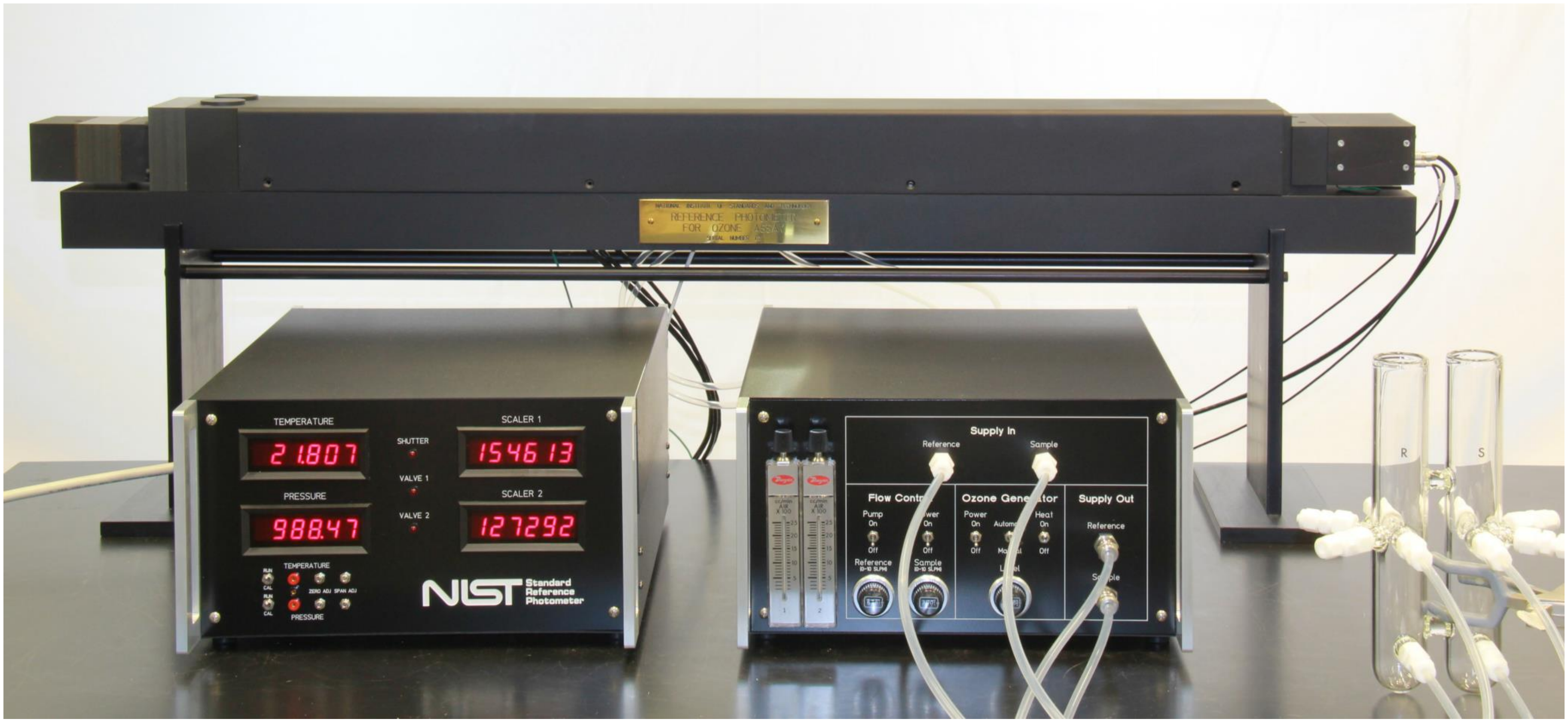
The NIST Standard Reference Photometer and its role in International Ozone Measurement Traceability



James E. Norris

Regional Workshop - Metrology Support for the Quality Assurance of Measurements of Air Quality Monitoring Networks

June 6, 2018

NIST Chemical Sciences Division

Outline

- Ozone Standards
- NIST Standard Reference Photometer
- U.S. Ozone Measurement Traceability
- NIST SRP Validation
- BIPM/NIST Collaboration
- International Ozone Measurement Comparability
- Ongoing Activities
- Summary

Ozone Measurement Instruments

- **Wet Chemistry Titration**
  - **neutral buffered potassium iodide (NBKI)**
  - **boric acid potassium iodide (BAKI)**
- **Chemiluminescence**
  - **reaction of O_3 with ethylene (C_2H_4)**
- **Gas Phase Titration**
  - **reaction of O_3 with NO**
- **UV Photometric**
  - **absorption at 253.7 nm**

U.S. EPA Study of Ozone Measurement Techniques

Early to middle 1970's

Included: **NBKI**
BAKI
GPT (excess NO)
GPT (excess O3)
UV Photometry

Study concluded: UV Photometry was more stable and consistent!

Led to: FRM changed from NBKI to UV Photometry (1976)!

UV Photometric Instruments

Derivation of Beer-Lambert Law equation used for calculating ozone mole fractions

$$C = \frac{-\ln T}{\alpha L} \times \left(\frac{T(sample)}{T(std)} \times \frac{P(std)}{P(sample)} \right)$$

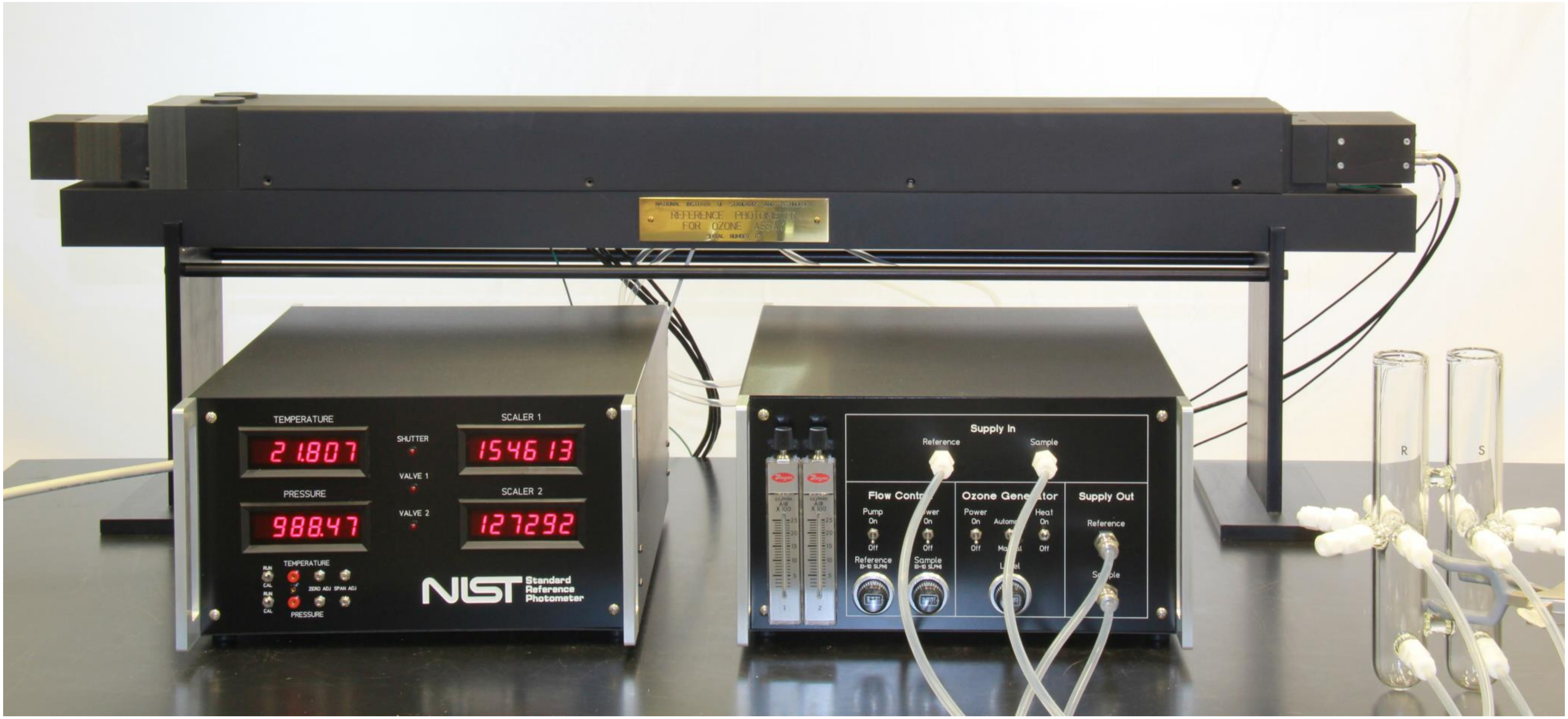
C = ozone concentration
T = transmittance (I/I^0)
α = ozone absorption coefficient (at STP)
L = optical path-length
$T_{(sample)}$ = sample gas temperature
$T_{(std)}$ = standard temperature
$P_{(std)}$ = standard pressure
$P_{(sample)}$ = sample gas pressure

NIST Standard Reference Photometer (SRP)

- U.S. EPA and NIST Collaboration (beginning 1981).
- UV Photometry (Absorption of 253.7 nm Hg Line).
- Custom Designed and Built Instrument.
- Measurement Range: 0 to 1000 nmol/mol (ppbv).
- Estimated Uncertainty: ± 1 ppbv (0 - 100 ppbv).
  ± 1% (100 - 1000 ppbv).
- NIST Ozone Reference Standard - 1982 to Present.
- Ozone Reference Standard for many other Countries.
- Official International Ozone Reference Standard.

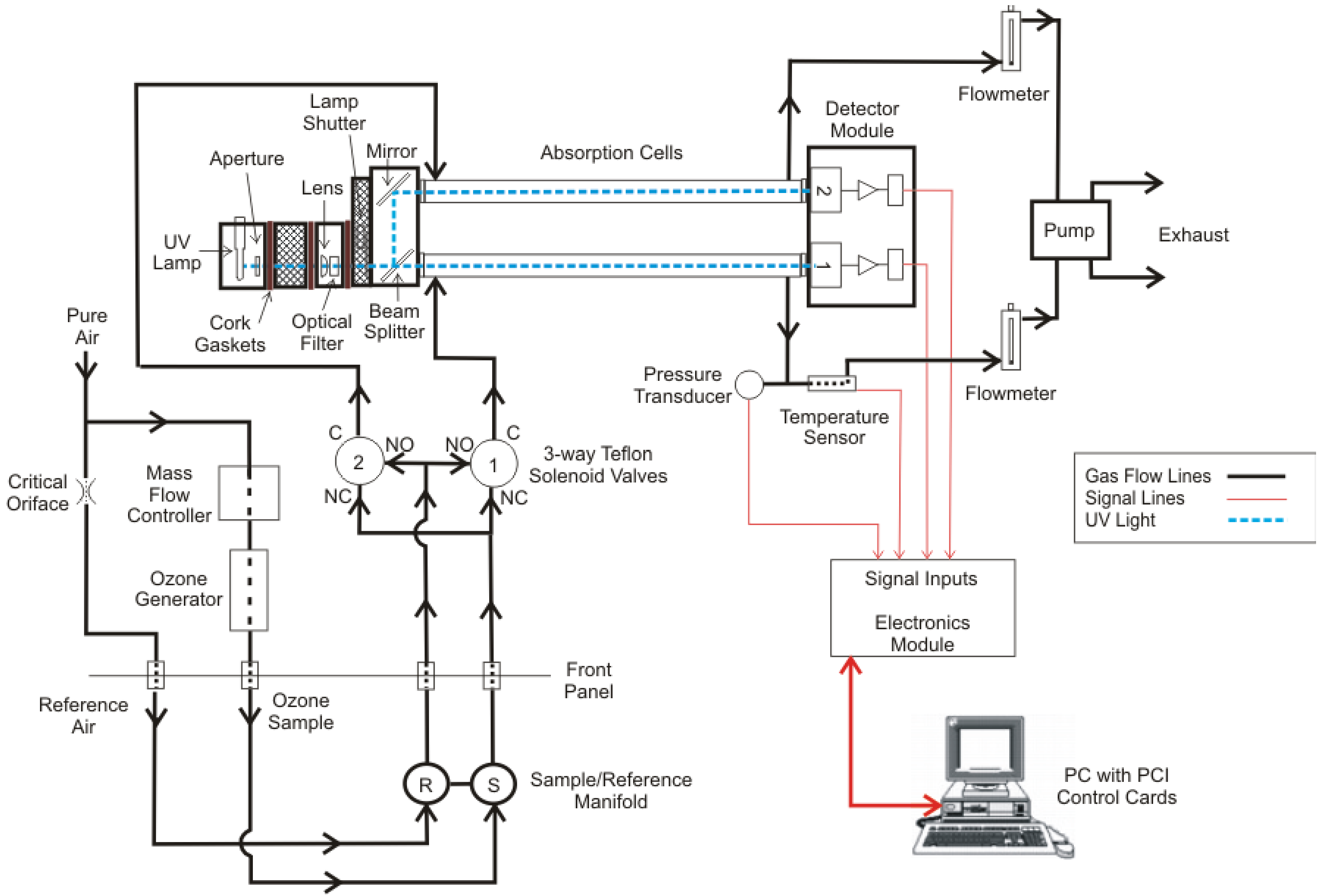
Arnold Bass and Jim Norris with SRP 2, circa 1984

NIST SRP 62



TEMPERATURE
21.807
PRESSURE
988.47
SHUTTER
VALVE 1
VALVE 2
SCALER 1
154613
SCALER 2
127292
NIST Standard Reference Photometer
Supply In
Reference
Sample
Supply Out
Reference

