

Through-the-Probe Criteria Pollutant Performance Audit Procedures

Volume V Audit Procedures Manual for Air Quality Monitoring

> QMB SOP Appendix E Revision 10

Quality Assurance Section

Quality Management Branch

Monitoring and Laboratory Division

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THROUGH-THE-PROBE CRITERIA POLLUTANT PERFORMANCE AUDIT PROCEDURES

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ACRONYMS AND DEFINITIONS

Acronym	Definition
AC	Alternating Current
AIS	Audit Information System
AQDA	Air Quality Data Action
CAN	Corrective Action Notification
CARB	California Air Resources Board
CE	Converter Efficiency
CO	Carbon Monoxide
°C	Degrees Celsius
H ₂ S	Hydrogen Sulfide
ID	Inside Diameter
kPa	kilopascal
lpm	Liters Per Minute
MFC	Mass Flow Controller
NAAQS	National Ambient Air Quality Standard
NIST	National Institute of Standards and Technology
NO	Nitric Oxide
NO ₂	Nitrogen Dioxide
NOx	Oxides of Nitrogen
NPAP	National Performance Audit Program
O ₃	Ozone
OD	Outside Diameter
PE	Performance Evaluation
POC	Parameter Occurrence Code
PQAO	Primary Quality Assurance Organization
PPB	Parts Per Billion
PPM	Parts Per Million
PSI	Pounds per Square Inch
QAPP	Quality Assurance Project Plan
QAS	Quality Assurance Section
SB	Superblend (cylinder)
SO ₂	Sulfur Dioxide
SOP	Standard Operating Procedure
TTP	Through-The-Probe
U.P.	Ultra Pure air
UPS	Uninterruptible Power Supply
U.S. EPA	United States Environmental Protection Agency
VAC	Volts Alternating Current
VOC	Volatile Organic Compound

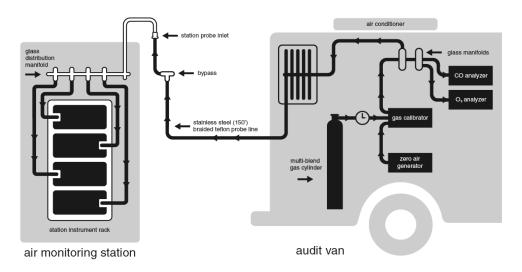
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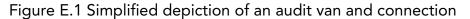
E.1.0 INTRODUCTION

The California Air Resources Board (CARB) Quality Assurance Section (QAS) is responsible for conducting through-the-probe (TTP) performance audits. These audits are required annually on all continuous gaseous analyzers in the ambient air monitoring network measuring for criteria pollutants. TTP audits of gaseous analyzers monitoring for ozone (O3), carbon monoxide (CO), nitrogen dioxide (NO2), hydrogen sulfide (H2S), and sulfur dioxide (SO2) are conducted in accordance with U.S. Environmental Protection Agency (U.S. EPA) requirements (Title 40 Code of Federal Regulations, Part 58, Appendix A). These audits verify the accuracy of the gaseous analyzers and ensure the integrity of the entire sampling system.

E.2.0 SUMMARY OF METHOD

For TTP audits, an audit van is driven by QAS staff to the ambient air monitoring station. Audit vans contain the necessary instrumentation and equipment to allow the audit to be conducted under the same conditions as the station instruments. As depicted in Figure E.1, various concentrations of pollutant gases are delivered from the van, through a presentation line, into the station sampling probe. QAS compares the results obtained from the station analyzer to the known values generated in the van to determine accuracy.

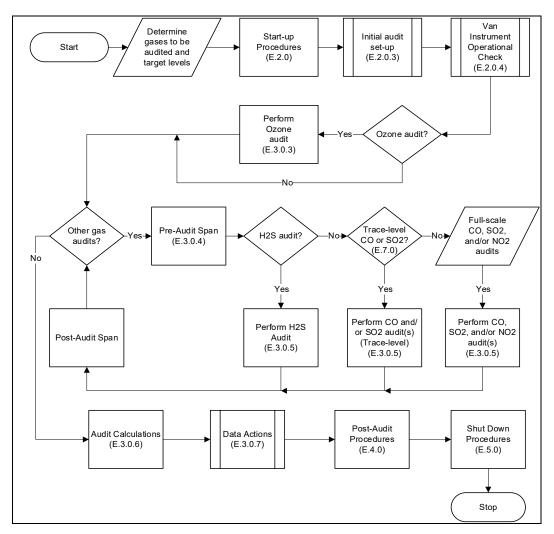




The TTP audit methodology exposes deficiencies due to poor analyzer response, pollutant scavenging contaminants, and sampling system leaks.

Deficiencies like these can cause the gaseous analyzers to fail an audit and possibly affect the quality of the ambient air data.

Figure E.2 (below) shows an overview of the audit process including decision making and a simplified order of operations.





E.3.0 INTERFERENCES

The interferences associated with this method include factors that can alter the concentration of audit gases. Such changes can be the result of loss (through leak or reactivity) or contamination. Interferences can be minimized by following these guidelines:

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- Take precautions to prevent the introduction of dirt or debris into the gas flow path. Ensure that the flow path's interior surfaces are clean, including manifolds, tubing, fittings, presentation line connections, etc.
- Use leak checks as required to identify and correct any leaks found within the flow system.
- Do not jeopardize the integrity of the flow path by opening connections unnecessarily or leaving fittings open and uncapped.
- Take all steps to minimize sampling and analysis residence times, including tubing and other flow path component lengths and diameters, dead spaces, leaks, unnecessary path resistance (due to sharp bends, kinks, etc.).
- Ensure the connection between the audit probe and station inlet allows for at least 1 liter per minute (lpm) of bypass. Improper bypass connections can allow entrainment of ambient air into the flow path, or pressurization of the system.
- Follow procedures for purging the cylinder pressure gauges to remove interference caused by either bleeding from the regulators or reaction of the gases in the gauges and lines.
- Water vapor can result in false positive analyzer readings and inaccurate dynamic dilution concentrations. To minimize this interference, use only well-dried zero air.

Ozone: The ultraviolet (UV) absorption method for detecting ozone is subject to interference from environmental contaminants such as sulfur dioxide, nitrogen dioxide, nitric oxide, water, volatile organic compounds (VOCs), and metal surfaces. The photometers in both the ozone standard and gas calibrator have been successfully tested for their ability to reject interference from most of these contaminants, and contain filters to assist in this process.

Carbon Monoxide: The carbon monoxide (CO) analyzer utilizes a band pass filter just before the infrared sensor, which allows the instrument to react only to infrared absorption in the wavelength (4.7 μ m) affected by CO. An analysis and comparison of the measure and reference signals and extraction of the ratio between them is performed to reject the effects of interfering gases. More information regarding the theory of operation for gas filter correlation analyzers can be found in the manufacturer's operations manual.

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E.4.0 PERSONNEL QUALIFICATIONS

All new CARB auditors undertake a one-year training program that is documented and monitored by the Quality Assurance Section (QAS) manager. The training includes in-office reading and coursework, handson field experience conducting audits, and shadowing an experienced auditor for one year along with several in-field evaluations by the QAS manager.

U.S. EPA reviews CARB's training program regularly for approval as an equivalent to U.S. EPA's national certification and recertification courses. Auditors should be familiar with the regulations and guidance cited in the references section (E.14.0) prior to conducting any audits without supervision. Each auditor is expected to have a minimum level of on-the-job training and familiarity with the audit equipment prior to conducting the audit.

E.5.0 HEALTH, SAFETY, AND CAUTIONS

All personnel must follow any general health and safety guidelines as described by the facility where the audit is conducted. All audit equipment, including audit vehicles, should be used only for the purpose and in the manner described in this standard operating procedure (SOP) and in the appropriate operator's manual. Gases from the equipment's vent and exhaust ports may contain ozone or other harmful compounds. Care should be taken to vent excess test gas outside of enclosed spaces or buildings whenever possible. Vehicles should be parked away from the air monitoring station when possible, taking note of wind direction and vehicle exhaust. Vehicles and generators should be left running only when necessary.

E.6.0 EQUIPMENT AND SUPPLIES

The current TTP audit system uses the following equipment:

- 1. Audit van with 240 VAC land-line and AC generator(s).
- 2. Voltage stabilized line conditioner, with battery backup.
- 3. U.S. EPA protocol compressed gas cylinders traceable to National Institute of Standards and Technology (NIST).
 - a. High CO (approximately 4 lpm or 16 lpm, depending on the targeted CO concentrations).

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- b. Low CO (approximately 1 lpm or 4 lpm, depending on the targeted CO concentrations).
- c. Ultra Pure (UP) zero air.
- d. Superblend #1 (SB #1): CO, NO, NOX, and SO2.
- e. Superblend #2 (SB #2): CO and H_2S .
- 4. Zero air generator.
- 5. Gas calibrator with an O_3 generator and photometer.
- 6. Ozone analyzer.
- 7. Carbon monoxide analyzer.
- 8. Oxides of Nitrogen analyzer (optional).

NOTE: The Oxides of Nitrogen analyzer is used for troubleshooting and diagnostic purposes only. Therefore, it is not calibrated on a regular basis.

