Comparison of Primary Standards/Scales of Key Greenhouse Gases between NOAA and NIST

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NIST

NOAA

Why and How could Gas Metrology Group Best Support Atmospheric Community

- In 2009 congress task NIST to support climate change research covering many facets

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

- develop SRMs containing real 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**

Historical Data for CH_4 SRM Lot Standards

SRM #	Y eval ppm	u Yeval ppm[a]	Cert. Conc. ppm[b]	Diff, ppm	% Diff	Years since Certified	Cert Year
1659							
11-1-CL	9.454	0.002	9.505 ± 0.080	-0.051	-0.53	30.4	1981
11-55-D	**9.718**	**0.002**	**9.764 ± 0.080**	**-0.046**	**-0.47**	**27.8**	**1983**
11-1-EL	9.577	0.002	9.584 ± 0.030	-0.007	-0.07	20.3	1991
11-FL-01	9.838	0.002	9.846 ± 0.020	-0.008	-0.08	14.0	1999
11-GL-01	9.865	0.002	9.863 ± 0.014	0.002	0.02	4.0	2003
1658							
12-1-B	0.9723	0.0001	0.9713 ± 0.010	0.0010	0.10	32.5	1979
12-11-C	0.9816	0.0001	0.9820 ± 0.010	-0.0004	-0.04	30.4	1981
12-5-D	0.9103	0.0001	0.9097 ± 0.010	0.0006	0.07	27.8	1983
12-FL-01	1.0770	0.0001	1.0787 ± 0.0022	-0.0017	-0.16	12.2	1999
1660							
13-8-C	3.848	0.001	3.863 ± 0.039	-0.015	-0.39	30.4	1981
13-1-D	3.893	0.001	3.890 ± 0.039	0.002	0.06	27.8	1983
13-1-EL	3.943	0.001	3.936 ± 0.008	0.007	0.17	16.0	1995

[a]Standard uncertainties at the 68 % confidence interval, k=1.

[b]Expanded uncertainties at the 95 % confidence interval, k=2.

NIST

Historical 1 ppm CH_4 SRM Recertification Data

Sample #	Original Certified Concentration	Reanalyzed Concentration	Difference (Reanal-Cert)	Date Certified	Date Reanalyzed	Years
SRM 1658 : 1 µmol/mol CH4 in Air						
12-11-A	0.951 ± 0.010	0.952 ± 0.010	0.001	9/16/1976	2/12/1979	1.5
12-11-A	0.951 ± 0.010	0.952 ± 0.010	0.001	9/16/1976	1/30/1980	3.4
12-23-A	0.951 ± 0.010	0.949 ± 0.010	-0.002	9/16/1976	3/31/1978	2.4
12-27-A	0.951 ± 0.010	0.951 ± 0.010	0.000	9/16/1976	1/30/1981	4.4
12-12-A	0.951 ± 0.010	0.950 ± 0.010	-0.001	9/16/1976	1/30/1981	4.4
12-14-A	0.951 ± 0.010	0.952 ± 0.010	0.001	9/16/1976	3/1/1983	6.5
12-08-A	0.951 ± 0.010	0.953 ± 0.010	0.002	9/16/1976	3/1/1983	6.5
12-22-A	0.951 ± 0.010	0.950 ± 0.010	-0.001	9/16/1976	8/15/1983	6.9
12-18-A	0.951 ± 0.010	0.952 ± 0.010	0.001	9/16/1976	3/11/1988	11.5
12-5-C	0.982 ± 0.010	0.982 ± 0.010	0.000	2/25/1981	3/20/1985	4.1
12-14-C	0.982 ± 0.010	0.985 ± 0.010	0.003	2/25/1981	3/11/1988	7.0
12-29-C	0.982 ± 0.010	0.984 ± 0.010	0.002	2/25/1981	12/22/1998	17.8
12-6-D	0.913 ± 0.010	0.910 ± 0.010	-0.003	10/26/1983	7/10/1995	11.7
12-6-D	0.913 ± 0.010	0.912 ± 0.010	-0.001	10/23/1983	12/7/1998	15.1
12-6-D	0.913 ± 0.010	0.913 ± 0.010	0.000	10/26/1983	7/17/2006	22.7
12-25-D	0.913 ± 0.010	0.911 ± 0.010	-0.002	10/26/1983	1/7/1998	14.2
12-24-D	0.913 ± 0.010	0.912 ± 0.010	-0.001	10/23/1983	12/11/1998	15.1
12-24-D	0.913 ± 0.010	0.914 ± 0.010	0.001	10/26/1983	6/12/2006	22.6