Schematic of SRP System



Uncertainty Estimation for SRP

Component (y)	Source	Distribution	Standard Uncertainty	Combined Standard Uncertainty μ(y)	Sensistivity Coefficient $c_i = \partial x/\partial y$	Contribution to μ(x), $\lvert c_i \rvert \cdot$ μ(y)/nmol mol^{-1}
Optical Path-length, L	Measurement scale Variability Divergence	Rectangular Rectangular Rectangular	0.0005 cm 0.003 cm. 0.52 cm	0.52 cm.	$-x/L_{opt}$	$2.89\times10^{-3}\,x$
Pressure, P	P Gauge P difference between cells	Rectangular Rectangular	0.029 kPa 0.017 kPa	0.034 kPa	$-x/P$	$3.37\times10^{-4}\,x$
Temperature, T	T probe T gradient	Rectangular Rectangular	0.029 K 0.058 K	0.07K	x/T	$2.29\times10^{-4}x$
Ratio of intensities, D	Scaler resolution Repeatability	Rectangular Triangular	8.0×10^{-6} 1.1×10^{-5}	1.4×10^{-5}	$x/D\ln(D)$	0.28
Absorption cross-section, σ	Conventional value		1.22×10^{-19} cm^2/molecule	1.22×10^{-19} cm^2/molecule	$-x/\sigma$	$1.06\times10^{-2}\,x$

summarised in one equation describing the uncertainty as a function of ozone mole fraction:

$$u(x) = \sqrt{(0.28)^2 + (1.1\cdot10^{-2}\,x)^2}\;nmol/mol$$

without the absorption cross-section uncertainty (for UV photometer comparisons):

$$u(x) = \sqrt{(0.28)^2 + (2.92\cdot10^{-3}\,x)^2}\;nmol/mol$$

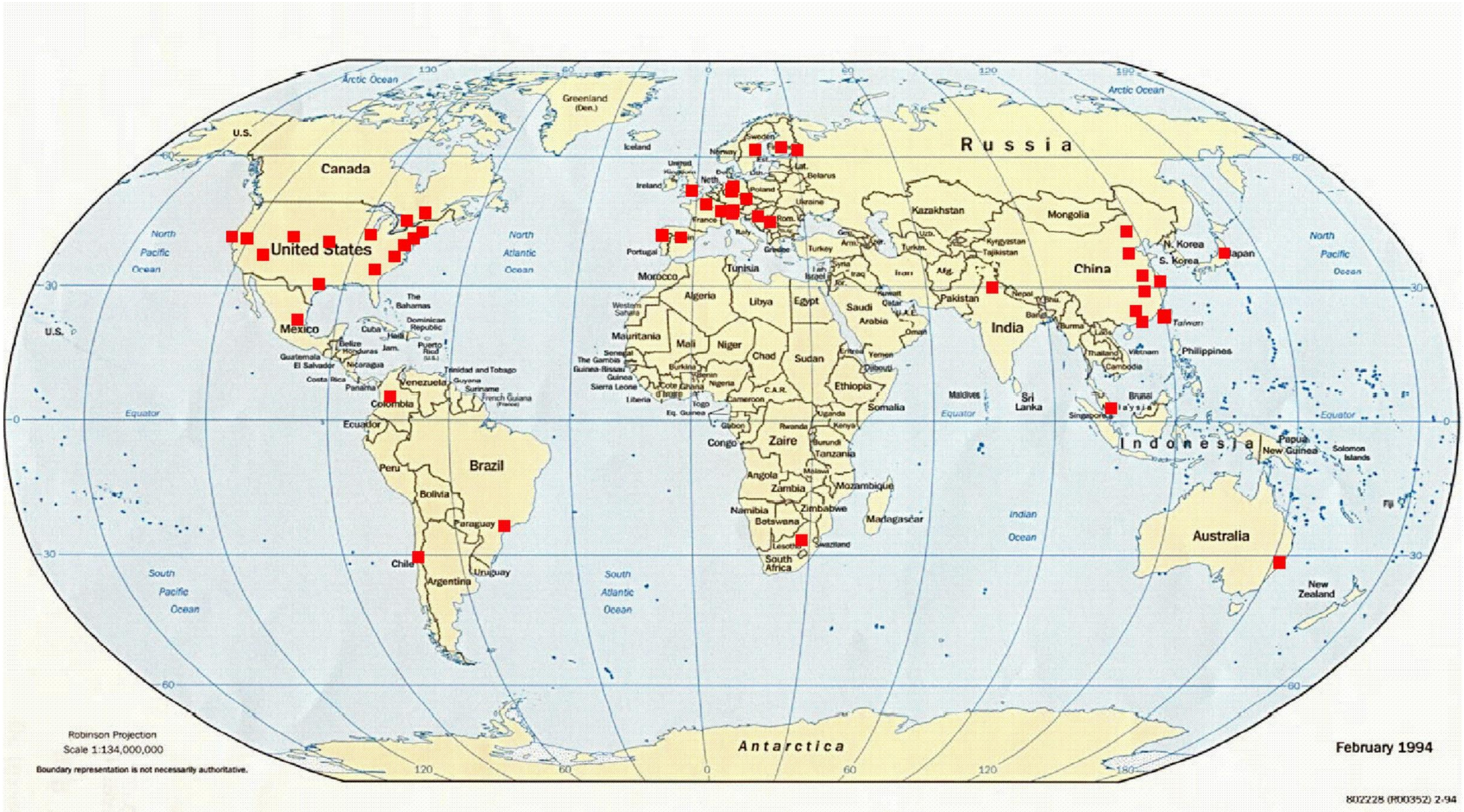
NIST SRPs
(United States Network)

SRP #	Agency	Location
0	NIST (Traveling Standard)	Gaithersburg, MD
1	EPA Office of Research and Development	Research Triangle Park, NC
2	NIST (National Standard)	Gaithersburg, MD
3	EPA Region 2 Laboratory	Edison, NJ
4	California Air Resources Board	Sacramento, CA
5	EPA Region 6 Laboratory	Houston, TX
6	EPA Region 5 Laboratory	Chicago, IL
7	EPA Office of Air Quality and Planning Stds.	Research Triangle Park, NC
8	EPA Region 8 Laboratory	Golden, CO
9	EPA Region 1 Laboratory	North Chelmsford, MA
10	EPA Region 4 Laboratory	Athens, GA
13	EPA Region 7 Laboratory	Kansas City, KS
36	EPA Region 9 Laboratory	Richmond, CA
61	EPA ORD/OAQPS	Research Triangle Park, NC

International NIST SRPs

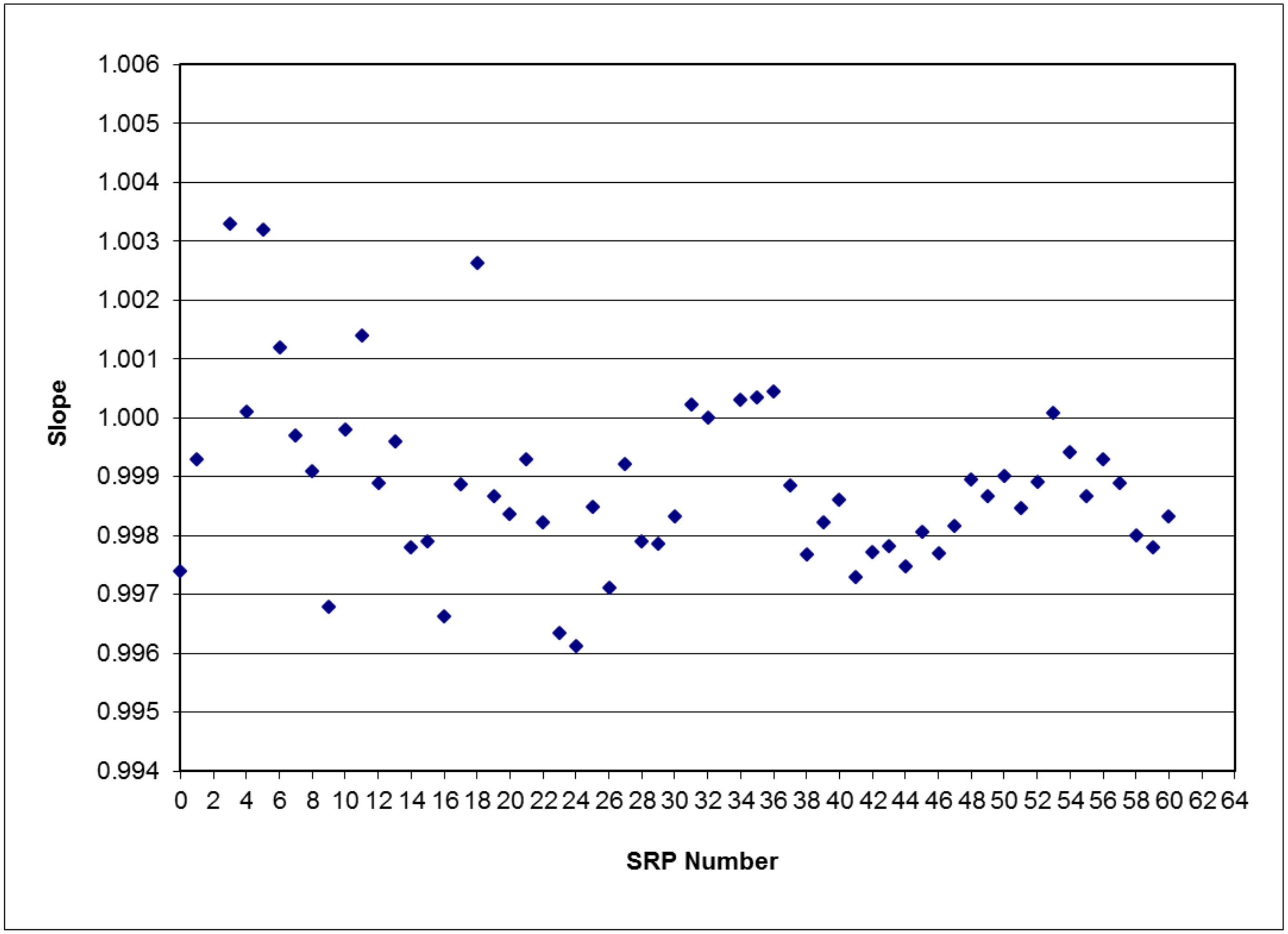
SRP #	Location	Organization
11	Stockholm, Sweden	ACES
14, 18	Bern, Switzerland	METAS
15, 23	Dubendorf, Switzerland	EMPA
12, 16	Ottawa, Canada	Environment Canada (12-OMOE)
17	Prague, Czech Republic	CHMI
20	London, United Kingdom	NPL
21	Sydney, Australia	NSW-EPA
22, 44	Madrid, Spain	ISCIII
24, 40	Paris, France	LNE
25	Lisbon, Portugal	IA
26	Vienna, Austria	EAA
27, 28, 31, 32, 33	Sevres, France	BIPM
19, 29	Langen, Germany	UBA-Germany (19-PTB)
30, 57	Kaohsiung, Taiwan, R.O.C.	Taiwan EPA
34	Hong Kong, S.A.R., China	Hong Kong EPD
35, 47	Tsukuba, Japan	NIES
37	Helsinki, Finland	FMI
38	St. Petersburg, Russia	VNIIM
39	Mexico City, Mexico	INE-CENICA
41	Beijing, China	NIM
42	Ispra, Italy	EC-JRC
43	New Delhi, India	NPLI
45	Santiago, Chile	CENMA
46	Singapore	NMC
48	Beijing, China	IERM (MEP)
49	Guangzhou, China	Guangdong EMC
50	Sao Paulo, Brazil	CETESB
51	Shanghai, China	Shanghai EMC
52	Nanjing, China	Jiangsu EMC
53	Jinan, China	Shandong EIMC
54	Belgrade, Serbia	DMDM
55	Medellin, Columbia	UN CALAIRE
56	Hangzhou, China	Zhejiang EMC
58	Zagreb, Croatia	DHMZ
59	Beijing, China	CNEMC (MEP)
60	Pretoria, South Africa	NMISA
62	Beijing, China	BMEMC

NIST SRP Network
(Worldwide)



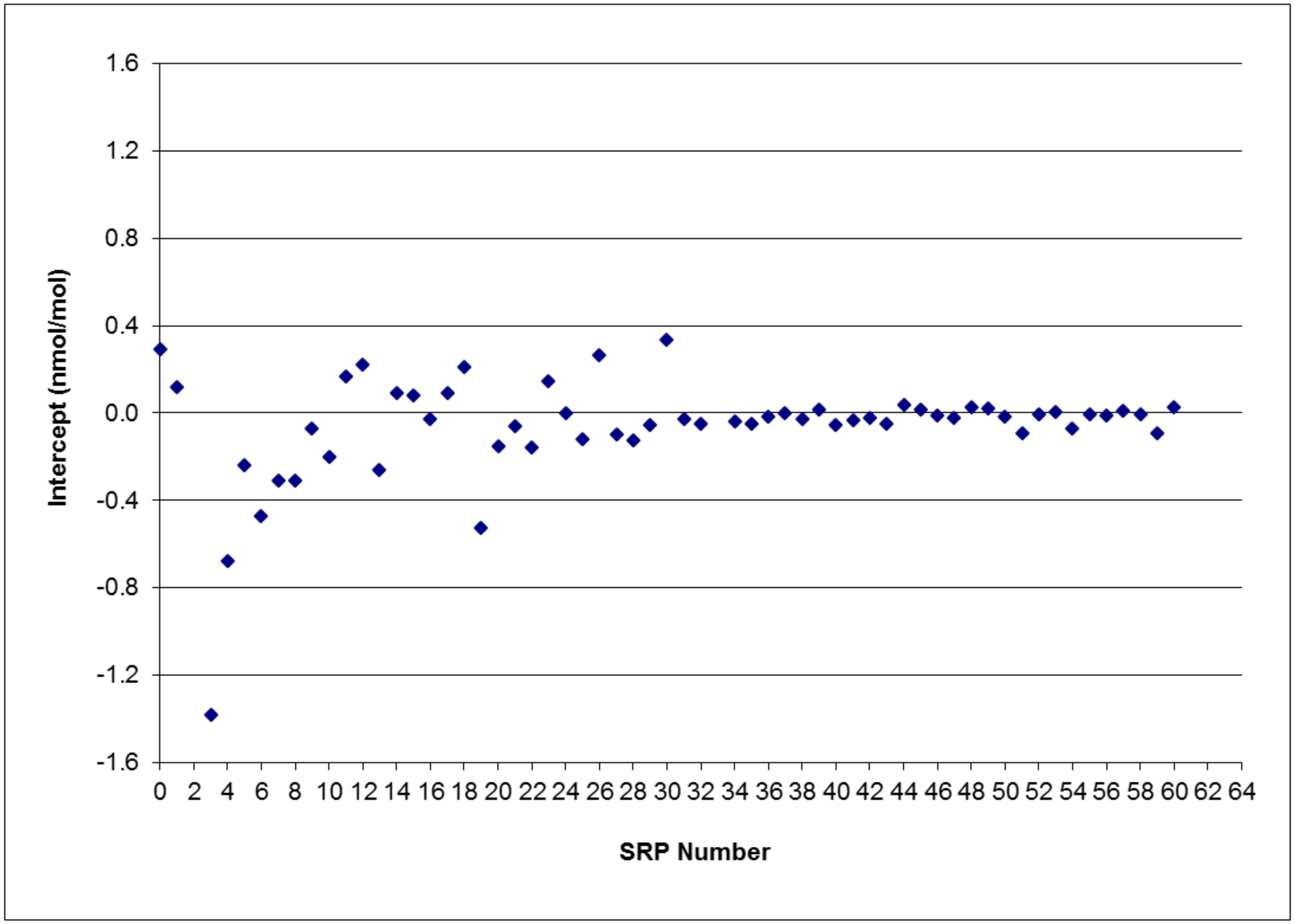
SRP Original Comparison vs. SRP 2

(Slopes)



Average Slope: 0.99887
Standard Deviation: 0.00148
Delta (Max – Min): 0.72%

SRP Original Comparison vs. SRP 2
(Intercepts)

