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Development of highly sensitive passive sampler for nitrogen dioxide using porous polyethylene membrane filter as turbulence limiting diffuser

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Abstract

A new design of passive sampler is described which is appropriate to reduce the sampling resolution of most formats of Palmes' tubes from weeks to 24 h or less. The sampler employs a flat-type porous polyethylene membrane filter as a diffuser, which controls mass transfer of the target analyte from ambient air to impregnated trapping filter. The new design is applicable to any analyte for which there is a paper Palmes' tube method, e.g. H_2S, OCS, NO, SO_2, O_3, organic acids, NH_3 and so on. As an example, the sampler for the determination of ambient atmospheric nitrogen dioxide (NO_2), employing a trapping filter impregnated with triethanolamine is described. Performance of the new sampler was evaluated in laboratory and field experiments. The sampling rate was measured directly at four kerb-side sites in Oxford, UK and Kanagawa, Japan, by comparing measured concentrations from the samplers with co-located automated NO_2 analyzers. Results showed mass transfer rate of NO_2 within the diffuser did not change with external wind speed (0.5–$2\,m\,s^{-1}$). The passive device had relatively higher sampling rate than those of previous samplers and gave equivalent results on NO_2 concentrations to the automated NO_2 analyzer at 24 h or less sampling duration. LOD and LOQ indicated possible application of these devices to sampling in urban intermediate, urban background and suburban areas.

Keywords: Passive sampler; Diffusion filter; Nitrogen dioxide; Turbulence; Sampling rate; Palmes' tube

1. Introduction

Passive air samplers are widely used for ambient monitoring for purposes ranging from occupational exposure (Vinzents, 1996) and outdoor air quality monitoring (Kirby et al., 2001) to indoor pollution monitoring for the conservation of cultural heritage monitoring (Ankersmit et al., 2005). They can be used for gases or particulates and for a large range

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of analytes (Appendix contains some example applications to demonstrate the wide application of this class of technique). One particular type of passive sampler (originally developed by Palmes et al. (1976) for workplace monitoring) called a "diffusion tube" or "Palmes' tube" is used extensively in UK, EU and USA primarily for NO_2. It is routinely used to determine the extent of polluted zones (Kirby et al., 1998; Glasius et al., 1999) and for comparison of national and international air quality standards (Van Reeuwijk et al., 1998) according to its ubiquitous, cost-effective and robust properties. Although there are different formats and methodologies of preparation which each brings difficulties in intercomparisons, all agree that these tubes over-sample in the outdoor environment (AQEG, 2004; Kirby et al., 2001; Ridge et al., 2005). Two potential sources of such enhancement have been identified. Firstly, eddy diffusion caused by air turbulence at the entrance of the sampling tube can lead to a shortening of the diffusion path length (Campbell et al., 1994; Gair and Penkett, 1995; Ridge et al., 2005; Koutrakis et al., 1993). Various approaches involving the use of turbulence baffles have been tried, but with mixed results (Gair and Penkett, 1995; Shooter et al., 1995). In essence, the root of this problem lies in the use of a column of gas (air) as the diffusion length, and could only be resolved if this were not used. The second source of positive bias is the disruption of the photo-stationary steady state in samplers not transparent to light ($\lambda \sim 315$ nm). In Palmes' tube type samplers, the time that the co-diffusing NO_2, O_3 and NO are in the tube is similar to, or greater than the residence time for reaction between the NO and O_3 molecules. Hence this reaction causes (excess) NO_2 formation, without the corresponding NO_2 loss from photolysis within the tube (Heal and Cape, 1999). The use of UV transparent Palmes' tubes is one way around this problem but quartz tubes undermine the economics of the samplers, and not all FEP is UV transparent. This issue is effectively one of kinetics, and could be resolved if the sampling rate of the passive sampler was much higher than the rate of the NO and O_3 reaction.

Sekine et al. (2001, 2002, 2004) have evaluated a performance of reactive passive sampler having porous polyethylene (PE) membrane cylinder, made of sintered PE particles, as a diffuser for the determination of formaldehyde and volatile organic compounds (VOCs) such as benzene, toluene, xylene, ethylbenzene, limonene and *p*-dichlorobenzene, and found the sampling rate of the sampler (89 $mL\,min^{-1}$ for formaldehyde, approx. 35 $mL\,min^{-1}$ for VOCs) was high enough to realize short-term sampling and was independent on the wind speed between 0.2 and 4 $m\,s^{-1}$. The work showed that the porous PE membrane not only had a high gas permeability, but also worked as a good turbulence baffle.

Then, the authors have prepared a flat type porous PE membrane filter to suit the trapping filter of the Palmes' tube and proposed the alternation of the diffuser from "tube" to "flat porous PE filter". The new passive sampler is applicable to any analyte for which there is a paper Palmes' tube method, e.g. H_2S, OCS, NO, SO_2, O_3, organic acids, NH_3 and so on. The aim of this paper is to discuss a potential alternation of the flat diffuser from the view point of diffusion and sorption processes and to demonstrate the use of the new design sampler for the determination of atmospheric concentrations of NO_2.

2. Experimental

2.1. Sampler construction

Fig. 1 shows a schematic view of the test sampler, alongside other samplers—the Palmes' tube and Ogawa sampler (Hirano et al., 1985; Koutrakis et al., 1993). It should be noted that whilst both the Palmes' tube and Ogawa samplers have tubes, the new sampler has a rod—it is simply a support for the trapping media. In this study the trapping filter for NO_2 was prepared by dipping Whatman#1, 13 mm φ filter into 10% v/v TEA in acetone solution. Two kinds of 13 mm φ of the flat porous PE membrane filters, #0.75 and #1.0 were prepared by sintering spherical PE powders. The #0.75 filter has a thickness of 0.75 mm with average pore size of 54 μm. The filter retains aerosol particles with larger than 25 μm of aerodynamic diameter in air. Pressure drop of the #0.75 filter was measured at an air flow of 100 $m^3\,m^{-2}\,min^{-1}$ and resulted in 76 mmHg (1010 Pa). On the other hand, the #1.0 filter has a thickness of 1.0 mm with an average pore size of 43 μm. Aerosol particles with an aerodynamic diameter of <20 μm pass through the filter. Pressure drop of the filter was 58 mmHg (7730 Pa) with an air flow of 100 $m^3\,m^{-2}\,min^{-1}$. The trapping filter and diffuser were retained by open center cap on the solid support (made of glass, PTFE or polyolefin). The solid support is a straight rod, so