- 9. Presentation line is 150 feet of 3/8 inch inside diameter (ID) Teflon[®] line with stainless steel over-braiding and rubber casing with one to two feet of ¼ inch outside diameter Teflon[®] line attached to the end.
- 10. Rotameter and glass tee for bypass flow.
- 11. Electronic barometer and temperature sensors.
- 12. Electronic chart recorder to document audit van temperature and audit van gaseous concentrations.
- 13. Audit software to record and store audit data, calculate results, and generate a report upon completion of the audit.

E.7.0 START-UP PROCEDURES

E.7.1 AUDIT VAN EXTERIOR

Open the generator compartment door(s) and verify that the oil is in the "safe" operating range for each generator. Park the vehicle on level ground and shut off generator before checking generator engine oil. Unscrew the fill cap and wipe oil off the dip-stick. Screw the cap back on,

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remove it and check the oil level on the dip-stick. The oil level should be in the "safe" operation range between the FULL and ADD marks on the dip stick. Add the correct type of oil, as necessary.

E.7.2 AUDIT VAN INTERIOR

If additional warm-up of instruments is required prior to starting the generator(s), turn on equipment, in the following order: the voltage stabilized line conditioner with battery backup, the zero air generator, the O_3 analyzer, the CO analyzer, and the gas dilution calibrator. The voltage stabilized line conditioner with battery backup should operate these instruments for up to one and a half hours, but the generator(s) or a land-line power source should be used during warm-up when possible. The zero air flowing through the system during the warm-up period should be free of moisture, as indicated by the "ready" light on the zero air generator.

- 1. Make certain that the generator/land-line power source selector is in the appropriate position (see generator operations manual located in the vehicle or online).
- 2. Check that all circuit breakers are in "on" position.
- 3. Start generator(s) and warm up for five minutes prior to placing electrical load on generator(s). If 240 VAC is available, use land-line power source in place of generator(s). After power source is stabilized, place the power control switch in appropriate position (See specific procedures in audit van.)
- 4. Turn "on" the power to the voltage stabilized line conditioner with battery backup (if not already on).
- 5. Turn "on" the power to the zero air generator (if not already on). Allow enough warm-up time for the humidity indicator to be "ready".
- 6. Turn "on" the power to the gas calibrator dilution unit (if not already on).
- 7. The following analyzers are used for audit(s) of the indicated gases:
 - a. O_3 : O_3 analyzer.
 - b. CO, H₂S, and SO₂: CO analyzer.
 - c. NO_2 : O_3 , CO, and NO/NO_x (optional) analyzers.

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NOTE: While the analyzers are in operation, the inside temperature of the van laboratory area should be maintained at 20-30 degrees Celsius (°C), Quality Assurance Handbook Volume 2, Section 7.2.2). Check temperature routinely and adjust climate controls as necessary to minimize fluctuations. U.S. EPA suggests maintaining temperatures within a standard deviation of $\leq \pm 2$ °C over a 24-hour period in order to provide a stable temperature environment for the analyzer.

- 8. Turn "on" the power to the electronic chart recorder.
- Allow a minimum warm-up time of one hour for the gas dilution calibrator and O₃ and CO (Picarro) analyzers, and three hours for the NO_x analyzer (or as recommended by the manufacturer).
- 10. For ozone and NO₂ audits, condition the van's presentation line by running a high level of ozone thru the system prior to arriving at the station. H₂S audits should also include pre-conditioning by flooding the system with H₂S before arrival.

E.7.3 INITIAL AUDIT SET-UP

- 1. Place safety cones around van as necessary to ensure public and worker safety. Chock the van wheels, if necessary.
- 2. Verify that the zero air generator and all instruments required for the audit are operating properly and warmed up.
- 3. Ensure that the Superblend cylinder concentrations for the current quarter have been correctly entered into the gas dilution calibrator.
- 4. Have the station operator place the station's data logger into audit or maintenance mode, or flag channels as appropriate.
- 5. Set the gas dilution calibrator to flow zero air through the van's presentation line. Be sure the amount of zero air is sufficient based on the flow requirements for all analyzers in the sampling train and the station's manifold configuration. Adjust the van's bypass rotameter to 0.3-0.4 liters per minute, if necessary.
- 6. Attach the presentation line to the station's gaseous probe inlet such that there is no entrainment of ambient air and bypass of at least one lpm of excess flow from the audit van. Use a rotameter to verify excess flow, as necessary.

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NOTE: Connections will vary from station to station. Common connections are: (1) through the calibration port on the station's glass inlet and (2) using the glass tee available in the audit van. Whatever the connection, be sure there is at least one lpm of bypass, and that ambient air is not entrained into the system, causing dilution of audit gases. A magnehelic can be used to ensure that the system's pressure has not changed.

7. Secure the presentation line to prevent movement during the audit.

E.7.4 VAN INSTRUMENT OPERATIONAL CHECK

If any of the analyzers fail to meet operational standards, consult the operator's manual to review the analyzer's test parameters and look up the troubleshooting guidelines. The operator's manual, instrument operation manuals, and standard operating procedures are located on the van's laptop and tablets in electronic form.

E.8.0 THROUGH-THE-PROBE AUDIT

E.8.1 <u>OVERVIEW</u>

To challenge the continuous gaseous analyzers measuring criteria pollutants, QAS conducts TTP audits by diluting known quantities of NIST traceable gases with up to 16 lpm of pure air to achieve concentrations of pollutants recorded at various levels. The TTP technique also serves to test the integrity of the entire sampling system. This is accomplished by introducing the diluted gas mixture into the monitoring station's probe inlet, where it is drawn through the sampling system by the gaseous analyzers.

A gas calibrator with an O_3 generator is used to control the dilution of O_3 and high concentration gases from U.S. EPA protocol compressed gas cylinders containing the following pollutants: CO, NO, NO_X, and SO₂ (SB #1); or CO and H₂S (SB #2). An ozone standard is used to determine a true O_3 concentration, which is used for auditing the station O_3 analyzer. An audit van CO analyzer is calibrated at a known high concentration and checked for linearity at a lower concentration. The zero response is calibrated using a zero air generator, and a cylinder of Ultra Pure zero air is used to verify the purity of the zero air generator. The switching of calibration cylinders may be achieved by manually moving the connections to each cylinder or through the use of solenoids, depending on the configuration of the audit van. After calibration, the CO analyzer is used to track the level of CO present in diluted gas samples. The CO

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analyzer response to the concentration of CO present in the diluted gas samples is used for auditing station CO analyzers. The audit van CO analyzer response also determines the true concentrations of all other pollutants present in the diluted sample, based on the ratios in the cylinder, which is used for auditing the respective analyzers.

E.8.2 DATA RETRIEVAL / RECORDING

The station instrument response for each sample gas delivered from the audit van (audit point) is noted from the data acquisition system used for collecting and storing the data-for-record. This data acquisition system may be a chart recorder, data logger, or computer.

NOTE: For each audit point, the station instrument response and van instrument display are both recorded on the Gaseous Audit Worksheet (Figure E.3) and entered into the Audit Information System (AIS) software program. AIS references calibration information (such as the O_3 line loss factor, O_3 standard slope and intercept, and gas cylinder certification data) to calculate the van's true response at each audit point. AIS then calculates the percent difference between the two responses for each audit point and compares it with the acceptance criteria to indicate results. At lower audit levels, the actual difference is also calculated for comparison.

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uditors:						_							۶) Po	st		Verif Dat	te:	
		* Audit Po	ints in leve	ls 1 or 2 wil	be evalu	ated and w	on't autor	natically be	subject to	corrective a	tion in 20	21					d Dev over 24 1	
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Target O3 (ppm)	Actual 03 (ppm)	Station Response		Van Reading	Target CO (ppm)	Actual CO (ppm)	Station		NO Station Response	NOx Station Response	O3 Target O3 (ppm)	NO Station Response	NOx Station Response	Pre-Audit CD	Van Reading	Target CO (ppm)	Actual CO (ppm)	Station Response
Zero			Zero		Zero									ZERO		ZERO		
			Hi CO		17.0 (101pm)									Hi CO		6.0		
0.130			Low CO		12.0 (13 lpm)	+	-				0.080			Low CO		4.0		\vdash
0.080			U.P.		4.0	+			<u> </u>		0.080			U.P.		3.0		\vdash
0.055				0 Van Reading	2.0						0.015	-		Post-Audit CO	Van Reading	2.0		
0.015			Hi CO		1.7						0.004	t.		Hi CO		0.72		
			Low CO		0.72													
0.005			U.P.		0.30	+								U.P.		Zeta our points, ba	and on range o	station's H25)
Zero			Zero		Zero	+								1				
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		Ozone		CO		SO ₂		NO2		H₂S				Standard	Stand			o/Span
Manufa	cturer:											Manufactu						
Model N	umber:											Model Num	ber:					
Serial N	umber:											Serial Num	ber:					
Last Cali	brated:											Last Calibra	ted:		(Jevel 8: 1/6 mo.)	(Level 1-2: 1/yr)		(1/m)
Instrument	Range:												G	Standard I. Gas Cylinder			Verification Gas C	
Slope /	Coeff.:							NO slope	NOx slope			Serial Num	ber:					
ntercept /	Offset:							NO Intercept	NOx Intercept			Cylinder Expir.	Date:					
Indicate	d Flow:											Station data adju corrected for an		Last Zero Air Check Date	Zero/ Checi		1-pt QC	check Frq
in-line Filter	change:											No Ves						
Span & 1-pt	Targets:	Span	1-pt QC	Span	1-pt QC	Span	1-pt QC	Span	1-pt QC	Span	1-pt QC			ses. ³ Verify slope/h 017) section 10.4 for gui				

Figure E.3 QA Gaseous Audit Worksheet

With current technology, many monitoring stations are using electronic data loggers that store data at the site, until collected, on a set schedule. The data from the electronic data logger is handled in the same manner as the strip chart data, except that it is read directly from an electronic display at each audit level. The responses are recorded by the auditor on the audit worksheet and entered into the audit software program. Station meta-data, such as calibration information, flows, and manifold pressure (if applicable), are also recorded onto the audit worksheet.