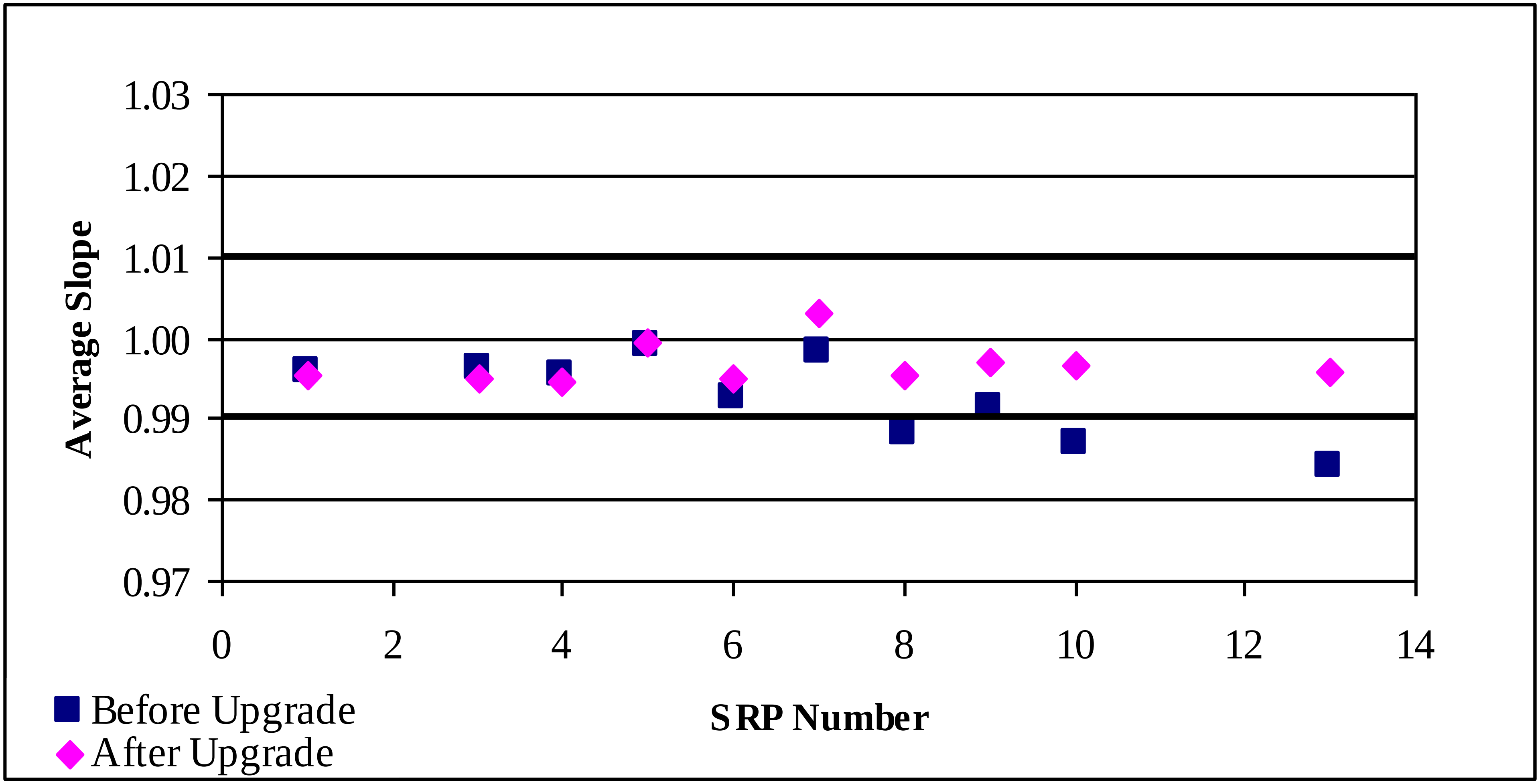


Average Intercept: - 0.064
Standard Deviation: 0.248
Delta (Max – Min): 1.715 nmol/mol

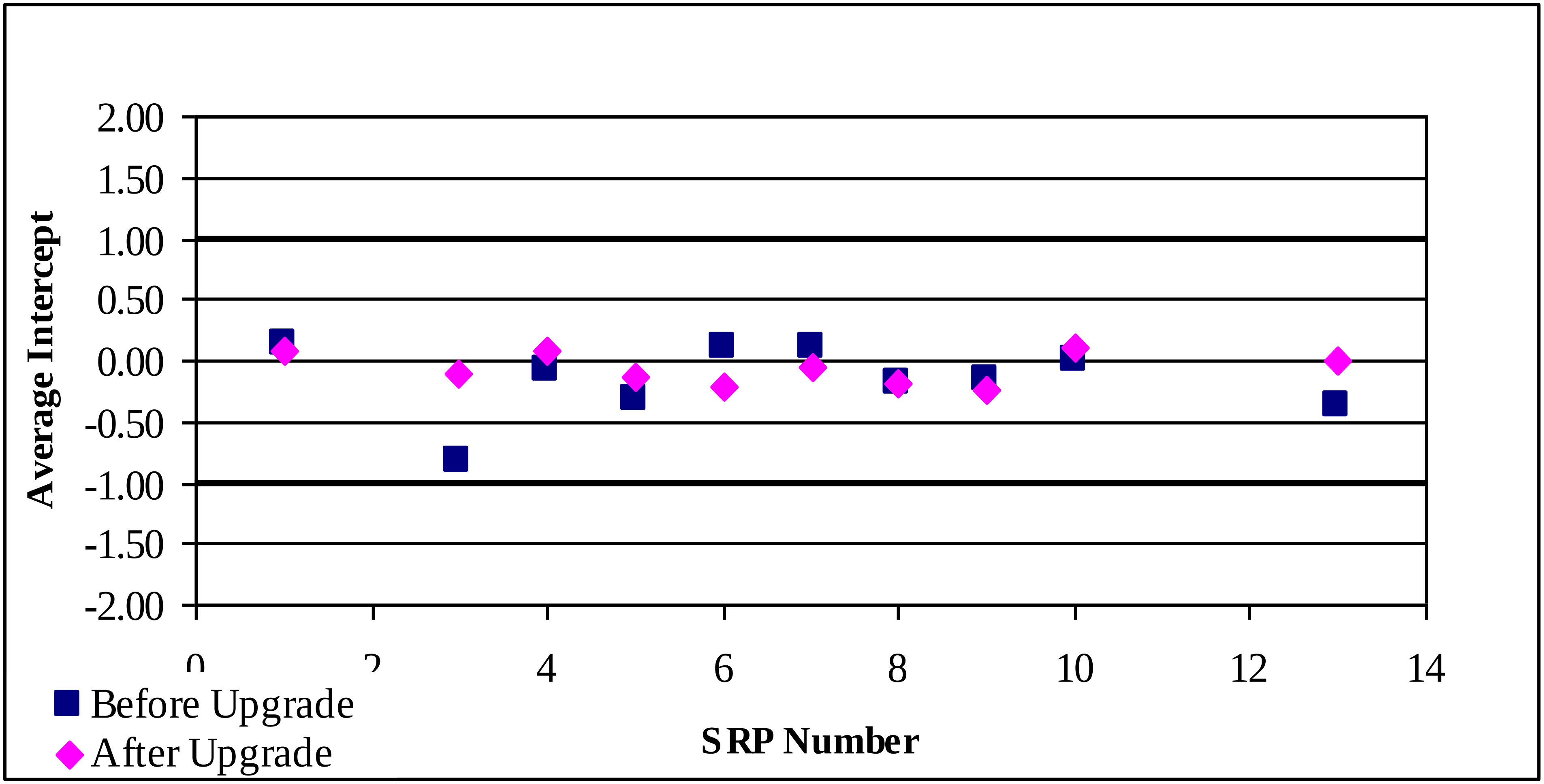
NIST SRP Electronics Upgrade Project
(1999-2000)

- **SRP 0-22 built with original electronics.**
  - **all have been upgraded.**
- **Driven by obsolete electronic components.**
  - **Several circuit chips were no longer produced.**
- **Consisted of complete electronics system redesign.**
  - **new Electronics module and Detector module.**
- **Improved V/f conversion rate (increased signal).**
  - **Increased from 1V in-10KHz out to 1V in-30KHz out.**
- **Included new dual external manifold.**
  - **Balanced pressure difference; improved intercepts.**
- **Included new version 4.0 control software.**
  - **Windows based VB code.**
- **Conference Proceeding Manuscript Available (A&WMA)**

U.S. EPA SRPs vs. NIST SRP 2 before and after electronics upgrade



U.S. EPA SRPs vs. NIST SRP 2 before and after electronics upgrade



NIST SRP Bias Upgrade
(2008-2010)

- Temperature and Optical Path-length Biases.
  - Determined by extensive SRP review by BIPM/NIST.
- Development of new light source block design.
  - Thermal Isolation of Heated Source Block.
  - Improved Collimation of Light Beam.
- Development of new absorption cells.
  - Optically sealed windows at 3° angle – fixed length.
  - Fused Quartz Inlet/Outlet Ports – No Teflon or O-rings.
  - Path-length measurement by Coordinate Measurement Machine.
- Measurement Quantification from each Bias Correction.
  - Independent Measurements after each Bias Upgrade.
- Manuscript available (*JAWMA*).

Derivation of Beer-Lambert Law equation used for calculating ozone mole fractions with the SRP

$$C = \frac{-\ln T}{\alpha L} \times \left(\frac{T(sample)}{T(std)} \times \frac{P(std)}{P(sample)} \right)$$

Optical Path-length Bias

- Multiple internal reflections in absorption cells from cell windows and optical filter.
- Path-length (L) is underestimated, C is overestimated.

Temperature Gradient Bias

- Sample and reference gases heated thru thermal transfer of heat from source lamp block.
- Sample Temperature [T(sample)] is underestimated, C is underestimated.

NIST SRP Bias Upgrade Project

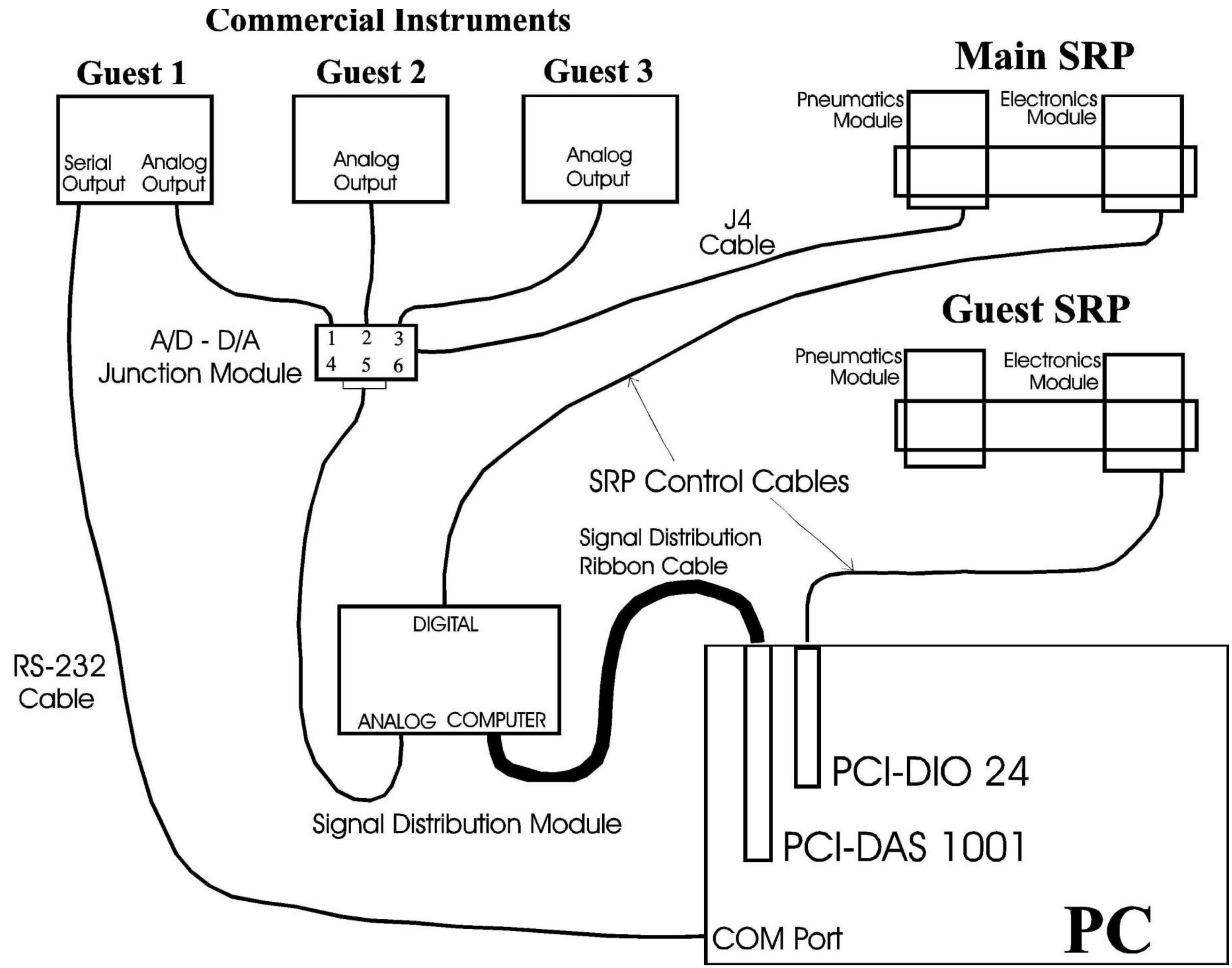
SRP Bias Upgrade (performed in steps).

1. Initial measurements.
2. New cells installed – set of measurements.
3. New source/optics block & shutter cover installed – final set of measurements.