NIST

Historical 10 ppm CH_4 SRM Recertification Data

Sample #	Original Certified Concentration	Reanalyzed Concentration	Difference (Reanal-Cert)	Date Certified	Date Reanalyzed	Years
SRM 1659 : 10 µmol/mol CH4 in Air						
11-5-A	9.43 ± 0.10	9.44 ± 0.10	0.01	9/16/1976	3/31/1978	1.5
11-5-A	9.43 ± 0.10	9.42 ± 0.10	-0.01	9/16/1976	1/28/1980	3.4
11-24-A	**9.43 ± 0.10**	**9.37 ± 0.10**	**-0.06**	**9/16/1976**	**6/7/1979**	**2.8**
11-15-A	9.43 ± 0.10	9.39 ± 0.10	-0.04	9/16/1976	1/28/1980	3.4
11-8-A	9.43 ± 0.10	9.43 ± 0.10	0.00	9/16/1976	1/23/1981	4.4
11-13-A	9.43 ± 0.10	9.43 ± 0.10	0.02	9/16/1976	1/23/1981	4.4
11-36-B	9.56 ± 0.08	9.56 ± 0.08	0.00	11/16/1979	2/3/1981	1.2
11-36-B	9.56 ± 0.08	9.56 ± 0.08	0.00	11/16/1979	3/19/1984	4.3
11-36-B	9.56 ± 0.08	9.56 ± 0.08	0.00	11/16/1979	2/15/1989	9.3
11-23-B	9.56 ± 0.08	9.56 ± 0.08	0.00	11/16/1979	2/15/1989	9.3
11-52-C	9.52 ± 0.08	9.52 ± 0.08	0.00	2/25/1981	3/20/1985	4.1
11-35-C	9.52 ± 0.08	9.52 ± 0.08	0.00	2/25/1981	3/14/1988	7.1
11-26-C	9.52 ± 0.08	9.52 ± 0.08	0.00	2/25/1981	2/15/1989	8.0
11-48-C	9.52 ± 0.08	9.52 ± 0.08	0.00	2/25/1981	2/15/1989	8.0
11-48-C	9.52 ± 0.08	9.49 ± 0.08	-0.03	2/25/1981	2/22/2000	19.0
11-49-C	9.52 ± 0.08	9.52 ± 0.08	0.00	2/25/1981	2/6/1996	15.0
11-17-D	9.79 ± 0.08	9.80 ± 0.08	0.01	10/26/1983	3/14/1988	4.4
11-17-D	9.79 ± 0.08	9.79 ± 0.08	0.00	10/26/1983	7/10/1995	11.7
11-17-D	9.79 ± 0.08	9.82 ± 0.08	0.03	10/26/1983	12/7/1998	15.1
11-10-D	9.79 ± 0.08	9.78 ± 0.08	-0.01	10/26/1983	2/15/1989	5.3
11-09-D	**9.79 ± 0.08**	**9.73 ± 0.08**	**-0.06**	**10/26/1983**	**5/16/2006**	**22.6**

NIST

Comparison of CH_4 Standards

2000	NIST 1998 PSMs Analyzed Value[a]	NOAA Value (CMDL83 scale)[b]	NOAA Value (NOAA04 scale)[c]
CH_4	1804 ± 7 nmol/mol	1781 ± 1 Δ = - 23 **(- 1.3 %)**	1802 ± 1 Δ = - 2 **(- 0.1%)**
	1664 ± 8 nmol/mol	1639 ± 1 Δ = - 25 **(- 1.5 %)**	1659 ± 1 Δ = - 5 **(- 0.3%)**

[a] Rhoderick, Dorko: ES&T, 2004; NIST1998 PSMs; k=2 (95%).
[b] Based on Rasmussen scale which was based on an NIST 10 ppm SRM (not NOAA scale).
[c] Dlugokencky, Myers, Lang, Masarie, Crotwell, Thoning, Hall, Elkins, Steele: JGR, 2005