E.8.3 OZONE AUDIT PROCEDURE

Ozone audits should be performed first, and the presentation line must be pre-conditioned (Section E.7.2, step 10).

1. Pre-Audit Zero Air: Introduce zero air from the audit van to the station through the presentation line. When the van and station readings are stable (at least ten minute chart trace, and stability at or below 0.5 parts per billion [ppb]), record the responses on the Gaseous Audit Worksheet and in AIS with the laptop. This will be the

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first zero audit point. Consult the CARB Audit Ranges document (example shown in Figure E.4) for the currently targeted O_3 audit points.

				EDA C	oncontrati	on Ranges, p										
Audit L	evel	03		CO	Uncentrati	N(SO2		AS Audit Poin based on a S					
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4	0	.040 - 0.069	0	0.900 - 2.99	9 ÓÓ	0.0080 - 0.0199		0.0080 - 0.0199			Full-Scale	Trace-Level				
5	0	.070 - 0.089	0	3.000 - 7.99	9	0.0200 - 0.0499 🔵 💭		0.0200 -	0.0499		0: 875 ppm	290 ppm				
6	-	.090 - 0.119		8.000 - 15.9		0.0500 - 0.0999 🔵 🥘		0.0500 -) •	10: 35 ppm 02: 17 ppm	35 ppm				
7	-	.120 - 0.139	<u> </u>	16.000 - 30.9		0.1000 - 0		0.1000 -			C: 850 ppm	14 ppm				
8	-	.140 - 0.169		31.000 - 39.9		0.3000 - 0.4999		0.1500 -			25: 17 ppm					
9 10	-	.170 - 0.189		40.000 - 49.9		0.5000 - 0		0.2600 -			Full-scale Annual					
		ARB	Full-Scale	Audit Points (ppm)		not automatically		Trace Leve	el Audit Po	oints (ppm)					
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0.130		NO/NO _x		NO		H ₂ S (0-200ppb)	H ₂ S	CO (0-5ppm)	SO ₂	1		NO				
	17.0 10 SPA 12.0 13 SPA	NO/NO _x	NO2	NO residual	SO2	H ₂ S (0-200ppb) (6.0 ppm C0) 0.120	н ₂ 5 (0-100ppb)	CO (0-5ppm) 2.0 1.3	SO2 (0-100ppb)	NO/NO _x	NO ₂	NO (residual) 0.077				
0.130	17.0 10 10 12.0 11 10 4.0	NO/NO _x 0.160	NO ₂	NO residual 0.080	SO2	H ₂ S (0-200ppb) (6.0 ppm C0) 0.120	H ₂ S (0-100ppb) 0.080	CO (0-5ppm) 2.0 1.3 0.70	SO ₂ (0-100ррь) 0.034	NO/NO _x	NO2	NO (residual)				
0.130	17.0 10 201 12.0 11 201 4.0 3.0	NO/NO _x 0.160 0.120	NO ₂ 0.080 0.030	NO residual 0.080 0.090	SO2	H ₂ S (0-200ppb) (6.0 ppm CO) 0.120 0.080	H ₂ S (0-100ppb) 0.080 0.060	СО (0-5ррт) 2.0 1.3 0.70 0.29	SO2 (0-100ppb)	NO/NO _x	NO ₂	NO (residual) 0.077				
0.130 0.080 0.055	17.0 10 504 12.0 11 504 4.0 3.0 2.0 1.7 0.72	NO/NO _x 0.160 0.120 0.080	NO ₂ 0.080 0.030 0.015	NO residual 0.080 0.090 0.065	0.078	H ₂ S (0-200ppb) (6.0 ppm CO) 0.120 0.080	H ₂ S (0-100ppb) 0.080 0.060	CO (0-5ppm) 2.0 1.3 0.70 0.29 0.13	5О ₂ (0-100ррb) 0.034 0.014	NO/NOx 0.157 0.085	0.080 0.030	NO (residual) 0.077 0.034				
0.130 0.080 0.055 0.015	17.0 1000 12.0 1100 4.0 3.0 2.0 1.7 0.72 0.30	NO/NO _x 0.160 0.120 0.080	NO ₂ 0.080 0.030 0.015	NO residual 0.080 0.090 0.065	0.078	H ₂ S (0-200ppb) (60 ppm CO) 0.120 0.080 0.040 0.014	H ₂ S (0-100ppb) 0.080 0.060 0.040 0.040	CO (0-5ppm) 2.0 1.3 0.70 0.29 0.13 0.08	SO ₂ (0-100ppb) 0.034 0.014 0.004	NO/NOx 0.157 0.085 0.010	0.080 0.030 0.004*	NO (residual) 0.077 0.034 0.006				
0.130 0.080 0.055 0.015 0.005*	17.0 1000 12.0 1100 4.0 3.0 2.0 1.7 0.72 0.30 0.11	NO/NO _x 0.160 0.120 0.080 0.068	NO2 0.080 0.030 0.015 0.004*	NO residual 0.080 0.090 0.065 0.064	SO ₂ 0.078 0.014 0.006 0.002*	H ₂ S (0-200ppb) (60 ppm C0) 0.120 0.080 0.040 0.040 0.014 There are no SP ranges	H ₂ S (0-100ppb) 0.080 0.060 0.040 0.014 A swith levels or for H ₂ S.	CO (0-5ppm) 2.0 1.3 0.70 0.29 0.13 0.08 0.04	SO ₂ (0-100ррь) 0.034 0.014 0.004 0.002	NO/NOx 0.157 0.085 0.010 0.010	NO2 0.080 0.030 0.004* 0.002*	NO (residual) 0.077 0.034 0.006 0.003				
0.130 0.080 0.055 0.015 0.005*	17.0 10000 12.0 11001 4.0 3.0 2.0 1.7 0.72 0.30 0.11 points are designed	NO/NO _x 0.160 0.120 0.080 0.068	NO2 0.080 0.030 0.015 0.004*	NO residual 0.080 0.090 0.065	0.078 0.078 0.014 0.006 0.002* uudit Program (N	H ₂ S (0-200ppb) (60 ppm C0) 0.120 0.080 0.040 0.040 0.014 There are no EP rangez	H ₂ S (0-100ppb) 0.080 0.060 0.040 0.014 A swith levels or for H ₂ S.	CO (0-5ppm) 2.0 1.3 0.70 0.29 0.13 0.08 0.04	SO ₂ (0-100ppb) 0.034 0.014 0.004	NO/NOx 0.157 0.085 0.010 0.010	NO2 0.080 0.030 0.004* 0.002*	NO (residual) 0.077 0.034 0.006 0.003				

Figure E.4 CARB Audit Ranges and Audit Points

- 2. Audit Points: Beginning with the highest O₃ audit point, use the gas dilution calibrator to generate ozone quantities within the desired audit ranges (based on the U.S. EPA Audit Levels). When the van and station readings are stable, record the responses on the Gaseous Audit Worksheet and in AIS with the laptop or tablet. Continue to introduce new ozone audit points as listed in Figure E.4, ensuring that the audit is completed within prescribed U.S. EPA audit levels.
- 3. Verify that all data entered into AIS matches the values on the Gaseous Audit Worksheet. The second auditor should review and verify that the worksheet and AIS entries match.
- 4. Inform operator of preliminary audit results. In the event AIS identifies a "fail" result, refer to Section E.8.7 (Performance Audit Failures).

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5. Proceed with the audit of other gaseous analyzers. If no further audits are to be conducted, follow Sections E.9.0 and E.10.0 for post-audit and shut down procedures.

E.8.4 CARBON MONOXIDE ANALZYER VERIFICATION PROCEDURE

The audit van CO analyzer is used during a performance audit to analyze the amount of CO present in a diluted gas sample. Before and after each audit (of a gas other than O_3), the CO analyzer is verified using a zero air generator, Ultra Pure air, and NIST-traceable CO gases at high and low concentrations. The pre-audit and post-audit CO analyzer responses are used in calculations to obtain true CO concentrations.

NOTE: If the CO analyzer response exceeds 0.25 ppm from the expected CO cylinder concentration for any of the verification points, the analyzer may require calibration or adjustment. Before calibration, be sure to troubleshoot, taking note of temperatures, pressures, flows, and warm-up conditions that may affect drift. Refer to the instrument specific operations manual for troubleshooting and calibration procedures.

Two multi-port glass manifolds in the audit van are used during a performance audit. One manifold is used to supply the van instruments with zero air, Ultra Pure zero air, and CO calibration (span) gases, or diluted Superblend #1 gases. The additional manifold supplies the station with zero air or diluted Superblend gases (as shown in Figure E.1). A three-way valve is used to isolate the manifolds during verification of the van's CO analyzer.

