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A high accuracy dilution system for generating low concentration reference standards of reactive gases

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ABSTRACT

We have developed a unique dynamic dilution system for generating high accuracy reference standards of reactive gases at concentrations which are unstable in high pressure cylinders. It uses state of the art 'Molbloc' flow elements and is capable of generating adjustable reference standards with an estimated relative expanded uncertainty lower than 1%. This is a significant development, improving the accuracy of primary reference gas mixtures used to provide and disseminate traceability for measurements of many key gaseous air pollutants.

1. Introduction

Protection of human health and the natural environment depends on the ability to measure harmful, toxic and carcinogenic substances. The exposure of the population to ambient pollutants such as oxides of sulphur and nitrogen, primarily originating from combustion sources, has decreased dramatically in recent decades [1], but is still a cause for concern since concentrations are no longer decreasing. Moreover, recent studies [2] show that the proportion of NO_2 to total NO_x in vehicle exhaust has increased in the last few years and this has been attributed to the use of oxidation catalysts and particle filters on light duty diesel vehicles. EU Directives regulate ambient concentrations of these gases and require routine automatic monitoring to be carried out by networks of stations across each EU Member State. As such it is essential to underpin these measurements with traceable reference standards and measurement systems [3–5]. Ideally, the standards used for calibration should be at low amount fractions to match expected ambient concentrations in order to reduce the uncertainty of field measurements [6].

The dissemination of primary standards of sulphur and nitrogen oxides at low amount fractions (<1 μmol/mol) by methods employing static gas standards is difficult because of their limited stability in high pressure cylinders. Dynamic methods based on dilution provide an alternative method to generate calibration gas mixtures and have the advantage that they may easily be tuned to produce variable amount fractions [7]. However, most commercially available systems are either limited to use with non-reactive gases or to generate reference mixtures with relatively large measurement uncertainties due to inaccuracies and instabilities in the dilution technology [8–13].

To address these problems we have developed a high accuracy dilution system for generating traceable, dynamic standards of sulphur dioxide (SO_2) and nitrogen monoxide (NO) between 100 and 10,000 nmol/mol to underpin certifications of these components and nitrogen dioxide (NO_2). It operates by taking continuous measurements of the mass flow rate of a primary reference gas mixture (PRGM) and a blank diluent gas using two high accuracy flow meters known as 'Molblocs' [14]. The two gases are blended at a manifold and sampled by a gas analyser. The system can

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generate reference standards with an estimated relative standard uncertainty lower than 0.5% (for amount fractions in the range 100–10,000 nmol/mol). In the following section we describe the design of the system and show how the uncertainty can be estimated. We then provide experimental results which validate its accuracy and performance.

2. Experimental

A schematic of the system is shown in Fig. 1. The calibration gas mixture is produced by blending a PRGM of the target gas with a diluent gas, which is either nitrogen (Air Products, BIP) or air (BOC, metrology grade). The diluent gas is passed through three filters containing silica gel, Purafil and charcoal (Thermo Fisher Scientific) to ensure it is nominally free from the target gas and other impurities such as water. The efficiency of the filters is checked once per year to ensure that >99% of residual target gases in the diluent are removed. This is particularly important since the presence of target gas in the diluent has a significant impact on the uncertainty at low amount fractions. The flow of the diluent can be regulated either by a 20 mg/s full-scale Viton seal thermal mass flow controller (MFC) (Brooks SLA5850-SE1AB1B2A1) or a 100 mg/s full-scale metal seal MFC (MKS 1479A53CR1BM), whereas the flow of the PRGM can be controlled by either a 0.2 mg/s full-scale Viton seal MFC (Brooks SLA5850-BC1-EA1AA0CA1B1) or a 2 mg/s full-scale metal seal MFC (Brooks SLA7950-S1EGG1B2A1). The mass flow of each gas is measured accurately with Molbloc-L laminar mass flow elements (DHI, models 1E3-VCR-V-Q and 5E3-VCR-V-Q for the diluent gas, and 5E1-VCR-V-Q and 1E2-VCR-V-Q for the PRGM), located upstream, and matched to the full scale setting of the mass flow controllers. These devices estimate the flow by means of Poiseuille's law [14]. According to this law, the mass flow of a compressible fluid in laminar flow through an annular pathway can be expressed as:

