Gas Sensing Metrology Group Greenhouse Gas/Climate Change Program

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How could Gas Metrology Group Best Support Atmospheric Community

- prepare new suites of ambient level standards for CO_2, CH_4, N_2O, CO, SF_6, halocarbons

- develop SRMs containing dry whole atmospheric air to support the measurement community

- WMO was in process of becoming member of the Consultative Committee on the Quantity of Material – Metrology in Chemistry (CCQM)

  - NOAA would eventually become WMO representative as they maintain the WMO calibration scales for CO_2, CH_4, N_2O

  - **NIST should support NOAA through comparison of standards**

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PSM and SRM Development

- develop new gravimetric primary standard mixture (PSM) suites with very low uncertainties; 0.01 % to 0.05 % relative to meet WMO Data Quality Objectives (DQO) - CO_2, CH_4, N_2O, CO, SF_6

- collaborate with atmospheric research laboratories to develop real air SRMs

- use new PSM suites to certify real air samples as SRMs

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Important Considerations in PSM Gravimetric Preparation

Uncertainty sources

- the component (ie: CO_2, CH_4) impurity in balance air
- uncertainty in the oxygen in balance air (curcial to a low uncertainty in the molecular mass of the balance air)
-

Sources of losses

- transfer lines in manifold (discovered w/ CO_2)
- losses of compounds to cylinder walls (CO_2)
- flow rate when transferring gases (discovered w/ N_2O)