- 1. The CO analyzer should be warmed-up based on the manufacturer's required warm-up period prior to calibration. The three-way valve should be in the "Sample" position prior to the audit.
- 2. If an O_3 audit was conducted prior to the CO analyzer calibration, the O_3 analyzer may either remain on or be turned off. If the O_3 analyzer is turned off, readjust the flow to the bypass rotameter to 0.3-0.4 lpm.
- 3. Once the CO analyzer response to the zero air is stable, record the result on the Gaseous Audit Worksheet under "CO Calibration." If the response to zero air is not within \pm 0.25 ppm of zero, the CO analyzer may need to be calibrated or adjusted (refer to the "NOTE" above).

NOTE: Stability determination for CO analyzers can vary depending on model and settings defined in the analyzer's software. Stability values below 0.1 ppm are typical and auditors should record results

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when the stability reading is as low as possible, with a straight-line chart trace of ten minutes or more. Refer to the instrument specific operations manual (located on the QA laptops) for troubleshooting procedures and more details.

- 4. Connect the "Span" line to the High CO cylinder, or if equipped, switch the High CO solenoid switch to the "on" position. Switch the 3-way valve to the "Span" position. Open the valve on the High CO gas cylinder and adjust the pressure regulator on the cylinder to 10 psi. Readjust the bypass to 0.3 to 0.4 lpm, using the appropriate needle valve.
- 5. Once the CO response is stable, record the result on the Gaseous Audit Worksheet under "CO Calibration." If the audit van CO response is not within ± 0.25 ppm of the certified values listed on the High CO cylinder, the CO analyzer may need to be calibrated (refer to the CO analyzer operator's manual).
- 6. Disconnect the "Span" line from the High CO and connect the line to the Low CO cylinder. Close the valve on the High CO cylinder. If the van is equipped with a solenoid, switch off the CO High, and then switch on the CO Low.
- 7. Open the valve on the Low CO gas cylinder and adjust the pressure regulator to 10 psi. Readjust the bypass flow to 0.3 to 0.4 lpm, if necessary.
- 8. When the "Low CO" response is stable, record the result on the Gaseous Audit Worksheet under "CO Calibration."
- 9. Disconnect the "Span" line from the Low CO cylinder and connect the line to the Ultra Pure air cylinder. Close the valve on the Low CO cylinder. If the van is equipped with a solenoid, switch off the CO Low then switch on the Ultra Pure. Open the valve on the Ultra Pure air cylinder and adjust the pressure regulator to 10 psi. Readjust the bypass to 0.3 to 0.4 lpm, if necessary.
- 10. When the CO response is stable, record the result on the Gaseous Audit Worksheet under "CO Calibration."
- 11. Close the valve on the Ultra Pure and disconnect the span line. If the van is equipped with a solenoid, put the switch for the Ultra Pure in the "off" position.

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- 12. Switch the 3-way valve back to the "Sample" position. Zero air should be flowing thru the system, to the station. Readjust the bypass to 0.3 to 0.4 lpm, if necessary.
- 13. Enter all values into the Audit Information System software, if not already done.
- 14. To continue with other gaseous performance audits, refer to the next Section.

E.8.5 <u>FULL AUDIT PROCEDURE</u>

NOTE: This procedure can be modified depending on the suite of analyzers present at the monitoring station. This procedure is designed for CO, NO₂, and SO₂ analyzers, or H₂S analyzers, in operation at ambient air monitoring stations. If any of these analyzers are not present, corresponding audit points should be skipped. Consult Figure E.4 for the targeted audit points.

NOTE: H_2S audits must be conducted separately from NO_2 and/or SO_2 audits due to the use of different Superblend cylinders and the interaction of the various gases. Use Superblend #2, which contains CO and H_2S concentrations. The van's presentation line should be conditioned by sampling H_2S for at least one hour, immediately prior to arriving at the station.

Consult with the station operator on their manifold setup and disconnect any analyzers that may be adversely affected by the introduction of H_2S at higher levels.

- 1. The van gas calibrator should be introducing zero air through the presentation line, to the station. Once stable, record the van and station readings into AIS.
- 2. Verification of the CO analyzer should have been performed as outlined in Section E.8.4. Consult Figure E.4 for the targeted audit points.
- 3. Pressure regulator bleeding procedures: To bleed the Superblend pressure regulator, open the valve located at the gas dilution calibrator inlet for at least ten seconds prior to the audit. This procedure will evacuate any NO₂ that has accumulated in the regulator and lines. After bleeding, adjust the regulator pressure to 25 psi.

NOTE: The regulator settings for span gases (10 psi) are different from the regulator setting for Superblend cylinders (25 psi).

4. Audit Points: Starting with the highest value audit point, introduce gas to the station by adjusting the target concentration and total flow on the gas dilution calibrator. Refer to the current CARB Audit Ranges document for the targeted audit points (Figure E.4).

NOTE: Depending on the Superblend cylinder concentrations and mass flow controller (MFC) sizes, multiple parameters can be audited using a single CO value, based on the ratios in the cylinder. Adjustments may be needed to stay within the desired U.S. EPA audit level ranges. Approximate concentrations can be found on Figure E.4, depending on the audit range.

NOTE: Depending on the Superblend cylinder concentration ratios, higher CO values may generate concentrations that may "overrange" analyzers in the station. Auditors should always be aware of the concentrations being generated and take precautions to avoid over-ranging station instruments when possible.

When the van and station analyzer readings are stable, record the responses from the van's CO analyzer and the station's analyzer(s) (or data logger) on the Gaseous Audit Worksheet and in AIS. The station's instrument response for all audit points should be stable, and recorded after a minimum of 10 minutes.

For ozone titration steps during an NO_2 audit, refer to the gas dilution calibrator's operating manual.

- 5. Audit Points (continued): Repeat Step 4 for the remaining audit points, ending with the lowest value audit point. After a minimum of 10 minutes, when the station readings are stable, record the responses on the Gaseous Audit Worksheet and in AIS with the laptop.
- 6. Post-audit zero air: After all audit points are completed and results are checked, set the gas dilution calibrator to introduce zero air to the station. Zero air should continue to flow to the station throughout the post-audit CO verification procedure.
- 7. Post-audit CO verification procedure: Switch the 3-way valve to the "Span" position. Open the High CO calibration cylinder. Connect the "Span" line to the High CO regulator or switch the High CO to the

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"on" position. Readjust the bypass to 0.3-0.4 lpm, if necessary. When the High CO reading is stable, record the response on the Gaseous Audit Worksheet under "CO Calibration," "Post-Audit CO Van Reading," and in AIS with the laptop.

- 8. Repeat step 7 using the Low CO cylinder to obtain a post-audit Low CO value.
- 9. Repeat step 7 using the Ultra Pure cylinder to obtain a post-audit Ultra Pure value.
- 10. Close the valves on all of the cylinders.
- 11. Switch the 3-way valve back to the "Sample" position. After the CO value has been stable (approximately 10 minutes), record the station zero value and audit zero air value in AIS.
- 12. Verify that all data entered into AIS match the values on the Gaseous Audit Worksheet. The second auditor should review and verify that the worksheet and AIS entries match.
- 13. Inform the station operator of preliminary audit results. In the event AIS identifies a "fail" result, follow Section E.8.7 (Performance Audit Failures).
- 14. Continue to Sections E.9.0 and E.10.0 for post-audit and shut down procedures.

E.8.6 ACTUAL AUDIT CONCENTRATION / CONVERTER EFFICIENCY DETERMINATION

After data is entered into AIS, actual audit concentrations and other values can be calculated. AIS performs these calculations using information from the selected standards file.

 Ozone: True O₃ value for each audit point, for comparison with the station response, is calculated by applying a slope and intercept (derived from the quarterly CARB Standards Laboratory certification) to the audit van O₃ analyzer's net display reading, and multiplying by one minus the O₃ quarterly line loss correction factor (see Section E.11.1).

True O₃ (ppm) =

(Display * Slope + Intercept) * (1 – Line Loss)

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where:

- Display = O₃ analyzer's display response (ppm)
- Slope = O₃ analyzer's slope
- Intercept = O₃ analyzer's intercept
- Line Loss = O₃ analyzer's line loss correction factor

The percent difference between actual audit (true O_3) concentration and the station response is determined by:

 $Percent Difference = \frac{Station Response-Actual Audit}{Actual Audit}$

For each audit point, this percent difference is compared against the control limit criteria. If the percent difference is greater than ± 10 percent, the audit will result in a failure.

- 2. Gases other than O₃: Actual audit (van) concentrations for each gaseous pollutant (except O₃), at each audit point, are determined using three factors:
 - a. CO Slope and Intercept
 - b. Dilution ratio from the Superblend cylinder
 - c. The indicated CO value from the audit display

The CO Slope and Intercept values are a regression calculation derived by comparing actual values to the expected values, using the following values generated during the CO analyzer verification procedure (Table E.1, Section E.8.4):

Actual Span ValueExpected Span ValueA1 = Pre-Audit Zero (CO) valueE1 = 0A2 = Pre-Audit High CO valueE2 = Expected High CO
cylinder concentrationA3 = Post-Audit High CO valueE3 = Expected High CO
cylinder concentrationA4 = Post-Audit Zero (CO) valueE4 = 0

Table E.1 Values Used in Calculations of CO Slope and Intercept

The CO Slope and Intercept can be generated, or verified, by using the following formulas in an Excel worksheet:

CO Slope = SLOPE(A1:A4, E1:E4) CO Intercept = INTERCEPT(A1:A4, E1:E4)

The dilution ratio for each gas in the Superblend cylinder is calculated as follows:

SB ratio = (gas concentration / CO concentration)

The indicated CO value (at each audit point) is then used to calculate the actual audit value using the following formula:

CO audit actual = (CO indicated - CO Intercept)/CO Slope

For gases other than CO, the following formula is used to calculate the actual audit concentration:

Gas audit actual = (CO audit actual) x (SB ratio)

The percent difference between actual audit concentration and the station response is determined by:

Percent Difference = <u>
Station Response-Actual Audit</u> <u>
Actual Audit</u>

For each audit point, this percent difference is compared against the control limit criteria. If the percent difference is greater than ± 15 percent the audit will result in a failure.

