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Development of traceable precision dynamic dilution method to generate dimethyl sulphide gas mixtures at sub-nanomole per mole levels for ambient measurement



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ABSTRACT

Dimethyl sulphide (DMS) is an important compound in global atmospheric chemistry and climate change. Traceable international standards are essential for measuring accurately the long-term global trend in ambient DMS. However, developing accurate gas standards for sub-nanomole per mole (nmol/mol) mole fractions of DMS in a cylinder is challenging, because DMS is reactive and unstable. In this study, a dynamic dilution method that is traceable and precise was developed to generate sub-nmol/mol DMS gas mixtures with a dynamic dilution system based on sonic nozzles and a long-term (> 5 years) stable 10 μmol/mol parent DMS primary standard gas mixtures (PSMs). The dynamic dilution system was calibrated with traceable methane PSMs, and its estimated dilution factors were used to calculate the mole fractions of the dynamically generated DMS gas mixtures. A dynamically generated DMS gas mixture and a 6 nmol/mol DMS PSM were analysed against each other by gas chromatography with flame-ionisation detection (GC/FID) to evaluate the dilution system. The mole fractions of the dynamically generated DMS gas mixture determined against a DMS PSM and calculated with the dilution factor agreed within 1% at 6 nmol/mol. In addition, the dynamically generated DMS gas mixtures at various mole fractions between 0.4 and 11.7 nmol/mol were analysed by GC/FID and evaluated for their linearity. The analytically determined mole fractions showed good linearity with the mole fractions calculated with the dilution factors. Results showed that the dynamic dilution method generates DMS gas mixtures ranging between 0.4 nmol/mol and 12 nmol/mol with relative expanded uncertainties of less than 2%. Therefore, the newly developed dynamic dilution method is a promising reference method for generating sub-nmol/mol DMS gas standards for accurate ambient measurements.

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1. Introduction

Dimethyl sulphide (DMS) is the most abundant sulphur species in the ocean. It is a reactive compound that plays an important role in the atmosphere by producing atmospheric aerosols. Atmospheric aerosols affect the Earth's radiation budget directly by scattering incoming solar radiation and indirectly by changing the radiative properties, amount, and lifetime of clouds by acting as cloud condensation nuclei (CCN) [1–3]. In 1987, Charlson et al. [2] proposed a possible climatic feedback loop, known as the CLAW

hypothesis, involving DMS emitted from oceanic phytoplankton. Because the CLAW hypothesis postulated that DMS is the main source of CCN formation in the remote marine environment, the relationships among DMS and marine bioproductivity, CCN, solar radiation, and climate feedback have been investigated [4–8]. Recent studies suggest that CCN formation in the remote marine environment may involve other complex factors, and thus the role of DMS in the atmosphere should be reconsidered in this light [9,10].

Because DMS plays important roles in atmospheric chemistry and climate change, it is monitored in the global network of the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) programme. The observation of ambient trends of reactive compounds is associated with large analytical uncertainties in the measurements because the instability of the compounds makes it difficult to obtain accurate values, especially

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at low concentrations. Therefore, it is critical to establish good calibration standards with small uncertainties to track ambient DMS trends accurately and understand the role of DMS in the atmosphere. At a WMO GAW Experts Workshop in 2006, the WMO GAW and the Gas Analysis Working Group (GAWG) of the Consultative Committee on Quantity of Material (CCQM) agreed on the necessity of stable gas standards for volatile organic compounds (VOCs), including DMS, to manage VOC measurements. In this agreement, the National Metrology Institute (NMI) members of CCQM GAWG were asked to develop VOC standards, investigate maintaining their long-term stability, and to consider supporting the Central Calibration Laboratory for selected VOCs [11]. The uncertainty of the calibration standard is a major uncertainty in evaluating performance, such as the limit of detection and linearity, of measurement techniques, and affects the data quality. Therefore, WMO GAW requires stable DMS standards with an uncertainty of less than 5% and a simple method that can be used in field measurements to achieve the data quality objective (better than 20% accuracy and 15% precision) for ambient DMS measurements [11]. The Korea Research Institute of Standards and Science (KRISS), the NMI of the Republic of Korea, has an important role in developing international DMS standards. For example, KRISS was the coordinating laboratory in the International Key Comparison (KC) conducted by the CCQM for measuring micromoles per mole ($\mu\text{mol/mol}$) mole fractions of DMS (CCQM K94). This KC will be extended to measure ambient trends in DMS in the future [12].

