CCQM Activities in the Gas Analysis Working Group

Since 1998, the Analytical Chemistry Division (ACD) has participated in 25 of 38 studies of the Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM) Gas Analysis Working Group (GAWG). The CCQM conducts international comparisons to establish equivalence among measurements made by national metrology institutes (NMIs). Intercomparisons in 2006 include studies involving carbon dioxide, oxygen, n*-hexane, nitric oxide, and hydrogen sulfide in gas cylinders.*

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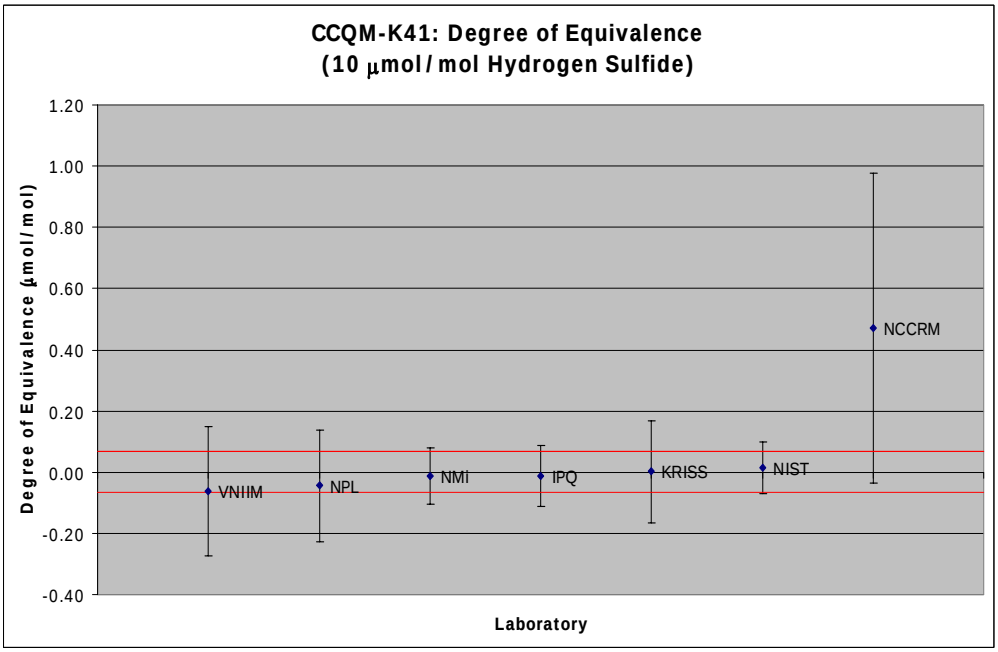
Studies in the GAWG typically take one of two forms. In measurement-capability studies, cylinders are distributed to laboratories for analysis and the agreement of results is assessed. In preparative-capability studies, participants prepare a cylinder to contain a certain concentration of the study gases, and the coordinating laboratory analyzes the samples under high-repeatability conditions to see whether the target was met. ACD participated in the following CCQM comparisons within the GAWG during the past year: CCQM-K52 360 µmol/mol Carbon Dioxide, CCQM-K53 100 µmol/mol Oxygen Preparative, CCQM-K54 100 µmol/mol *n*-Hexane in Methane Preparative, and CCQM-P73 50 µmol/mol to 70 µmol/mol Nitric Oxide Preparative Study. In addition, ACD completed the final reporting for the CCQM-K41 10 µmol/mol Hydrogen Sulfide.

Results are not yet available for two of these studies, CCQM-K52 and K53. CCQM-52 is a study in which capabilities are assessed for measurement of atmospheric-concentration carbon dioxide in air at concentrations of 350 µmol/mol and higher. A total of 18 NMIs participated in this study. CCQM-K53 is a primary standard preparative study in which NMIs were instructed to prepare a primary standard containing oxygen at an amount-of-substance fraction of 100 µmol/mol. This study is intended to underpin the NMIs' preparative capabilities, and also to validate purity assessment. A total of 12 NMIs are participating in the study.

A Draft A report was provided at the Fall 2006 meeting of the GAWG for CCQM-K54 *n*-Hexane in Methane. This study was designed to test preparative capabilities for the syringe injection technique of preparing volatile organic compound (VOC) gas standards. A total of 9 NMIs participated in this study. The results from the NIST-prepared cylinder show excellent agreement with the regression line calculated from the results.

Preliminary results were available for CCQM-P73 Nitric Oxide in Nitrogen Preparative Study. NIST prepared primary standards at nitric acid mole fractions of 43 µmol/mol and 67 µmol/mol in nitrogen. The results from the NIST-prepared cylinders showed excellent agreement with the target values.

In 2005, ACD coordinated CCQM-K41 10 µmol/mol Hydrogen Sulfide, and results were reported to the CCQM GAWG this past year. This key comparison was intended to compare the capabilities for the preparation and value assignment of gas standards for hydrogen sulfide in nitrogen. The nominal amount-of-substance fraction of the comparison standard was 10 µmol/mol, which is close to regulatory levels in most countries. Participants in this study were Russia (VNIIM), England (NPL), the Netherlands (NMi), Portugal (IPQ), Korea (KRISS), China (NCCRM), and NIST. The Key Comparison Reference Value was calculated from the participants' data and thus represents a consensus value. (Cylinders could not be prepared gravimetrically because hydrogen sulfide may be absorbed onto the walls of the cylinder and has been



shown to be unstable in cylinders at the comparison concentration.) Gas mixtures were procured from a vendor, analyzed by NIST to determine stability, and then those determined to be stable were shipped to the participants for analysis. After analysis, the cylinders were returned to NIST for reanalysis. Through this process, NIST could accurately track the stability of the gas mixtures. In parallel, NIST also analyzed a stable reference, a hydrogen sulfide gas mixture that has been shown to be stable over many years. Using the stability data, the participants' analytical results, and NIST's analysis of the stable reference, a consensus value could be calculated which represents the concentration of the stable reference. The key comparison demonstrated that the results of the laboratories agreed within 0.5 % relative to the consensus value. A subset of 6 participants' results agreed with the consensus value to better than 0.25 %.

Impact: The results from these studies will be used to benchmark the appropriate Comparability and Measurement Claims (CMCs) of the participating NMIs.

Future Plans: Key comparisons planned for the coming year include: CCQM-K46 40 µmol/mol Ammonia in Nitrogen, CCQM-K51 5 µmol/mol Carbon Monoxide in Nitrogen, and CCQM-QM-K1 Ozone Reference Photometer Ongoing Comparison.