

Review-Ozone Transfer Standard Guidance

Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone
Technical Assistance Document

DRAFT May, 2009

Table 4-1 6-Day Initial Ozone Verification

Site	Level 1	Level 2	Level 3	Mean (ppb)	St. Dev.	Range (ppb)	CV	CV ²	CV ³
S1820001	0	1	1	1.920					
S1820001	31	81	0	0.000 (Median = 684)					
S1820001	798	798	1	0.000					
S1820001	260	260	0	0.000					
S1820001	480	481	1	0.000					
S1820001	0	1	1	0.000					
S1820001	80	80	0	0.000					
S1820001	90	90	0	0.000					
S1820001	204	204	0	0.000					
S1820001	282	288	4	1.584					
S1820001	448	452	3	0.000					
S2220001	0	1	1	0.000					
S2220001	80	80	1	1.200					
S2220001	89	86	1	1.200					
S2220001	262	268	2	0.000					
S2220001	380	382	2	0.000					
S2220001	482	482	1	0.000					
S2220001	0	0	0	0.000					
S2220001	80	81	1	1.100					
S2220001	90	91	1	1.100					
S2220001	201	201	0	0.000					
S2220001	281	282	1	0.200					
S2220001	481	482	2	0.400					
S2220001	0	0	0	0.000					
S2220001	80	80	1	1.100					
S2220001	90	89	1	1.100					
S2220001	198	197	1	0.000					
S2220001	282	282	0	0.000					
S2220001	481	481	0	0.000					
S2220001	0	0	0	0.000					
S2220001	51	50	0	1.000					
S2220001	91	90	1	1.000					
S2220001	208	208	1	0.000					
S2220001	380	380	0	0.000					
S2220001	481	481	0	0.000					
S2220001	481	481	0	0.000					
Avg	0.0000	0.0187	0.7027	0.0041					



Background

- Original document developed in 1979
 - Not many standards available
 - People were building their own
 - SRPs were not around yet
- Why Now
 - Newer/better technology
 - Newer terminology
 - Some methods no longer used

Guidance Document at:
<http://www.epa.gov/ttn/amtic/srpqa.html>

Transfer Standard Workgroup

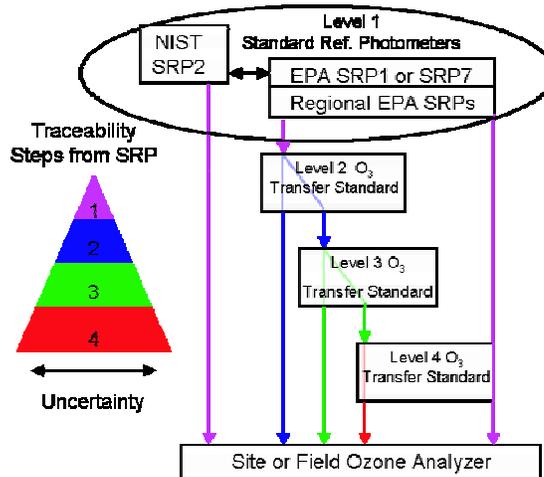
Brian Lee
 Chris Stgermain
 Donald Hammond
 James Regehr
 Joseph Delwiche
 Mark Shanis
 Paul Nichols
 Rayna Broadway
 Stephanie McCarthy
 David Malorin
 Michael Copeland
 Louie Pounds

Brian Spreadborough
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 Don Gourley
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 Lynn Geter
 Paul Groff
 Randy Dillard
 Scott Hamilton
 Michael Tolocka
 Anna Kelley
 Scott Moore

Thanks

New Model for Ozone Standards



What Have We Done

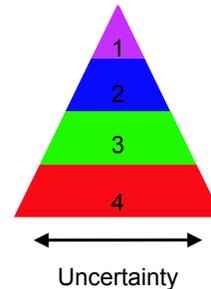
- Language- included a glossary
 - Using Levels starting from family of SRPs
 - Replaced “certification” with “verification”
- Consolidated to 4 sections from 6
- Removed Old Methods
 - Boric Acid Potassium Iodide
 - GPT with Excess Nitrogen Oxide
 - GPT with Excess Ozone
- “Softened” Qualification
- Nothing changed with verification procedure



What are we going to do?

- Adding Uncertainty
 - Trying to determine a way to add an uncertainty estimate at each level
 - If the additive uncertainty reaches some unacceptable value then you fix and you can't go below that transfer standard level.
 - Develop in a user friendly way (e.g. a Transfers Standard DASC tool on the Web?)

Traceability Steps from SRP



What do you think?