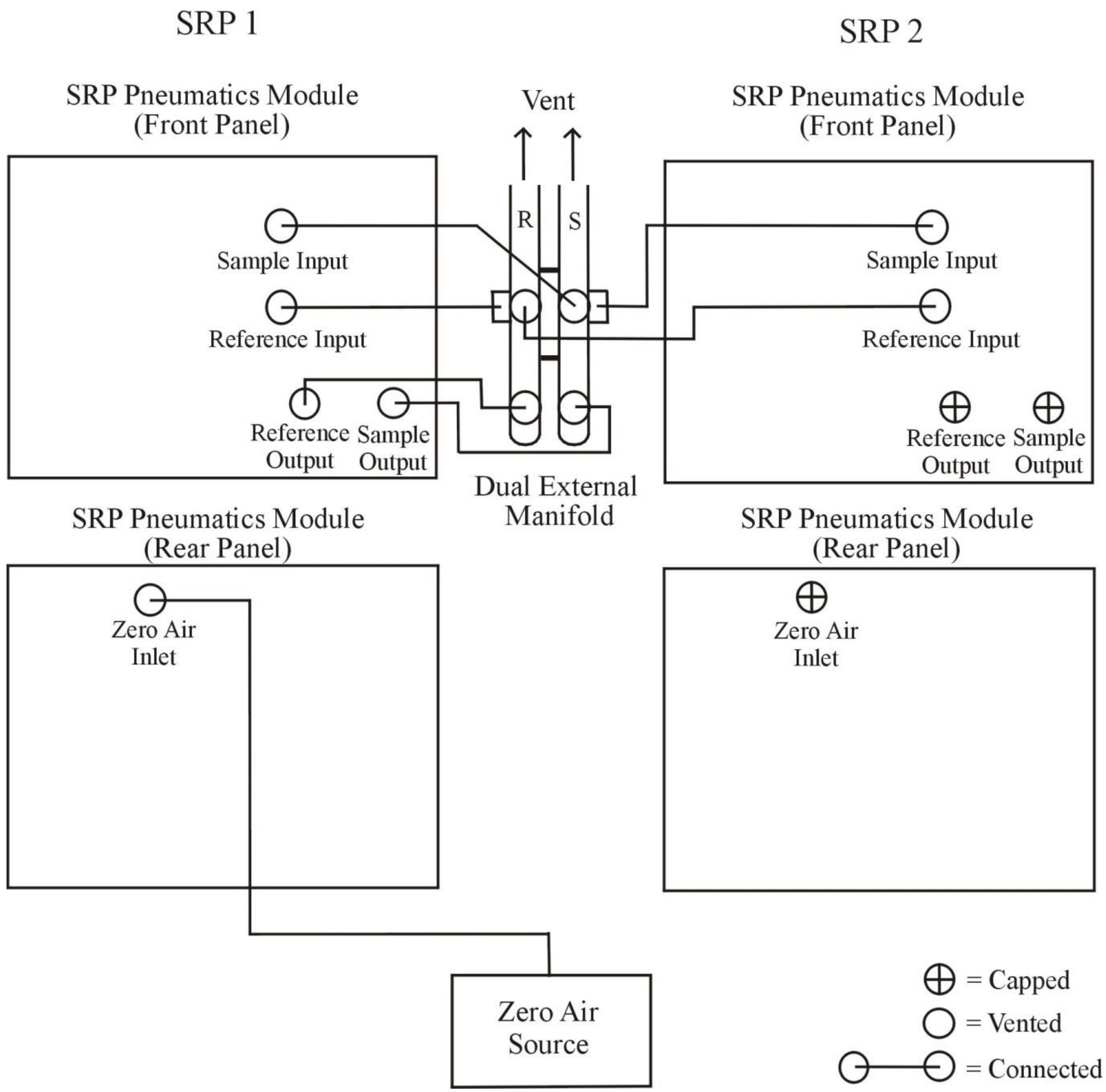
- 36 of 38 SRPs upgraded so far, including SRP 2.
    - 8 directly vs. SRP 2 at NIST.
    - 11 using SRP 0 as transfer.
    - SRP 32 vs. SRP 27 (data not corrected to SRP 0 or SRP 2).
- 6 SRPs upgraded by BIPM (Data not available)!
- 9 SRPs upgraded by USEPA (Data not available)!
- 25 new SRPs built new with bias upgrade included.

- Average shift in slope from new cells (optical bias): - 0.70%.
- Average shift in slope from new source (temp. grad. bias): + 0.39%.
- Average net change in slope from bias upgrade: - 0.30%.
- No noticeable change in the intercepts.
- Overall agreement in all SRPs before bias upgrade: 0.72%.
- Overall agreement in all bias upgraded SRPs: 0.33%.

Signal Connections to the SRP Control System



Current SRP vs. SRP Sampling Configuration



1 O3 Generator
1 sample manifold
1 reference manifold
Zero air to one SRPs

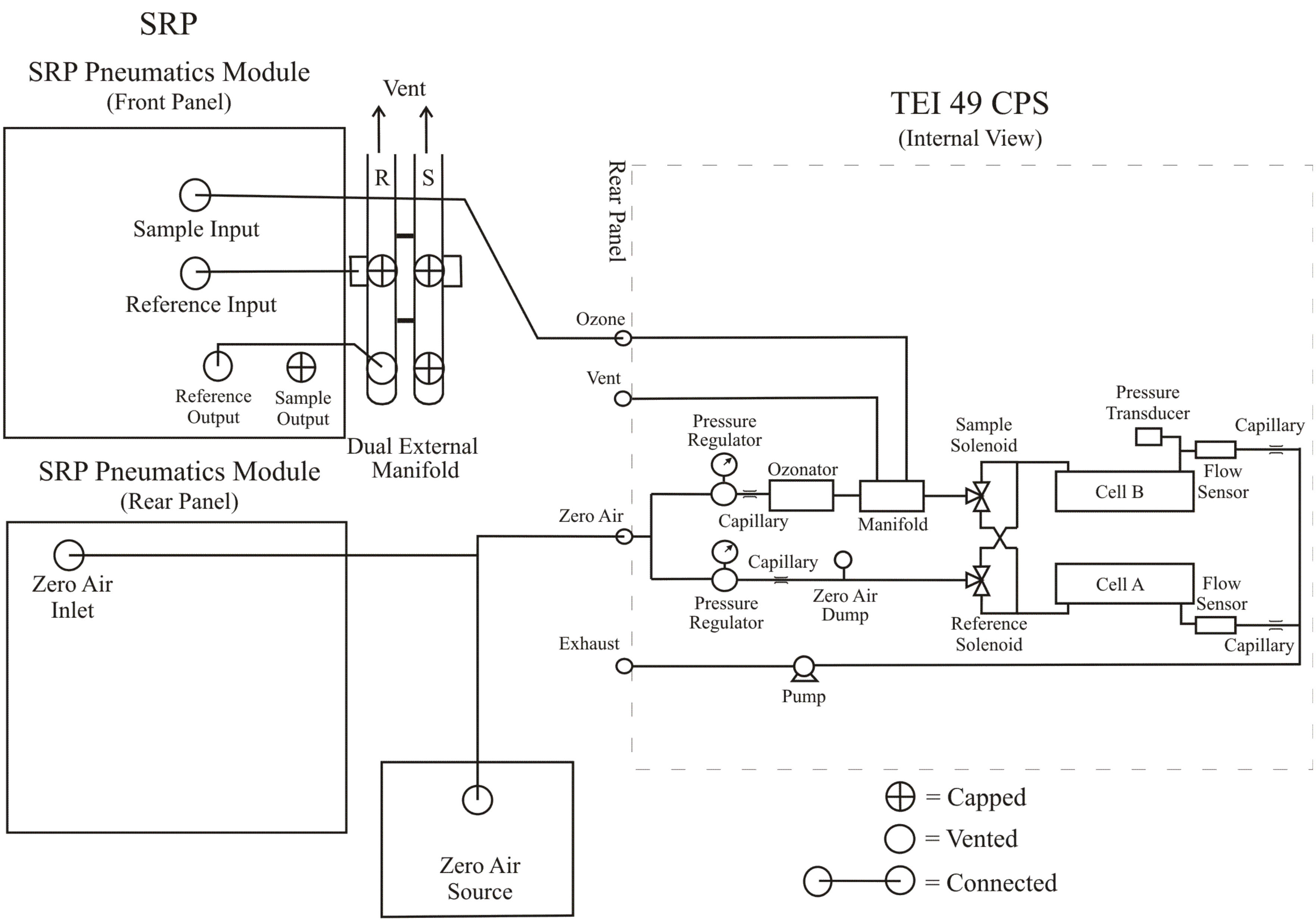
Sample/reference lines same length

Pressure values for sample and reference balanced

Lower uncertainty
Lower intercepts

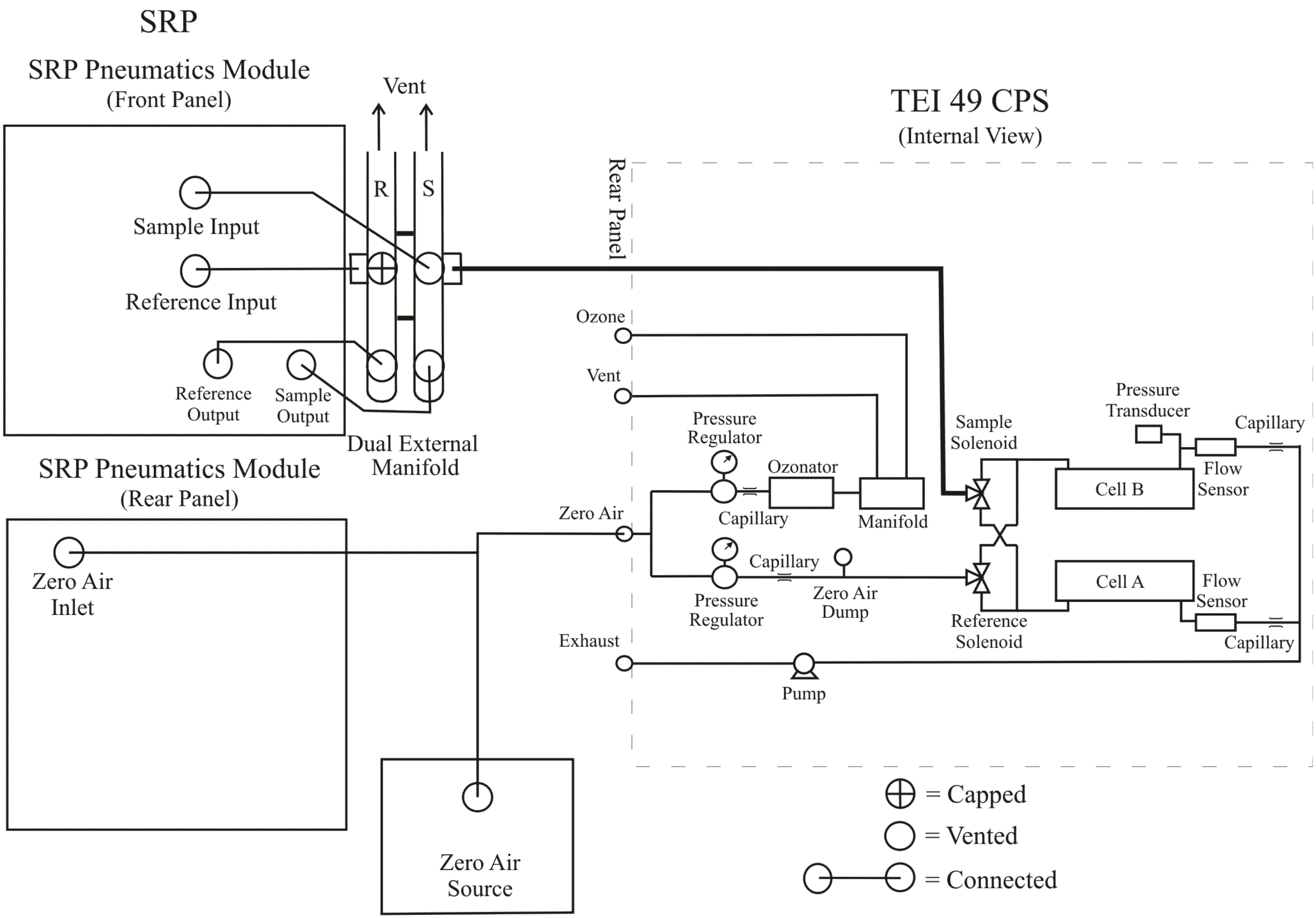
Calibration of TEI 49 CPS vs. NIST SRP

(Configuration 1)



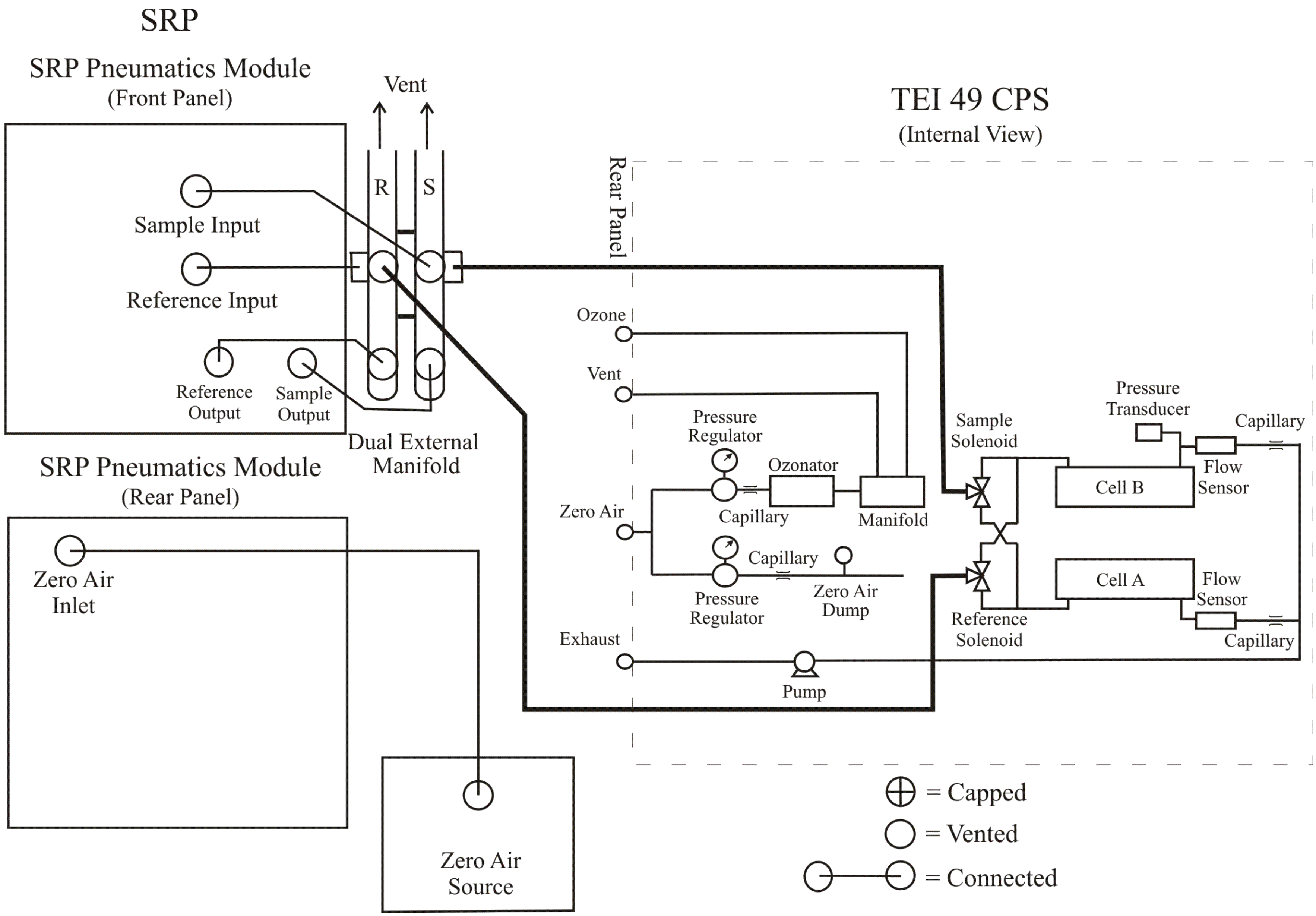
NIST Chemical Sciences Division

Calibration of TEI 49 CPS vs. NIST SRP
(Configuration 2)