3. **Converter Efficiency**: The converted NO₂ concentration is used at each point to determine NO/NO_x analyzer converter efficiency. The converter efficiency is calculated as follows:

Percent CE =
$$\frac{\Delta NO - \Delta NO_x}{\Delta NO_x} \times 100$$

where:

CE = Converter Efficiency

 $\Delta NO = ([NO] \text{ original} - [NO] \text{ remainder})/NO Slope$

 $\Delta NO_X = ([NO_X] \text{ original} - [NO_X] \text{ remainder})/NO_X \text{ Slope}$

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Calculated converter efficiencies (for chemiluminescent analyzers) less than 96 percent or greater than 104 percent result in a failure.

4. **True NO₂ Concentrations**: True ambient level concentrations for NO₂ are calculated using the following formulae:

 $Van NO_2 = \frac{NO [O_3 Off] - NO [O_3 On]}{NO Slope} \times 100$

Station $NO_2 =$

(NO_x [O₃ On] - NO_x Zero Average) - (NO [O₃ On] - NO Zero Average)

E.8.7 PERFORMANCE AUDIT FAILURES

 In the event of a "fail" audit result, an investigation is necessary to determine the possible cause(s) of the failure. It may be necessary to inspect all aspects of the audit, beginning with the van operation and ending with the station operation.

NOTE: If the cause for the failure is determined during any point in the investigation, resolve the problem (if possible) and resume the audit. If the source of the problem is from the station, the site operator should be notified of the "As Is" failure, and an "AUDIT ACTION ITEM NOTIFICATION" worksheet (Figure E.5) should be filled out. If the cause of the failure is determined to be the audit van set-up, the problem should be resolved and the audit restarted. Delete the results of the first audit.

- 2. Beginning with the audit van, all instruments need to be checked to verify proper operation. This will include all of the following, unless the cause of the failure is discovered and resolved at any point during the investigation process.
 - a. Is the airflow set correctly on the gas dilution calibrator? What values do the mass flow controllers indicate? Is the targeted gas value entered correctly for the appropriate audit point (including units)? Does the analyzer display correspond with the targeted level and range? Check the cylinder concentrations in AIS and the gas dilution calibrator. Are the appropriate valves and regulators open, with pressures sufficient for proper operation?
 - b. Is the zero air generator operating correctly? Is there sufficient output pressure (40-45 psi) to maintain a constant pressure of 30-

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35 psi to the calibrator? Is the regulator pressure set at 30 psi? Is there sufficient pressure in the gas cylinder (at least 200 psi)? Is the by-pass rotameter set for a flow of 0.3-0.4 lpm? Is the correct gas port selected? Is the 3-way valve (SPAN/SAMPLE) in the correct position?

- c. Are all lines correctly connected to the manifolds and/or probe line? Are the lines to the instruments connected? Are there any apparent leaks? Are the filters installed correctly and filter holders sealed? Is ambient air being entrained into the system and diluting the audit concentrations?
- 3. When these checks have been completed and all instruments checked for proper operation, the next step is to verify that the station is receiving enough flow to their inlet probe. This flow can be easily checked with a mass flow meter or rotameter. If there is not enough flow to the inlet probe, disconnect any booster pump that the station may be using. The van flow needs to be at least one lpm greater than the station flow requirement.
- 4. If the cause for the failure still cannot be determined, check the flow path of the audit gas from the station inlet probe to the back of the station instruments. Make certain to check all lines and in-line filters for leaks or breaks.
- 5. If the cause for the failure cannot be determined during this examination, remove the "Line" from the station inlet probe and connect it to the station's instrument manifold (if present, otherwise proceed to step 6). Take care to ensure proper bypass. Recheck the instruments for the proper response.
- 6. If the instrument still indicates a failure, remove the "Line" from the instrument manifold and check for the response at the back of the instrument using a glass tee and a bypass.
- 7. If the cause for the failed condition cannot be determined after a thorough investigation, take pictures of the audit set-up. The pictures should show how the "Line" is connected to the station's inlet probe and the sampling system from the inlet probe to the instruments. Document all trouble shooting measures performed.
- 8. When the investigation is completed, proceed with an Air Quality Data Action (AQDA) Request or Corrective Action Notification (CAN) as described in Sections E.9.2 and E.9.3, if appropriate. If the cause

for the failed condition is determined and corrected, proceed with the scheduled gaseous audit.

9. An incomplete audit or audit failure may require rescheduling. Contact the QAS manager or audit scheduler as soon as possible to discuss options, make a determination, and initiate a re-scheduling process, if necessary.

	QA	AUDIT WORKS	HEET	
	AUDIT AC	TION ITEM NO	TIFICATION	
Site Name:			Date:	
Operator:		District		
Auditors:		Parame	eter(s):	
Make	Model	Sampler Informati	ON Last Cal Date	Cal Equip Cert Date
Make	Model	Senary to Number	Last car bate	car Equip Cert Date
Air Quality Dat	al Power ng or malfunctionin ta Action (AQDA) wi	Failure Oth	to discontinue audit Re-audit to be perfo	Unit Malfunction
No action will t		upporting photos sav	ed to:	
Auditor Signature: _			-	

Figure E.5 Audit Action Item Notification Form

E.9.0 POST-AUDIT PROCEDURES

E.9.1 COMPILING PRELIMINARY AUDIT RESULTS

- 1. Auditors responsible for data entry and review should sign the completed Gaseous Audit Worksheet. The second auditor should review and verify that the worksheet and AIS entries match.
- 2. Notify the operator of preliminary audit results. A copy of the report will be provided electronically after review, via email.

E.9.2 <u>AIR QUALITY DATA ACTION (AQDA) REQUEST</u>

AQDA Requests are issued when the audit reveals that the station's analyzer(s) are not operating within federal critical criteria or CARB control limits. Refer to the SOP for Air Quality Data Action Requests (Volume V, Appendix AO) for guidance.

E.9.3 CORRECTIVE ACTION NOTIFICATION (CAN)

CANs are issued to document issues that may impact or may potentially impact data quality, completeness, storage, or reporting. Refer to the SOP for Corrective Action Notifications (Volume V, Appendix AN) for guidance.

E.10.0 SHUT DOWN PROCEDURES - AUDIT VAN

E.10.1 INTERIOR

- 1. After reviewing the audit report, log out of the AIS program and shut down the computer.
- 2. Turn off the power to the gas calibrator, zero air system, and applicable analyzers.
- 3. Turn off the power to the APC Smart Uninterruptible Power Supply (UPS) line conditioner.
- 4. Close the valves and regulators on all compressed gas cylinders.
- 5. After turning off all overhead lighting and climate controls, shut down the generator(s).

E.10.2 EXTERIOR

- 1. Disconnect the presentation line from the station inlet and inform the operator that the station's data logger can be put back on line.
- 2. Reel the "Line" into the audit van. Make certain the end of the "Line" is placed into the "Line" cradle, and lock the hose reel into position.
- 3. Secure the ladder and safety cones.
- 4. Remove the wheel chocks.

E.11.0 AUDIT VAN CALIBRATION CHECKS AND PROCEDURES

E.11.1 INSTRUMENT AND GAS RECERTIFICATION

- 1. O_3 analyzer and transfer standard– The CARB Standards Laboratory re-certifies the UV Photometer against a Standard Reference Photometer quarterly. The slope and intercept derived from the recertification are used in the calculation of audit van "True" O_3 values.
- Compressed Gases The High CO, Low CO, and SB #1 cylinders meet U.S EPA protocol gas criteria and are valid until the expiration date provided by the manufacturer. It is good practice to verify the concentrations of new cylinders by the Standards Laboratory along with the current inventory on an annual basis. SB #2 cylinders are certified in accordance with manufacturer recommendations.

E.11.2 <u>O₃ LINE LOSS INTRODUCTION</u>

The purpose of the line loss procedure is to determine the percentage of ozone that is lost as it transits through the 150-foot presentation line, while accounting for the instability and reactivity of ozone. The Audit Information System uses this percentage to calculate an actual concentration of ozone that is leaving our presentation line and being presented into the inlet of the air monitoring station. Line loss is determined at the start of each quarter. Two lines are used during the test. These are referred to as the "Inside" and "Outside" lines.

To obtain percent line loss, it is necessary to take the inside line ozone response value and subtract it from the outside line ozone response value.

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- Inside: The "inside" value for each test point is derived from values taken while the audit van is in its normal operating configuration, where the ozone analyzer line is connected to the van's instrument manifold.
- Outside: The "outside" value for each test point is derived from values taken while the end of the audit van's presentation line is connected directly to the van's ozone analyzer.

