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Technical note

Laser-induced fluorescence instrument for measuring atmospheric SO_2

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Abstract

We report on the development of a high-sensitive detection system for measuring atmospheric SO_2 using a laser-induced fluorescence (LIF) technique at around 220 nm. Second harmonics of a tunable broad-band optical parametric oscillator (OPO) pumped by the third harmonic of a Nd:YAG laser is used as a fluorescence excitation source. The laser wavelength is alternatively tuned to the peak and the bottom wavelengths in the photoabsorption spectrum of SO_2 at 220.6 and 220.2 nm, respectively, and the difference signal at the two wavelengths is used to extract the SO_2 concentration. This procedure can give a good selectivity for SO_2 and avoid interferences of fluorescent or particulate species other than SO_2 in the sample air. The SO_2 instrument developed has a sensitivity of 5 pptv in 60 s and $S/N = 2$. The practical performance of the detection system is tested in the suburban area. The inter-comparisons between the LIF instrument and a commercial instrument using Xe flash lamp excitation for the fluorescence detection have been performed. The correlation between two instruments is measured up to 70 ppbv. A good linear relationship between the LIF measurements and commercial instrument measurements is obtained.

Keywords: Sulfur dioxide; OPO; Detection limit; Instrument development

1. Introduction

In the atmosphere, sulfur in both gaseous and aerosol forms impacts regional and global chemistry, climate change, as well as the health of various living organism. Anthropogenic emissions in the form of SO_2 are about 75% of the total sulfur emission budget (Brasseur et al., 1999). The source of SO_2 is primarily from coal and petroleum combustion, petroleum refining and metal smelting operations. The anthropogenic emissions of SO_2 are converted to H_2SO_4, which is the dominant precursor responsible for acid precipitation. The acidic precipitation in the form of rain, fogs, and mists has long been implicated in playing some role in forest decline and foliar damage. SO_2 is also a common intermediate in the oxidation of all the reduced sulfur compounds such as dimethylsulfide (DMS), hydrogen sulfide (H_2S), carbon disulfide (CS_2), etc. The released sulfur compounds are converted to sulfuric acid (H_2SO_4) through the gaseous SO_2 form.

The mixing ratios of SO_2 in polluted urban and rural areas, particularly near power plants, smelters or paper mills, may exceed several parts per billion by volume (10^{-9}, ppbv). In the remote troposphere, the concentrations of SO_2 are typically less than 100 parts per trillion by volume (10^{-12}, pptv). To provide useful information

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with which we may broaden our understanding of the sulfur cycles, measurement techniques must be sensitive, precise, and accurate enough to qualify the SO_2 concentrations over the wide range from several hundred ppbv to several pptv. Measurements of SO_2 in the remote marine atmosphere are extremely important for elucidating the long-range transport of sulfur compounds far from source regions, and understanding of atmospheric sulfur oxidation and deposition. For example, Yvon and Saltzman (1996) measured the concentrations of SO_2 and its biogenic precursor DMS in the tropical Pacific marine boundary layer, and analyzed the atmospheric sulfur cycling. Tu et al. (2004) measured the SO_2 concentrations on transit flights during the NASA Transport and Chemical Evolution over the Pacific mission (TRACE-P), and investigated the long-range transport of SO_2 in the Pacific.

Various techniques for the detection of atmospheric SO_2 have been used. In the Gas-Phase Sulfur Intercomparison Experiment (GASIE), seven techniques for the field measurement of trace SO_2 were compared simultaneously over 1 month in 1994 using samples produced in situ by dynamic dilution (Stecher et al., 1997). The seven techniques were aqueous chemiluminescence (estimated detection limit: 3 pptv in 10–35 min with 500 l sample gas) (Jaeschke et al., 1997), pulsed fluorescence detector (described later) (Luke, 1997), isotope dilution-gas chromatograph mass spectrometer (1 pptv in 3–8 min with 1.7 l gas) (Bandy et al., 1993), mist chamber ion chromatograph (5–47 pptv in 5–30 min with 400 l gas) (Talbot et al., 1997), diffusion denuder sulfur chemiluminescence detector (10 pptv in 3 min with 3 l gas) (Benner et al., 1997), high performance liquid chromatography fluorescence detector (4 pptv in 4 min with 6 l gas) (Gallagher et al., 1997), and carbonate filter ion chromatograph (3–12 pptv in 90 min with 6000 l gas) (Ferek et al., 1997).

