

Accelerated Test Method to Quantify Changes in the Composition of CO₂/Air Reference Gases in Cylinders

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National Metrology Institutes and Central Calibration Laboratories continue to develop and disseminate reference materials needed to meet demanding scientific and regulatory needs for quantifying greenhouse gas emissions. The stability of these reference materials and measurement methodologies are central to anchoring values traceable to the SI. For atmospheric CO₂ concentrations, long-term stability of assigned values is critical to the longevity of the gas standards[1] and continue to be researched by NMIs and CCLs.[2] At NIST, a multidisciplinary effort is underway examining the stability of CO₂-containing natural air in various compressed gas metal cylinders typically used in the dissemination of these gas standards.[3] Here, we focus on the pressure dependence of desorption of CO₂ from cylinder walls – an effect that can alter the composition of a reference gas mixture as the cylinder is discharged and pressure is reduced. Additionally, co-adsorption of gas impurities is also being examined. Using new technologies that enable sensitive, real-time measurements of gaseous composition, we have developed an experimental method and thermodynamic model for quantifying gas composition as cylinder contents are discharged to extend its useful life to lower pressures.

To illustrate, we present experiments in which cylinders are discharged at rates much faster than during normal use but under near-isothermal conditions. These data reveal a relatively large desorption of CO₂ below a threshold partial pressure which depends on temperature. While the underlying cause of the rise in CO₂ mole fraction has been demonstrated[4], the exact mechanism is difficult to elucidate. To better understand this effect, we introduce a thermodynamic model that includes a simple description of the adsorption equilibrium of CO₂ on the inner cylinder surface. Despite its simplicity, the model can quantify the rise in CO₂ mole fraction as the cylinder discharges. Furthermore, by incorporating competitive adsorption in this model, we can also predict and describe non-monotonic changes in CO₂ composition when two or more gases in the mixture adsorb to the cylinder surface (e.g., water and CO₂). We have used this approach to quantify the capacity and relative affinity of CO₂ to adsorb on metal surfaces as a function of temperature and partial pressure. In general, this experimental and theoretical approach enables rapid quantification of the minimum useful pressure of reference standards for CO₂ and other relevant gases. We envision this approach to support a variety of new gas mixtures. Its targeted application by standards organizations and user communities will help ensure adherence to increasingly stringent amount-of-substance specifications.

References:

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