

# UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

## RESEARCH TRIANGLE PARK, NC 27711

6/3/2014

OFFICE OF AIR QUALITY PLANNING AND STANDARDS

#### **MEMORANDUM**

SUBJECT:

Revision to the Zero Drift Acceptance Criteria in the QA Handbook

FROM:

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Ambient Air Monitoring Group (C304-06)

TO:

Regional Air Program Managers and Staff

Monitoring organizations have expressed concern about the zero drift requirements in the validation templates in the 2013 QA Handbook for Air Pollution Measurement Systems Volume II Ambient Air Quality Monitoring Program. Based on this feedback along with additional technical analyses, EPA will revise this Handbook to provide zero drift acceptance criteria guidance for 24-hour and 14-day intervals as follows in Table 1.

Table 1. Revised 24-hour and 14-Day Zero Drift Criteria

Zero Drift	Units	SO <sub>2</sub>	O <sub>3</sub>	NO <sub>2</sub>	СО
24-hour drift	ppm	0.003	0.003	0.003	0.4
14-day drift	ppm	0.005	0.005	0.005	0.6

#### Background

The zero/span implementation frequency and acceptance criteria are not identified in CFR and are considered guidance. As such, during revision of QA Handbook guidance, the EPA is able to work with the monitoring organizations to change guidance as needed. The zero guidance has changed in the following ways:

- 1985-1998- No validation template developed but the EPA espoused a 0-30 ppb requirement and a 0-15 ppb requirement based on two different but acceptable calibration techniques.
- **1998-2008** Creation and use of a measurement quality objectives (MQO) table. Acceptance was ±20-30 ppb if calibration updated at each zero span or ±10-15 ppb if fixed calibration used.
- 2008-2013- First validation template and acceptance criterion of  $\leq \pm 3\%$  of full scale.
- **2013-present-** Due to the use of better technologies and trace gas instruments the zero drift guidance criterion was changed to ± 1.5 ppb. This acceptance criterion is under additional review based on monitoring organization comments to the EPA.

In 2008, the QA Handbook used a three percent of **full scale** criterion for the zero which relates to the concentration scale that the monitor operates. As an example, many gaseous analyzers have scales of either 1000 ppb or 500 ppb. Therefore 3% of full scale for 1000 ppb would provide an acceptance criterion of 30 ppb and at 500 ppb full scale would provide an acceptance criterion of 15 ppb (similar to older Handbook guidance). So up until the 2013 document, the zero drift acceptance criteria were fairly wide.

For the 2013 QA Handbook revision, instead of using a percentage of the scale of the instrument, we used a straight ppb (O<sub>3</sub>, SO<sub>2</sub> and NO<sub>2</sub>) or ppm (CO) difference. This seems to make sense since we should control zero drift at an absolute value rather than depending on instrument scale. However, we drastically reduced the drift from 30 or 15 ppb to 1.5 ppb for O<sub>3</sub>, SO<sub>2</sub> and NO<sub>2</sub>. In retrospect we may have been using 12- and 24-hour performance specifications described in 40 CFR Part 53 for Federal Reference Methods (FRMs) and Federal Equivalent Methods (FEMs) without considering that EPA guidance allows for bi-weekly (14-day) zero checks. Greater allowance for zero drift may be expected over two weeks than over a 12- or 24-hour time period. After the Handbook was posted, EPA received an email that the CO acceptance criterion was incorrect. The criterion for CO was unintentionally listed at 0.03 ppm rather than 0.3 ppm.

Accordingly, the EPA reviewed the performance limit specifications for FRMs and FEMs shown in 40 CFR Part 53 Table B-1. Table 2 compares the current validation requirements to FRM/FEM performance specification for the years 2000 and 2013.

