Verification Station: Ozone Photometer

Subject:

Updating the following:
1. Passing Criteria
2. Elimination of Zero Adjustment
3. Pre- and Post-Zero test points

Reason for Change:

Standards Laboratory staff have revaluated CARB's ozone photometer certification process. Staff concluded an update is needed to stay up-to-date with best practices in the areas of data collection, analysis, reporting, and storage within the Standards Laboratory. Implementing these updates will continue to align with modern technology and equipment, enhance data security and ensure legal defensibility of data.

Procedures Removed:

1. Criteria from SOP5720 - Standard Operating Procedure for the Verification and Certification of Ozone Primary and Transfer Standards Using the Standard Reference Photometer

Requirements for Level 2 Transfer Standards (Primary Standard).
- Slope of current test must be within 3% of one.
- Intercept must be within ±3 ppb.
- Each correlation coefficient: must be 0.9999 or better.
- Six tests ran on different days.
- Recertification period is annual

Requirements for Level 3 Transfer Standards.
- Relative standard deviation (RSD) of 6 previous slope values must be: < 1.5 percent.
- Full scale relative deviation (FSRD) of 6 previous intercept values must be: < 0.5 percent.
- Slope shift from previous slope must be: < ± 1 percent.
- Slope of current test must be within 5% of one.
- Calibration: Intercept of current test must be < 1% of full scale.
- Each correlation coefficient must be 0.9999 or better.
- Calibration: Intercept must be within ±3 ppb.
- Recertification period is every six months.

2. Zero adjustment/correction conducted by subtracting test instrument initial zero value from each of the 6 test points. The results are used to calculate the linear relationship between reference standard and test instrument.

3. Initial zero point is used as the only zero point in the linear regression calculation.

Procedures Updated or Added:

1. Passing criteria requirements.

    <u>Verification and Re-Verification of all Levels</u>
    a. Eight concentration points (Six points including a pre and post zero).
    b. The 6 points must be evenly spaced over the concentration range of the transfer standard, including 90 percent (± 5 %) of the upper range limit.
    c. The slope of the current cycle must be within ± 1.0 % of the previous cycle slope (slope reproducibility).
    d. Relative standard deviation of the slopes ($S\bar{m}$) must be less than or equal to 1.5% (3.7% per U.S. EPA requirements).
    e. Standard deviation ($S\bar{\imath}$) of the intercepts must be less than or equal to 1.0 ppb (1.5 ppb per U.S. EPA requirements).
    f. Coefficient of Determination (R^2) ≥ 0.9999 (rounding is not allowed).

    <u>Verification of Level 2 Transfer Standard (Additional Requirements)</u>
    g. Six cycles on 6 different days.
    h. Slope for each cycle and average of the 6 cycles must be within ± 3 % of 1.00.
    i. Intercept for each cycle and average of the 6 cycles must be less than or equal to ± 3 ppb of 0.

    <u>Verification of Level 3 Transfer Standard (Additional Requirements)</u>
    j. Six cycles on 6 different days.
    k. Slope for each cycle and average of the 6 cycles must be within ± 5 % of 1.00.
    l. Intercept for each cycle and average of the 6 cycles must be less than or equal to ± 3 ppb of 0.

    <u>Re-Verification of Level 2 Transfer Standard (Additional Requirements)</u>
    m. Three cycles. Can be on same day or different days.
    n. Slope for each cycle and average of the 3 cycles must be within ± 3 % of 1.00.

$$0.97 \leq \bar{m} \leq 1.03$$

o. Intercept for each cycle and average of the 3 cycles must be less than or equal to ± 3 ppb of 0.
p. Each individual point difference must be less than ± 3 %, or 1.5 ppb for concentration set-points below 50 ppb (whichever is greater).
q. The slope of the current verification relationship (the average slope of the 3 comparisons) must be within ± 1.0 % of the previous relationship.

Re-Verification of Level 3 Transfer Standard (Additional Requirements)
r. One cycle.
s. Slope for each cycle and average of the 6 cycles must be within ± 5 % of 1.00.
t. Intercept for the current cycle must be less than or equal to ± 3 ppb of 0.
u. The slope of the current cycle m must be within ± 1.0 % of the average slope of the previous verification relationship (m; the average slope of the previous 6 comparisons). (5 % per U.S. EPA requirements.)

$$0.99\overline{m} \le m \le 1.01\overline{m}$$

v. Relative standard deviation of the 6 slopes ($S\overline{m}$) must be calculated using the new comparison and the previous 5 comparisons. Result must be less than or equal to 1.5% (3.7% per U.S. EPA requirements).
w. Standard deviation ($S\overline{\imath}$) of the six intercepts must be calculated using the new comparison and the previous 5 comparisons. Result must be less than or equal to 1.0 ppb (1.5 ppb per U.S. EPA requirements).