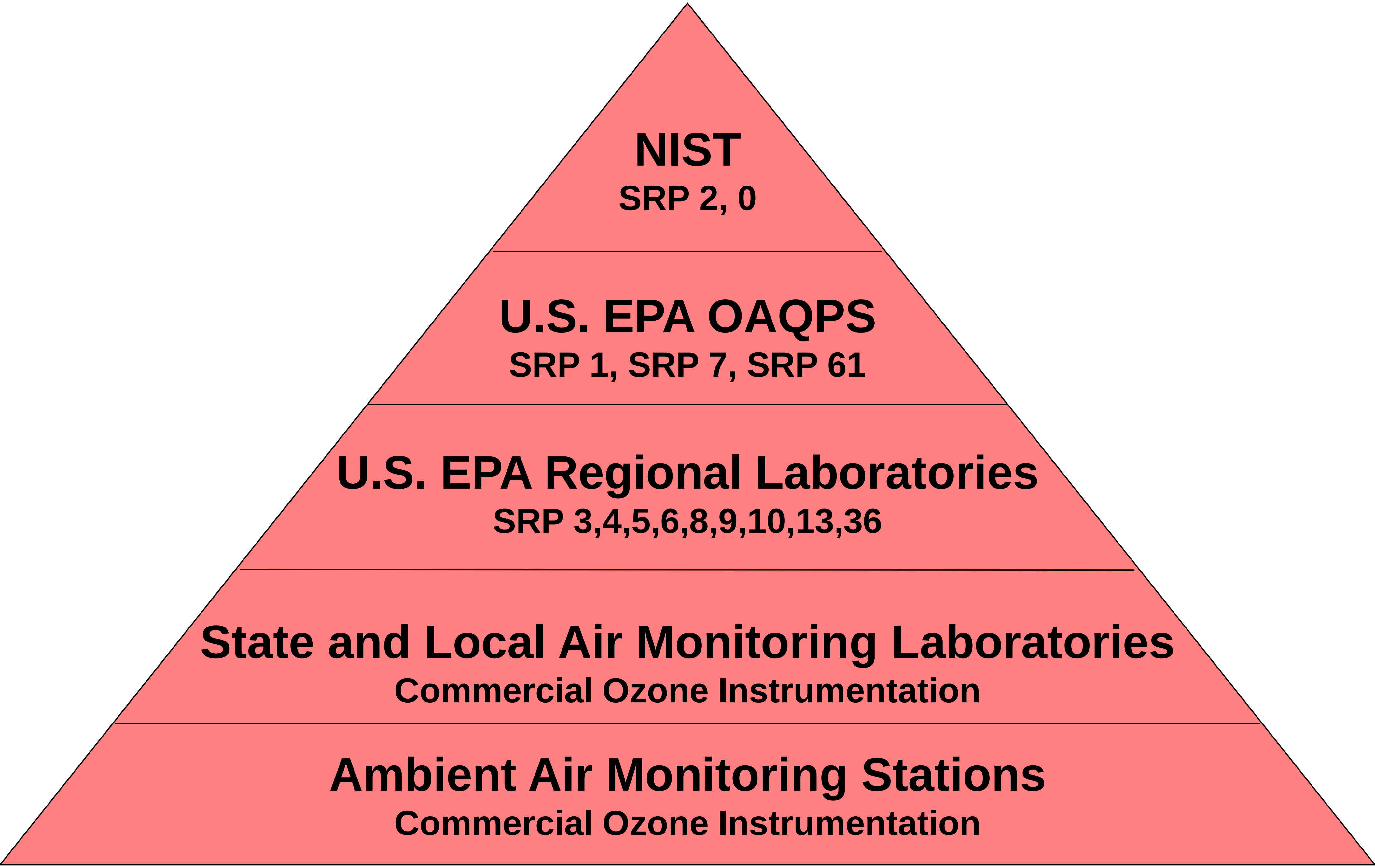


Calibration of TEI 49 CPS vs. NIST SRP

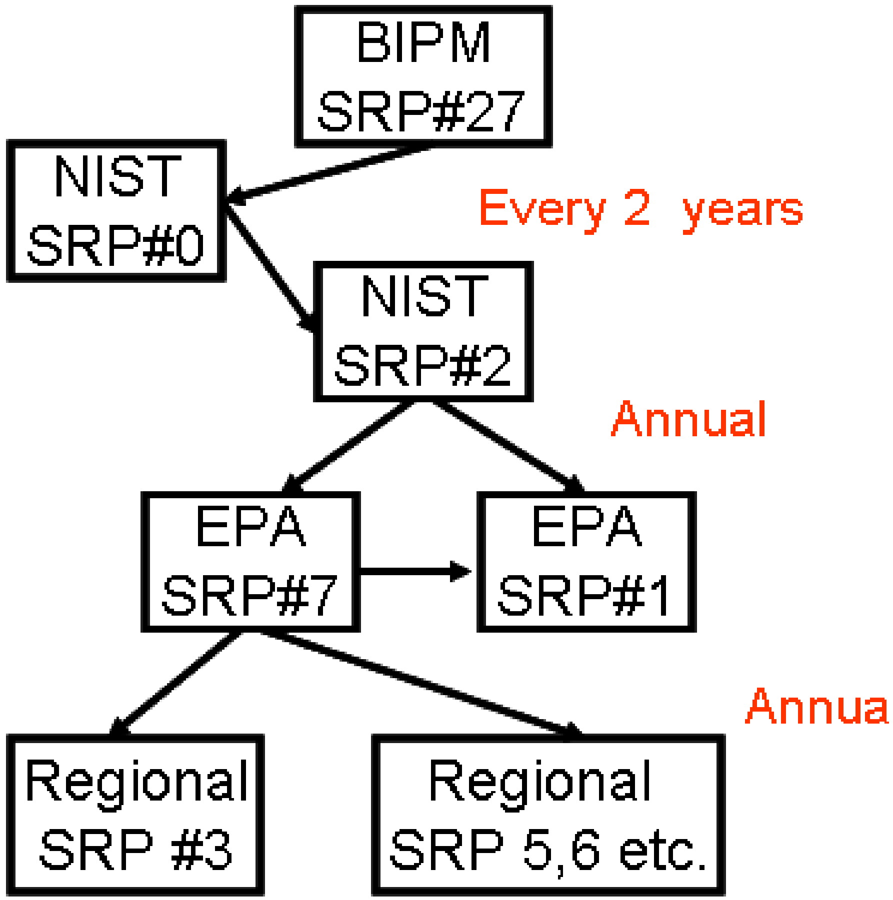
(Configuration 3)



Ozone Traceability in the United States

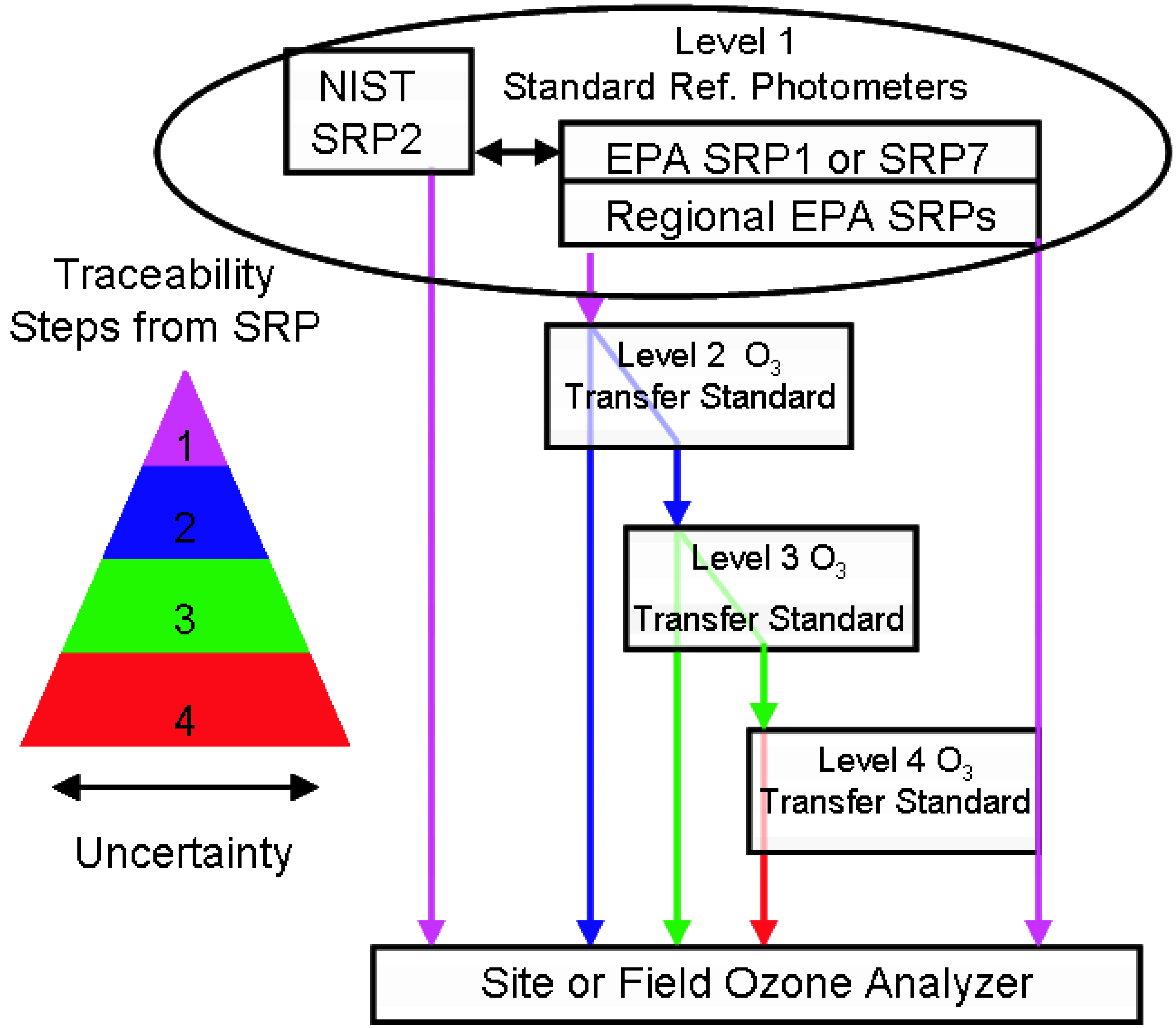


U.S. Family of Level 1 Ozone Standards (NIST SRPs)



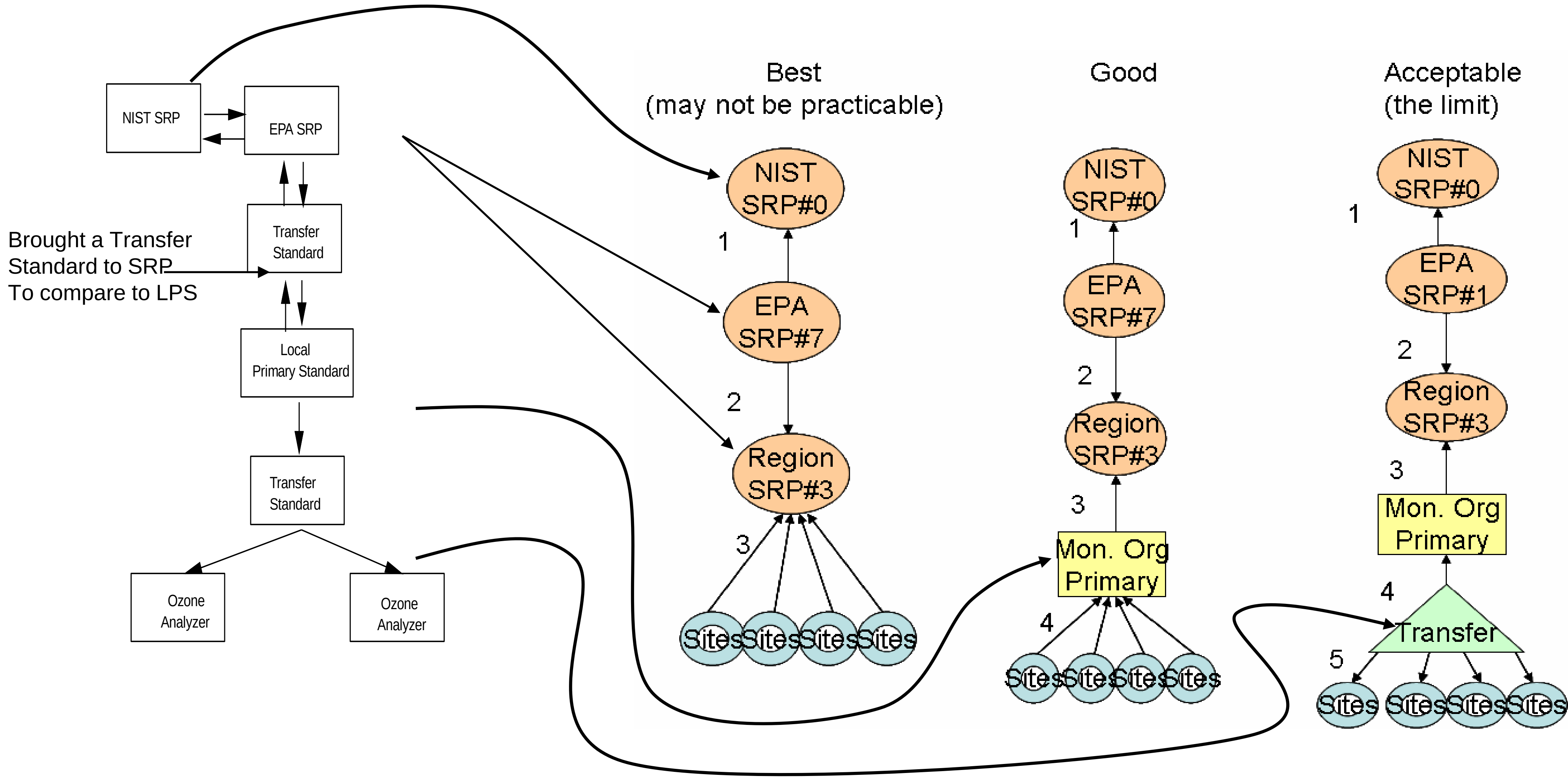
EPA Requirement: Agreement within ± 1% (Slope), ± 1 ppbv (Intercept).