Ambient DMS has been observed at levels of several picomoles per mole (pmol/mol) or sub-nanomoles per mole (nmol/mol) in the remote atmosphere [13–17]. Establishing traceable DMS standards is important to ensure the reliability of results reported by various laboratories. Researchers prepare DMS standards in the target concentration range or purchase commercial standards. Various types of standards, such as a gas standard in a cylinder [18], a diluted gas standard from a high-pressure cylinder [19,20], a diluted gas standard from permeation or diffusion of a parent gas [21–23], adsorbent tube standards [24,25], a liquid solution standard [26], and an isotopically labelled internal standard [27,28], have been used to quantify DMS. However, these standards are associated with considerable uncertainties. For example, instruments calibrated with gas standards in cylinders without dilution were used for a measurement range much lower than the concentration of the gas standards. Diluted gas standards from high-pressure cylinders and permeation tubes were used without evaluating their dilution uncertainties. Adsorbent tube standards and liquid solution standards are complicated to prepare and maintain, and isotopically labelled internal standards are not cost effective.

A widely used method of gas standard preparation is the gravimetric method [29], in which high-purity gases or liquids are weighed and transferred into cylinders [30]. For preparing pmol/mol or nmol/mol gas standards by the gravimetric method, the high-purity gases or liquids must be diluted multiple times to reduce uncertainties from handling trace amounts and the unexpected losses of target compounds. However, multiple dilutions are laborious and time-consuming for preparing sub- nmol/mol gas standard mixtures in cylinders. In addition, maintaining target mole fractions in cylinders is a major challenge in preparing and distributing standard gas mixtures of reactive compounds. To overcome these problems, a traceable dynamic dilution method may be a promising alternative to gravimetric preparation.

The goal of this study is to develop a dynamic dilution method that can generate DMS gas standard mixtures at less than 10 nmol/mol with a relative expanded uncertainty of 3% (confidence interval of 95%, $k=2$). Stable $10 \mu\text{mol/mol}$ DMS primary standard gas mixtures (PSMs) were diluted by a precision dynamic dilution system to generate reliable sub- nmol/mol DMS gas mixtures. The

long-term stability of the $10 \mu\text{mol/mol}$ DMS PSMs in cylinders was evaluated. Dilution factors of the dynamic dilution system were calculated by using traceable methane PSMs and a methane analyser. The dilution factors were then used to determine the mole fraction of dynamically generated gas mixtures. The methane analyser was calibrated against traceable methane PSMs, and then was used to determine the dilution factors and to check the operational consistency of the dynamic dilution system in real time during the dynamic dilution process. Dynamically generated DMS gas mixtures were compared with 6 nmol/mol DMS PSM in a cylinder to evaluate the applicability of the dynamic dilution system. In addition, DMS gas mixtures ranging between 0.4 and 11.7 nmol/mol were dynamically generated to evaluate the linearity of the dynamic dilution system.

2. Materials and methods

2.1. Materials

2.1.1. Gas cylinders

Gas cylinders with 6 L internal volume (Luxfer, Australia) were used for preparing $10 \mu\text{mol/mol}$ DMS PSMs in 2005 and 2009. Since 2010, new gas cylinders with a 10 L internal volume (Luxfer, United Kingdom), have been used to prepare $10 \mu\text{mol/mol}$ DMS PSMs. The cylinders were aluminium and fitted with nickel-plated valves (Hamai, Japan).

2.1.2. Regulators and tubing

Stainless steel, single-stage, diaphragm regulators (Rotarex, France) were used for DMS analysis. Sulfinert treated stainless steel tubing and traps (Restek Corporation, USA) were used in the cryogenic pre-concentration unit and sampling paths to minimise adsorption loss of DMS.

2.1.3. Gas filling system

A custom-designed gas filling system was used to introduce parent gases and diluent gases into cylinders. The system consists of a manifold, gate valves, a vacuum pump, and pressure gauges. A pre-estimated amount of the gases was transferred from both source and balance gases to a sample cylinder.

2.1.4. Weighing apparatus

Liquid reagent injected into the empty gas cylinder was weighed on a chemical balance (XP205, Mettler Toledo, Switzerland) with 0.01 mg resolution. An automated top-pan balance (XP26003L, Mettler Toledo) with 26 kg capacity and 1 mg resolution was used for weighing cylinders before and after gas filling. A cylinder rotary exchange mechanism was used for automating the balance to achieve acceptable relative uncertainties (several parts per million) during the long weighing cycles [31].

2.1.5. DMS reagent and N_2 diluent gas

Liquid DMS reagent ($> 99.0\%$) was purchased from Sigma-Aldrich (USA). The neat liquid was analysed for impurities including total hydrocarbons, water, and total sulphur compounds by gas chromatography with flame-ionisation detector (GC/FID; 6890N, Agilent Technologies, USA), Karl Fischer coulometer (831 KF, Metrohm, Switzerland), and gas chromatography (GC; 7890B, Agilent Technologies) with a sulphur chemiluminescence detector (Antek 7090, PAC, USA). The purity of the DMS reagent was estimated as 99.45% with a relative expanded uncertainty of 0.07% (Table 1). High-purity (99.9999%) diluent N_2 gas (Deokyang Co., Ltd., Korea) was used to prepare and dilute the DMS gas standards. DMS content in the diluent N_2 gas was analysed by GC with an atomic emission detector (AED, Joint Analytical Systems GmbH,

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