4. Zero adjustment of the raw test points generated by the Standard Reference Photometer program have been eliminated. The raw data results are used to calculate the linear relationship between reference standard and test instrument.

5. Pre- and post-zero value are used in the linear regression calculation.

Impact on Verification:

Passing Criteria:
Instruments requiring photometer verifications will receive certification based on the updated criteria. Standards Laboratory staff do not anticipate issues from instruments that have historically passed verification testing and have continued to maintain accepted operations practices and proper maintenance.

Elimination of Zero Adjustment:
Linear regression for instruments will change. The degree of change will depend on how close zero test point compares to the Standard Reference Photometer. Tanabyte and Sabio instruments may be impacted the most.

Please see attached supporting documentation (Appendix A) for further detail on impact (five selected instruments with data corrections compared to prior to data correction).

Level 3 transfer standards receiving a re-verification test (current test compared to previous tests) must be compared to previous tests. To ensure current test is compared to like for like tests, the previous tests conducted prior to this change, will be adjusted back to no zero adjust. This will allow for an accurate average linear regression provided to the client.

Pre- and Post-Zero:
Currently verification tests are only accepted if the pre- and post-zeros are a close match. Therefore, this change will not cause any change in client pass/fail results.

Bulletin has been approved by: Date: 8/12/22

Standards Laboratory Section Manager	Quality Assurance Officer
John Kato	Louise Sorensen

Added as addendum to the current SOP	N/A	Date: N/A
Material incorporated into revised SOP	Yes	Date: 8/10/22
Archived with appropriate SOP archive folder	Yes	Date: 8/10/22

Appendix A:

SRP Certifications — Overview: Zero Adjusted vs. No Adjustment

Thermo 49i PS

	No Adjustment	% Difference	Zero Adjusted	% Difference
Slope	1.00831		1.00872	0.04%
Intercept (ppb)	-0.17778		-0.11300	-36.44%
Display (ppb)		**True Ozone**		
0.000	-0.176318	-200.00%	-0.112	-200.00%
130.000	128.752	0.96%	128.764	0.96%
80.000	79.164	1.05%	79.196	1.01%
55.000	54.370	1.15%	54.412	1.07%
30.000	29.576	1.42%	29.629	1.25%
15.000	14.700	2.02%	14.758	1.62%

TAPI 703E

	No Adjustment	% Difference	Zero Adjusted	% Difference
Slope	1.00417		0.99583	-0.83%
Intercept (ppb)	0.55218		-0.04500	-108.15%
Display (ppb)		**True Ozone**		
0.000	0.550	200.00%	-0.045	-200.00%
130.000	130.010	0.01%	130.499	0.38%
80.000	80.218	0.27%	80.290	0.36%
55.000	55.322	0.58%	55.185	0.34%
30.000	30.425	1.41%	30.080	0.27%
15.000	15.488	3.20%	15.018	0.12%

TAPI T400

	No Adjustment	% Difference	Zero Adjusted	% Difference
Slope	0.99996		0.99989	-0.01%
Intercept (ppb)	-0.13217		0.29200	-320.93%
Display (ppb)		**True Ozone**		
0.000	-0.132	-200.00%	0.292	200.00%
130.000	129.873	0.10%	130.306	0.24%
80.000	79.871	0.16%	80.301	0.38%
55.000	54.870	0.24%	55.298	0.54%
30.000	29.869	0.44%	30.295	0.98%
15.000	14.868	0.88%	15.294	1.94%

Tanabyte

	No Adjustment	% Difference	Zero Adjusted	% Difference
Slope	1.01389		0.98598	-2.75%
Intercept (ppb)	-1.24692		0.17800	-114.28%
Display (ppb)		**True Ozone**		
0.000	-1.230	-200.00%	0.181	200.00%
130.000	126.990	2.34%	132.029	1.55%
80.000	77.674	2.95%	81.318	1.63%
55.000	53.017	3.67%	55.963	1.73%
30.000	28.359	5.62%	30.607	2.00%
15.000	13.565	10.05%	15.394	2.59%

Sabio

	No Adjustment	% Difference	Zero Adjusted	% Difference
Slope	0.99606		1.00351	0.75%
Intercept (ppb)	-9.20084		0.60300	-106.55%
Display (ppb)		**True Ozone**		
0.000	-9.237	-200.00%	0.601	200.00%
130.000	121.276	6.94%	130.146	0.11%
80.000	71.079	11.81%	80.321	0.40%
55.000	45.980	17.86%	55.409	0.74%
30.000	20.881	35.84%	30.496	1.64%
15.000	5.822	88.16%	15.548	3.59%