Effect of variation in argon content of calibration gases on determination of atmospheric carbon dioxide

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ABSTRACT

Carbon dioxide (CO_2) is a greenhouse gas that makes by far the largest contribution to the global warming of the Earth's atmosphere. For the measurements of atmospheric CO_2 a non-dispersive infrared analyzer (NDIR) and gas chromatography are conventionally being used. We explored whether and to what degree argon content can influence the determination of atmospheric CO_2 using the comparison of CO_2 concentrations between the sample gas mixtures with varying Ar amounts at 0 and 18.6 mmol mol^{-1} and the calibration gas mixtures with Ar at 8.4, 9.1, and 9.3 mmol mol^{-1}. We newly discovered that variation of Ar content in calibration gas mixtures could undermine accuracy for precise and accurate determination of atmospheric CO_2 in background air. The differences in CO_2 concentration due to the variation of Ar content in the calibration gas mixtures were negligible (<±0.03 μmol mol^{-1}) for NDIR systems whereas they noticeably increased (<±1.09 μmol mol^{-1}) especially for the modified GC systems to enhance instrumental sensitivity. We found that the thermal mass flow controller is the main source of the differences although such differences appeared only in the presence of a flow restrictor in GC systems. For reliable monitoring of real atmospheric CO_2 samples, one should use calibration gas mixtures that contain Ar content close to the level (9.332 mmol mol^{-1}) in the ambient air as possible. Practical guidelines were highlighted relating to selection of appropriate analytical approaches for the accurate and precise measurements of atmospheric CO_2. In addition, theoretical implications from the findings were addressed.

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1. Introduction

Carbon dioxide (CO_2) is a greenhouse gas that makes the key contribution to the global warming of the Earth's atmosphere. The atmospheric concentration of CO_2 remarkably increased from approximately 280 μmol mol^{-1} (ppmv) during the pre-industrial era to a global average of 379 μmol mol^{-1} in 2005. Atmospheric CO_2 monitoring started in 1958 to establish that the CO_2 concentration was rising and to document its rate of increase. During the past decade, increase in CO_2 is responsible for 84% of the increase in global radiative forcing. Such increase is due primarily to emissions from fossil fuel combustion [1].

Although CO_2 monitoring has been conducted in many parts of the world and on a voluntary basis, a number of strict criteria exist in order to establish and maintain the data quality for atmospheric CO_2 measurements. The Global Atmospheric Watch (GAW) under the World Meteorological Organization (WMO) has set the target precision of the atmospheric CO_2 measurement programme

to 0.1 μmol mol^{-1} (parts per million as volumetric fraction) in the Northern Hemisphere and 0.05 μmol mol^{-1} in the Southern Hemisphere [2,3].

There are at least 3 major quality elements for guaranteeing CO_2 data reliability: (i) best available analytical method to ensure repeatability and reproducibility (precision, measurement uncertainty); (ii) the closeness of measured data to true values (accuracy); and (iii) establishment of a chain to be capable of tracing any sources of systematic errors from true values (traceability) [4].

Valid analytical approaches need to be well established prior to applications to real observations of atmospheric CO_2. Any valid method for the determination of CO_2 in gas mixtures requires basically not only calibration gas mixtures but also appropriate analytical equipment. Quantitative determination of CO_2 in gas mixtures is realized by comparison of instrumental response signals from calibration and sample gas mixtures using appropriate equipment [5].

The available analytical systems frequently used in practice to date for the measurement of atmospheric CO_2 are a non-dispersive infrared analyzer (NDIR) and a gas chromatograph (GC) equipped with a methanizer and a flame ionization

detector (FID) or with thermal conductivity detector (TCD) [6,7].

Potential sources of measurement uncertainties for CO_2 measurements come mostly from sample gas mixtures, calibration gas mixtures, instrumental drift, changes of environmental conditions, and matrix effects due to the interactions among these factors [8]. As far as CO_2 calibration gases are concerned, it is impossible in reality to prepare such calibration gases in which background composition is exactly identical to that of natural ambient air due to the presence of a number of minor constituents including Ne (18.2 μmol mol^{-1}), CH$_4$ (1.5 μmol mol^{-1}), and Xe (0.1 μmol mol^{-1}), and other trace elements. CO_2 calibration gases therefore must best simulate natural atmospheric composition as possible. In practice, simulated air is gravimetrically prepared with the mixture of N_2 and O_2 near to the levels found in dried ambient air (0.78083 mol mol^{-1} N_2 and 0.20944 mol mol^{-1} O_2). Depending on analytical goals, argon (Ar), an important noble gas found in ambient air, may need to be added (approximately 10 mmol mol^{-1}) to the mixture of N_2 and O_2. The best accurate value for Ar content in dried ambient air is reportedly 9.332 mmol mol^{-1} [9].