An atmospheric pressure ionization mass spectrometer (APIMS) has been developed to determine atmospheric SO_2 by Thornton et al. (2002) using a chemical ionization mass spectrometry (CIMS) technique. They have used radioactive nickel-63 for an electron source to produce secondary ions. They continuously added $^{34}S^{16}O_2$ as an internal standard. Their detection limit was <1 pptv in 1-s integration time. They indicated that the sensitivity of the CIMS technique was strongly dependent on water vapor in the air and the necessity of a dryer in the air inlet was suggested especially for marine boundary layer measurements. The CIMS approach for the determination of SO_2 has been also reported by several groups (Jost et al., 2003; Hunton et al., 2000; Reiner et al., 1998; Eisele and Berresheim, 1992). Differential optical absorption spectrometry (DOAS) measurements of atmospheric SO_2 were performed by Platt and Perner. The detection limit of SO_2 was estimated to be 10 pptv in 20-min measurement with 5-km optical path (Platt and Perner, 1980).

Fluorescence detection methods with the optical excitation to electronically excited states of SO_2 have been used for the determination of SO_2 concentrations in air. In the 1970's Okabe and co-workers (Okabe et al., 1973; Schwartz et al., 1974) used the atomic resonance line of Cd (228.8 nm) or Zn (213.8 nm) discharge lamp for the optical excitation sources. Excited SO_2 molecules fluoresce in a broad band continuum from 240 to 420 nm, with an emission peak at approximately 320 nm. A bandpass filter was used to isolate the emission radiation and transmit it to an orthogonally oriented photomultiplier tube (PMT). They found that the detector response was linear from at least 8.6 ppbv to 1.8 ppmv. The detection limit was several ppbv levels in 1-min integration time. In the commercial pulsed fluorescence (PF) detector for SO_2, Thermo Environmental Instruments (Franklin, Massachusetts) Model 43S, SO_2 molecules are electronically excited with the output of a xenon flash lamp pulsed at 10 Hz with 130 μs time width (Thermo Environmental Instruments, Inc., 1992). This instrument is called a Thermo Electron 43S. In this instrument a series of refractive interference filters isolates and passes excitation radiation in the 190–230 nm wavelength range of the xenon flash lamp. The emission from SO_2 is monitored with a gated PMT. The sampling window gate is delayed by 30 μs from the start of the Xe flash lamp trigger to avoid the electrical noise associated with the flash. Luke (1997) succeeded to detect as little as 30 pptv SO_2 in a 25-min sampling interval using a modified Thermo Electron 43S instrument in the GASIE intercomparison experiment, although the specification of the original instrument is 200 pptv in 3-min detection time. The laser-induced fluorescence (LIF) detection of SO_2 was tested in the laboratory by Bradshaw et al. (1982) to provide an assessment for the atmospheric detection. The excitation wavelength was 222.2 nm. The laser system consisted of a Nd:YAG laser pumped dye laser, the fundamental of which was frequency doubled and this output, in turn, was then frequency mixed with the Nd:YAG fundamental at 1064 nm. Based on the laboratory experiments, they estimated the detection limit of SO_2 to be several pptv in 1-min integration time with the laser energy of 1 mJ at 222.2 nm and the repetition rate of 10 Hz for the excitation laser light and 6 PMTs for fluorescence detection.

Here, we describe design and performance of an LIF instrument for SO_2 detection that uses frequency-doubled light of a broad-band optical parametric oscillator (OPO). We have used a two-wavelength measurement technique to extract the concentration of SO_2 to avoid the interferences by other fluorescent species. The detection limit of the instrument for SO_2 is 5 pptv in 60-s integration time and $S/N = 2$.