Advances in metrology for energy-containing gases and emerging demands

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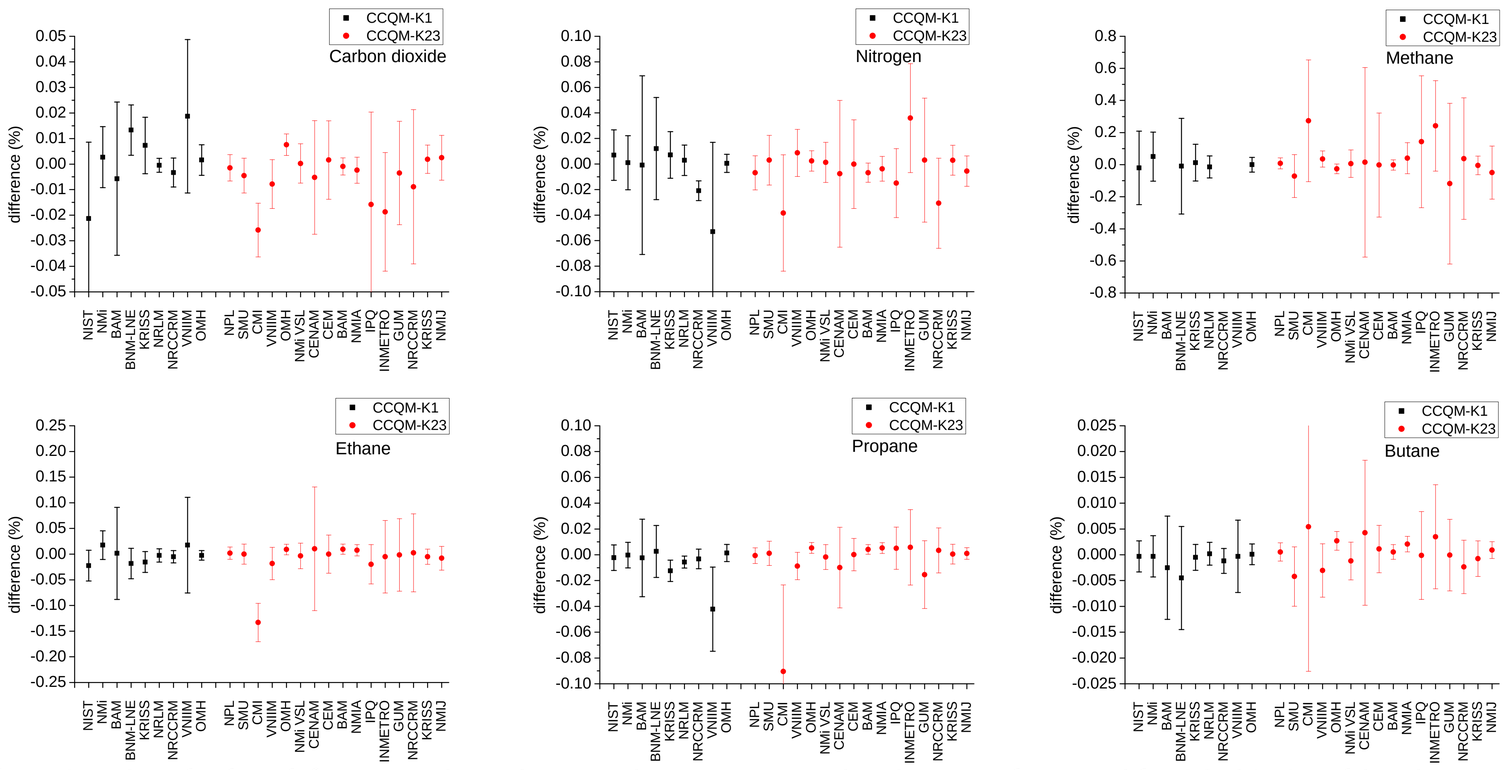
Abstract

Metrological services related to energy gases have been supported by the programme of key comparisons of the CCQM-GAWG since its conception in 1993. Most of the key comparisons have been performed on natural gas composition measurement, which is key to the calculation of natural gas properties. Furthermore, comparisons have been organised on sulphur-containing components, non-conventional energy gases (refinery gas, LPG) and on the liquid injection in the preparation of Primary Standard gas Mixtures. The use of non-conventional and renewable energy gases requires the use of spectroscopic techniques and dynamic primary gas standards for providing services in these areas to meet industry demand in assessing fuel quality with established specifications. These emerging challenges concern especially the measurement of the concentrations of impurities, such as silicon and halogenated compounds in biomethane and upgraded biogas and many others.

