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Metrology for Nitrogen Dioxide: A study on the effects of water vapour within primary reference materials of NO_2

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Nitrogen dioxide (NO_2) is one of the key reactive trace gas species found within Earth's atmosphere. A toxic pollutant and respiratory irritant, NO_2 plays a key role in atmospheric chemical cycles that have implications not only for regional air quality but also on the global scale through climate forcing. Consequently, NO_2 is a regulated pollutant and is measured at both national and global scales in order to enforce legislation that is aimed at curbing emissions and assess the accuracy of climate models.

Key to maintaining the comparability of the measurement infrastructure of NO_2 is the use of accurate and stable reference materials that are traceable to the SI, commonly realised by the production of static gravimetrically prepared calibration standards. However, due to the reactivity of NO_2 with ubiquitous trace impurity water vapour in particular, static calibration standards of NO_2 are affected by the formation of nitric acid (HNO_3) which causes the amount fraction of NO_2 to decay significantly from its gravimetric value over time. Therefore to improve the state-of-the-art of NO_2 reference materials, consideration should be given to understanding and characterising the chemistry within static reference standards of NO_2, with a particular focus on the formation of HNO_3.

This work presents FT-IR spectroscopic measurements of gravimetrically prepared mixtures of NO_2 and water vapour and their stability over time. Implications of the formation of HNO_3 will be discussed as well as the possibility of exploiting this chemistry in a positive fashion, for developing static reference standards of HNO_3.