2011	NIST 2010 PSM[d] Value	NOAA (NOAA 04 scale)		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%)**

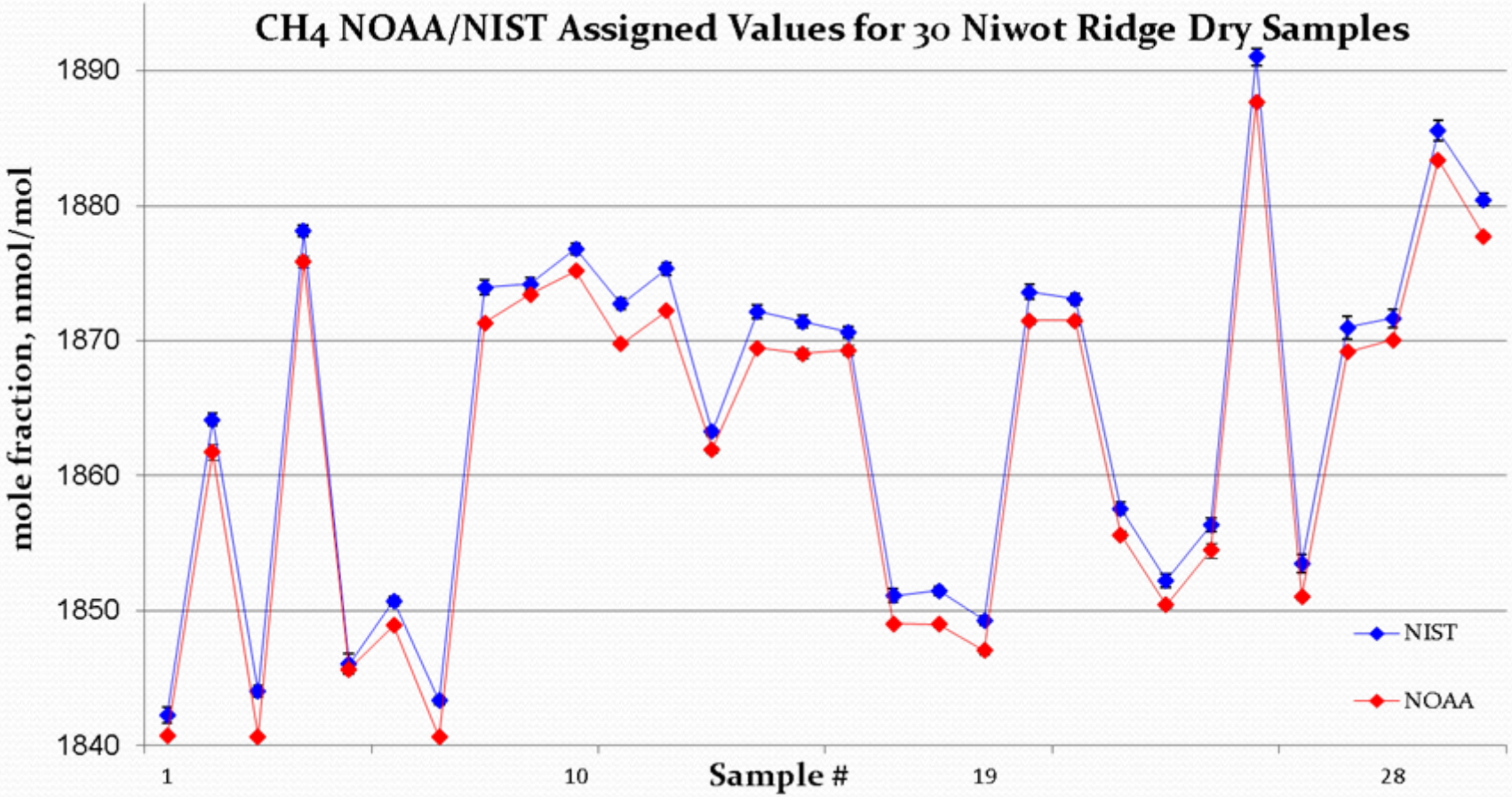
[d] Rhoderick, Carney, Guenther, *Anal Chem*, accepted March 22,2012.
http://dx.doi.org/10.1021/ac300526v

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

NIST

NOAA

SRM 1720: Methane



Analysis of NOAA mixtures/NIST N_2O PSM

2000	NIST 1998 PSMs Analyzed Value[a]	NOAA Value (NOAA 2000 scale)	NOAA Value (NOAA 2006 scale)[b]
N_2O NOAA #1	317.6 ± 1.6 nmol/mol	313.6 ± 2.0 Δ = - 4.0 **(- 1.3 %)**	313.4 ± 2.0 Δ = - 4.2 **(- 1.3%)**
NOAA #2	294.0 ± 1.9 nmol/mol	287.9 ± 2.0 Δ = - 6.1 **(- 2.1 %)**	287.7 ± 2.0 Δ = - 6.3 **(- 2.1%)**

[a] Rhoderick, Dorko: ES&T, 2004; NIST1998 PSMs
[b] Hall, Dutton, Elkins: JGR, 2007