Equivalence of national natural gas standards

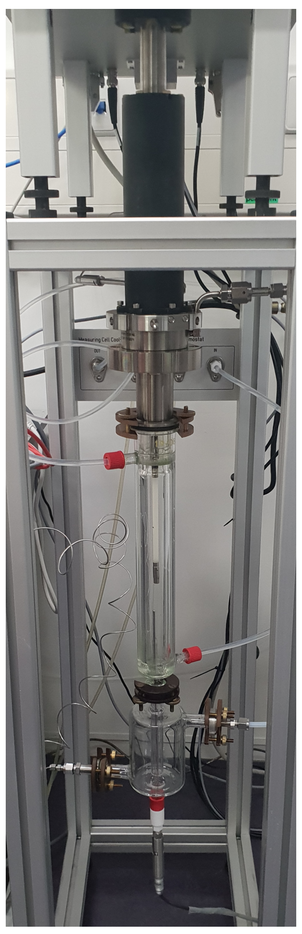
The degrees-of-equivalence of are shown for the amount fractions of six components in type II natural gas in CCQM-K1 and CCQM-K23. Over the years, the number of NMIs providing services has increased. The measurement capabilities are very similar.



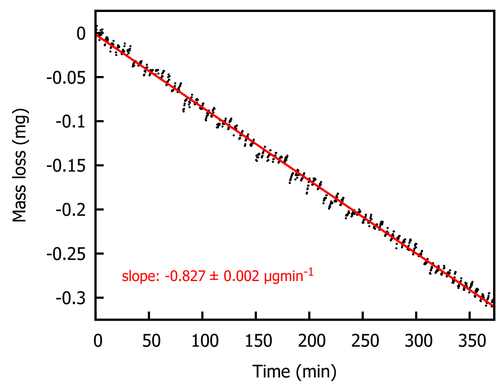
The KCRV is calculated from gravimetric gas mixture preparation in accordance with ISO 6142, taking into account the effects of, e.g., molar masses and the purity of the materials.

Reactive components in biogas and biomethane

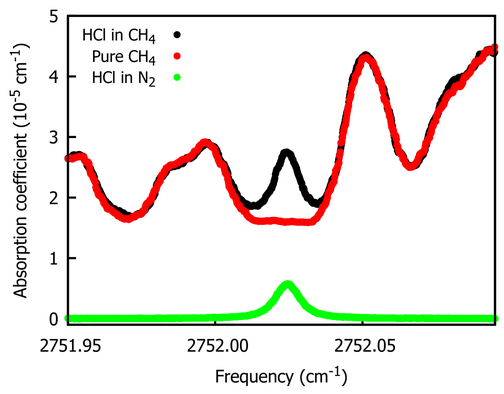
Gas standards for ammonia (NH_3), hydrogen chloride (HCl) and hydrogen fluoride (HF) require dynamic gravimetric preparation techniques and laser spectroscopy to establish metrological traceability at the required amount fraction levels. All molecules appear in the European biomethane specification (EN 16723).



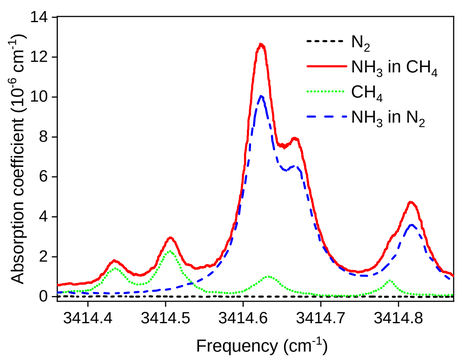
Primary gravimetric dynamic gas standard based on permeation



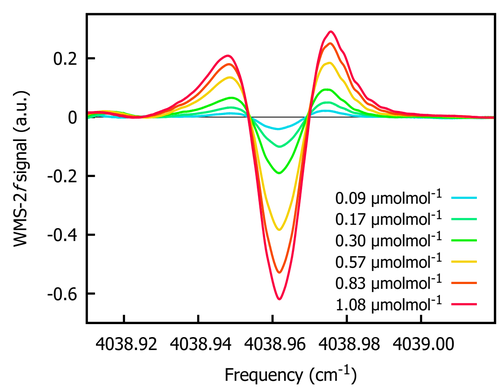
Permeation rate of HCl at 39.3 °C



Measurements of CH_4 background (red), HCl in N_2 (green) and HCl in CH_4 (black) using CRDS and OPO light source