The difference, which should be a negative value, is then divided by the inside line ozone response value. The result is multiplied by 100 so it can be expressed as a percentage. This is repeated for all audit point concentrations. Currently there are five test points: 130 ppb, 80 ppb, 55 ppb, 30 ppb, and 15 ppb. Once a percent line loss has been determined for each of these concentrations, an average of the five values are taken. This overall line loss percentage is averaged with the previous quarter's line loss percentage to obtain a new percent line loss for the current quarter. These steps are summarized on the worksheet (see example in Figure E.6).

	Ozon		Worksheet helter Temp Ver	ification
Analyze	r Model:	T400	Date: 1/12/2021	Quarter: 1
	ID #:	12345	Van: C	Year: 2021
Т	est Point (TP)	Inside Line (ppb)	Outside Line (ppb)	% Difference
1	130 ppb	130.3	130.4	-0.0767
2	80 ppb	79.3	79.0	0.3783
3	55 ppb	54.6	54.2	0.7326
4	30 ppb	29.9	29.8	0.3344
5	15 ppb	14.6	14.1	3.4247
Aver Diffe	rienty Current Loss -	VT123	rter Line Loss rature Verification Van Temp (indicated):	
	p Sensor ID#:		A sudde The second for all such a dis-	24.0
	td Sensor ID#:	57 Int: -0.019	Audit Temp (indicated): Audit Temp (actual): Temperature – (van Indicated - au	

Figure E.6 O₃ Line Loss Worksheet

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E.11.3 O₃ LINE LOSS BACKGROUND

As ozone audit levels have declined in recent years, the line loss procedure has been forced to evolve. At the lowest point of 15 ppb, the percent difference for a fixed inside-versus-outside difference (1 ppb for example) is more than three times of what it would be at the old low point of 55 ppb. Another way of stating this is that just 1 ppb of line loss at all points will now result in a failed line loss. With currently technology, any particular point generated will oscillate within the 1 ppb range. This continues to be the case despite several mitigation measures. There is more "noise" than the small percentage of ozone line loss.

The API T700U ozone generator and dilution system tends to be more backpressure sensitive than the Environics ozone generator and dilution system that was used in the past. Additionally, the API T700U has an onboard photometer that, via a feedback loop, attempts to hold the concentration steady. The feedback loop has a bit of lag time and thus a set value still oscillates, usually within the one ppb range.

The audit van ozone analyzer for record, API T400, is more tolerant of backpressure variations than the API T700U. However, the T400 reacts adversely to interruptions in the type of air it is receiving. When a stream of ozone and zero air mixture is interrupted with ambient (higher humidity) air, it then takes the T400 more than 10-20 minutes to restabilize on the initial value. This tends to be the case even when the interruption is short, on the order of seconds.

In order to mitigate these compounding issues, several adjustments were made to the line loss procedure. To deal with the oscillatory nature of the ozone generation, the feedback feature for ozone generation on the API T700 has been turned off. It is possible to drive the ozone generation with a fixed voltage to the lamp for each point. Readings are taken at 15-second intervals and averaged over five minutes for each configuration (inside line / outside line) and for each of the five audit point concentrations. However, the steady drive voltage at each concentration is still producing an oscillatory behavior in the ozone generated. To compensate for the backpressure sensitivity, it is now possible to monitor and adjust backpressure so that both instruments (API T700 and API T400) experience the same backpressure in either the inside line or outside line configuration. (See Figure E.7).

To avoid introduction of ambient air during the process of switching configuration from inside line to outside line or outside line to inside line,

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a three-way valve has been added. This resulted in a significant improvement. Figure E.7 depicts the setup.

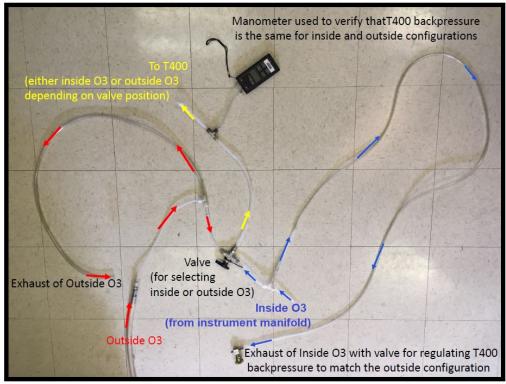


Figure E.7 O₃ Line Loss Configuration

E.11.4 O₃ LINE LOSS PROCEDURE

There are three main procedures used in determining ozone line loss each quarter:

- Condition the lines used in the procedure
- Determine the voltages used for each test point
- Record ozone values based on the test point voltages

NOTE: Line loss should be performed after the quarterly certification and re-installation of the van's ozone analyzer.

- 1. Turn on instrumentation in the audit van and allow for a 30 minute warm-up period. At this stage (for steps 1 through 12), no changes to the normal audit configuration are needed.
- 2. Set the API T700U to generate 400 ppb ozone at a 16 lpm flow rate, and allow a minimum of two hours to condition the line.

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- 3. Before continuing, ensure that the API T400 has settled on a steady ozone value. This is done by looking at the electronic strip chart. If the value is still climbing, more warmup time will be required.
- 4. In addition to having a steady value, it is important that the value on the API T400 be within 5% of the audit point value. The API T400 will read a lower, but more accurate, ozone value than the ozone value that appears on the API T700U. The API T400 is the ozone analyzer for record despite the fact that the API T700U ozone generator has a built in photometer. If the difference is greater than 5% then the desired audit point concentration, the API T700U desired ozone value will need to be increased so that audit points remain in the range dictated by the U.S. EPA.
- Once a steady value is attained, change the concentration to 130 ppb or slightly higher (as needed) on the API T700U. Wait a minimum of 10 minutes or until the concentration has stabilized on the API T400. Make sure the reading is within 5% of 130 ppb.
- 6. On the API T700U, navigate through the test parameters using the touch screen until the O₃ GEN DRIVE value is reached and make note of this voltage. This value will be needed later.
- 7. Repeat steps 5 and 6 for the 80 ppb and 55 ppb concentrations. Do not do this for the last two concentrations, as the ozone fractionator activates at these concentrations on the API T700U resulting in O_3 gen drive voltages that are much higher than needed for these concentrations. The ozone fractionator mixes higher concentration ozone air at one part for every four parts of zero air to reach a desired concentration.
- 8. Run the API T700U on O₃ gen drive mode (Refer to the User Manual to set the gen drive mode). This disables the iterative photometer feedback loop and allows for less oscillation around the desired concentration. Enter the voltage noted earlier for the high point, 130 ppb. Verify that after ten minutes the API T400 is registering a concentration that is within 5% of 130 ppb. Adjust the O₃ gen drive value if necessary and make note of the new value.
- 9. Repeat step 8 for the next two concentrations at 80 ppb and 55 ppb.
- 10. A decrease in three millivolts reduces ozone generated by approximately one ppb. With this in mind, enter an O₃ gen drive value that is approximately 75 millivolts lower than the value entered

for the 55 ppb point. Verify that after ten minutes the API T400 is registering a concentration that is within 5% of 30 ppb. Adjust the value as necessary and make note of this value.

- 11. Repeat step 10 to obtain a 15 ppb voltage, keeping in mind that the initial reduction in the O₃ gen drive value will need to be approximately 45 millivolts lower than the O₃ gen drive value that was determined for the 30 ppb point.
- 12. Obtaining functional O_3 gen drive values for the five concentrations must be repeated for each van and for each quarter. This is because the lamp that generates ozone degrades over time and requires a greater voltage to produce the same ozone concentration.
- 13. The line loss kit is pictured in Figure E.7. It is kept in a black plastic suitcase that is labeled "Line Loss". Prior to performing a line loss procedure, the auditor should become familiar with the layout and connection of the Teflon[®] and Tygon[®] (exhaust) tubes as well as the correct location of the three-way valve, exhaust valve, and manometer.
- 14. During the line loss procedure, there is only one connection in the audit van that is changed or interrupted from normal auditing configuration. This the connection at the back of the ozone analyzer. At this connection, the flow is moving from the instrument manifold into the API T400 ozone analyzer. Undo the connection at the back of the API T400, and insert the assembled line loss kit into this connection. Once all fittings are snug, verify that the kit's manometer is registering slightly positive pressure; approximately 0.05 kilopascals (kPa). The audit vans have a manometer that is connected to the presentation line manifold. It will read a backpressure of 3.25 kPa, but this value can change by as much as 0.5 kPa per analyzer if other analyzers are turned off or on. Fewer analyzers being on increases the backpressure on the presentation line manifold.
- 15. Run 400 ppb for at least ten minutes for either position of the kit's inside/outside ozone valve. This conditions the short segments of Teflon[®] tubing that are a part of the line loss kit and helps alleviate any unwanted bias. This is the end of the setup, and the actual line loss procedure can begin.
- 16. On the API T700U, enter the O₃ gen drive voltage that was determined to produce the 130ppb point. Begin with the kit's inside/outside ozone valve in the inside position.

