Metrology Labs Measure Primary Gas Moisture Standards
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It took three years for EURAMET (European Association of National Metrology Institutes) to finally complete the all-important moisture standards, which were compared across four-countries and five metrology labs who establishing a needed baseline standard. Participating labs are shown in Table 1. The purpose of this study was to both establish the much-needed baseline and to determine whether any of the different methods used by the participating labs displayed any measurement aberrations.

Abbreviation	Participant	Country
NIST	National Institute of Standards and Technology	US
NPL-GMTA	National Physical Laboratory Gas Metrology and Trace Analysis Group	UK
NPL-TH	National Physical Laboratory Temperature and Humidity Group	UK
PTB	Physikalisch-Technische Bundesanstalt	Germany
NMIJ	National Metrology Institute of Japan	Japan

Table 1. Participating metrology labs

Typically, there are two approaches that one can take when attempting to make such a comparison. (1) comparing the measuring capabilities of the various labs or (2) comparing the labs capability to provide accurate and stable standards. In the former, the coordinating laboratory would provide a cylinder to be measured by the participating labs and the results compared. In the latter, each of the participating labs would prepare a gas standard and ship it to the coordinating lab for measurement and comparison.

However, for moisture standards, neither of these approaches will work because this process involves dynamic standards which cannot be "shipped in a cylinder." Dr. Graham Leggett, Product Manager / Environmental Division, of Tiger Optics, explains that, "Due to the chemical properties of water, it is not possible to produce accurate standards that can be stored in gas cylinders. The only way in which standards for water vapor can be produced is using a dynamic method. For example, NPL (UK) uses a gravimetric method involving a permeation tube and an associated dilution system. Such dynamic systems are complex and large. They are permanent installations that cannot be transported for comparison purposes."

The next question for EURAMET, in designing the study, was, which analyzer to use. The analyzer would need to meet accuracy requirements over a wide dynamic range (10 ppb to 2000 ppb over the range 10 – 2000 nmol/mol.) EURAMET choose the Tiger Optics LaserTrace + analyzer with the back-up compact HALO instrument, also from Tiger Optics, as the

instrument to conduct the study. The LaserTrace was well known to EURAMET from previous studies comparing instruments from various vendors.

The LaserTrace+ uses CRDS technology. As the EURAMET report explains,

"CRDS operates by tuning a laser source to the unique molecular fingerprint of the target compound. By measuring the time it takes the light to "ring-down", an accurate molecular count is received in milliseconds. A continuous wave diode laser emits a directed beam of light energy through an ultrahigh reflective mirror into the absorption cell (cavity). The light reflects back and forward between two ultra-high reflective mirrors multiple times. When the photodiode detects a preset level of light energy, the light source is shuttered or diverted from the cavity. On each successive pass, a small amount of light or ring-down signal emits through the second mirror and is sensed by the light detector. Once the light 'rings down', the detector achieves a point of zero light energy in milliseconds, and the measurement is complete."

Methodologies for the moisture standards differed at the participating labs. The NIST facility utilized a low frost point generator (LFPG) that saturates an inert gas stream with water vapor by flowing the gas over a plane surface of isothermal ice at known temperature and pressure. By ensuring that the inlet gas stream has reached thermodynamic equilibrium with the generator saturator, the mole fraction of water vapor in the gas phase can be calculated.

The NPL-GMTA trace water vapor facility generated an adjustable level of trace water (between 2 – 2000 nmol/mol) by using measurements of mass loss from a permeation device coupled with a dilution system based on an array of flow orifices. The NPL-TH used a low frost point generator (LFG). The LFG is a primary standard of dew-point and frost-point temperature in the range from +20 °C to –90 °C (and experimentally down to -100 °C). Realization of the frost point is by saturation of air at selected controlled temperatures, and controlled pressure. The value of the generated frost point was ascertained from measurements made using platinum resistance thermometers .

The PTB lab generated volume fractions of water vapor with a coulometric trace humidity generator (CTHG). The CTHG operates on the principle of Faraday's law of electrolysis and is based on the processes of generating a zero gas stream, generating a defined quantity of H_2 and O_2, drying the gas flow from the electrolysis cell, and recombining the generated hydrogen and oxygen back into H_2O on a Pt/Pd-catalyst.