Summary Table

Requirement	Frequency	Acceptance Criteria	Information /Action
Regional Standard Reference Photometer (SRP) (Level 1 Standard)			
Verification	1/year	Regression slope = 1.00 ± 0.01 and intercept $< \pm 1$ ppb	This is usually at a Regional Office and is compared against the traveling EPA SRP
Ozone Level 2 Transfer Standard			
Qualification	Upon receipt of transfer standard	$\pm 4\%$ or ± 4 ppb (whichever greater)	Transfer Standard Doc EPA XXXX App B
Verification (6x6)	After qualification and upon receipt/adjustment/repair	RSD of six slopes 3.7% Std. Dev. of 6 intercepts 1.5	Transfer Standard Doc XXX Section 4.1
Verification/reverification to SRP Min- 6 points 7 replicates	After qualification and upon receipt/adjustment/repair 1/year	Each individual point difference $\leq \pm 3\%$	Level 2 standard usually transported to EPA Region's SRP for comparison
(if recertified via a transfer standard)*	1/year	Regression slopes = 1.00 ± 0.03 and two intercepts are 0 ± 3 ppb	
Ozone Transfer Standards Levels 3 and Greater			
Qualification	Upon receipt of transfer standard	$\pm 4\%$ or ± 4 ppb (whichever greater)	Transfer Standard Doc EPA XXXX App B
Verification (6x6)	After qualification and upon receipt/adjustment/repair	RSD of six slopes 3.7% Std. Dev. of 6 intercepts 1.5	Transfer Standard Doc XXX Section 4.1
Reverification to Level 2 standard	Beginning and end of O3 season or 1/6 months whichever less	New slope = ± 0.05 of previous and RSD of six slopes 3.7% Std. Dev. of 6 intercepts 1.5	Transfer Standard Doc XXX Section 4.2

Recommendations On Use Of Specific Types Of Transfer Standard Devices

- **Level-2** standards and/or standards used in the verification of other transfer standards include both a generation device and a photometer.
- **Level-3** standards be, at a minimum, a photometer. The level 3 standard can be a photometer and generator but should not be just a generator.
- **Level-4** and greater can be a ozone generation device.

What Else?

- Strongly suggest bringing the monitoring organizations “bench standard” to the SRP not a surrogate
- No adjustments- Suggesting that verifications be accomplished without adjustments. Allows for “drift and fix” paradigm.

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Questions

- Does the guidance seem reasonable?
- Specific Comments?
- What are your concerns?

Please provide any and all comments by June 19
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Developing model for traceability calculations

1. Would like to include uncertainty of higher level photometer comparisons in verifications.
2. Existing least-squares model assumes that for a given photometer verification, the higher level photometer measures without error. Would like to relax this assumption.

Proposed Approach

The current approach is a linear regression where:

$$Y = \alpha + \beta X + e$$

Y = reading of lower level photometer

X = reading of higher level photometer

If normal errors, $e \sim N(0, \sigma^2)$

The proposed approach:

Introduce regression parameters specific to each photometer (α_x, β_x), (α_y, β_y), where $\alpha_x, \alpha_y, \beta_x, \beta_y$ would be regression parameters for regression of X or Y on true (unknown) ozone concentration.

Estimate parameters of (α_y, β_y) in highest level comparison using assumption that highest level photometer measures without error (this can also be considered to be an assumption of the current approach).

In lower level comparisons apply regression model allowing for error in both X and Y and use relationship $\alpha = \alpha_y - \beta \alpha_x$, $\beta = \beta_y / \beta_x$ to estimate slope and intercept of lower level photometer, given previous estimates for higher level photometer.

- Suppose four-level traceability chain, with acceptance criteria for regression slope at each level being 1 ± 0.05 .
- For each verification, simulate 6 ozone readings over 0-1000 ppb at approximately SRP1/SRP7 precision
- All photometers tested have bias $\beta=1.04$

Photometer	True values			Estimated values current approach		Estimated values proposed approach	
	α	β	Cumulative bias	α	β	α	β
NIST	0	1	1.00	0	1	0	1
Level 1	0	1.04	1.04	-0.476	1.041	-0.476	1.041
Level 2	0	1.04	1.08	-0.044	1.002	-0.521	1.042
Level 3	0	1.04	1.12	-0.686	1.002	-1.208	1.044
Level 4	0	1.04	1.17	0.259	1.000	-0.948	1.043

- For current approach:
 - the first comparison suggests bias, but not others.
- For proposed approach:
 - All comparisons suggest bias, although none exceed bounds of acceptance criteria.
 - Cumulative bias exceeds acceptance criteria by second comparison.