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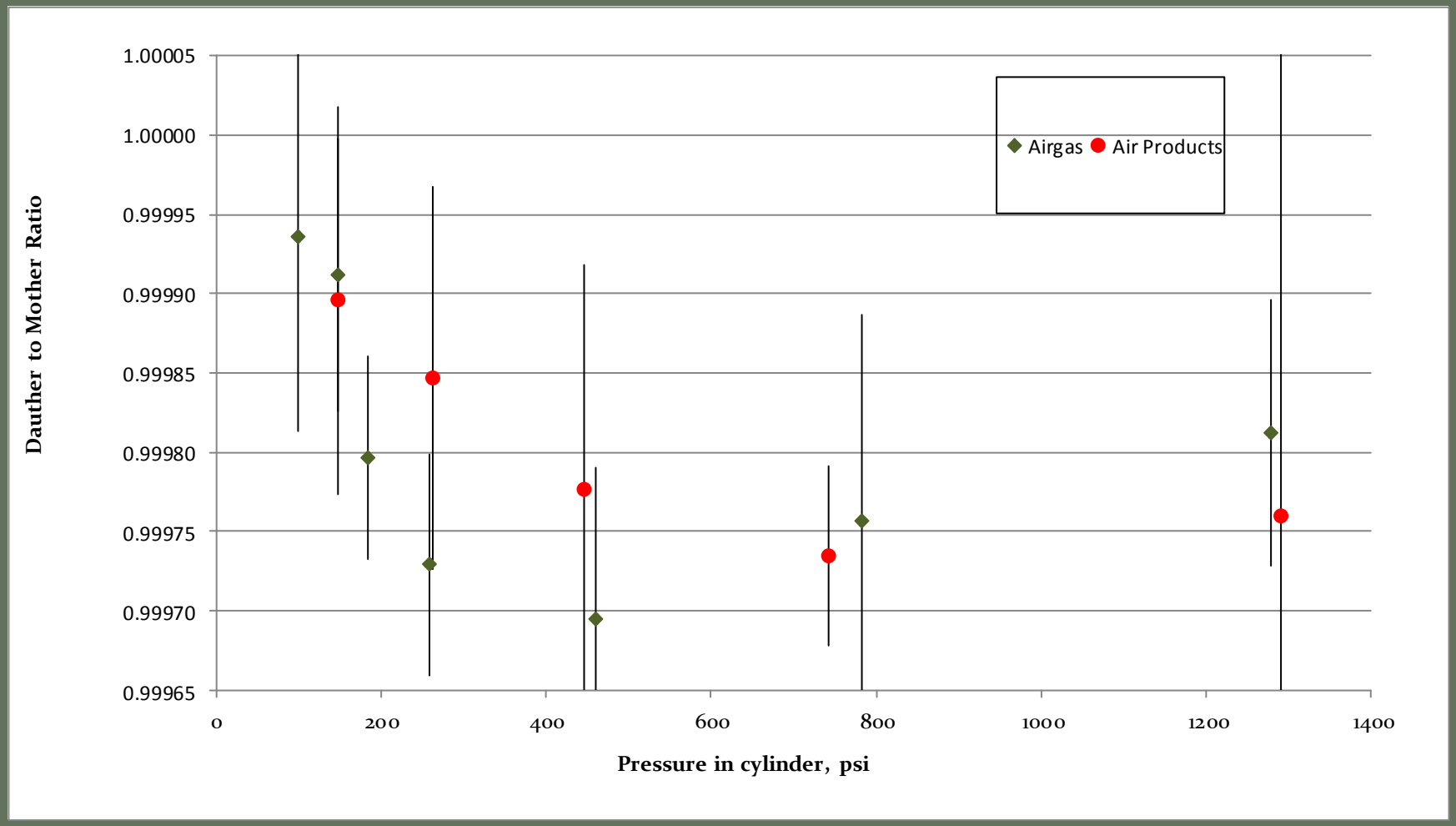
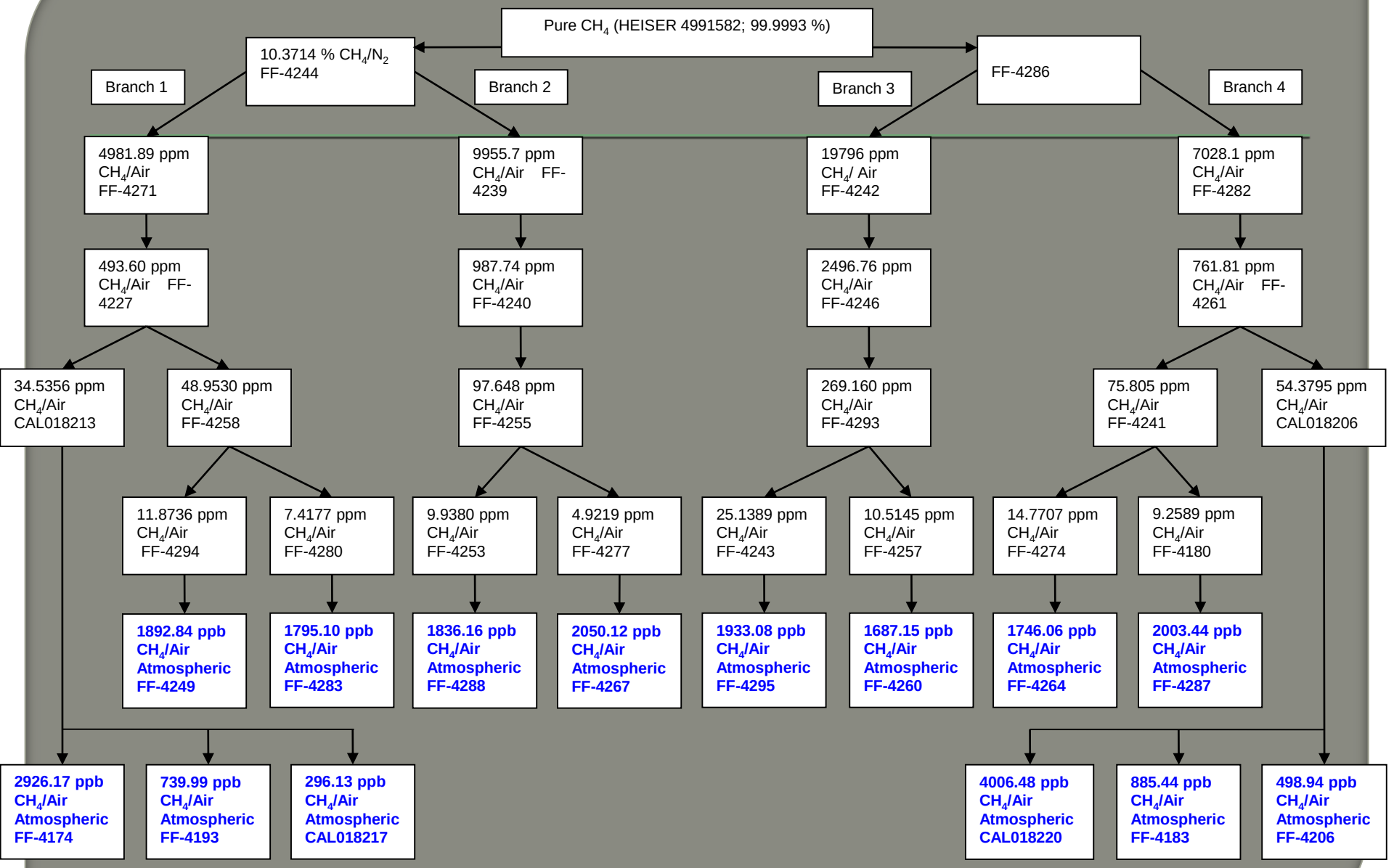
CO_2 Loss Studies – Daughter/Mother Test