The NMIJ lab generated the trace water vapor in N_2 using a magnetic suspension balance/diffusion-tube humidity generator (MSB/DTG) developed at NMIJ. The generation chamber of the DTG was attached to the bottom of the MSB. The MSB consisted of magnetic suspension coupling and an analytical balance. A diffusion cell in the generation chamber was magnetically suspended from the measuring load of the magnetic suspension coupling without contact with the analytical balance using the permanent magnet and the electromagnet. The water vapor from the diffusion cell was mixed with the dry nitrogen. The evaporation rates of water vapor from the diffusion cell was measured as the mass-change rates of the diffusion cell using the MSB. The total flow rates of the dry nitrogen were accurately and precisely measured using a flow measurement system.

Results plotted in the graph below (Figure 1) show that the measurements deviated less than 2 percent over the course of the three-year, multinational inter-laboratory comparison, thereby permitting the facilities to establish a baseline for future work. It demonstrates

comparability of standards produced by the participating laboratories as well as validates the performance of the Lasertrace+ instrument.

Full details of the inter-comparison can be found in *EURAMET 1002: International comparability in measurements of trace water vapour*, P J Brewer, M J T Milton, P M Harris, S A Bell, M Stevens, G Scace, H Abe and P Mackrodt, published in June 2011. The report can be downloaded via the following links: http://publications.npl.co.uk/dbtwwpd/exec/dbtwpub.dll?&QB0=AND&QF0=ID&QI0=%205834%20&TN=NPLPUBS&RF=WFullRecordDetails&DL=0&RL=0&NP=4&AC=QBE_QUERY

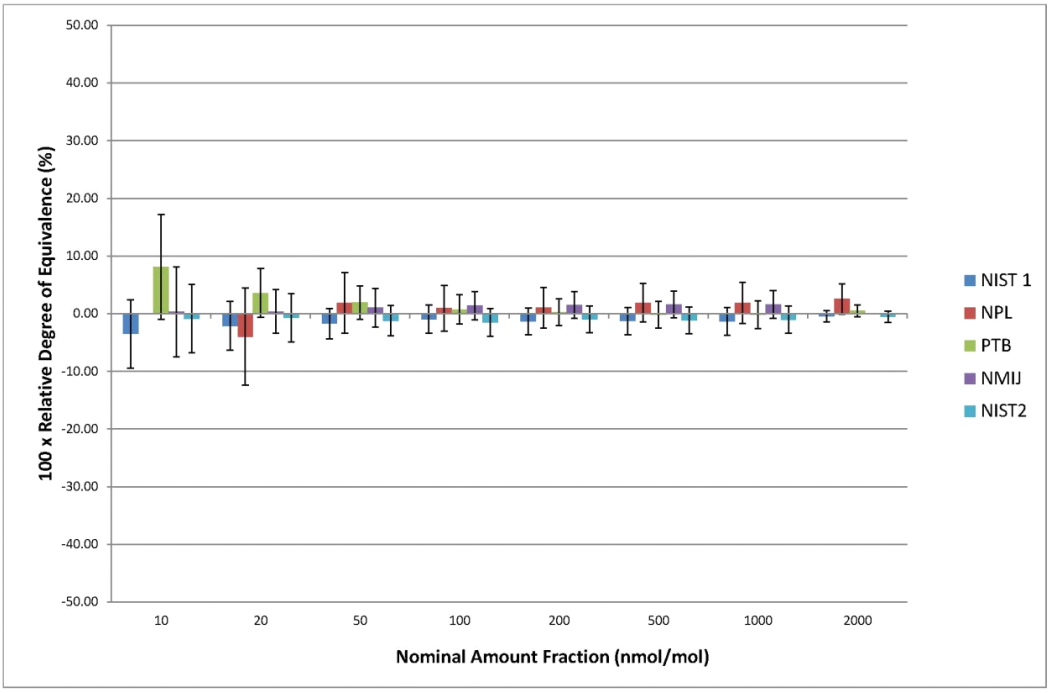

Figure 1. Relative degree of equivalence for each NMI using travelling standard 1 at each amount fraction. Source: EURAMET 1002: "International comparability in measurements of trace water vapour," http://publications.npl.co.uk/dbtw-wpd/exec/dbtwpub.dll?&QB0=AND&QF0=ID&QI0=%205834%20&TN=NPLPUBS&RF=WFullRecordDetails&DL=0&RL=0&NP=4&AC=QBE_QUERY