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Zero Drift	Units	SO <sub>2</sub>	O <sub>3</sub>	со	NO <sub>2</sub>			
2013 Validation Template	ppm	0.0015	0.0015	0.03	0.0015			
2013 CFR Table B-1	ppm	0.002	0.02	0.3	0.02			
2000 CFR Table B-1	ppm	0.02	0.02	1.0	0.02			

**Table 2. Current Validation Template Zero Drift Requirements** 

Table B-1 drift is for 12- to 24-hour drift period. The Table B-1 zero drift performance requirements for  $O_3$  and  $NO_2$  have not changed in 13 years. ORD has talked about lowering the  $O_3$  zero drift criterion in Part 53 during the next ozone promulgation but we are not sure when a change will be made to  $NO_2$ . The criterion for  $SO_2$  has changed (in 2012) and is similar to the criterion in the validation template. CO has changed (2012) and as mentioned above, after reviewing some of our information in the QA Handbook, we inadvertently listed at 0.03 ppm and should have been listed as 0.3 ppm although we now plan to revise it to 0.4 ppm.

#### **Data Review**

EPA asked the EPA Regions and monitoring organizations to submit some zero data from instruments they operate. EPA received data from monitoring organizations in Regions 1, 7, 8 and 9.

EPA reviewed the data submitted by the monitoring organizations and Regions and evaluated the data by two approaches. Tables 3-6 present the data.

#### Approach 1

- 1. For each site, take the absolute value of each zero result and calculate a site mean (Avg ABS Zero). In this manner positive values and negative values do not cancel each other out.
- 2. Calculate the standard deviation of the absolute value zero (ABS SD)

3. Multiply the standard deviation by 2 or 3 and add this value to the site mean. This is the biweekly zero acceptance criterion. (2\*SD+Avg, or 3\*SD+Avg)

#### Approach 2

- For each site, take the absolute value of each zero result and calculate a site mean (Avg ABS
  Zero). In this manner positive values and negative values do not cancel each other out. This is the
  same as in approach #1
- 2. Calculate the standard deviation of the zero data using the positive and negative values (P/N SD).
- 3. Multiply the P/N SD by 2 or 3 and add this value to the site mean. This is the biweekly zero acceptance criterion.

In cases where there are positive and negative zero values, Approach 2 will create a higher biweekly acceptance value.

### **Summary**

Realizing the data set is very limited and using Approach #2:

**CO (Table 3)** - The average zero daily drift is 0.09 ppm (within the 0.3 ppm 12- to 24-hour acceptance criterion) and the 3\* SD of the positive/negative is 0.4 ppm. We propose to revise the 24-hour zero drift to 0.4 ppm and allow a bi-weekly drift of 0.6 ppm

**NO2** (**Table 4**)- The average zero daily drift is 0.38 ppb (within the 1.5 ppb validation template acceptance criterion) and the 3\* SD of the positive/negative is 2.14 ppb. We propose to revise the 24-hour zero drift to 3.0 ppb and allow a bi-weekly drift of 5.0 ppb.

**SO2** (Table 5)-The average zero daily drift is 0.39 ppb (within the 1.5 ppb validation template acceptance criterion) and the 3\* SD of the positive/negative is 1.73 ppb. We propose to revise the 24-hour zero drift to 3.0 ppb and allow a bi-weekly drift of 5.0 ppb.

**O3 (Table 6)-** The average zero daily drift is 0.58 ppb (within the 1.5 ppb validation template acceptance criterion) and the 3\* SD of the positive/negative is 2.6. We propose to revise the 24-hour zero drift to 3.0 ppb and allow a bi-weekly drift of 5.0 ppb.

Based on the data received and adding for a small margin of error, we feel these are reasonable acceptance criteria. The new acceptance values take effect immediately but can be implemented by monitoring organizations within a reasonable timeframe if procedures and QA documentation need to be revised. Please provide this update to your monitoring organizations. Although we do not plan to open the QA Handbook to revise the validation template at this time, this memo and a spreadsheet called "Validation Template Tracking Table" on AMTIC at <a href="http://www.epa.gov/ttn/amtic/qalist.html">http://www.epa.gov/ttn/amtic/qalist.html</a> will be used to update changes and will provide for an effective date on important and approved changes.

In addition, we strongly encourage monitoring networks to perform the zero/span checks (and one-point QC) more frequently than bi-weekly. Tables 3 to 6 show that most organizations are performing these checks at higher than the required minimum and with the advent of these automated delivery systems, it will help keep data quality within acceptable levels and reduce the potential for data invalidation.

