



## Investigation of nitrous acid concentration in an indoor environment using an in-situ monitoring system

Seung Shik Park<sup>a,\*</sup>, Jin H. Hong<sup>b</sup>, Jai H. Lee<sup>b</sup>, Young J. Kim<sup>b</sup>, Sung Y. Cho<sup>a</sup>, Seung J. Kim<sup>a</sup>

<sup>a</sup> Department of Environmental Engineering, Chonnam National University, 300 Yongbong-dong, Buk-ku, Gwangju 500-757, Republic of Korea

<sup>b</sup> Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology, 1 Oryong-dong, Buk-ku, Gwangju 500-712, Republic of Korea

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### ABSTRACT

An in-situ measurement system for the determination of nitrous acid (HONO) was developed and used at an indoor residential environment. The system uses a diffusion scrubber to sample gaseous HONO and the peroxyxynitrite-induced luminol chemiluminescent method to quantify the amount of HONO. In this system, the detection limit of HONO, estimated as three times the noise level of the scrubbing solution blank, was 120 pptv for a 2-min integrated sample. Indoor HONO and NO<sub>x</sub> concentrations were determined for 7 days in the living room of an apartment with a gas range for cooking in the kitchen. Close examination of the relationships among HONO, NO, and NO<sub>2</sub> concentrations during both the background and combustion periods confirm that the observed HONO was formed not only by direct emission from gas combustion, but also from heterogeneous reactions of NO<sub>2</sub> with H<sub>2</sub>O on indoor surfaces. The average ratio of HONO to NO<sub>2</sub> over the study period was  $0.12 \pm 0.05$ . The HONO/NO<sub>2</sub> concentration ratio was 0.04–0.08 during the combustion period, whereas it was 0.10–0.25 after combustion had stopped. This suggests that HONO was generated through different production processes, both during combustion and after the completion of combustion. The controlled combustion experiments indicate that the burning rate is an important factor to determine the peak HONO concentration. In darkness, HONO had a nearly constant removal rate for all of the combustion experiments, whereas the removal rates of NO and NO<sub>2</sub> depended on the burning rates of the gas range. Combustion experiments conducted at the fixed burning rate setting show also that ventilation decreased HONO concentration. This indicates that the airflow rate of the range hood fan is an important factor to control the concentration of indoor air pollutants.

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### 1. Introduction

Recently, attention has turned to greater consideration of indoor environments because most people spend 80–90% of their time indoors. The use of unvented combustion appliances in homes leads to high indoor concentrations of nitrogen oxides, i.e., NO and NO<sub>2</sub>, causing a potential indoor air quality problem (Goldstein et al., 1988; Ross, 1996;

Farrow et al., 1997). Nitrous acid (HONO) in indoor air is formed by both direct emissions from combustion processes (Pitts et al., 1989; Febo and Perrino, 1991) and the heterogeneous reaction of NO<sub>2</sub> with water vapor on surface materials (Jenkin et al., 1988; Brauer et al., 1990; Spengler et al., 1993; Spicer et al., 1993; Weschler et al., 1994; Wainman et al., 2001; Khoder, 2002; Lee et al., 2002). Controlled chamber studies have demonstrated that the heterogeneous reaction between NO<sub>2</sub> and H<sub>2</sub>O with surfaces is an important pathway for HONO production indoors, and its reaction rate is first order with respect to

\* Corresponding author. Fax: +82 62 530 1859.

E-mail address: [park8162@chonnam.ac.kr](mailto:park8162@chonnam.ac.kr) (S.S. Park).

NO<sub>2</sub> (Pitts et al., 1984; Jenkin et al., 1988; Brink and Spolestra, 1998; Kleffmann et al., 1998; Goodman et al., 1999; Wainman et al., 2001).

HONO is potentially involved in the formation of carcinogenic nitrosamines (Pitts et al., 1978) and could cause adverse effects to mucous membranes and lung function when people are exposed to higher HONO concentrations than those present in typical indoor residential environments (Beckett et al., 1995; Rasmussen et al., 1995). Therefore, the adverse health effects of HONO exposure and occurrences of high HONO levels indoors suggest the need for HONO measurements in indoor environments.

Since the first measurement of HONO had been made by employing differential optical absorption spectroscopy (DOAS) (Perner and Platt, 1979), a variety of other techniques have been developed. These techniques include UV-photofragmentation/laser-induced fluorescence sensor (Rodgers and Davis, 1989), chemiluminescent method (Brauer et al., 1990; Kanda and Taira, 1990), annular denuder/ion chromatography (Ferm and Sjodin, 1985; Febo et al., 1993; Leaderer et al., 1999; Lee et al., 2002), diffusion scrubber sampler/ion chromatography with UV detection (Dasgupta, 1993; Simon and Dasgupta, 1995), and coil sampler/dinitrophenylhydrazine (DNPH) with high performance liquid chromatography (Zhou et al., 1999). These methods have their own advantages and limitations, which were briefly discussed in Zhou et al. (1999). Of these techniques, some techniques suffer from poor detection limit, long integration time and tedious labor. In the present study a continuous analyzer coupling a diffusion scrubber with luminol chemiluminescent method was developed to overcome the limitations of other instrumentations mentioned above and applied in indoor environment.