Measurement of the NH_3 in CH_4



Background corrected WMS-2f spectra of HF in CH_4 collected at 100 mbar in the ppb and low ppm range

Acknowledgement

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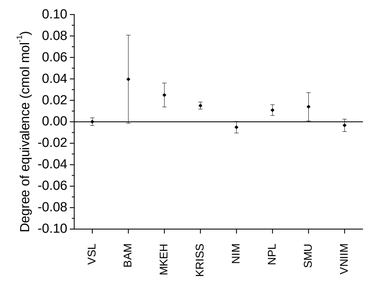
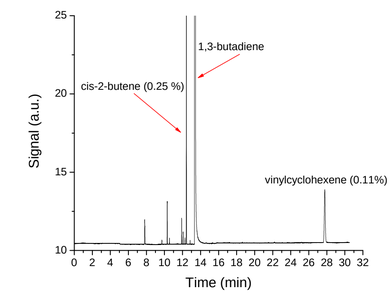
Refinery gas

One of the ways to diversify the gas supply is to use energy gases from industrial processes, such as refinery, coke oven, blast furnace or synthesis gas. One key comparison (CCQM-K77) has been organised dedicated to the total composition of refinery gas.



One of the challenging amount fractions is that of 1,3-butadiene which is affected by the formation of dimers.

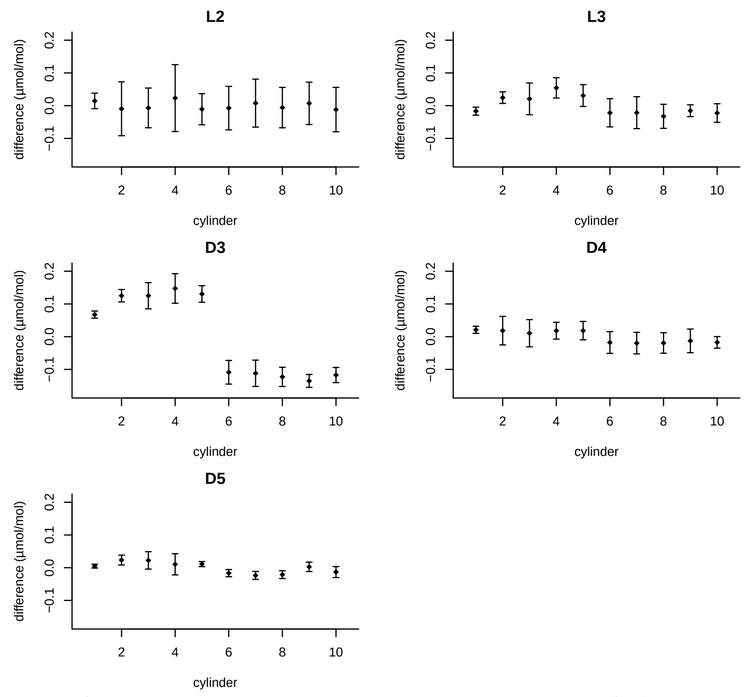


The chromatogram from the purity analysis shows clearly the presence of vinylcyclohexene (one of the possible dimers).

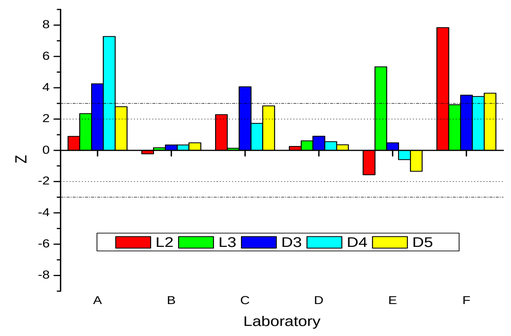
The KCRV is obtained as in the natural gas key comparisons.

Siloxanes in methane

Siloxanes appear in biomethane and form SiO_2-deposits in the gas transmission infrastructure. Hence, the silicon concentration is part of the biomethane specification EN 16723. Siloxanes are reactive components, showing reactions among themselves and with (metal) surfaces. A suite of 10 gas mixtures has been prepared containing 5 of the most volatile siloxanes (L2, L3, D3, D4, and D5) using gravimetric dilution from multi-component parents to study cylinder treatment effects.



Six of the mixtures have been used in a proficiency test.



The assigned values were obtained from analysis using freshly prepared traceable gas standards. Z-scores were used to assess the performance of the labs.