Atmospheric Environment 67 (2013) 112–119

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

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

Development of a new LOPAP instrument for the detection of O_3 in the atmosphere

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HIGHLIGHTS

- ► A simple instrument for the detection of O_3 is presented.
- ► Sensitive, selective and absolute quantification by Lambert–Beer's law.
- ► Single interferences studied can be negligible for atmospheric conditions.
- ► Successful validation in the atmosphere and in a complex smog chamber experiment.

ARTICLE INFO

Article history:
Received 6 July 2012
Received in revised form
9 October 2012
Accepted 10 October 2012

Keywords:
Ozone
Instrument development
Interferences
Intercomparison

ABSTRACT

A simple O_3-LOPAP (Long Path Absorption Photometer) instrument for the selective detection of O_3 in the atmosphere is presented, which is mainly intended to be used as an extension of a recently developed NO_2-LOPAP. O_3 is sampled in a stripping coil by a selective chemical reaction with the highly absorbing Indigo dye. The reduction of the optical absorption of the dye is detected in a liquid core waveguide. The instrument has a detection limit of 0.4 ppbv, an accuracy of 10%, a precision of 2% for 6 min time resolution and allows the absolute quantification of O_3 according to Lambert–Beer's law. Interferences towards nitrogen oxides (NO and NO_2), N_2O_5, H_2O_2 and several VOCs were quantified in the laboratory and found to be negligible for atmospheric conditions. The new instrument was successfully validated against a commercial UV-absorption instrument during an urban field campaign and against the FTIR technique in a smog chamber under complex photosmog conditions. For the UV-absorption instrument significant positive interferences towards aromatic species were observed in the smog chamber.

1. Introduction

Due to its direct adverse effects on humans, animals and plants and due to its UV absorbing properties, ozone (O_3) is of crucial importance for life on Earth. Especially, photochemical O_3 formation in the troposphere during "summer smog" episodes and its destruction in the stratosphere after polar winter ("ozone hole") have attracted considerable public and scientific attention in the past. Due to its health effects, a threshold limit average daytime value of 120 $\mu g\ m^{-3}$ ($\sim$60 ppbv) not to be exceeded more than 25 days per year was introduced in the European Union in 2010 (Directive, 2002/3/EC, 2002).

The environmental importance of ozone has led to routine measurements in the atmosphere by different techniques which started with primary studies of the chemist Schönbein (1844). Today, ozone is typically measured by in-situ instruments using the UV-absorption of ozone at 254 nm. Standard UV-absorption instruments have a typical detection limit of 1–2 ppbv for a time response of <1 min (Dunlea et al., 2006). The simplicity of the method and the absolute quantification of O_3 with Lambert–Beer's law have resulted in this technique being typically recommended, by e.g. DIN, ISO, EPA, EU (ISO 13964, 1998; McElroy et al., 1997). However, it is well known that atmospheric trace gases, which absorb in the UV (e.g. aromatic hydrocarbons), can interfere in the detection of O_3. For that reason, the instruments use two channels. In one channel, ozone is destroyed, e.g. on heated metal surfaces or manganese dioxide, and only the interfering species are quantified. In the other channel, the sum of ozone and the interferences are measured. From the difference between the two channels, the ozone concentration is determined. While this interference correction typically works well under atmospheric conditions (Kleindienst et al., 1993; Dunlea et al., 2006; Williams et al., 2006), interferences towards sticky aromatic species – also undesirably removed in the interference channel of the instrument – are still

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1352-2310/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.atmosenv.2012.10.058

observed under laboratory conditions, when high trace gas levels are used (Kleindienst et al., 1993).

In addition to UV-absorption, chemiluminescence techniques based on gas phase reactions of O_3 with NO or ethene and liquid phase reactions, e.g. with Coumarine, Luminol or Indigo-disulfonate are also used for the detection of ozone in the atmosphere (Stedman et al., 1972; Gregory et al., 1983; Takeuchi et al., 1990; Ridley et al., 1992; Jiménez et al., 1997), even though absolute calibration is not possible for these techniques. However, the sensitivity and time response of these instruments can be very high, with detection limits down to 10 pptv for seconds time response (Ridley et al., 1992). Besides compact in-situ instruments, O_3 is also measured by the path averaging FTIR and DOAS techniques (Dunlea et al., 2006). The detection limits and time responses of FTIR and DOAS instruments are typically a few ppbv and ~10 min, respectively, depending on the optical path length, visibility of the atmosphere and the concentration levels (Williams et al., 2006; Dunlea et al., 2006).