Measurement efforts have indicated that HONO concentrations are higher indoors than outdoors, even in homes in which no combustion source is present (Brauer et al., 1990, 1991; Leaderer et al., 1999; Khoder, 2002; Lee et al., 2002), suggesting that indoor HONO could be formed from ambient NO<sub>2</sub> infiltrating from outdoors. In Albuquerque, New Mexico, 24-h average HONO concentrations in homes with gas cooking ranges ranged from 2 to 8 ppb (Spengler et al., 1993). Indoor HONO concentrations were 5.5 and 2.4 ppb in homes with and without gas ranges, respectively (Leaderer et al., 1999). High time-resolution measurements of HONO showed that time-averaged HONO concentrations are typically 5–15 ppb (Wainman et al., 2001), with peak HONO concentrations as high as 100 ppb (Goldstein et al., 1988; Brauer et al., 1990).

Unlike in industrialized countries such as the United States and Japan, more than 60% of population in Korea inhabit in large-scale apartment complex. Gas ranges are typically used for cooking in these homes and are the most common. Normally, an air ventilation system is located atop the gas range in the kitchen. We developed an instrument to continuously measure HONO concentrations in indoor environments. The instrument uses a diffusion scrubber and the luminol chemiluminescence method to collect and quantify, respectively, gaseous HONO. Our aim was to characterize HONO concentrations in the indoor environment of an occupied apartment, to investigate the

emission sources of the observed HONO, and to understand NO, NO<sub>2</sub>, and HONO production in the living room in relation to the burning rates of the gas range and the operating conditions of range hood fan.

## 2. Experimental section

### 2.1. A new HONO measurement method

We developed an in-situ monitoring system to measure nitrous acid (HONO). The system is composed of three main parts: a sampling part, automated sample injection ports, and an analytical part (Fig. 1). In the sampling part, a diffusion scrubber collects HONO, which is transferred to the respective stream channel. The instrument has two separate channels to account for the background level of HONO ("blank") of the scrubbing solution (0.1 M Na<sub>2</sub>HPO<sub>4</sub>). One channel is used to transfer the scrubbing solution to a six-port valve; the other channel carries the actual sample solution containing HONO. The difference between the sampled solution (containing HONO and possible interference from gaseous compounds and water impurities) and the original scrubbing solution (background) gives the actual HONO concentration. For automated sample injection, the sample and blank scrubbing solutions are alternately injected into the analytical part through a six-port valve. Sample loads and injection durations are controlled by a timer. Finally, the luminol chemiluminescent method is used to quantify the HONO in the analytical part. The method is based on the reaction of peroxyxynitrous acid (ONOOH) and luminol reagent (C<sub>8</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub>) to produce chemiluminescent light, which is detected by a photomultiplier (PMT) to quantify HONO.

#### 2.1.1. Sampling part of gaseous HONO

Air is sampled by a vacuum pump at a flow rate of 1 L min<sup>-1</sup>, set using a flow meter that was calibrated in the laboratory using a primary flow standard. The air samples then pass through a diffusion scrubber in which gaseous HONO is separated from the sample air. The diffusion scrubber is made of 60 cm long double tubing. The inner tube is a porous membrane with a diameter of 5.5 mm and a thickness of 1.55 mm, and the outer tube is 0.2 mm thick glass. Diffusion scrubbers have widely been used to collect soluble gases. Dasgupta (1993) reviewed several requirements in regard to the membrane properties of diffusion scrubbers, e.g., fractional surface porosity, wall thickness, and pore size. The membrane that we used was manufactured by Membrana (Germany) and was appropriate for the above requirements (e.g., surface porosity: 0.7, pore size: 0.2 μm, inner diameter: 5.5 mm). The scrubbing solution (0.1 M phosphate buffer) flows at a rate of 0.63 mL min<sup>-1</sup> between the porous membrane and the glass tubing. As the samples pass through the diffusion scrubber, gaseous HONO is absorbed on the surface of the porous membrane tubing and diffused across from the inside to the outside of the membrane. The HONO dissolved in the scrubbing solution transfers to the automated sample injection part. The aerosol particles pass to the end of the diffusion scrubber and are expelled to the air. The scrubbing solution in the second channel (see Fig. 1) goes directly into the

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