In order to guarantee high precision and accuracy of the measured data in gas analysis, it is of great importance to apply the identical amounts of sample and calibration gas mixtures to an analytical system for every run. For this goal, it is imperative to maintain flow rates of a sample gas as constant as possible. A mass flow meter and/or controller (MFC) are thus commonly used to minimize the variation of gas flow rates. Thermal mass flow controller (TMFC) is widely used to control due to merits that it is possible to directly measure relatively small mass flow rate of a gas with high precision and that no calibration needed against temperature and pressure. It is to be recognized that different gas species may result in different volumetric flow rates due to the nature of a thermal mass flow controller (TMFC) and that as a consequence, a gas species with different matrices are subject to different volumetric flow rates. In other words, if TMFC is used for different gas or different composition of a gas mixture from the initially calibration gas (e.g., N_2), the TMFC could lead to an important source of measurement uncertainty. In other words, depending on varying composition of gas mixtures, the gas flow rates are subject to change through the TMFC. The TMFCs should be calibrated prior to its usage for gas analysis [10]. As long as appropriate calibrations are conducted against the specific gas mixtures, the TMFC can maintain the mass flow rate of a gas unchanged throughout gas analysis. Without additional calibrations, the volumetric flow rate of an analyte through the TMFC may be altered by different matrices of gas mixtures depending upon the presence and the levels of other constituents. Best accuracy can ensure solely by conducting calibration processes appropriately under real operating conditions. However, it is not unusual to apply the TMFC to an analytical system without additional calibration because commercially available TMFCs in the market are initially one-point calibrated against high-purity inert gas (e.g., N_2). Moreover, it is practically impossible to calibrate the TMFC as to a number of different samples prior to analysis and to prepare all RMs with the identical matrices to those of the sample gas mixtures to be analyzed.

We report for the first time the initial findings from the investigation on whether and to which degree Ar as a matrix constituent (ranging from 0 to 18.6 mmol mol^{-1}) can influence CO_2 determination in gas mixtures using calibration gas mixtures prepared in different matrices through comparisons between analytical systems. This study explored a total of 5 different analytical systems after some modifications made to conventional systems, aiming at probing potential effects of Ar on instrumental sensitivity and precision of atmospheric CO_2 determination: (i) a conventional NDIR analyzer; (ii) a modified NDIR; (iii) a conventional GC-FID; and (iv) a modified GC-FID; and (iv) a modified GC-TCD. Based on these find-

ings, practical implications and reliable analytical approach to the measurements of atmospheric CO_2 were suggested.

2. Experimental

2.1. Preparation of calibration and sample gas mixtures

The gravimetric method is officially a primary method that ensures international traceability for the preparation of calibration gas mixtures. A total of 5 gas mixtures (3 calibration gas mixtures and 2 sample gas mixtures) containing atmospheric-level CO_2 were prepared in the 30-L stainless-steel gas cylinders under ambient conditions (1.0 atm, 25 ± 2 °C) by a gravimetric technique [11]. Detailed description of the preparation procedures by this technique is found elsewhere [12]. A total of 4 source gases were used as the mother gases for each constituent. All source gases were of high purity grade: CO_2 (0.9999 mol mol^{-1} Matheson Co., USA), N_2 (0.9999 mol mol^{-1}, Deokyang Energen Co., South Korea); O_2 (0.99999 mol mol^{-1}, Prexair Co., Rep. South Korea), and Ar (0.99999 mol mol^{-1} Deokyang Energen Co., South Korea). The compositions and concentrations of gaseous impurities contained in the mother gases were determined as summarized in Supporting Information. A total of 6 calibration and sample gas cylinders were used in this study. The compositions and concentrations of the calibration and sample gas mixtures prepared by this technique are presented in Table 1. R and S stand for calibration and sample gas mixtures, respectively. The second calibration gas mixture ($R_{2,NDIR}$) was used exclusively for the NDIR whereas $R_{2,GC}$ for the GC systems only. $R_{2,GC}$ is a standard reference material (SRM) purchased from the Global Monitoring Division (GMD) under the National Oceanic & Atmospheric Administration (NOAA; Boulder, Colorado, USA) in September 2001. For of the SRM, the GMD/NOAA indicated that the SRM has CO_2 at 383.36 ± 0.04 μmol mol^{-1} as the World Meteorological Organization (WMO) mole fraction scale [4]. Information on the gravimetric concentrations for N_2 and O_2 (GMD/NOAA) were not available from the provider. The cylinders contain 4 major constituents in common: CO_2 (380–392 μmol mol^{-1}), N_2 (0.775–0.783 mol mol^{-1}), O_2 (0.205–0.216 mol mol^{-1}), and Ar (zero-18.6 mmol mol^{-1}). The sample gas mixtures were prepared in the different Ar matrices (0 and 18.6 mmol mol^{-1}). The amount of Ar in S_1 indicates only trace amount (<0.022 mmol mol^{-1}) estimated from the impurities analysis. For the calibration gas mixtures, the expanded uncertainty values ($U = ku_c$) at a coverage factor (k) of 2 for the preparation of 5 different CO_2 concentrations using a computer software (GUM Workbench Version 2.3) fall within 0.06 μmol mol^{-1} [13,14].

2.2. NDIR analytical systems

The modified NDIR analytical system is identical to the conventional one except a pressure control system (Fig. 1). The system compartments are comprised of an NDIR analyzer (Siemens Ultramat 6, Germany), two commercially available TMFCs (Brooks 5850E, Japan), and the pressure control system. The NDIR analyzer for measuring atmospheric CO_2 used in this study is of an open-path cell type. The NDIR analyzer determine the amount of CO_2 with a characteristic wavelength region of 2349 ± 50 cm^{-1} by measuring the difference in the intensities in the infrared radiation (2349 ± 50 cm^{-1}) passing through a sample cell relative to that through a reference cell. The TMFC has been initially calibrated against N_2 at a volumetric flow rate of 1000 mL min^{-1} by the manufacturer. The modified NDIR analyzer adopted a pressure control system which consists of a damping chamber and a pressure controller (a pressure sensor, an indicator, and a pressure relief valve). To make corrections for the drift of the instrumental signals during