U.S. Ambient Air Ozone Traceability Scheme



Courtesy USEPA

Possible Scenarios of Ozone Traceability



International SRP Network Traceability

as of 2002

Canada

SRP 12 (MOE)
SRP 16 (EC)

1 - 2 years

NIST SRP 2 or SRP 0

2 - ? years

Asia- Pacific

SRP 21 (NSW-EPA)

SRP 30 (TEPA)

2 - ? years

Europe

SRP 11 (ACES - Sweden)
SRP 14, 18 (METAS - Switzerland)
SRP 15, 23 (EMPA - Switzerland)
SRP 17 (CHMI - Czech Republic)
SRP 19 (PTB - Germany)
SRP 20 (NPL - United Kingdom)
SRP 22 (ISCIII - Spain)
SRP 24 (LNE – France)
SRP 25 (IA – Portugal)
SRP 26 (UBA – Austria)
SRP 29 (UBA-Germany)

Bureau International des Poids et Mesures

Bureau International des Poids et Mesures
(International Bureau of Weights and Measures)

The task of the BIPM is to ensure world-wide uniformity of measurements and their traceability to the International System of Units (SI).

It does this with the authority of the Convention of the Metre, a diplomatic treaty between fifty-one nations, and it operates through a series of Consultative Committees, whose members are the national metrology laboratories of the Member States of the Convention, and through its own Laboratory work.

The BIPM carries out measurement-related research. It takes part in, and organizes, international comparisons of national measurement standards, and it carries out calibrations for Member States.

Source – BIPM website

Consultative Committees under the International Committee for Weights and Measures (CIPM)

CCAUV: Consultative Committee for Acoustics, Ultrasound and Vibration
CCEM: Consultative Committee for Electricity and Magnetism
CCL: Consultative Committee for Length
CCM: Consultative Committee for Mass and Related Quantities
CCPR: Consultative Committee for Photometry and Radiometry
CCQM: Consultative Committee for Amount of Substance (Metrology in Chemistry)
CCRI: Consultative Committee for Ionizing Radiation
CCT: Consultative Committee for Thermometry
CCTF: Consultative Committee for Time and Frequency
CCU: Consultative Committee for Units

Source – BIPM website

CCQM Working Groups and Steering Group

(CAWG) - CCQM Working Group on Cell Analysis

(NAWG) - CCQM Working Group on Nucleic Acid Analysis

(SPWG) - CCQM Strategic Planning Working Group

(KCWG) - CCQM Working Group on Key Comparisons and CMC Quality

(IAWG) - CCQM Working Group on Inorganic Analysis

(BAWG) - CCQM Working Group on Bioanalysis

(EAWG) - CCQM Working Group on Electrochemical Analysis

(GAWG) - CCQM Working Group on Gas Analysis

(OAWG) - CCQM Working Group on Organic Analysis

(PAWG) - CCQM Working Group on Protein Analysis

(SAWG) - CCQM Working Group on Surface Analysis

(MBSG) - ad hoc Steering Group on Microbial Measurements

CCQM ad hoc Working Group on the Mole

Source – BIPM website

CCQM Key Comparison Database
Example (gases)

CCQM-K1.a
Carbon monoxide (CO) in Nitrogen (N2)
1994 - 1995, Approved for equivalence
Results available

CCQM-K1.b
Carbon dioxide (CO2) in Nitrogen (N2)
1993 - 1994, Approved for equivalence
Results available

CCQM-K1.c
Nitrogen monoxide (NO) in Nitrogen (N2)
1995 - 1996, Approved for equivalence
Results available

CCQM-K1.d
Sulfur dioxide (SO2) in Nitrogen (N2)
1996 - 1997, Approved for equivalence
Results available

CCQM-K1.e
Natural gas type I
1996 - 1997, Approved for equivalence
Results available

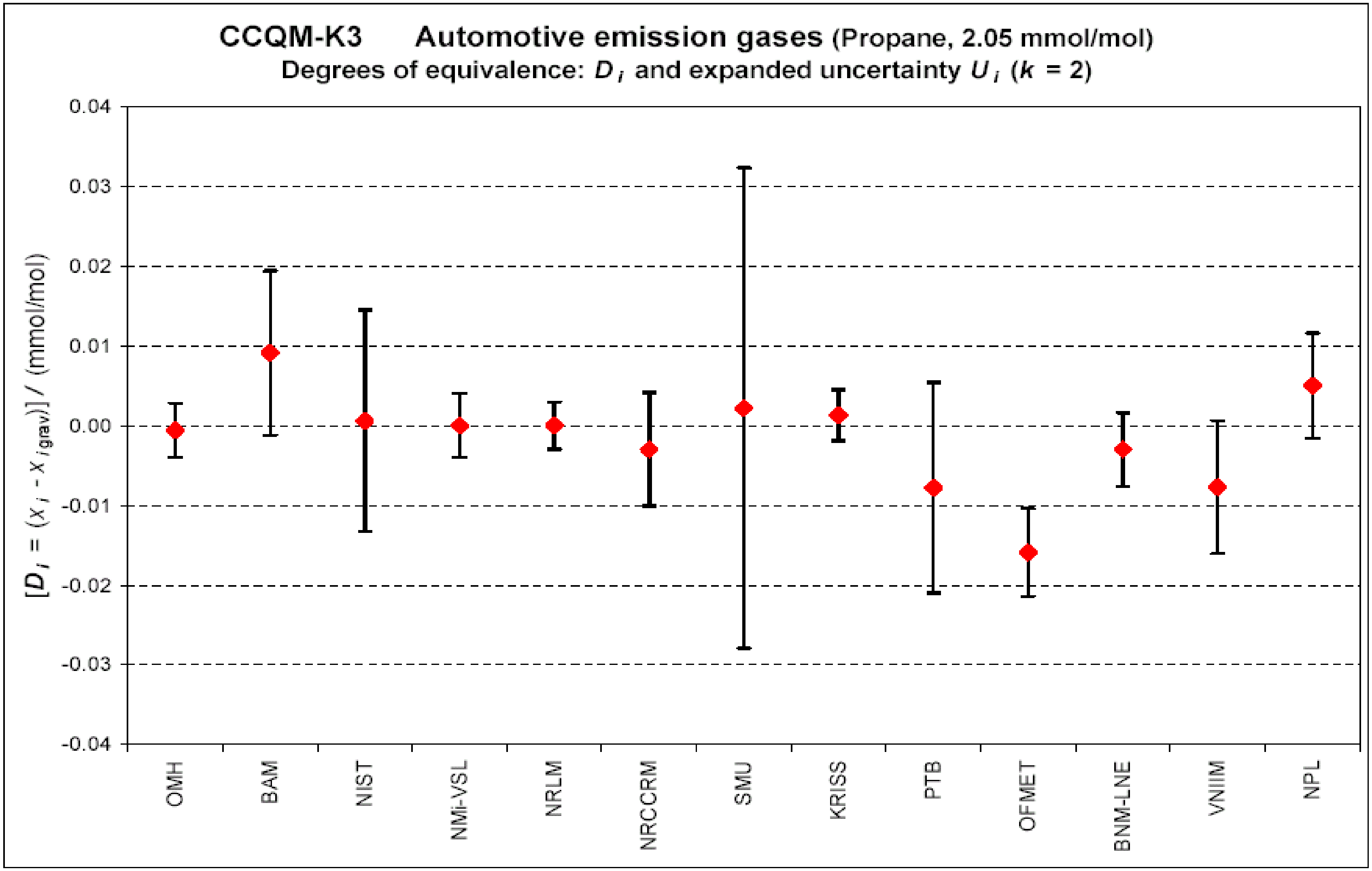
CCQM-K1.f
Natural gas type II
1996 - 1997, Approved for equivalence
Results available

CCQM-K1.g
Natural gas type III
1996 - 1997, Approved for equivalence
Results available

CCQM-K3
Automotive emission gases
1998 - 1999, Approved for equivalence
Results available

Source – BIPM website

Automotive Emission Gases



Source – BIPM website

BIPM – NIST Ozone Collaboration

- Delivery of SRP 27 and SRP 28.
- Detailed Training during assembly of SRP 31 and SRP 32.
- SRP 33 assembled at BIPM using BIPM machined parts.
- Detailed Review of SRP – publication available (*Metrologia*).
    - Temperature Measurement Bias: - 0.4% estimate.
    - Optical Path-length Bias: + 0.5% estimate.
- SRP Bias Upgrade Project – publication available (*JAWMA*).
- Develop International Ozone Traceability System through CCQM.
    - CCQM – P28 - Ozone Ambient Level Pilot Study – publication available.
    - BIPM.QM-K1, CCQM Key Comparison 2007- Present.

International Ozone Measurement Traceability

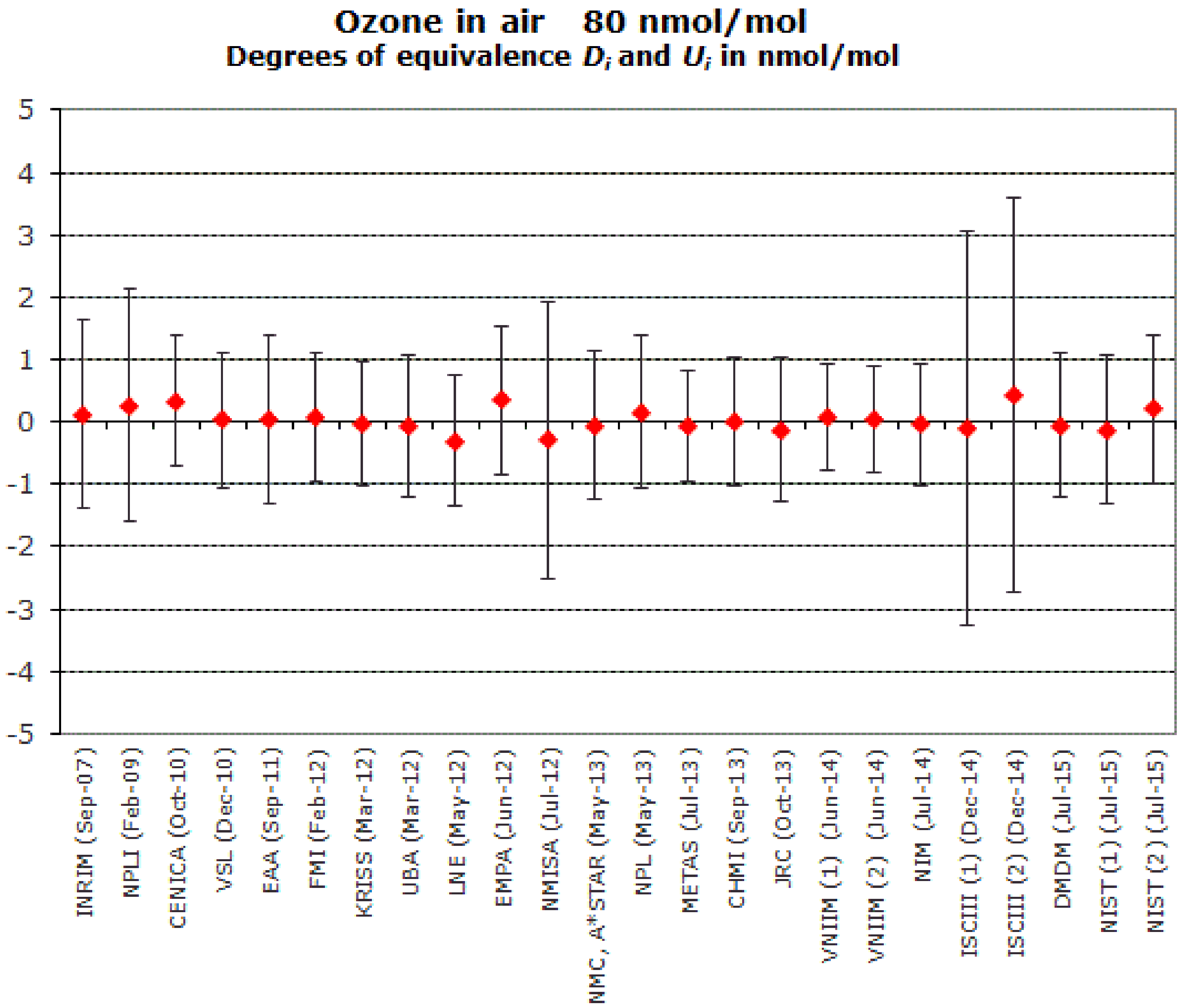
- CCQM – P28 - Ozone Ambient Level Pilot Study.

  (publication available, *Metrologia*)

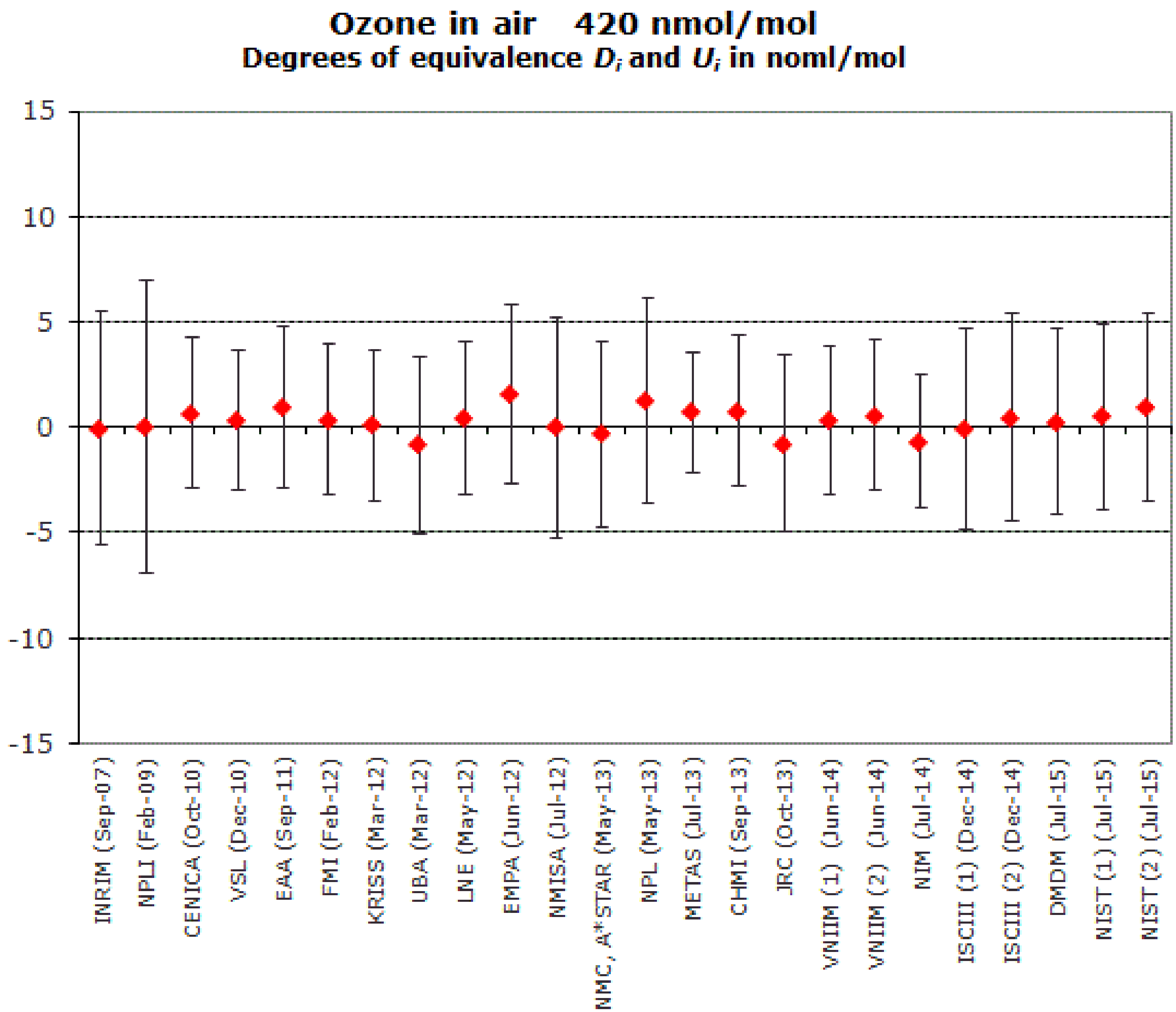
- BIPM.QM-K1, CCQM Key Comparison 2007- Present

