Atmospheric Environment 66 (2013) 1–7

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Development and evaluation of optical fiber NH_3 sensors for application in air quality monitoring

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HIGHLIGHTS

- Optical fiber NH_3 sensors have been developed.
- The feasibility of using the sensors for air quality monitoring has been investigated.
- The sensors are reversible, can be used for continuous monitoring NH_3 in air.
- The sensors are highly sensitive, can detect NH_3 in ppbv level.
- Cross responses of the sensors to moisture, CO_2 and temperature change have been investigated.

ARTICLE INFO

Article history:
Received 23 November 2011
Received in revised form
22 June 2012
Accepted 23 June 2012

Keywords:
Optical fiber chemical sensor
Ammonia sensor
Air quality monitoring
Concentrated animal feeding
Manure
Feedlot

ABSTRACT

Ammonia is a major air pollutant emitted from agricultural practices. Sources of ammonia include manure from animal feeding operations and fertilizer from cropping systems. Sensor technologies with capability of continuous real time monitoring of ammonia concentration in air are needed to qualify ammonia emissions from agricultural activities and further evaluate human and animal health effects, study ammonia environmental chemistry, and provide baseline data for air quality standard. We have developed fiber optic ammonia sensors using different sensing reagents and different polymers for immobilizing sensing reagents. The reversible fiber optic sensors have detection limits down to low ppbv levels. The response time of these sensors ranges from seconds to tens minutes depending on transducer design. In this paper, we report our results in the development and evaluation of fiber optic sensor technologies for air quality monitoring. The effect of change of temperature, humidity and carbon dioxide concentration on fiber optic ammonia sensors has been investigated. Carbon dioxide in air was found not interfere the fiber optic sensors for monitoring NH_3. However, the change of humidity can cause interferences to some fiber optic NH_3 sensors depending on the sensor's transducer design. The sensitivity of fiber optic NH_3 sensors was found depends on temperature. Methods and techniques for eliminating these interferences have been proposed.

1. Introduction

Ammonia emission from agricultural activities has attracted increased attention in recent years due to the adaptation of large scale concentrated animal feeding practices and the rural development which brought residents closer to the animal feeding operation (AFO) facilities (Rhoades et al., 2010; Wathes et al., 1997; Gates et al., 2008). Ammonia from AFO has been implicated to the formation of fine aerosol particles. US EPA also recognizes that ammonia in the atmosphere is indirectly involved in the formation of ground ozone (http://www.epa.gov/region9/animalwaste/problem.html). Metal oxide aerosol particles can catalyze the oxidation of ammonia in air to form NO_x, which are precursors of ground ozone (Renard et al., 2004; Yuan et al., 1994). In order to understand ammonia atmospheric chemistry, to develop ammonia emission control techniques, as well as to provide baseline data for air quality standards, it is necessary to develop technologies for continuous, real-time, long-term monitoring ammonia spatial distribution.

Present state-of-the-art techniques for monitoring NH_3 concentration in air quality programs depend on field-sampling/lab-analysis (Cole et al., 2005; Phillips et al., 2001; McGinn et al., 2003) or the use of expensive instruments (Mukhtar et al., 2009; Maeda and Takenaka, 1993; Roberts et al., 1988). The first method requires frequent field trips and has a high labor-cost. It is too expensive to obtain high time/spatial-resolution distribution of NH_3

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http://dx.doi.org/10.1016/j.atmosenv.2012.06.072

concentration in air with this method. Chemiluminescence analyzers are presently available for continuously monitoring trace NH_3 concentration in air (Mukhtar et al., 2009; Maeda and Takenaka, 1993). However, these instruments are expensive, and monitoring hundreds of sites using such instruments in air quality monitoring programs is difficult and cost prohibitive.

There are several sensor technologies reported for detecting/monitoring ammonia gas (Malyshev and Pislyakov, 2003; Marquis and Vetelino, 2001; Varghese et al., 2003; Yuan and El-Sherif, 2003; Jin et al., 2001; Morales-Bahnik et al., 1994; Huang and Tao, 2011; Tao et al., 2008, 2006, 2007; Guo and Tao, 2007). Among the reported sensor technologies, fiber optic NH_3 sensors have the advantages of high sensitivity, fast response, reversible sensing, robustness, low cost of both fabrication and operation, compatibility with present fiber optic communication techniques for forming sensor network and communicating obtained information of NH_3 spatial and time distribution among interested parties.

The challenges in developing a sensor for continuous, long-term NH_3 monitoring in air include: 1) low analyte concentration (sub-ppmv), 2) continuously changing sample matrix (moisture and CO_2), and 3) continuously changing sample temperature. Although many fiber optic NH_3 sensors have been reported, there has been no systematic study of the effect of these parameters (relative humidity, CO_2, temperature) on the NH_3 sensors.

We have been developing fiber optic sensor technologies for applications of monitoring trace ammonia (Huang and Tao, 2011; Tao et al., 2008, 2006, 2007; Guo and Tao, 2007). These sensors are sensitive, and can detect NH_3 in air to low ppbv level. The sensors also have fast response. This paper reports our continued efforts to evaluate the potential of fiber optic NH_3 sensors for applications in air quality monitoring, and the development of approaches to eliminate potential interferences. These include assessing the sensitivity of fiber optic NH_3 sensors for air quality monitoring, investigating the effect of air composition change (humidity, CO_2) and temperature on sensor's response to ammonia. The approaches for eliminating potential interferences are also discussed.

