopy (e.g. Alicke et al., 2002) with detection limits of 84 ppt (Alicke et al., 2003). Laser-induced detection of the OH fragment following the photofragmentation of HONO with a sensitivity of 10 ppt in 5 min has also been developed (Liao et al., 2006). Cavity ring-down spectroscopy has also been proposed as a method for HONO detection (Wang and Zhang, 2000) but has not been used for field measurements to our knowledge.

We propose a new strategy for HONO detection based on thermal dissociation (TD) coupled to chemiluminescent (CL) detection of NO (TD-CL). The method has the potential to provide an order of magnitude higher time resolution than any of the above techniques with comparable detection limits. We describe laboratory tests of the proposed design and evaluate factors affecting the instrument response and potential interferences. Modifications to the prototype are proposed that will improve the instrument's prospects for successful field measurements.

2. Thermal dissociation—chemiluminescence detection of HONO

In recent work, Day et al. (2002) show the use of gas phase TD of peroxy nitrates (ΣPNs), alkyl nitrates (ΣANs) and nitric acid (HNO_3) followed by the detection of the NO_2 fragment by LIF is an accurate and sensitive method for detection of these species. We follow a similar strategy for the detection of HONO. Upon heating, HONO molecules thermally dissociate to yield NO and OH (Fig. 1)

$$\mathrm{HONO + heat \rightarrow OH + NO.} \tag{1}$$

The NO fragment is then detected using the CL reaction with O_3. Commercial instruments for NO detection with sensitivities of 50 ppt in 3 s or 10 ppt in 60 s (Eco Physics, CLD 780 TR) are available and designs with sensitivities of 1–2 ppt in 10 s have been developed (e.g. Ridley and Grahek, 1990). Sensitive and accurate detection of HONO requires three additional elements: an inlet, a method of calibration, and a method of accounting for secondary chemistry affecting the amount of NO arriving at the detection region. These three elements are described below.

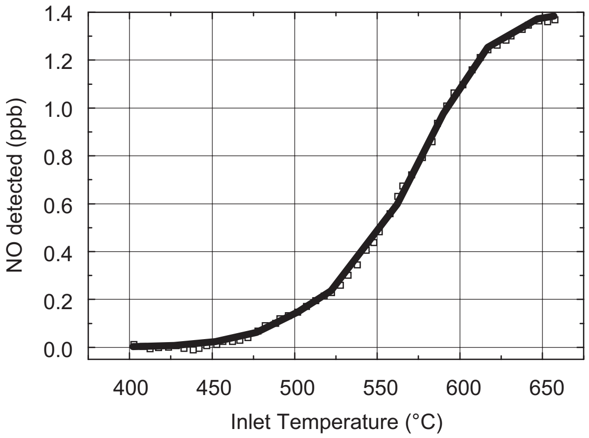

Fig. 1. Nitric oxide detected by chemiluminescence during a temperature ramp (400–670 °C) of 1.39 ppb of nitrous acid in zero air along with a model temperature ramp. The model used to produce this figure is discussed below.

2.1. Inlet

We use an inlet similar to the one described by Day et al. (2002). Air is taken in through a $\frac{1}{4}$ in (6.4 mm) OD quartz tube and is rapidly heated, producing an enhancement in NO over the ambient background. In our laboratory experiments we used a two-channel system which sampled air at approximately 2 standard liters per minute through 15 cm of PFA tubing heated to approximately 50 °C to prevent losses of HONO to the walls of the inlet and then split into two equal flows directed through a 120 cm long section of 6.4 mm OD (3.8 mm ID) long quartz tubing (see Fig. 2). The first channel is set at ambient temperature and is used to measure NO and the second channel is heated to the temperature at which HONO dissociated (640 °C) and used to measure the sum of NO and HONO. Nichrome wire wrapped around the first 25 cm of the quartz tubing resistively heats that segment and the remaining ~100 cm is used to cool the gas. Quartz tubing surrounds the heated section to