Expanded uncertainties at 2σ (coverage factor k=2)

2012	NIST 2011 PSM Value	NOAA Result (NOAA 2006A)	SIO (Scripps)	
N_2O	317.95 ± 0.07 nmol/mol	318.02 ± 0.10 Δ = + 0.07 **(+0.02%)**	317.75 ± 0.16 Δ = -0.20 **(-0.06%)**	

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

NIST

NOAA

Important Considerations

Source of losses

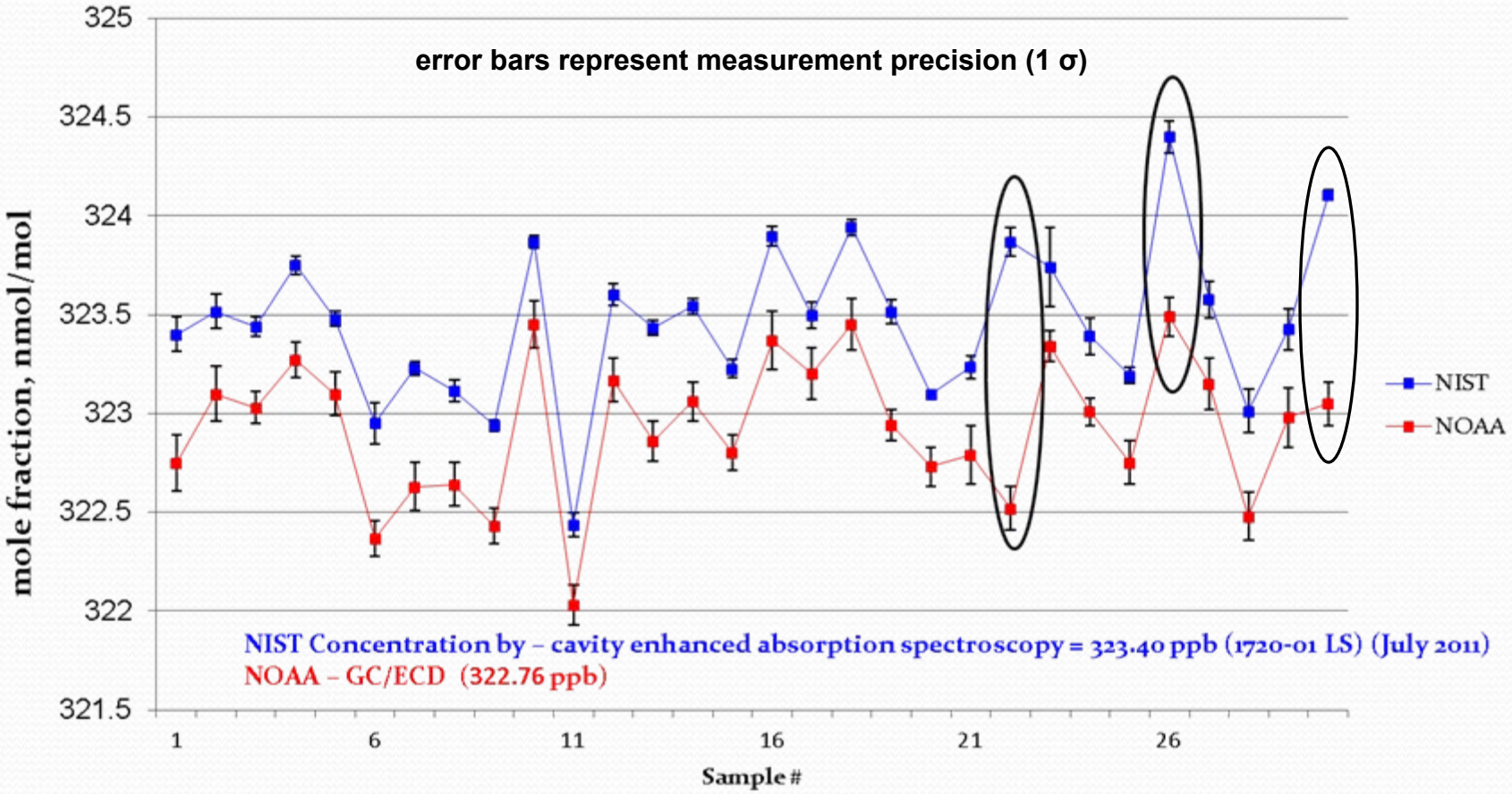
- flow rate when transferring gases (discovered w/ N_2O)

  - during prep of level 2 PSMs (1 % concentration) transfer lines cold and sweating during parent transfer; PSMs did not pass utest in Genline; N_2O freezing out??