  (data available at www.BIPM.org under KCDB)

BIPM.QM-K1, ozone at ambient level results



BIPM.QM-K1, ozone at ambient level results



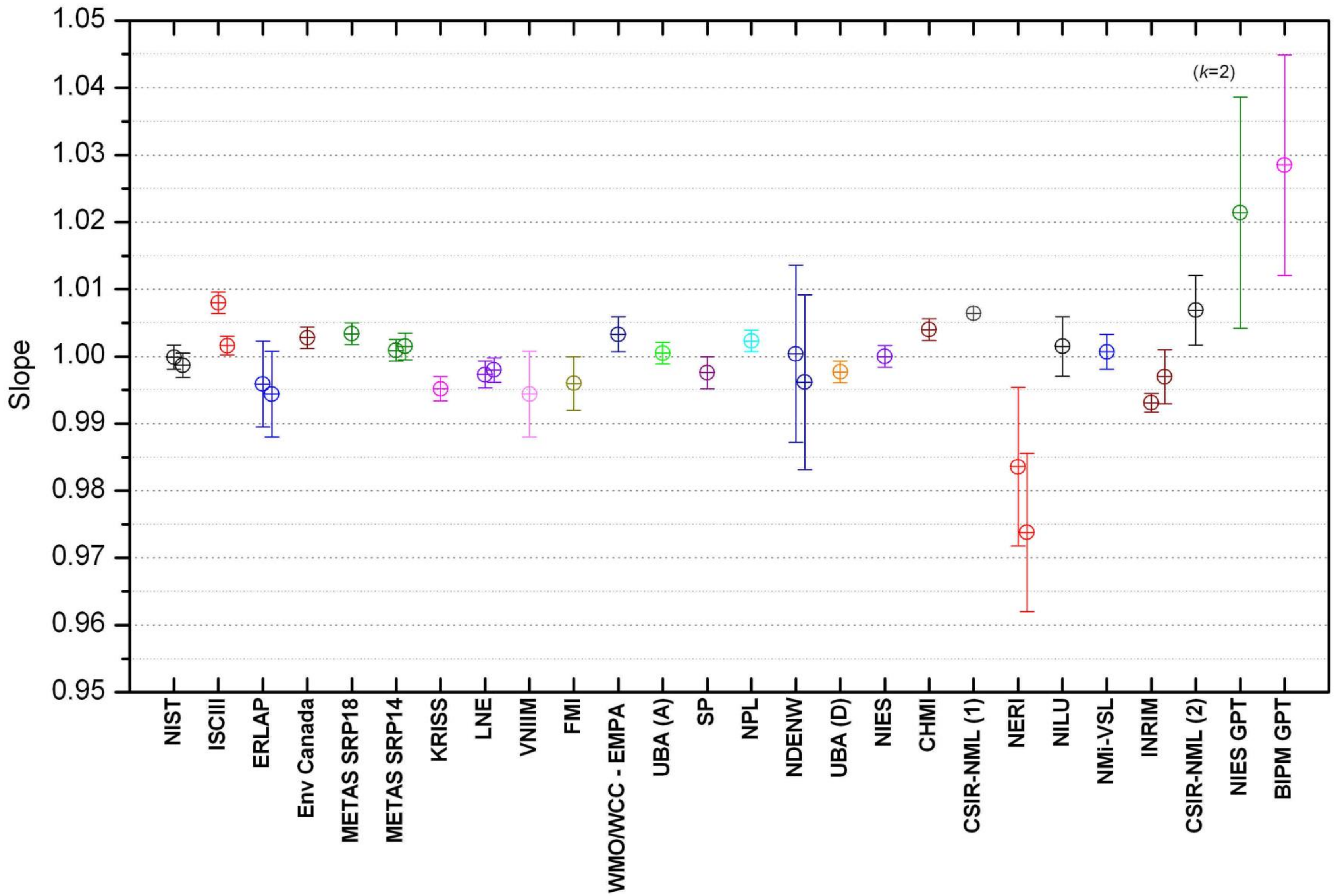
CCQM-P28 Instrumentation

Date	Institute	Country	Instrument to be brought to BIPM	Protocol followed	National Standard (if different)
July 2003	NIST	USA	SRP 0	B	SRP 2
Sept 8-12, 2003	ISC III	Spain	TECO 49C	B	SRP 22
Sept 22-26, 2003	EC-JRC	EC	TECO 49CPS	B	UMEG
Oct 20-24, 2003	Env. Canada	Canada	SRP 16	A	
Nov 3-7, 2003	IGF	Poland	ML9811	A	
Nov 17-21, 2003	METAS	Switzerland	SRP 18	B	SRP 14
Dec 1-5, 2003	KRISS	Korea	KRISS-1	A	
Jan 12-16, 2004	NILU	Norway	ML9811	A	
Jan 26-30, 2004	IMGC	Italy	KRISS-2	A	
Feb 2-6, 2004	LNE	France	TEI-49CPS	B	SRP 24
Feb 16-20, 2004	VNIIM	Russia	Dasibi 1003AH	A	
Mar 1-5, 2004	FMI	Finland	TEI-49CPS	A	
Mar 15-19, 2004	WCC-EMPA	WMO	SRP 15 / SRP 23	B	
Mar 29- Apr 2, 2004	UBA	Austria	TEI 49C-PS	B	SRP 26
May 3-7, 2004	SP	Sweden	Environment SA	A	(BAKI?)
May 24-28, 2004	NPL	UK	SRP 20	A	
June 7-11, 2004	IEM-DEP	Hungary	TE 49C	B	UMEG
June 21-25, 2004	UBA	Germany	SRP 29	A	
July 5-9, 2004	NIES	Japan	TEI-49C-PS	B	GPT
Sept 6-10, 2004	BIPM		GPT	A	
Sept 20-24, 2004	CHMI	Czech Rep	SRP 17	A	

Courtesy BIPM

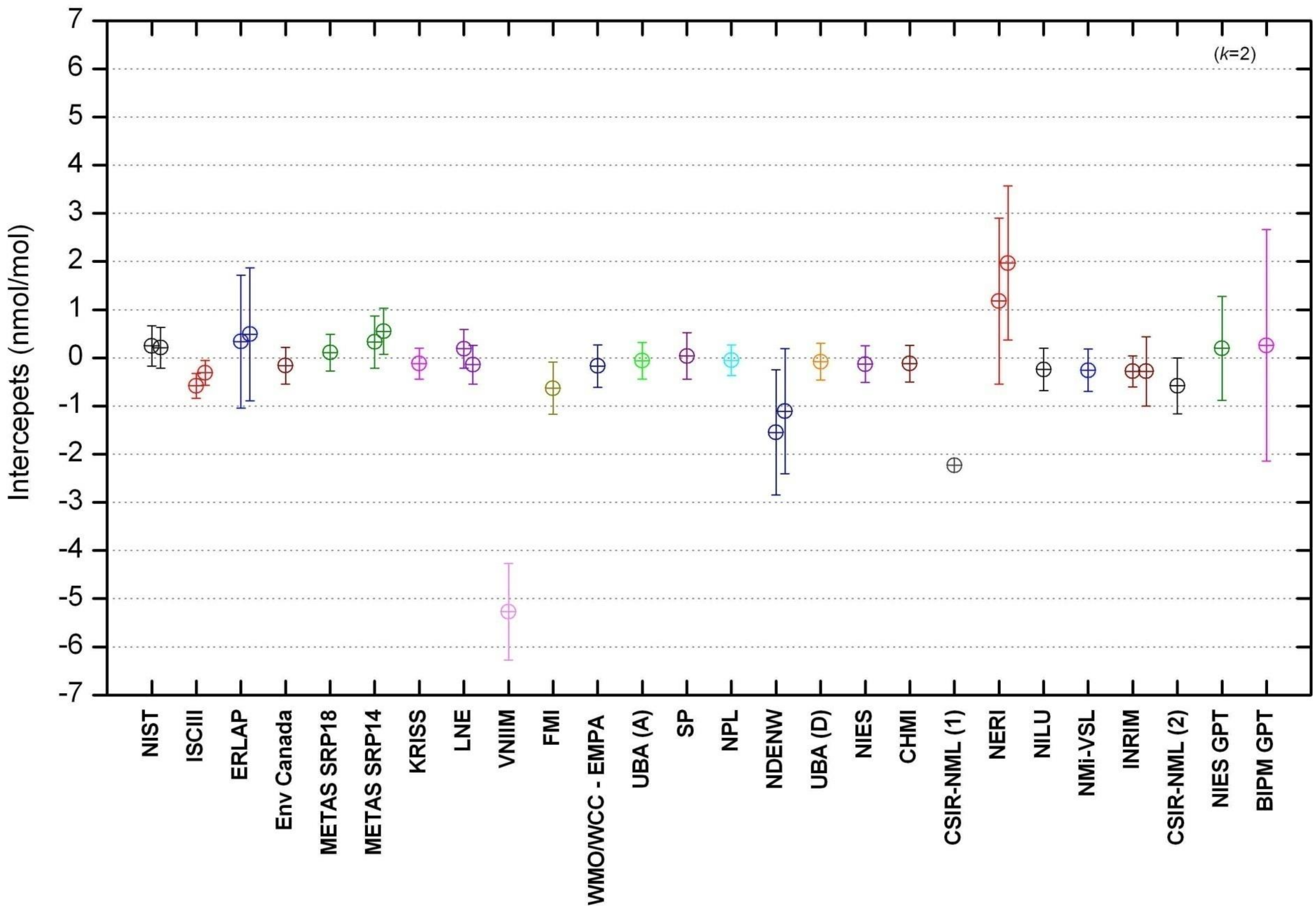
CCQM – P28 - Ozone Ambient Level Pilot Study

(slopes)



CCQM – P28 - Ozone Ambient Level Pilot Study

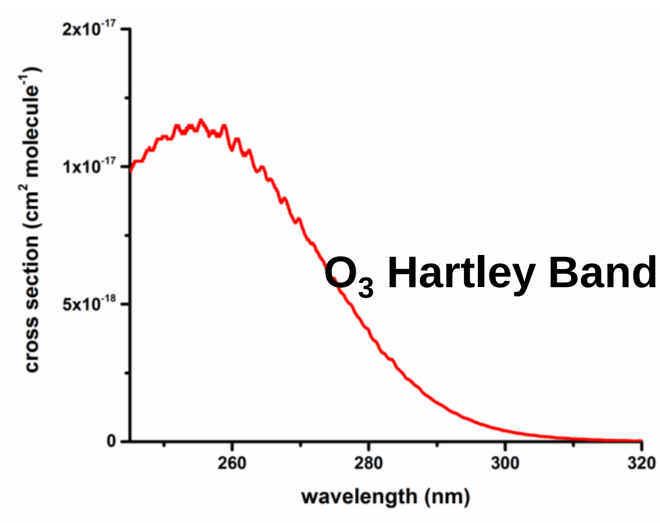
(intercepts)

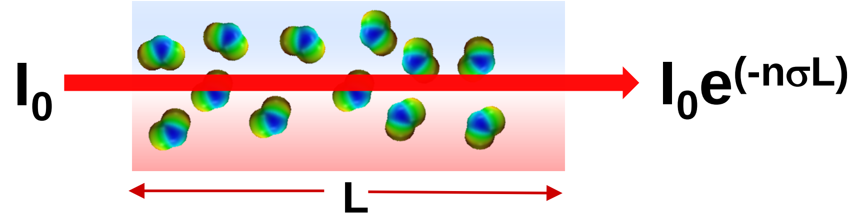


Redetermination of the Ozone Absorption Cross-section

CCQM-GAWG Ozone Cross Section Task Group

Joseph T. Hodges,[1] Joële Viallon & Robert Wielgosz,[2]
[1]National Institute of Standards and Technology
[2]Bureau Internationale des Poids et Mesures