Recently, a sensitive and selective NO_2-LOPAP instrument (Long Path Absorption Photometer) has been developed and successfully validated in our group (Villena et al., 2011, 2012). The only significant interference towards O_3 is suppressed using a scrubber, in which O_3 is quantitatively sampled in a stripping coil by the selective reaction with the blue Indigo dye, while NO_2 is almost unaffected. This reaction was originally used to quantify O_3 in the liquid phase (Bader and Hoigné, 1981) and was later applied in passive samplers (Grosjean and Hisham, 1992; Scherren and Adema, 1996; Garcia et al., 2010), in a discontinuous bubbler method (Bergshoeff et al., 1984) and in a stopped flow approach (Toda et al., 2003) to measure O_3 in the atmosphere. In the present study, the Indigo method is used for the continuous sensitive quantification of O_3 in the gas phase also by the LOPAP technique. A two channel instrument was developed to characterize and optimize the instrument's performance. However, later it is planned to use only the one channel ozone scrubber from the NO_2-LOPAP instrument for the sensitive and selective quantification of O_3 and NO_2 in the atmosphere.

2. Experimental section

The O_3-LOPAP instrument consists of two separate units. (1) The external sampling unit, directly situated at the sampling site (i.e. in the atmosphere), which avoids the use of any sampling lines. (2) The detection unit (19″ instrument) where the Indigo absorption is quantified using a liquid core wave guide. Both units are connected by a temperature controlled sampling line, through which liquid reagents, zero gas and the liquid from the thermostat are transferred (Fig. 1).

2.1. Sampling unit

In the external sampling unit two similar vertical glass stripping coils are connected in series (see Fig. 1). Each of the two stripping coils has 25 coils with 40 mm outer coil diameter, an inner glass

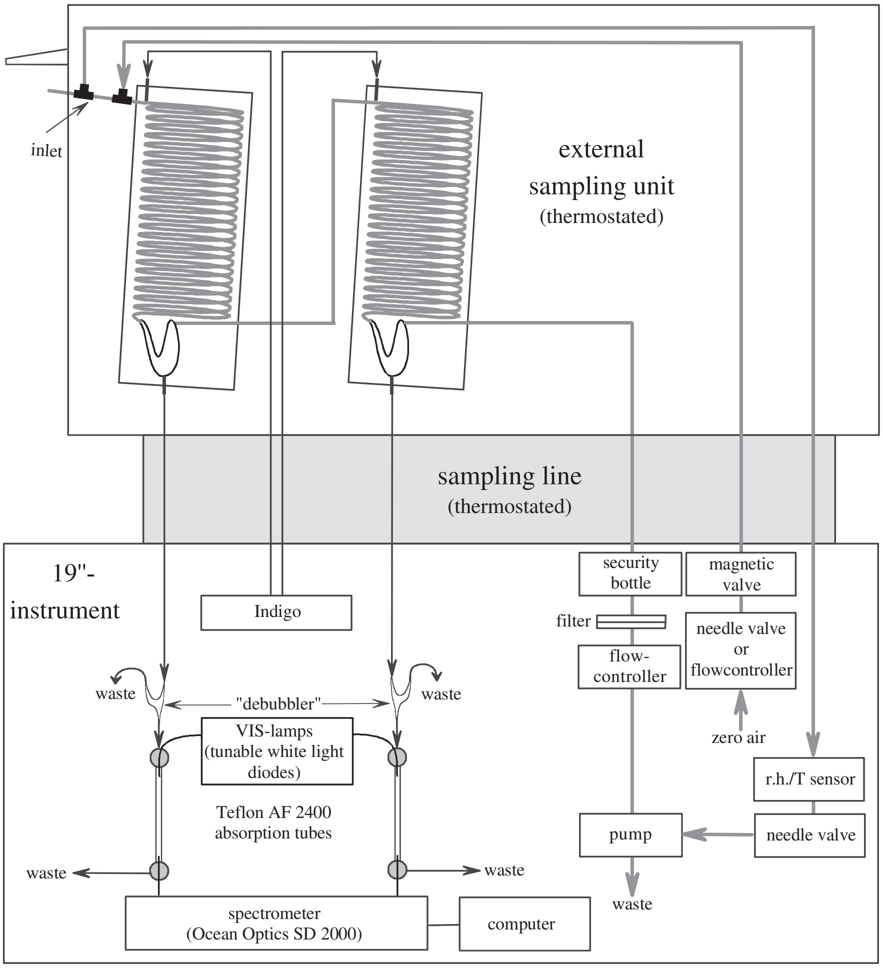

Fig. 1. Schematic setup of the O_3-LOPAP instrument.