Methane PSM Preparation Scheme



Analysis of NIST PSMs by other Labs

	NIST Grav Value	NOAA	SIO (Scripps)	KRISS
CH_4	1836.16 ± 0.75 nmol/mol	1833.62 ± 0.75 Δ = - 2.54 **(0.14%)**		1838.5 ± 0.9 Δ = + 2.3 **(0.13%)**
N_2O	317.95 ± 0.05 nmol/mol	318.02 ± 0.10 Δ = + 0.07 **(0.02%)**	317.75 ± 0.16 Δ = - 0.20 **(0.06%)**	
CO_2	Future			
CO	Future			
SF_6	Future			

Standard uncertainties at 1σ (coverage factor *k*=1)

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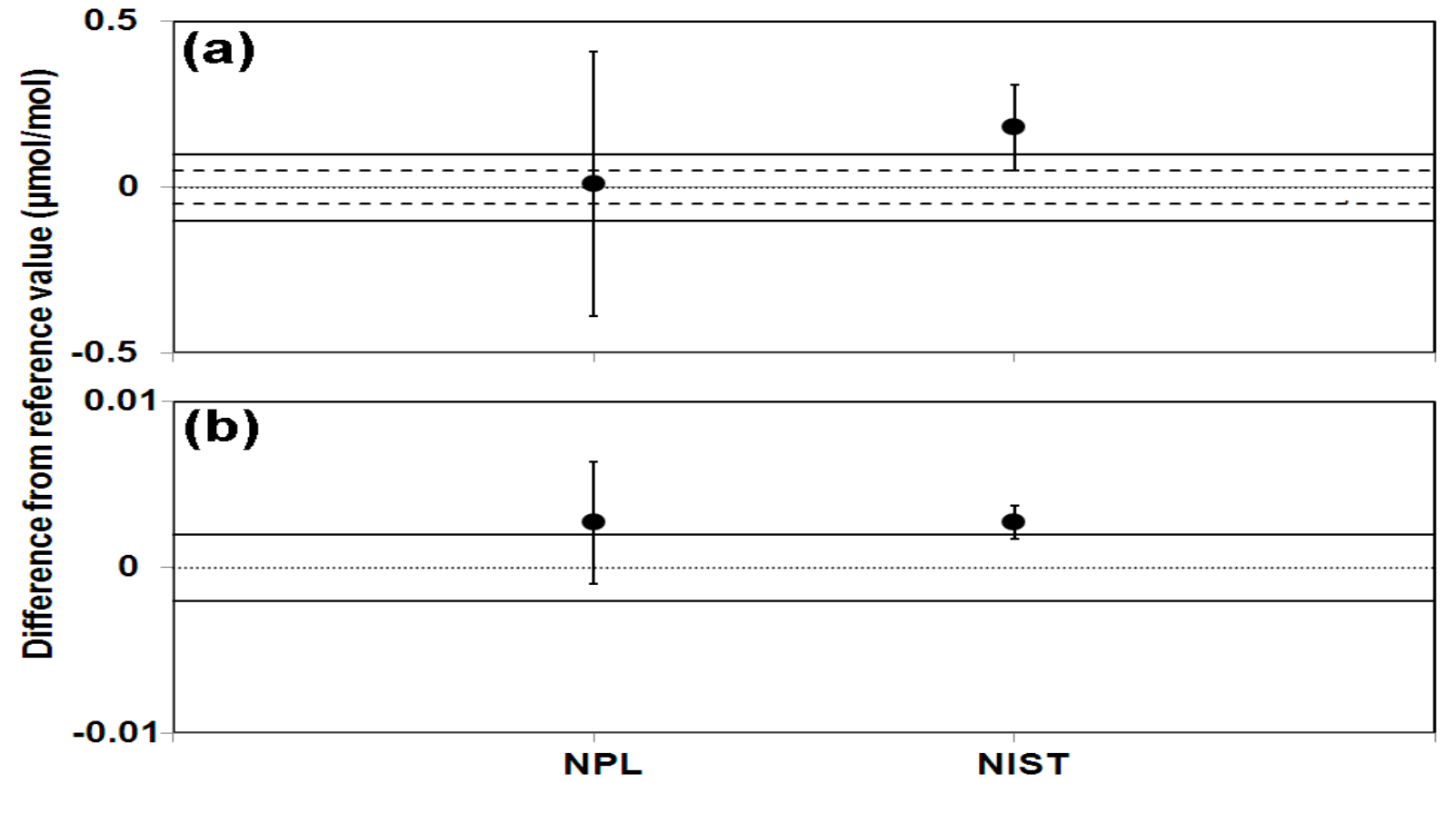
NIST, NOAA, NPL Comparisons