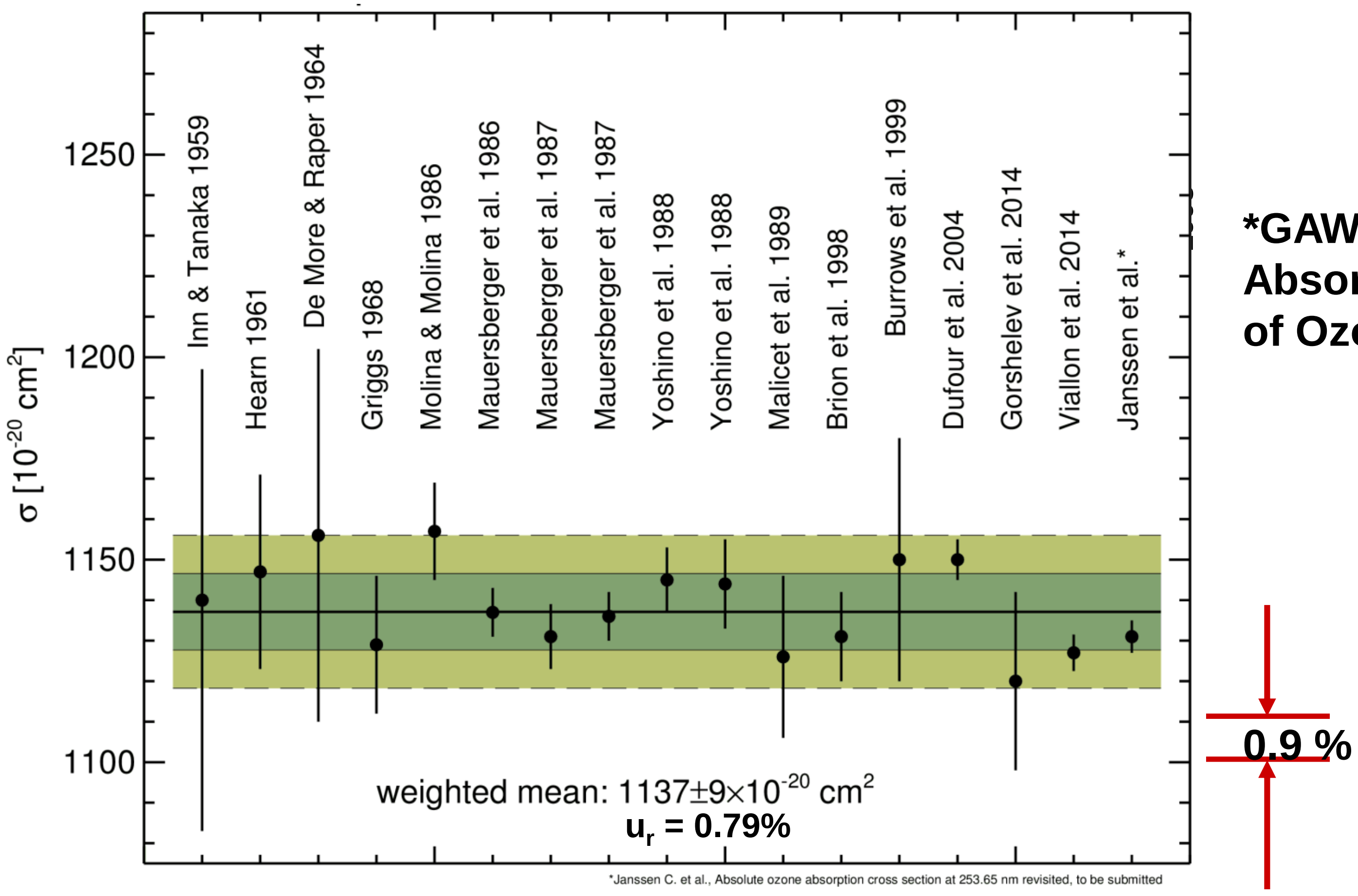




CCQM-GAWG Meeting, BIPM April 24-25, 2017

NIST

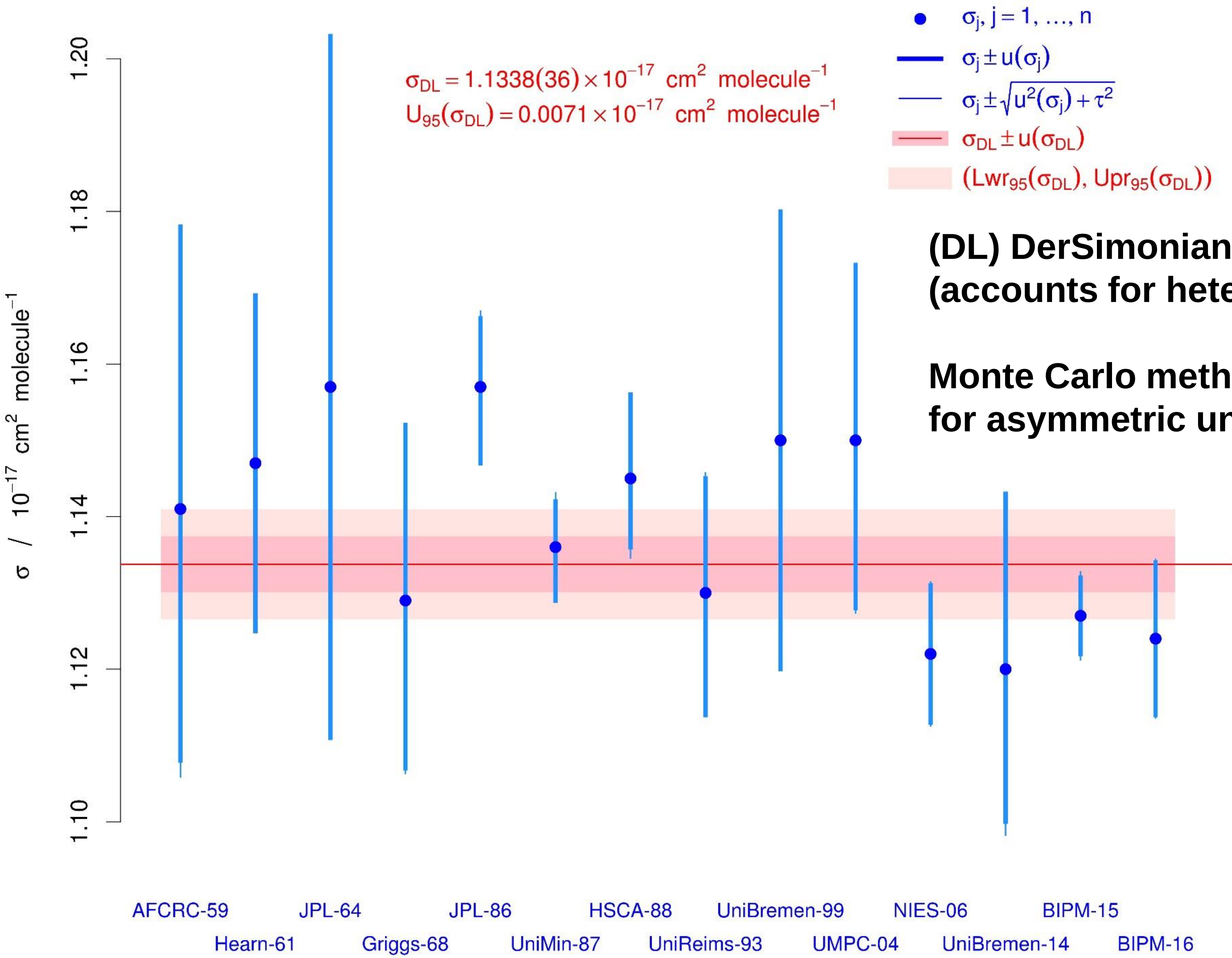
Room-temperature ozone cross sections at 253.65 nm*



***GAW 218**
Absorption Cross Sections
of Ozone (ACSO) Status Report

NIST

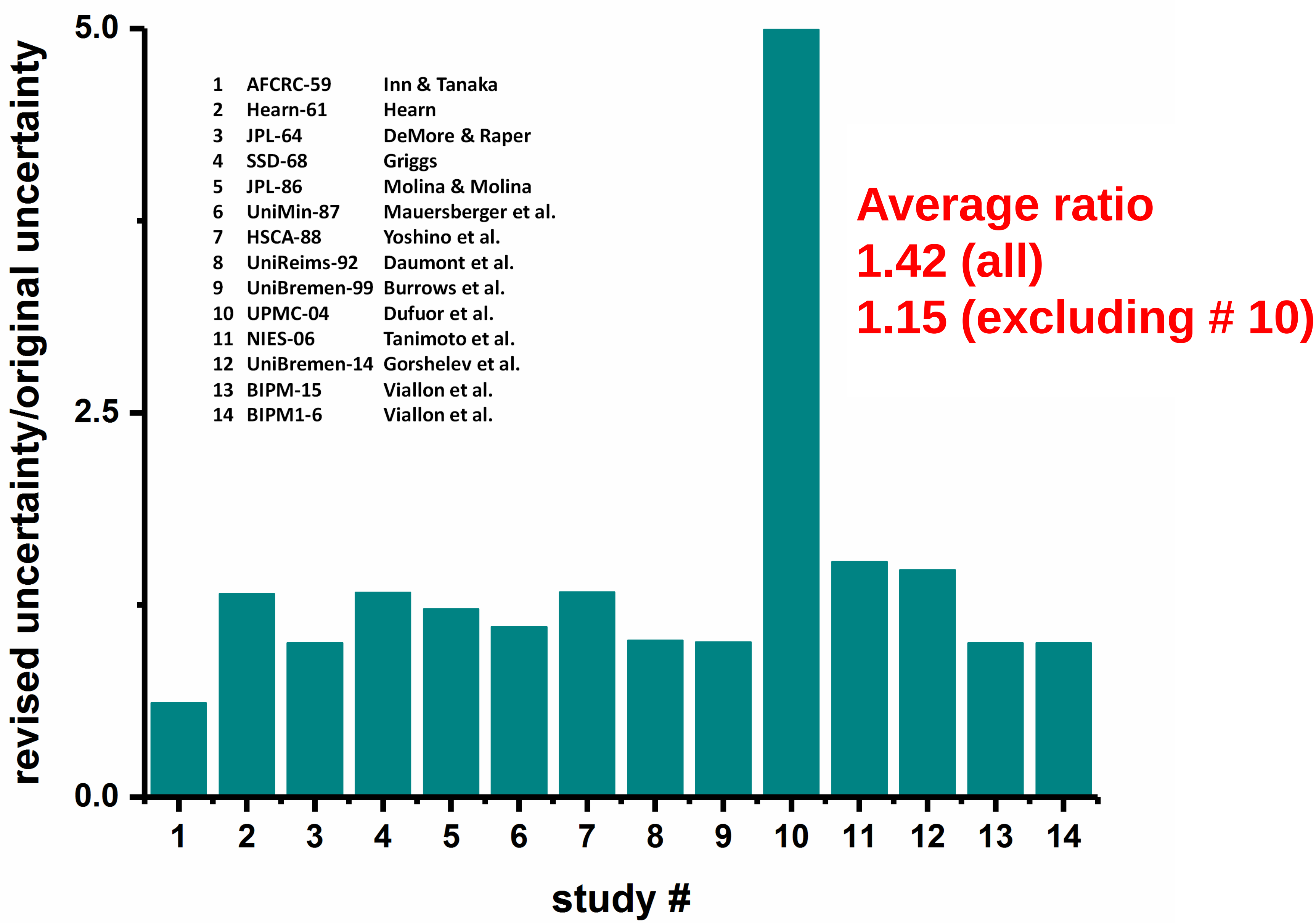
Statistical Analysis, Possolo (NIST)



(DL) DerSimonian-Laird (accounts for heterogeneity)

Monte Carlo method used to account for asymmetric uncertainties

Change in Assigned Uncertainties



NIST

Results for O_3 254 nm Cross section

Source	consensus value	relative to Hearn	standard relative unc.
Hearn	1.147×10^{-17} cm^2/molec. (Hearn)		1.9 %
ACSO/GAW	1.137×10^{-17} cm^2/molec. (ACSO/GAW)	-0.9 %	0.8 %
This work	1.1338×10^{-17} cm^2/molec.	-1.15 %	0.32 % (DL); 0.25 % (std. weighting)

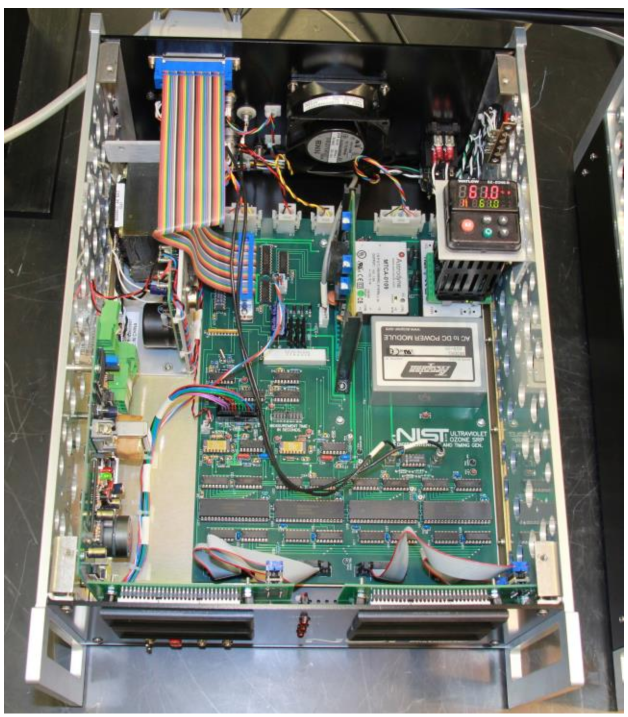
Monte Carlo, DerSimonian-Laird (DL) analysis provided asymmetrical pdf for uncertainties and confidence intervals.

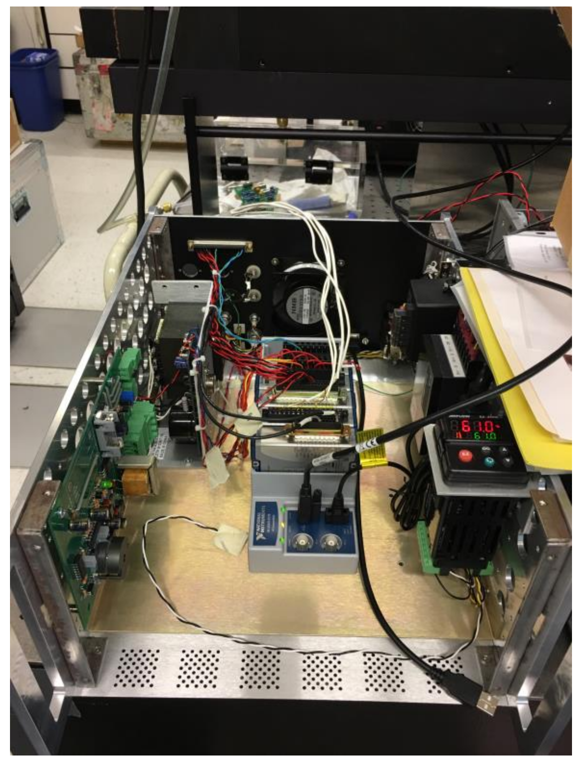
Standard weighting vs. DL analysis yields only a 0.05 % relative difference in cross section.

NIST

Update of SRP Electronics System

- Need based on obsolete components.
- NI cDAQ components to be used.
- Additional temperature sensors to be used, 2 for each cell.
- Additional pressure transducer available.
- O3 Conductor software (Lab View based) currently being updated for use with new electronics.
- Remote operation of sample pump.





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Summary

- **NIST Standard Reference Photometer**
  - Stable, Accurate Ozone Reference Standard for 35 Years.
  - Network agreement maintained within 1%.
  - Upgrade projects have improved agreement.
  - Maintained in 28 Countries, designated National Standard in 16 Countries.
  - Total of 62 instruments Worldwide (currently).
- **BIPM – NIST Collaboration**
  - Detailed Training and Study of SRP.
  - Developed International Traceability through CCQM.
  - Research with GPT, UV Laser, Cross-section redetermination.
  - Electronics update.
- **Ozone Traceability**
  - US Traceability well established.
  - CCQM Ozone Key Comparisons
    - P28 Pilot Study Completed – Results Published.
    - BIPM.QM-K1 Official Key Comparison (ongoing).