

Status of NIST Methane SRMs and Standards

J. Rhoderick

NIST, Gas Metrology Group, CSTL, NIST, 100 Bureau Drive, Gaithersburg, MD 20899; 301-975-3937, Fax: 301-977-8392, E-mail: George.Rhoderick@nist.gov

Methane is an important component in the greenhouse gas arena. The Gas Metrology Group at the National Institute of Standards and Technology (NIST) has provided methane in air Standard Reference Materials (SRMs) for over 30 years. Three of these SRMs widely bracket the amount-of-substance fraction (concentration) of methane in the atmosphere; 10 $\mu\text{mol/mol}$ (ppm), 4 ppm and 1 ppm. Much work has been done over the past 10 years to insure the accuracy of both these SRMs and the Gas Metrology Groups internal primary standards (PSMs). In the past five years, the Gas Metrology Group at NIST has developed PSMs to bracket the atmospheric concentration level. A suite of 8 PSMs covering a range from 1.00 ppm to 2.50 ppm were prepared. A linear regression from the analysis of these PSMs yields an average residual of 0.10 % between the gravimetric and analyzed values. One of the major improvements in the preparation of the PSMs has been the ability to analyze the balance air used. Improvements in the instrument and measurement techniques has made it possible to determine trace methane in the matrix air to as low as 0.001 ppm, and we continue to drive the detection limit lower. The international Consultative Committee for Amount of Substance-Metrology in Chemistry (CCQM) conducted a pilot comparison, P-41, for Greenhouse Gases which included methane. This intercomparison between other National Measurement Institutes (NMIs) has shown that there is very good agreement between the NMI's reported methane values at the 1.8 ppm level. The NMI Van Swinden Laboratorium B.V. in Delft, the Netherlands, prepared mixtures and assigned a methane value to each mixture. Each of 9 participating NMIs and 2 WMO labs, NOAA and CSIRO-AR, received a methane mixture, analyzed, and reported a value for the methane. The NIST reported value agreed to within -0.30 % of the reference value. After reassessment of the NIST data from the analysis of its sample mixture from NMI, including impurities of methane in the air balance gas of its primary standard mixtures (PSMs), NIST agrees with two other NMIs to within 0.05 % relative to the reference value.

Table 1. Results of CCQM P-41 Methane Comparison

Laboratory	Nmi Reference Value, ppm	Nmi Reference Uncertainty, ppm	Laboratory Value, ppm	Laboratory Uncertainty, ppm	Difference, ppm (Lab - Nmi)
IMGC	1.814	0.004	1.855	0.074	0.041
CENAM	1.801	0.004	1.871	0.102	0.07
CEM	1.792	0.004	1.796	0.026	0.004
NOAA ^a (WMO)	1.801	0.004	1.769	0.001	-0.031
NIST	1.801	0.004	1.796	0.010	-0.005
NIST^b	1.801	0.004	1.802	0.005	0.0009
KRISS	1.800	0.004	1.792	0.002	-0.008
CSIRO-AR (WMO)	1.801	0.004	1.771	No Uncertainty	-0.03
NMIJ	1.801	0.004	1.780	0.009	-0.021
Nmi VSL	1.803	0.004	1.802	0.030	-0.038
CSIRO-NML	1.799	0.004	1.810	0.020	0.011
NPL	1.803	0.004	1.802	0.018	-0.001

^a Uncertainty is relative to the WMO scale.

^b NIST reassessed value.