  - remade level 2, transferring at slow rate and all pass utest

SRM 1720: N2O

NOAA and NIST assigned values to samples (July 2011)

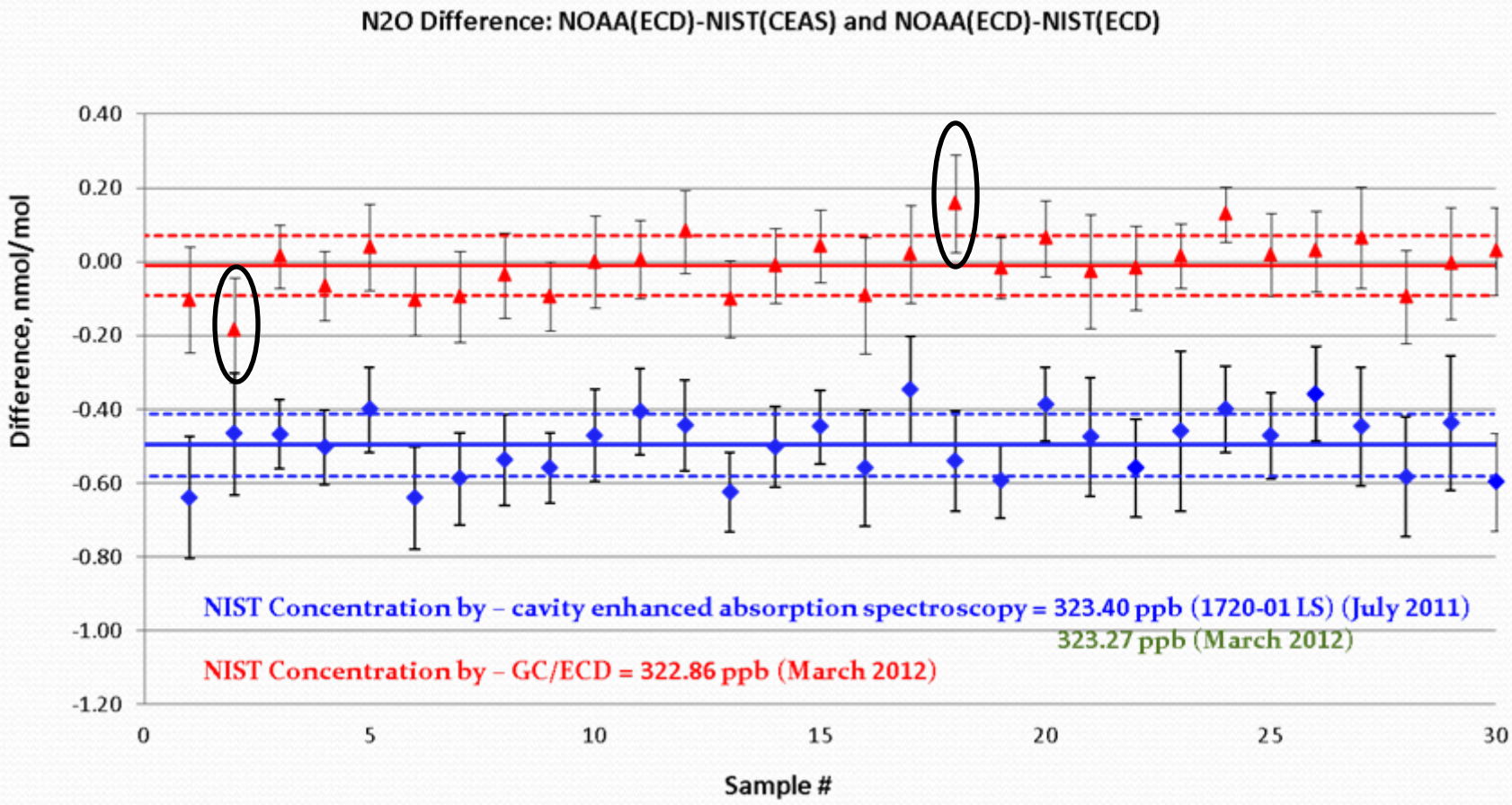