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- 17. Wait ten minutes. During these initial ten minutes, take note of the kit's manometer reading and the van's presentation manifold manometer reading. After minimum of ten minutes have passed, begin recording the (inside, 130 ppb point) values off the API T400 at 15 second intervals. Continue to record these values every 15 seconds for 5 minutes. An average is taken of these 20 readings. An Excel[®] spreadsheet has been created to aid with recording and calculations. The spreadsheet can be found in the Cabinet/Ozone Line Loss folder, along with each quarter's results.
- 18. Keeping the API T700U O₃ gen drive value the same, turn the kit's inside/outside ozone valve to the outside position. Take note of the kit's manometer reading and the van's presentation manifold manometer reading. If the difference is more than 0.01 kPa on the kit's manometer, then an adjustment on the kit's exhaust valve (refer to Figure E.7). The backpressure on the van's presentation manifold manometer should also read within 0.01 kPa. It can be adjusted using the audit van's bypass valve if necessary.
- 19. Wait ten minutes, then begin recording the (outside, 130 ppb point) values from the API T400 at 15 second intervals. Continue to record these values every 15 seconds for 5 minutes. An average is taken of these 20 readings in the Excel[®] spreadsheet.
- 20. Determine the inside value, then the outside value for the remaining points. Repeat steps 16 through 19 with the O₃ gen drive values that that were determined to produce 80 ppb, 55 ppb, 30 ppb, and lastly 15 ppb.
- 21. Any point that results in a line gain (outside concentration > inside concentration) must be repeated. Any gain is the result of oscillation, or noise, offsetting the small ozone line loss, and is not possible due to the known properties of ozone.
- 22. Once all five points have a calculated line loss, however small, the procedure is finished. The Excel[®] spreadsheet calculates all the values that need to be entered on the line loss worksheet (Figure E.6). Transcribe the values to the worksheet. Review and sign it.
- 23. Reconnect the one connection at the back of the API T400 that was disconnected when the line loss kit was inserted.
- 24. Place all components of the line loss kit into its suitcase.

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- 25. Verify that the audit van is left in the configuration it was found before the procedure.
- 26. If no other auditors plan on working in the van, power down all instruments.
- 27. Turn in the completed quarterly line loss worksheet to the manager for verification and approval. Upon approval, the line loss percentage should be given to the AIS administrator for entry into the Standards File.

E.11.5 <u>PREVENTATIVE MAINTENANCE</u>

Preventative maintenance should be performed quarterly. The most common steps are listed below. Refer to the maintenance SOP (currently under development) for more detail.

- 1. At the end of each quarter perform 90-day maintenance on all audit vans. The vehicle and onboard electrical generators are subject to a safety inspection and/or routine maintenance by a certified service facility.
- 2. Replace particulate filters on all gaseous analyzers quarterly or as needed. Follow all manufacturer's recommended maintenance schedules as outlined in the operator's manuals.
- Document test parameter functions on all gaseous analyzers quarterly, or as needed. Leak check all analyzers annually, or as needed.

E.12.0 ADDENDUM – TRACE-LEVEL THROUGH-THE-PROBE AUDIT

E.12.1 <u>OVERVIEW</u>

Trace-level analyzers are ultra-sensitive and designed to measure lower levels of gases than ambient-level analyzers. For CO, a trace-level analyzer typically ranges from 0 to 5 ppm, while an ambient-level analyzer ranges from 0 to 20 (or 50) ppm. For SO₂, trace-level analyzers are typically 0 to 100 ppb, while ambient-level analyzers can range up to 500 ppb. The audit van CO analyzer is used during a performance audit to analyze the amount of CO or SO₂ present in a trace-level diluted gas sample.

The audit procedures for trace-level audits are similar to "regular" (full-scale) audits with the following points of note:

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- Trace Superblend CO concentrations are lower
- Trace High and Low CO cylinder concentrations are lower
- Instrument warm-up and stability periods can be longer
- Temperature and pressure fluctuations may affect analyzer drift
- Exceedances of audit criteria at low audit levels do not automatically invalidate data
- Audit data is entered on a separate worksheet (refer to Figure E.8) designed specifically for trace-level audit points and levels.

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				* Audit Poi	ints in level	s 1 or 2 wil	l be eval	luated and wo	n't automat	ically b	subject to	corrective act	tion in 2021			Dev over 24 hours
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0.015			• H	i CO		0.1	3									
			- LO	w CO		0.0	8							0.004*		
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Model Numb												Number:				
Serial Numb												Number:				
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Figure E.8 Trace-Level Gaseous Audit Worksheet

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E.12.2 TRACE-LEVEL CO ANALYZER VERIFICATION PROCEDURE

Before and after each audit, the trace-level CO analyzer is verified using a zero air generator, Ultra Pure air, and NIST traceable CO gases at concentrations of approximately 4 (High CO) and 1 (Low CO) ppm. The pre-audit and post-audit CO analyzer responses are used in calculations to obtain true CO concentrations.

NOTE: If the CO analyzer drift exceeds 0.25 ppm for any of the verification points the analyzer may require calibration or adjustment. Before calibration, be sure to troubleshoot, taking note of temperatures, pressures, flows, and (especially) warm-up conditions that may affect drift. Refer to the instrument specific operations manual for troubleshooting, adjustment, and calibration procedures.

Refer to Figure E.4 for CARB Audit Ranges and Trace-Level Audit Points.

Refer to Section E.8.4, steps 4 through 14, for the CO analyzer verification procedure while using trace-level High and Low CO cylinders.

E.12.3 TRACE-LEVEL CO AND SO₂ AUDIT PROCEDURE

Refer to Section E.8.5 for the Trace-Level CO and/or SO_2 Audit Procedure, and follow the steps using the trace-level Superblend cylinder.

E.13.0 ADDENDUM – SELECTING AUDIT RANGES

E.13.1 <u>OVERVIEW</u>

The Annual Performance Evaluation (PE) includes ten audit levels for the gaseous pollutants of O₃, CO, NO₂, or SO₂. In accordance with federal criteria, the evaluation is made by challenging the monitor with audit gas standards of known concentration from at least three audit levels. One point must be within two to three times the method detection limit of the instruments within the PQAO's network, the second point will be less than or equal to the 99th percentile of the data at the site or the network of sites in the PQAO or the next highest audit concentration level. The third point can be around the primary NAAQS or the highest 3- year concentration at the site or the network of sites in the PQAO. An additional 4th level is encouraged by U.S. EPA for those agencies that would like to confirm the monitors' linearity at the higher end of the operational range. Due to the audit levels being expanded to allow for lower concentration audits to support NCore and trace-level work, U.S.

EPA issued a Technical Memorandum suggesting expanded acceptance criteria for levels 1 and 2 audit ranges in February, 2011.

E.13.2 <u>AUDIT LEVELS</u>

The audit levels for Annual Performance Evaluations are defined in 40 CFR Part 58, Appendix A, section 3.1.2.1, and are shown in Table E.2 below. Audits conducted for the National Performance Audit Program (NPAP) use the same range of audit levels.

		Concentratio	n Range (ppm)	
Audit Level	O ₃	SO ₂	NO ₂	CO
1	0.004-0.0059	0.0003-0.0029	0.0003-0.0029	0.020-0.059
2	0.006-0.019	0.0030-0.0049	0.0030-0.0049	0.060-0.199
3	0.020-0.039	0.0050-0.0079	0.0050-0.0079	0.200-0.899
4	0.040-0.069	0.0080-0.0199	0.0080-0.0199	0.900-2.999
5	0.070-0.089	0.0200-0.0499	0.0200-0.0499	3.000-7.999
6	0.090-0.119	0.0500-0.0999	0.0500-0.0999	8.000-15.999
7	0.120-0.139	0.1000-0.1499	0.1000-0.2999	16.000-30.999
8	0.140-0.169	0.1500-0.2599	0.3000-0.4999	31.000-39.999
9	0.170-0.189	0.2600-0.7999	0.5000-0.7999	40.000-49.999
10	0.190-0.259	0.8000-1.000	0.8000-1.000	50.000-60.000

Table E.2 Audit Levels and Concentration Ranges

E.13.3 <u>SELECTING AUDIT RANGES</u>

Audit points used in the Annual PE must fall within ranges set by the criteria outlined in the Overview (refer to Section E.13.1), and is also defined in 40 CFR Part 58, Appendix A, section 3.1.2.1. By using this criteria, the low, mid, and high audit point targets can be identified. Auditing in a fourth level is encouraged. Additionally, the audit levels selected do not have to be consecutive.

E.13.3.1 <u>POINT ONE</u>

One point must be within two to three times the method detection limit of the instruments within the PQAOs network.

Monitoring organizations can use Federal methods detection limits (MDLs) listed in AQS, or alternate methods' detection limits that the organization has developed and reported to AQS, to identify the low audit level selected for the annual performance evaluation. The selection of the audit level can be performed at the site level or the network level.

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U.S. EPA issued guidance for using the MDLs through a Technical Note, dated May 3, 2016 (see References, Section E.14.0). The memo also provides information on the statistics that can be used to identify the appropriate concentration for 1-point QC checks and the second annual PE audit level (99th percentile). It is important that the low audit level be selected with detection limits and monitoring objectives kept in mind.