$$f = \frac{(P_1 - P_2) \cdot \rho_{(P,T)}}{\eta_{(P,T)}} \times C_G \tag{1}$$

where f is the mass flow (mg/s), P_1 is the upstream absolute pressure (Pa), P_2 is downstream absolute pressure (Pa), $\eta_{(P,T)}$ and $\rho_{(P,T)}$ are the dynamic viscosity (Pa.s) and the density of the gas (mg/m^3), respectively, at pressure P (Pa) and temperature T (K) and C_G is the geometrical constant of Molbloc flow path defined as:

$$C_G = \frac{\pi R H^3}{6L}\left(\frac{\Delta M}{m}\right) \tag{2}$$

where R is the flow passage radius (m), H is the gap between piston and cylinder (m), and L is the length of the laminar flow path (m). The ratio of ΔM to m is a calibration coefficient of the Molbloc obtained by the manufacturer. ΔM is the mass difference flowing through a Molbloc element obtained gravimetrically (mg) whereas m is the average mass obtained from Molbloc measurements (mg). This ratio attempts to take into account the differences in the dimensions and geometry of the manufactured parts with respect to the designed prototype and will be very close to one in most cases.

Each Molbloc measures the upstream and downstream pressures using built-in, high precision reference pressure transducers (RPTs). An ohmic measurement system reads the resistance of the Molbloc platinum resistance thermometers from which the temperature of the Molbloc is determined. The mass flow of the gas through each Molbloc is determined using the upstream and downstream pressures and the temperature. Two pressure regulators (LNI Schmidlin SA) are set to maintain equal input pressures of nominally 3.0 bar (absolute) to each Molbloc (to ensure they are operating at a pressure within the range in which they were calibrated). The RPTs in each Molbloc are programmed for the appropriate balance gas, purged with the gas to be used and set equal prior to measurement. A two-way valve is used to either flow the generated reference gas or gas mixture under test into an analyser. Two lines venting to atmosphere ensure that the blend and test mixture are flowing continuously in order to maintain an equilibrium. The excess flow of the blended gas is matched to that of the test mixture to ensure there is no change in upstream pressure to the analyser. Two shut off valves on each input to the blending manifold allow the Molblocs to be isolated under pressure for routine leak checks. All manifolds are constructed of stainless steel tubing and the surface area is kept to a minimum by using short tubing lengths to reduce contamination effects from build-up or release of the target gas in the system. The components in the system have been mounted on a dual

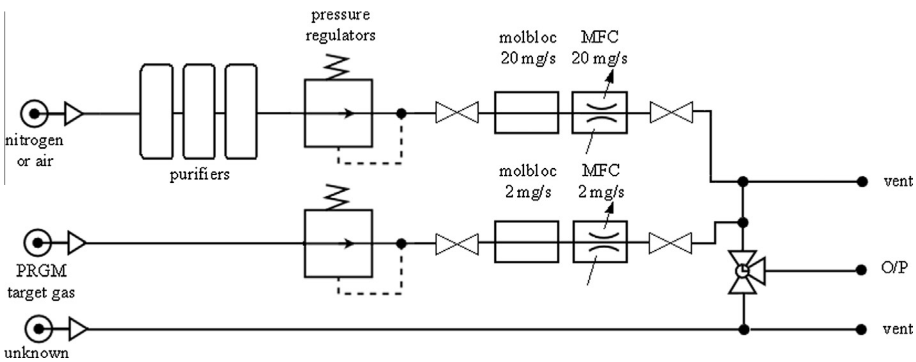

Fig. 1. Schematic of the high accuracy dilution system. The output (O/P) is connected to a gas analyser. A two-way valve is used to alternate the flow of the blend and unknown to the analyser. MFC represents a mass flow controller.