average diff (n=27) = - 0.50 nmol/mol
sd = 0.08 nmol/mol

SRM 1720: N_2O

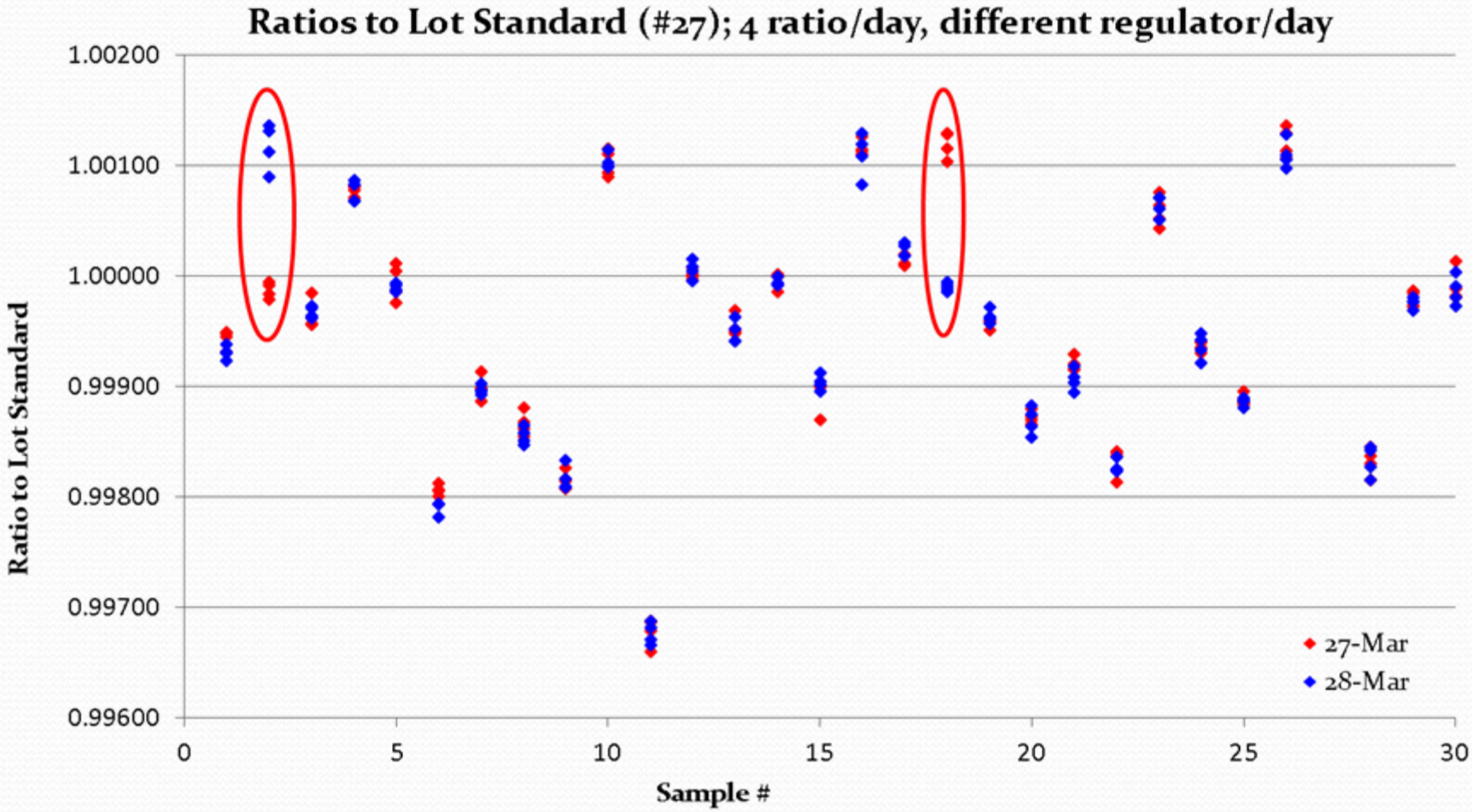
average (n=30) = - 0.50 nmol/mol
sd = ± 0.08 nmol/mol