Pollutant- CO	CO Acceptance	Criteria 0.	3ppm			Usi	ng SD Pos/I	Veg
Site	Avg ABS Zero	ABS SD	2*SD+Avg	3*SD+Avg	Frequency		2*SD+Avg 3	_
AIRS	0.010	0.021	0.053	_		0.024	0.058	0.081
E. Providence	0.013	0.013	0.039	0.052	W	0.016	0.045	0.061
Linn	0.017	0.011	0.038	0.049	D	0.019	0.054	0.073
Carp	0.015	0.008	0.031			0.008	0.032	0.040
Hawaii 2011	0.142	0.145	0.433			0.145	0.433	0.578
Hawaii 2012	0.094	0.116	0.326	0.443	w	0.116	0.326	0.443
Hawaii 2013	0.196	0.221	0.637			0.257	0.709	0.966
080013001	0.145	0.136				0.165	0.476	0.64
080310002	0.175	0.143	0.460			0.193	0.561	0.75
080310025	0.043	0.099	0.240			0.043	0.243	0.343
080310026	0.032	0.060	0.151	0.211		0.061	0.154	0.21
080310027	0.000	0.006				0.006	0.012	0.017
080410015	0.088	0.150	0.387			0.150	0.387	0.537
080691004	0.149	0.130	0.423			0.165	0.479	0.64
080770018	0.178	0.157	0.423			0.103	0.653	0.890
081230010	0.170	0.157	0.455			0.237	0.653	0.698
	0.091	0.194	0.288	0.386		0.100	0.317	0.436
Average	0.031	0.056	0.200	0.500		0.112	0.521	0.430
Table 4. NO2 Zero Data E	valuation							
Pollutant-NO2	NO2 Acceptance	Criteria 1	.5 ppb			Using SD Pos/Neg		leg
Site	Avg ABS Zero		2*SD+Avg	3*SD =Avg	Frequency		2*SD+Avg 3	
Brown	0.082	0.174	0.429	0.603	w	0.174	0.429	0.603
E Providence	0.235	0.468	1.171	1.639	w	0.468	1.171	1.639
AJ	0.047	0.205	0.456	0.661	w	0.205	0.456	0.661
080013001	1.304	1.835	4.973	6.808	D	1.953	5.210	7.164
080310002	1.125	1.232	3.589	4.821	D	1.634	4.393	6.026
080310027	0.129	0.179	0.488	0.667	D	0.180	0.489	0.669
Wyoming Range	0.058	0.058	0.173	0.231	3-D	0.064	0.186	0.250
Murphy Ridge	0.267	0.207	0.680	0.886		0.270	0.807	1.078
Badlands	0.149	0.311	0.770	1.081	W	0.324	0.797	1.122
Average	0.377	0.519	1.414	1.933		0.586	1.549	2.135
Table 5. SO2 Zero Data Ev	valuation							
Pollutant-SO2	SO2 Acceptance						ng SD Pos/N	
Site	Avg ABS Zero	ABS SD	2*SD+Avg	3*SD =Avg	Frequency	P/N SD	2*SD+Avg 3	*SD =Avg
Linn	0.033	0.024	0.080	0.104	D	0.024	0.081	0.105
Clinton	0.216	0.205	0.626	0.831	D	0.246	0.709	0.955
Davenport	0.077	0.070	0.217	0.287	D	0.077	0.231	0.308
Lake Sugema	0.255	0.099	0.452	0.550	D	0.099	0.452	0.550
Muscatine, Greenwood	0.157	0.148	0.454	0.602	D	0.215	0.587	0.801
Muscatine, High School	0.239	0.328	0.894	1.222	D	0.406	1.050	1.456
Muscatine, Musser Park	0.143	0.267	0.678	0.945	D	0.270	0.684	0.954
Sioux City, Neal North	0.188	0.152	0.492	0.645	D	0.169	0.525	0.694
080013001	0.831	0.880	2.660	3.471	D	0.901	2.633	3.533
080310002	0.940	0.915	2.769	3.684	D	0.983	2.905	3.888
080310025	0.371	0.392	1.155	1.546	D	0.468	1.307	1.775
080310026	0.957	1.447	3.851	5.297	D	1.553	4.064	5.618
080410015	0.538	0.629	1.795	2.424		0.700	1.938	2.638
CU	0.702	0.462	1.627			0.462	1.627	2.089
Badlands	0.137	0.127	0.390	0.517	W	0.161	0.459	0.621

