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OFFICE OF AIR QUALITY PLANNING AND STANDARDS

Technical Note- Clarifications and Guidance on Gaseous Pollutant Methods

01/30 /2018

During recent revisions to the QA Regulations (March 2016) and the QA Handbook (January 2017), EPA has received questions from the monitoring community on a few topics that will be addressed in this technical memo. OAQPS and ORD both agree with the clarifications and guidance below and will eventually reflect this information in future method revisions. These clarifications and guidance are effective immediately.

Concentration Requirement for NO Cylinder Standards

The NO_2 method, 40 CFR Part 50 Appendix F Section 1.3.1 requires a *"gas cylinder standard containing 50 to 100 ppm NO in N_2 with less than 1 ppm NO_2."* This method has not been revised in some time and there are NIST traceable standards lower than 50 ppm NO in N_2 on the market that are now suitable for use in this method. Therefore, lower standards that are NIST traceable may be used for calibrations.

Concentration Requirement for SO_2 Cylinder Standards

The SO_2 method, 40 CFR Part 50 Appendix A-1 Section 4.1.6.1 requires a *"SO_2 gas concentration transfer standard having a certified SO_2 concentration of not less than 10 ppm, in N2, traceable to a NIST Standard Reference Material (SRM)"*. This method has not been revised in some time and there are NIST traceable standards lower than 10 ppm in N_2 on the market that are now suitable for use in this method. Therefore, lower standards that are considered EPA protocol gas and NIST traceable may be used for calibrations. The transfer standard requirements for calibrations do not apply to the standards used for the 1-point QC checks or annual performance evaluations and therefore, lower concentration standards can be used for these checks as long as the gasses used are EPA protocol gas and NIST traceable.

Calibration Acceptance Criteria Language

For the O_3 (40 CFR part 50 App D Sec 4.5.5.6), SO_2 (40 CFR Part 50 App C Sec. 4.2.9) and CO (40 CFR Part 50 App C Sec 4.4.7) methods, the following sentence can be found:

"Compute (or calculate) the linear regression slope and intercept and plot the regression line to verify that no point deviates from this line by more than 2 percent of the maximum concentration tested"

The CFR criteria could be interpreted that you can take the highest test concentration (for example 400 ppb for ozone with full scale at 500 ppb) and take 2 percent of that value (8 ppb) and allow every calibration point to diverge from the calibration line by 8 ppb.

Since 2008, the QA Handbook has guidance that suggests:

"For the gaseous pollutants the verification/calibration is considered acceptable if all calibration points fall within 2% of the full scale, best fit straight line.

In this case, all calibration points are used to develop the calibration regression line. Once the line is developed no individual point may deviate from the line by two percent. In addition, because the Handbook allows for calibrations at lower concentrations than full scale[1], EPA will be adding a 1.5 ppb difference for O_3, SO_2 and NO_2 and 0.03 ppm CO difference acceptance criteria for those monitoring organization that plan to calibrate at lower concentrations. If either acceptance criteria pass, the calibration will be acceptable. EPA suggests that monitoring organizations use the Handbook language.

NO2 Dynamic Parameter Specifications (40 CFR Part 50 Appendix F Sec 1.4)

Monitoring organization have found it difficult to meet both the residence times and dynamic parameter requirements when calibrating or auditing at lower levels.

1.4 *Dynamic parameter specification.*

1.4.1 The O_3 generator air flowrate (F_0) and NO flowrate (F_{NO}) must be adjusted such that the following relationship holds:

$P_R = [NO]_{RC} \times t_R \geq 2.75$ ppm-minutes

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} < 2 \text{ minutes}$$

where:
P_R = dynamic parameter specification, determined empirically, to insure complete reaction of the available O_3, ppm-minute
$[NO]_{RC}$ = NO concentration in the reaction chamber, ppm
t_R = residence time of the reactant gases in the reaction chamber, minute
$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm
F_{NO} = NO flowrate, scm^3/min
F_O = O_3 generator air flowrate, scm^3/min
V_{RC} = volume of the reaction chamber, scm^3

With the allowance of a lower the gas standard (20 ppm NO), ORD demonstrated their calibration system in the following configurations (see Figure 1.) can meet the residence times and the dynamic parameter specifications. Therefore, with the ability to use lower concentration gas standards these parameters can be met. However, as the method gets reviewed, ORD will review the requirements for the dynamic parameter specification.

[1] The QA Handbook is using the term "calibration scale" to denote a range for calibration based on routine concentrations measured at monitoring organization sites.

Figure 1. Dynamic parameter and residence time information							
NO conc	PPB	200	200	400	400	500	500
O3 conc	PPB	180	10	300	10	400	10
F_{NO}	SCCM	84.5	84.8	169.1	169.2	210.5	210.5
F_{O}	SCCM	129	27.8	129.1	27.8	129	27.8
FZA-Act	LPM	8.31	8.42	8.24	8.34	8.2	8.3
t_R	Minutes	0.627635	1.190053	0.449363	0.680203	0.394698	0.562316
$[NO]_{RC}$		7.915691	15.06217	11.34138	17.17766	12.40059	17.66681
P_R	ppm/Min	4.968162	17.92478	5.096395	11.6843	4.894489	9.934335
P_R must be	≥2.75	ok	ok	ok	ok	ok	ok
V_{RC} (cm3)		$[NO]_{STD}$					
134		20	ppm				