Analysis of dry whole air sample: a) CO_2, b) CH_4

NIST and NPL points as a difference from the NOAA value



SRM 1720 Northern Hemisphere Air

- Samples pumped (February 2010) by NOAA's Global Monitoring Division, Earth Science Research Laboratory
- Sampling facility at Niwot Ridge, Colorado

February 9, 2010

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Just a Perspective

Maryland, February 6, 2010

Maryland, February 12, 2010

SRM 1721 Southern Hemisphere Air

- Samples pumped by the National Institute of Water and Atmospheric Research (NIWA) in Wellington, New Zealand
- National Institute Research Station at Baring Head, New Zealand (south end of North Island)

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Instrumentation for Measurement of SRM 1720 samples

	NIST	NOAA
CO_2	Picarro CRDS GC/FID/Methanation	NDIR
CH_4	GC/FID	GC/FID
N_2O	LGR off axis ICOS (4th gen. cavity enhanced absorption spec)	GC/ECD
CO	LGR	
SF_6	GC/ECD	GC/ECD

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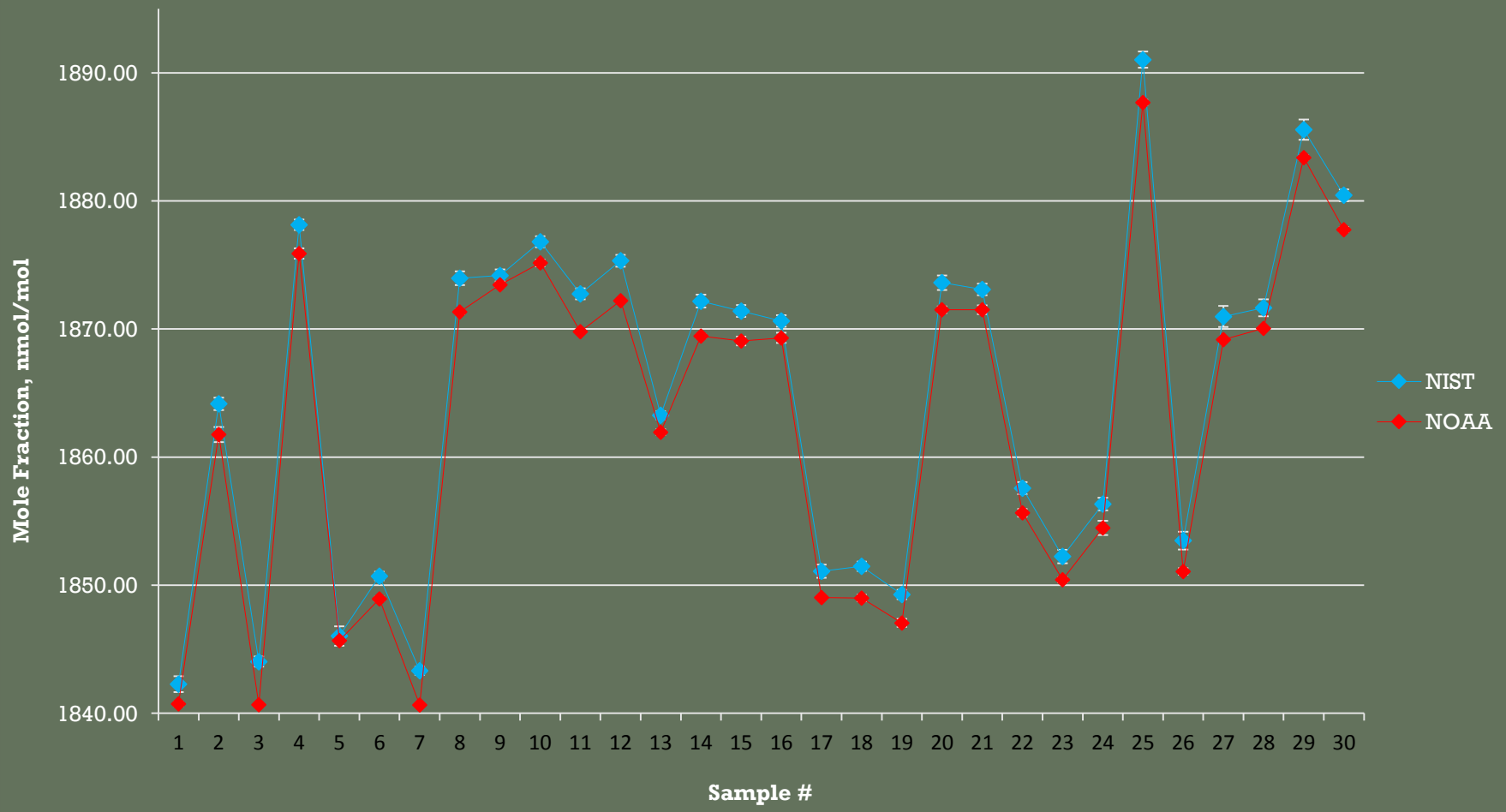
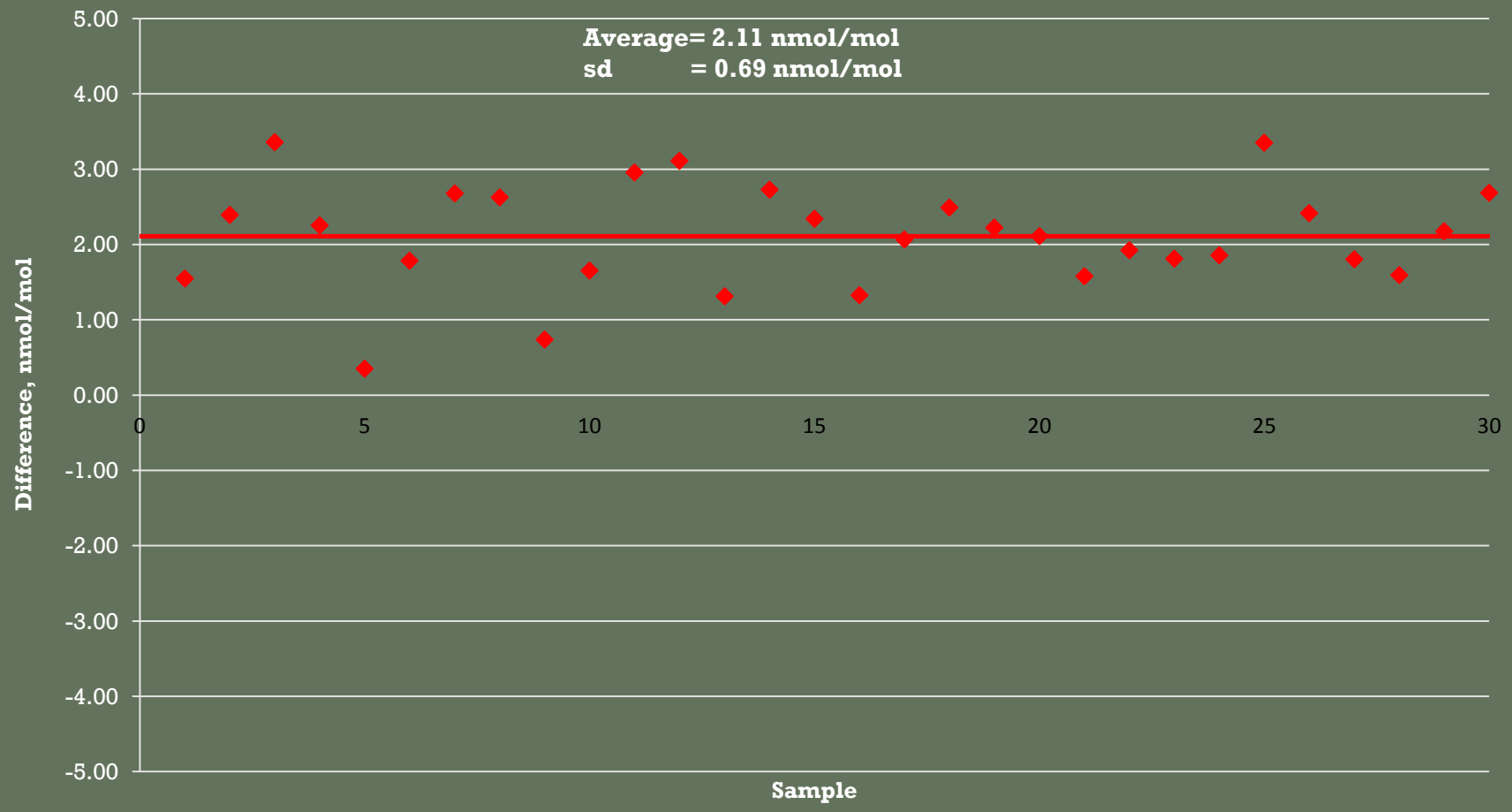
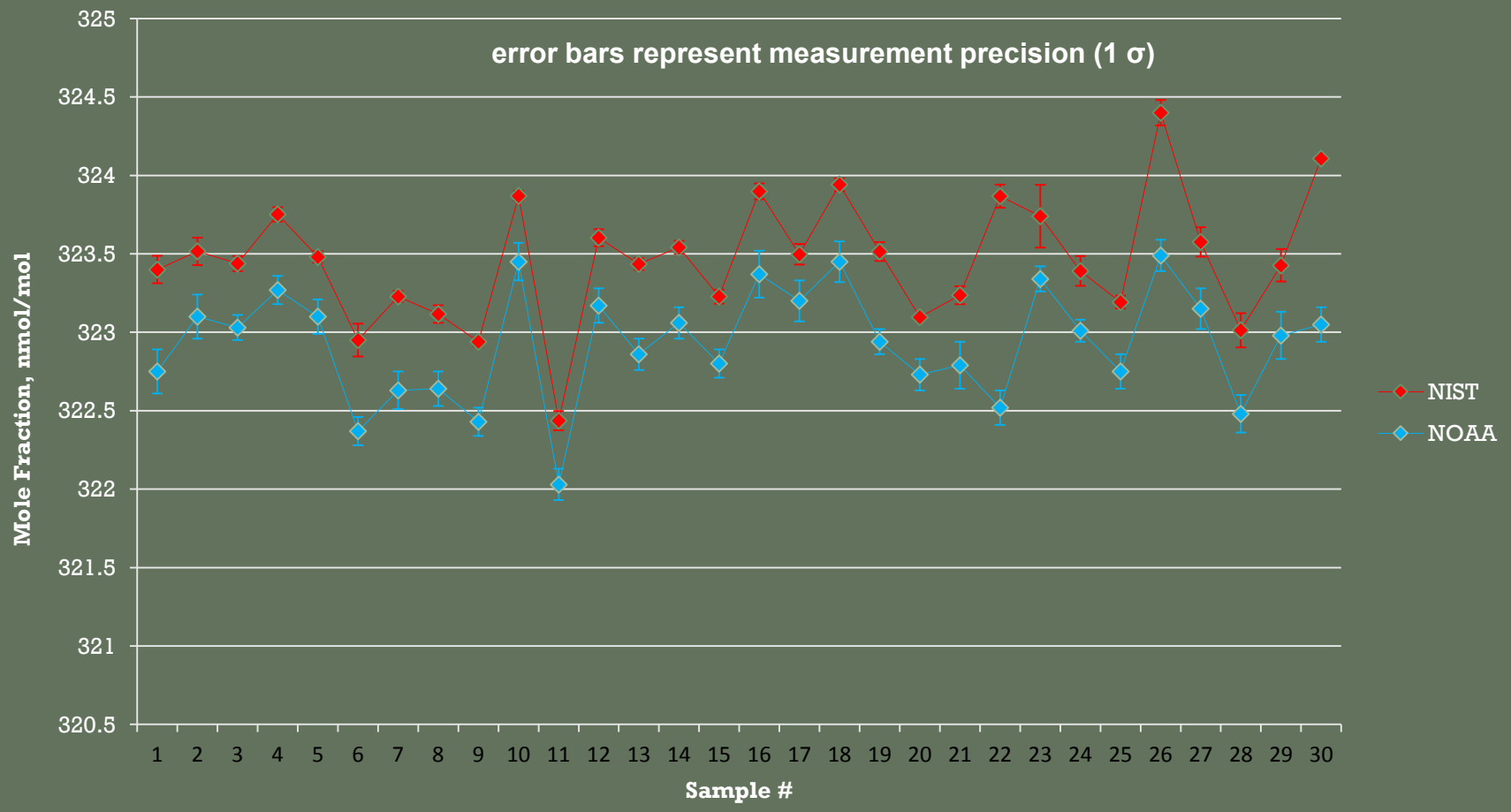
SRM 1720: Methane