average (n=30) = - 0.01 nmol/mol
sd = ± 0.08 nmol/mol

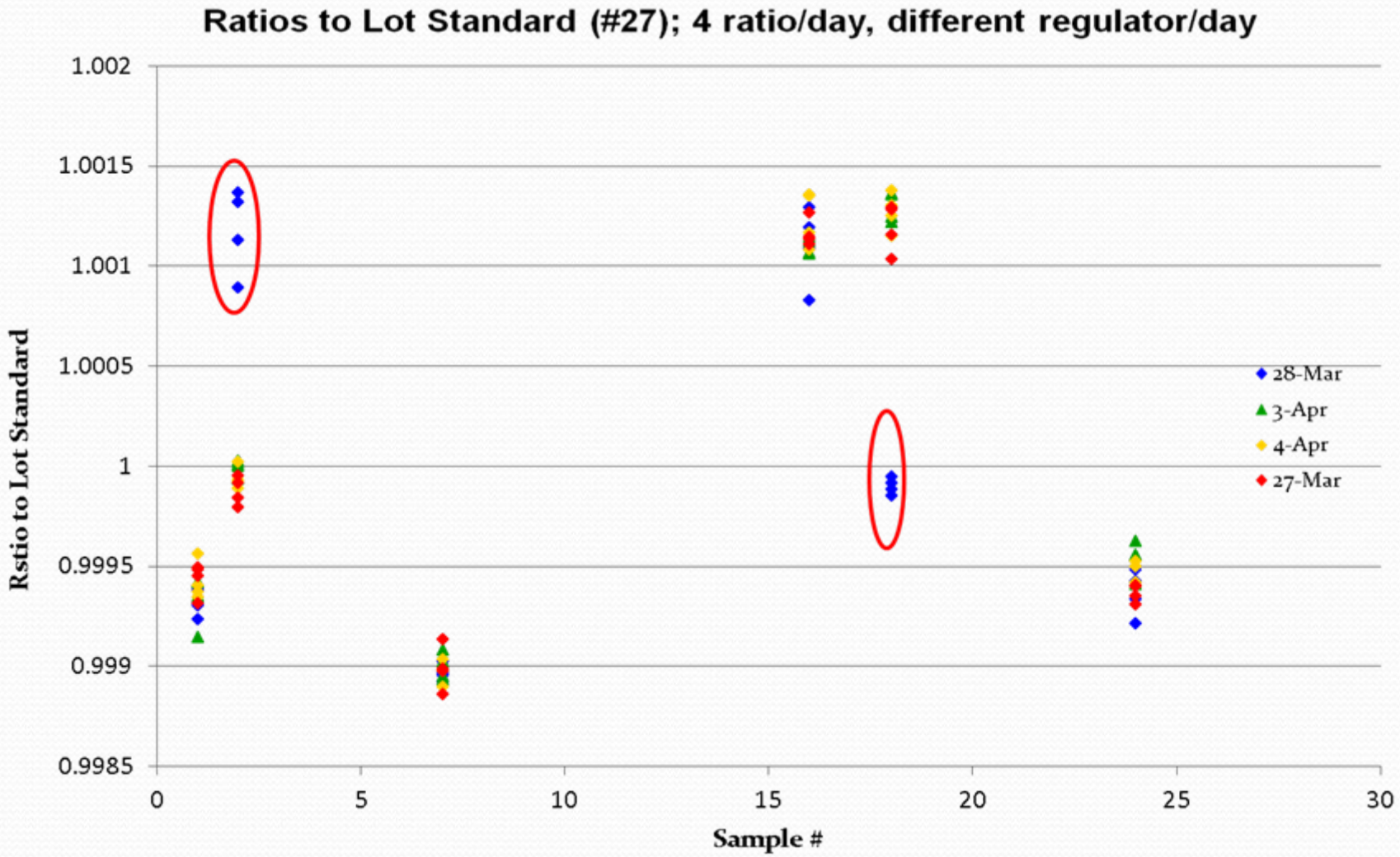


Regulator issue??