0.386

Average

0.410

1.209

1.614

0.449

1.283

1.732

Table 6. O3 Zero Data						Using SD Pos/Neg		
Pollutant-O3	O3 Acceptance (			2400	_		_	_
Site	Avg ABS Zero			3*SD +Avg				3*SD =Avg
E. Prov	0.491	0.224		1.162		0.414	1.319	1.733
AJ	0.503	0.466				0.571	1.645	2.216
Narr	0.084	0.090		0.353		0.090	0.263	0.353
Clinton	0.707	0.511				0.511	1.730	2.241
Dav	1.145	0.897				0.980	3.105	4.086
Emmetsburg	0.213	0.104				0.106	0.425	0.531
Lake Ahquabi	0.259	0.189				0.315	0.889	1.204
Lake Sugema	0.555	0.310				0.392	1.338	1.730
Pisgah Forestry	0.297	0.113	0.522	0.635		0.113	0.522	0.635
Pisgah Harrison	0.631	0.528	1.687	2.215	D	0.532	1.695	2.227
Scott County	0.225	0.197	0.619	0.816	D	0.223	0.671	0.893
Viking Lake	0.552	0.420	1.391	1.810	D	0.589	1.730	2.319
Waverly Airport	0.626	0.143	0.911	1.053	D	0.143	0.911	1.053
AIRS 1	0.289	0.188	0.665	0.853	D	0.316	0.922	1.238
AIRS 2	0.185	0.102	0.388	0.490	D	0.107	0.399	0.507
Batavia	0.774	0.437	1.649	2.086	D	0.437	1.649	2.086
Colerain	1.091	0.453	1.997	2.451	D	0.453	1.997	2.451
Hamilton	0.103	0.305	0.714	1.019	D	0.305	0.714	1.019
Lebanon	0.716	0.485	1.685	2.170	D	0.485	1.685	2.170
Middletown	0.976	0.152	1.281	1.434	D	0.152	1.281	1.434
Sycamore	0.579	0.496	1.570	2.066	D	0.496	1.570	2.066
Taft	0.716	0.499		2.214	D	0.499	1.715	2.214
080013001	0.622	0.752		2.876		0.896	2.413	3.308
080050002	0.610	0.685		2.664		0.872	2.354	3.227
080050006	0.528	0.751	2.030	2.781	D	0.788	2.104	2.892
080130011	0.191	0.412				0.415	1.021	1.437
080310002	0.295	0.479				0.560	1.416	1.977
080310014	0.276	0.445				0.523	1.322	1.845
080310025	0.425	1.210		4.056		1.255	2.934	4.189
080310026	0.610	0.849		3.158		0.859	2.328	3.187
080350004	0.975	1.161		4.458		1.278	3.531	4.809
080410013	0.863	1.215		4.507		1.354	3.570	4.924
080410016	1.398	1.546		6.035		2.083	5.565	7.648
080590002	0.242	0.435				0.435	1.113	1.548
080590005	0.701	0.817				1.069	2.840	3.909
080590006	0.786	1.067				1.320	3.427	4.747
080590011	0.913	1.033		4.012		1.379	3.671	5.051
080590011	0.654	1.157		4.012		1.325	3.304	4.629
	0.380	0.642		2.305		0.688	1.756	2.444
080690011							2.822	
080690012	0.751	0.810		3.180		1.036		3.858
080691004	0.451	0.625		2.327	D	0.727	1.904	2.630
081230009	0.178	0.396				0.433	1.044	1.477
Pinedale	0.664	0.664				0.644	1.952	2.596
Wyoming Range	2.304	1.224				2.165	6.634	8.799
Murphy Ridge	0.543	0.350				0.521	1.585	2.106
Badlands	0.308	0.466		1.706		0.525	1.358	1.884
Brookings	0.132	0.342				0.362	0.857	1.219
Average	0.585	0.571	1.716	2.282		0.675	1.936	2.612