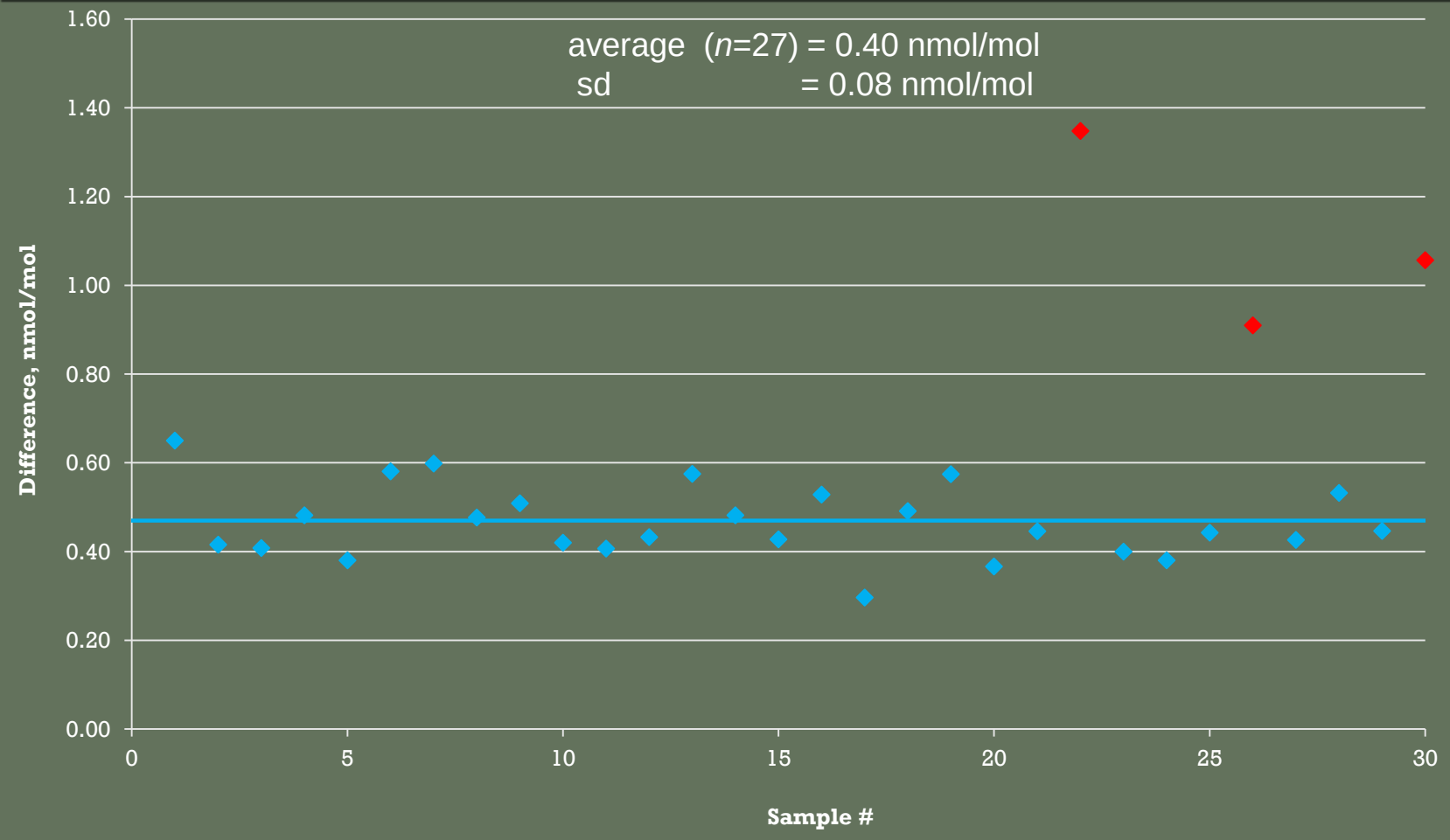
SRM 1720: Methane



SRM 1720: N_2O

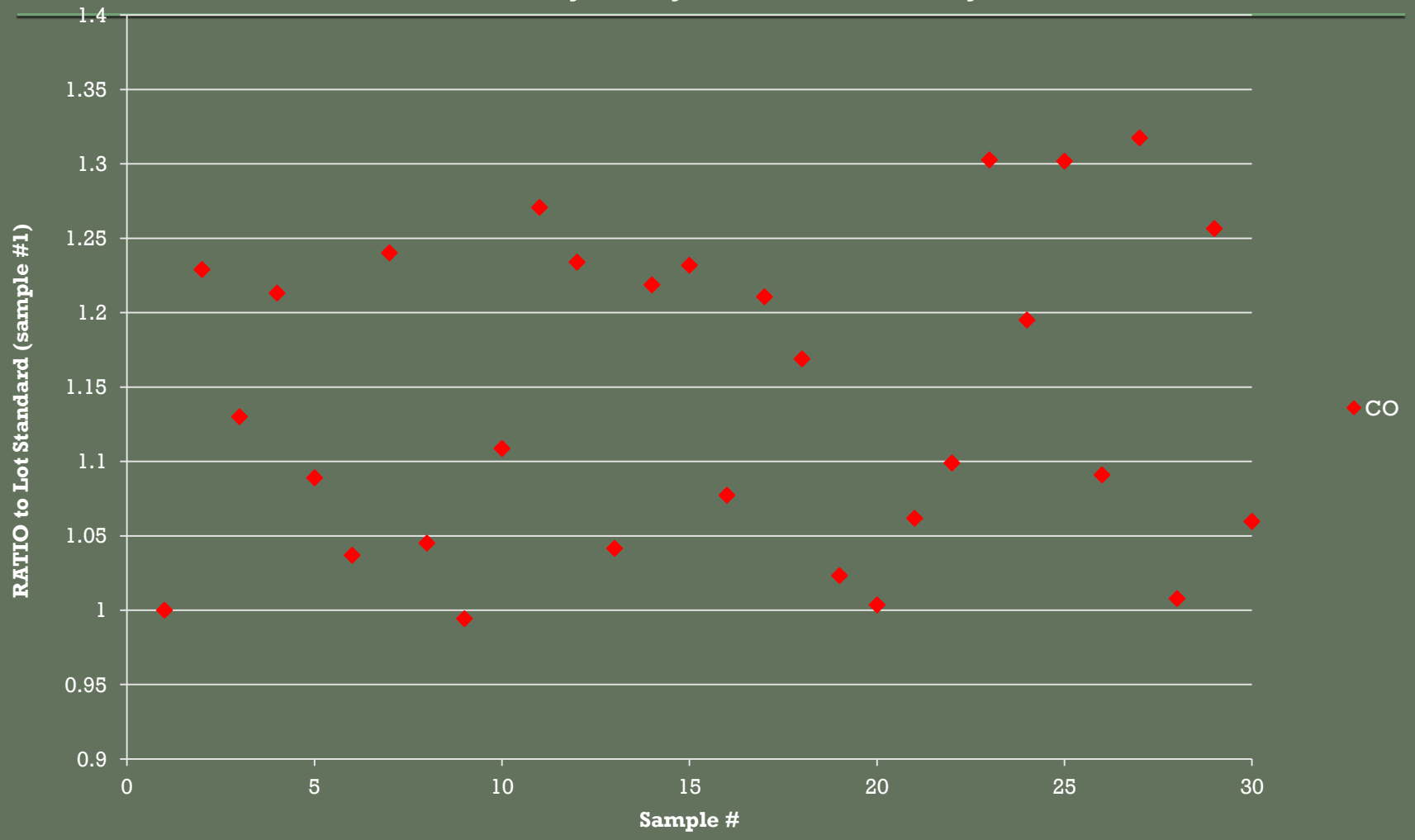

error bars represent measurement precision (1 σ)
Mole Fraction, nmol/mol
325
324.5
324
323.5
323
322.5
322
321.5
321
320.5
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
Sample #
NIST
NOAA

SRM 1720: N_2O


average (n=27) = 0.40 nmol/mol
sd = 0.08 nmol/mol
Difference, nmol/mol
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0
5
10
15
20
25
30
Sample #

SRM 1720 : CO

Results from analysis by LGR – CEAS system



Projected Typical Certified Values for SRM 1720

	NIST, Amount Fraction[a]	NOAA Amount Fraction[a]	WMO Data Quality Objective[b]
CO_2	394. xx ± 0.10 µmol/mol	394.08 ± 0.20 µmol/mol	± 0.1 µmol/mol
CH_4	1878.1 ± 1.0 nmol/mol	1875.9 ± 1.5 nmol/mol	± 2 nmol/mol
N_2O	323.52 ± 0.20 nmol/mol	323.10 ± 1.0 nmol/mol	± 0.1 nmol/mol
CO	≈ 200 ± 4 nmol/mol (vary 35 % sample to sample)		± 2 nmol/mol
SF_6	≈ 7 ± 0.04 pmol/mol	7.16 ± 0.04 pmol/mol	± 0.02 pmol/mol

[a] Expanded uncertainty at *k*=2 coverage factor, 95 % confidence interval.
[b] Standard uncertainty at 1 σ (*k*=1 coverage factor).

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Additional SRM and certified mixture Developments

- SRM 1718 : 1 μmol/mol N_2O in synthetic air

- SRM 1722: Ambient halocarbons in dry, whole air (candidates collected at Niwot Ridge, CO)
  - CFC-12, CFC-11, CFC-113, HFC-134a, HCFC-22, HCFC-142b and also considering CFC-114, HFC-152a, HCFC-141b, HCFC-143

- Certification of working standards for MEGA Cities – CO_2 and CH_4; CO probably as informational value at this time

Additional Standards Support

- WMO/GAW-Volatile Organic Compounds (VOC)
  - Central Calibration Laboratory (CCL) for monoterpenes
  - support the CCL, National Physical Laboratory (NPL, UK), for hydrocarbons
- WMO/GAW/CCL for ground level ozone