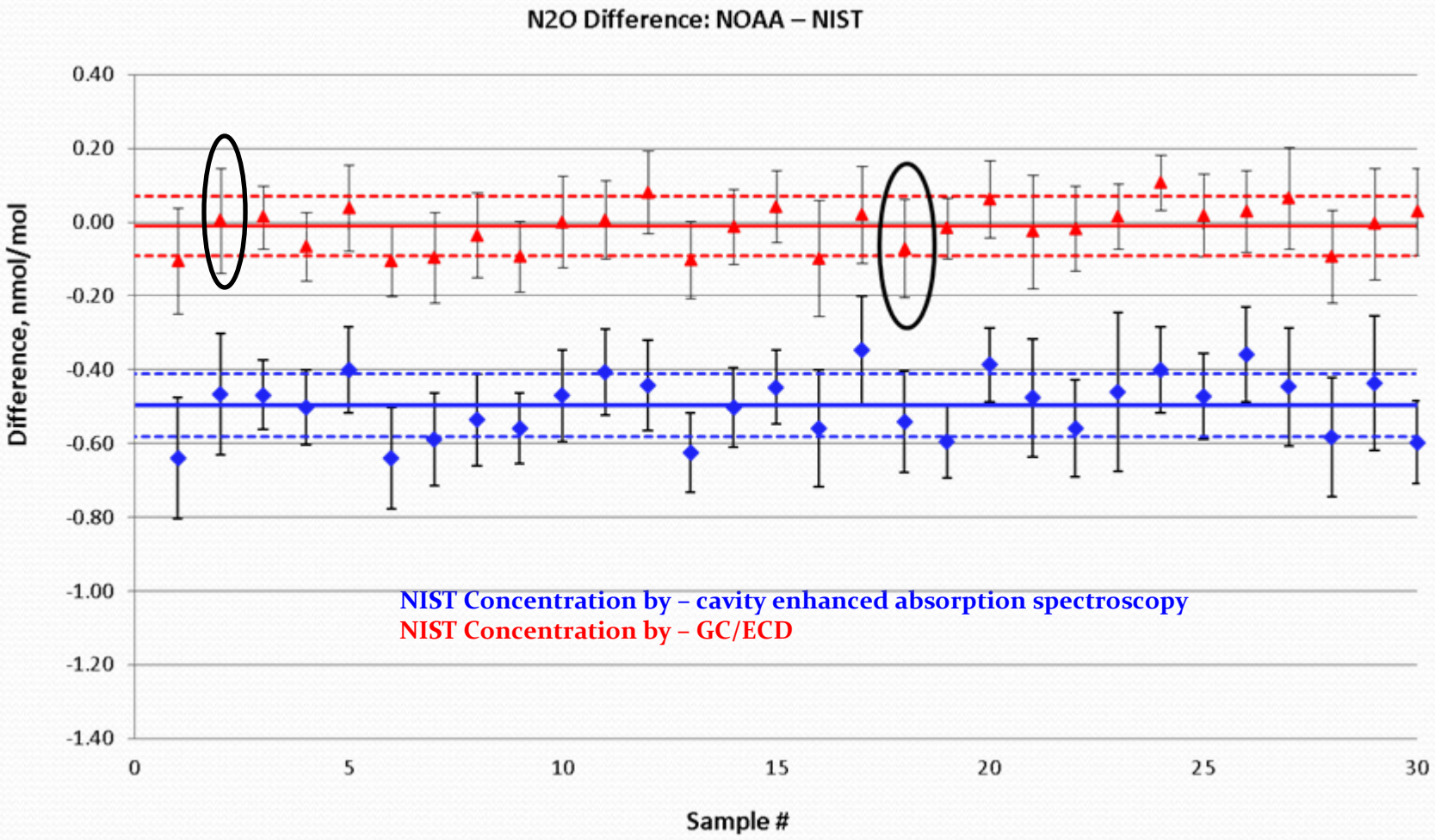
Probably not since 2 regulators used, analyzing 2 samples at time



Additional Comparisons by CEAS



Additional Comparisons by CEAS



Important Considerations

Source of losses

transfer lines in manifold; found 0.2 ppm loss of CO_2

- changed from flexible braided stainless steel over teflon tubing to 0.64 cm stainless steel tubing

losses of compounds to cylinder walls (CO_2)

- CO_2 losses of $\geq$ 0.2 µmol/mol

CO_2 Loss Studies

Transfer Lines

Mother Cylinder	Daughter Cylinder	Pressure	Transfer Line	CO_2 Loss ppm
FB03265	CAL018224	650	ss	0.144
CAL018224	FB03343	300	teflon	0.266

Cylinder Walls

- Transferred ≈ 13.8 bar of 388.65 µmol/mol CO_2/air mother PSM to cylinders
- Analyze the daughter against the mother; stainless steel transfer lines

Cylinder	µmol/mol Loss CO_2	
CAL018224	- 0.39	(treated for CO_2 service)
FB03343	- 0.31	(treated for CO_2 service)
APEX994663	- 0.12	(treated for low level VOC service, Ni plated valve)

CO_2 Loss Studies

- 13.8 bar of mother cylinder (CC12989 – 393.2 µmol/mol CO_2/Air) transferred into:

Cylinder	µmol/mol Loss CO_2
APEX1005718	- 0.08
APEX1005723	- 0.12
APEX1005679	- 0.08
APEX1005706	- 0.04
APEX1005720	- 0.08

PSMs prepared in these cylinders still predicted a - 0.6 µmol/mole CO_2 loss (0.2 % relative) based on difference from NOAA scale.

Since the primary standards were at 110 bar, the next wall effects study will try to determine if there is a pressure component to these losses.

Summary and Future

- Comparisons between NOAA scale and NIST PSMs are in good agreement for CH_4 and N_2O
- CO2, CO and SF_6 comparisons as PSMs completed
- Other comparisons for halocarbons in the future