2. Experimental

2.1. Instruments

An optical fiber compatible ultraviolet/visible (UV/Vis) spectrometer (Redtide620, OceanOptics, Inc., Dunedin, FL) and an optical fiber compatible light source (LS-1, OceanOptics, Inc.) were used for measuring optical absorption response of optical fiber sensor probes. A dynamic gas calibrator (Thermo Scientific Model 146i, Franklin, MA) was used to dilute a standard NH_3 gas sample with compressed air to make test air samples. A tube furnace (MTI Model GSL-1500X-50, MTI Corp., Richmond, CA) was used to heat air gas samples during some experiments for testing the effect of varying temperature.

2.2. Fiber optic NH_3 sensors

A fiber optic NH_3 sensor consists of the optical fiber compatible light source, the optical fiber compatible UV/Vis spectrometer, and a bent optical fiber probe having a specially tailored coating on the surface of the bent fiber core. The two ends of the bent optical fiber probe are connected to the light source and spectrometer, respectively.

Two fiber optic sensors investigated in this work were developed from our previous works (Huang and Tao, 2011; Tao et al., 2006). Two additional fiber optic sensor techniques, which have potential in applications of monitoring trace NH_3, were also investigated. The transducers of the two fiber optic NH_3 sensors developed from our previous works are: 1) a bent optical fiber probe coated with a bromocreasol purple (BCP) doped sol–gel silica polymer (Tao et al., 2006), 2) a bent optical fiber probe having a dual layer poly (methylmethacrylate) (PMMA)/chlorophenol red (CPR) coatings (Huang and Tao, 2011). The transducer of one of the new sensors is a bent optical fiber probe having a polyaniline coating. The transducer of the second new sensor is a bent optical fiber probe having a Fe(III)-porphyrin complex doped PMMA coating. The sensing mechanisms (chemical reactions) of these two new sensors are similar to those already reported by other research groups (Yuan and El-Sherif, 2003; Jin et al., 2001; Morales-Bahnik et al., 1994).

The BCP-doped sol–gel silica coated sensor probe and the dual PMMA/CPR coated probe were made by following our previously reported procedures (Huang and Tao, 2011; Tao et al., 2006). In order to make a polyaniline coated bent optical fiber sensor probe, 2.0 mL of an acidic solution (1.0 M HCl) containing 0.10 M aniline was mixed with 2.0 mL of 0.10 M $NH_4S_2O_8$ solution. A pre-cleaned bent optical fiber probe was inserted into the mixed solution for 12 h. During the oxidization polymerization process, a thin layer of polyaniline was formed on the surface of the bent optical fiber core. This procedure is similar to a reported method for preparing a polyaniline membrane based NH_3 sensor (Yuan and El-Sherif, 2003; Jin et al., 2001). Fifty milligram of a Fe(III)-porphyrin complex (Fe(III) meso-tetra-(o-dichlorophenyl) porphine chloride, Frontier Scientific, Inc, Logan, UT) was dissolved together with 0.20 g PMMA resin in 4.0 mL acetone to form a coating solution. A dip-coating method was followed to coat a Fe(III)-porphyrin doped PMMA membrane on a bent optical fiber probe (Huang and Tao, 2011; Guo and Tao, 2007; Tao et al., 2006).

2.3. Laboratory set-up for testing the sensor probes and test method

The laboratory set-up for testing the sensor probes is diagrammatically shown in Fig. 1. A bent optical fiber sensor probe to be tested was set inside a laboratory-made climate chamber. Light from the light source was injected into the bent optical fiber sensor probe from one end. The light transmitted through the probe is detected by the optical fiber compatible spectrometer and converted to absorbance signal with a computer program provided by the spectrometer maker.

Compressed air was used to dilute a standard NH_3 gas sample to make test air samples of different NH_3 concentration. The

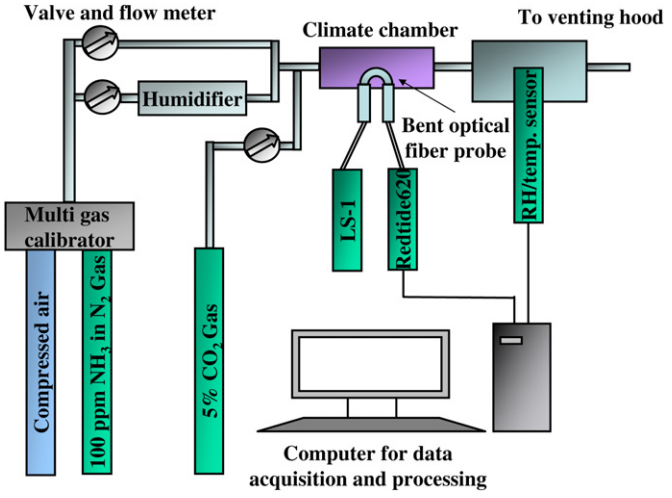

Fig. 1. A schematic diagram shows the laboratory setup for testing the fiber optic NH_3 sensor probes exposed to air samples of different composition at different temperatures.