The Federal MDL for each monitoring method, by parameter, can be found here:

https://aqs.epa.gov/aqsweb/documents/codetables/methods_criteria.ht ml

Monitor data (Monitor Listing) is published by U.S. EPA approximately every six months here:

https://aqs.epa.gov/aqsweb/airdata/download_files.html

The methods reported to AQS for monitors in California can be derived by performing the following steps:

- 1. Download the <u>"Monitor Listing" zip file</u> and extract the data.
- 2. Using Microsoft Excel[®], open the .csv (Comma Separated Values) file.
- 3. Filter out or delete all rows that do not have 6 for the "State Code" (California).
- 4. Filter out or delete all rows with parameter codes other than 44201 (O_3) , 42101 (CO), 42602 (NO₂), and 42401 (SO₂).
- 5. Filter out or delete all rows with a "Last Sample Date" older than one or two years.
- 6. Review the remaining data and remove any rows or columns that are not relevant (monitors that are no longer active, or will not be audited).
- 7. Sort the data by parameter and method code.
- 8. Add and populate three columns for "FED MDL", "FED MDL *3", and "AUDIT LEVEL". A fourth column for "ALT MDL" can be entered if an alternative method for generating the MDL is being used.

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NOTE: The method codes can be filtered for uniqueness, but it is helpful to keep in mind the number of sites using a particular method code, as well as the monitoring objective, when selecting audit levels. Sorting by PQAO can also help identify the number of monitors (by POC) using each method.

An example of the remaining data, formatted for review, is found in Figure E.9, below:

				А	UDIT F	POINT 1			
					# CARB	# NON- CARB			
					PQAO	PQAO			
	Parameter	Parameter Code	Units	Method Code	sites (2019)	sites (2019)	Federal MDL	MDL *3	Audit Level
ſ				047	8	20	0.005	0.015	2
	O3	44201		087	85	22	0.005	0.015	2
		44201	ppm	190	0	2	0.003	0.009	2
				199	6	0	0.0006	0.0018	1

<u> </u>	42101	ppm	054	4	17	0.5	1.5	4
			093	3	0	0.5	1.5	4
			106	0	8	0.5	1.5	4
			158	0	15	0.5	1.5	4
			554	3	3	0.04	0.12	2
			593	8	2	0.02	0.06	2

			074	4	50	1	3	2
			099	28	6	2.7	8.1	4
	42602 p		157	0	2	5	15	4
		ppb	200	5	0	0.1	0.3	1
			212	2	2	0.04	0.12	1
			599	3	0	0.05	0.15	1

SO2			060	2	11	2	6	3
	42401	ppb	100	1	0	0.4	1.2	1
			560	3	7	0.2	0.6	1
			600	3	0	0.2	0.6	1

Figure E.9 Example of Audit Levels by Method Code Using MDLs

NOTE: Many, but not all of the method codes associated with trace gas instruments have a method code in the range between 500 and 600.

Once the low level audit range requirements have been identified, the mid and high audit levels must be determined.

E.13.3.2 <u>POINT TWO</u>

...the second point will be less than or equal to the 99th percentile of the data at the site or the network of sites in the PQAO or the next highest audit concentration level.

U.S. EPA has provided data for gaseous pollutant statistics by monitor, including the 99th percentile, for each site here:

https://aqs.epa.gov/aqsweb/airdata/download_files.html#Annual

Download "annual_conc_by_monitor" for the each of the last 3 <u>complete</u> years. For each of the 3 files:

- 1. Filter out/delete all states except California (6).
- 2. Filter out/delete all parameters except 42101 (CO), 42401 (SO₂), 42602 (NO₂), 44201 (O₃).
- 3. Filter out/delete all pollutant standards except 1-hour statistics, and the Ozone 8-hour standard for comparison.
- 4. Verify that the data has been certified, and there are no unusual exceptions or qualifiers.
- 5. Delete/hide unnecessary columns.
- 6. Add a column for PQAO, and populate it for each site.
- 7. Sort by: PQAO, then by Parameter Code (smallest to largest), then by Pollutant Standard, and finally by 1st Max Value (largest to smallest).
- 8. Identify the median 99th percentile value and highest 1st Max Value for each PQAO, within each parameter, for each year.
- 9. Summarize the data in a separate table (see Figure E.10).

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AUDIT	⁻ POII	NT 2	
Pollutant Standard	Year	Median 99th Percentile	Audit Level
	2019	0.075	5
Ozone 1-hour 1979	2018	0.086	5
	2017	0.080	5
	2019	0.066	4
Ozone 8-hour 2015	2018	0.074	5
	2017	0.071	5

	2019	0.862	3
CO 1-hour 1971	2018	0.800	З
	2017	0.850	3

	2019	32.8	5
NO2 1-hour	2018	37.2	5
	2017	36.2	5

	2019	3.0	2
SO2 1-hour 2010	2018	2.0	1
	2017	2.0	1

Figure E.10 Example of Data Summary Showing the Median 99th Percentile

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The U.S. EPA's AQS database should be queried for the most recent data (by site and/or PQAO) to identify the 99th percentile for each gaseous parameter. It may be valuable to review the average 99th percentile and the highest 99th percentile values for comparison to the median. Additionally, the highest concentration from each site (the 1st Max Value) for the previous three years should be identified, and included in the decision-making process for choosing the range for audit point three.

E.13.3.3 POINT THREE

The third point can be around the primary NAAQS or the highest 3-year concentration at the site or the network of sites in the PQAO.

The Clean Air Act requires the U.S. EPA to set a NAAQS for pollutants considered harmful to public health and the environment. The Clean Air Act identifies two types of national ambient air quality standards. *Primary standards* provide public health protection, including protecting the health of "sensitive" populations such as asthmatics, children, and the elderly. *Secondary standards* provide public welfare protection, including protection, against decreased visibility and damage to animals, crops, vegetation, and buildings.

The U.S. EPA has set NAAQS for six principal pollutants, which are called "criteria" air pollutants. Periodically, the standards are reviewed and may be revised. The current NAAQS standards can be found here:

https://www.epa.gov/criteria-air-pollutants/naaqs-table

Although there are number of different methods used to determine the NAAQS (i.e., rolling 8-hour averages etc.), the hourly concentration data can be used to establish audit points 2 and 3 for all gaseous pollutants.

Therefore, the current hourly Primary NAAQS standards are:

- CO: 35 ppm
- NO₂: 100 ppb
- O₃: 70 ppb (8-hour)
- SO₂: 75 ppb

The highest 3-year concentration data can also be used in determining the third audit level.

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NOTE: From the Technical Note- Guidance on Identifying Annual PE Audit Levels Using Method Detection Limits and the 99th Percentile (May 3, 2016), it is not a requirement to use three years of data so PQAOs may want to establish audit levels based on the previous year. However, the data set should be large enough to justify the selection of audits points and be consistent in its implementation from year to year.

After the relevant data has been gathered, a summary table similar to the one in Figure E.11 can be generated.

	AUI	DIT POINT 3		
		Highest	Audit	NAAQS
Pollutant Standard	Year	1st Max Value	Level	(Audit Level)
	2019	0.167	8	
Ozone 1-hour 1979	2018	0.135	7	N/A
	2017	0.158	8	
	2019	0.093	6	70nnh
Ozone 8-hour 2015	2018	0.115	6	70ppb (5)
	2017	0.136	7	(3)

CO 1-hour 1971	2019	35	8	
	2018	20.782	7	35 ppm (8)
	2017	8.689	6	

NO2 1-hour	2019	88.7	6	
	2018	75.9	6	100 ppb (7)
	2017	73.6	6	

SO2 1-hour 2010	2019	9.4	4		
	2018	9.9	4	75 ppb (6)	
	2017	76.0	6		

Figure E.11 Example of Data Summary Showing the Highest 1st Max Value

Using the lowest and highest audit levels for each parameter (and method code) as a guide, select three or more levels that meet the criteria outlined in 40 CFR Part 58, Appendix A, Section 3.1.2.1. As

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described in the rule, more than three PE points are encouraged, which could alleviate concerns about exceeding the acceptance criteria at low level points, and may help better understand how to best troubleshoot any failed individual point.

E.13.4 SELECTING AUDIT TARGETS

Once the audit levels have been selected, calculations must be done to determine the ideal audit targets. The use of a Superblend cylinder (with CO, NO, NO_x, and SO₂ concentrations) means that multiple parameters can be audited at a time, but consideration must be given to completing the audit in an efficient manner, and ideally with the fewest number of steps. The following factors will play a role in identifying the most efficient targets when auditing a site with more than one gaseous parameter:

- Superblend cylinder concentrations: determines the minimum and maximum values possible given the target flows.
- Mass Flow Controller (MFC) sizes in the gas dilution calibrator.
- Flow rates: the total flow and gas flow through the gas dilution calibrator, based on the sizes of the MFCs.
- NO₂ titration points: should be selected to coincide with ozone audit points, thereby conditioning the O₃ generator.
- The mid-point of the audit level range: especially important at the lowest audit levels when targeting a small concentration in a narrow range.
- Trace-level audits versus full-scale audits: multiple Superblend cylinders may be required to achieve a wider range of targets.

An Excel[®] spreadsheet (Expected Concentration Calculator, Figure E.12) has been generated to help perform some of the calculations. By inputting cylinder concentrations along with total air flow, various concentrations can be identified, given fixed MFC sizes. This allows the user to pick Superblend concentrations that meet the target audit levels. By changing the total air flow, maximum and minimum concentrations can also be shown. The calculator is available here:

S:\Cabinet\FORMS and WORKSHEETS - QA\Technical Appendices - Excel worksheets\Expected Concentration Calculator

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	ΜΔΙ		ORTS									
Port		entration		Gas ID								
1		00	%	AIR			\sim	л да	004			
2		875	PPM	CO			UΥ	'L #1	234	50		
2		35	PPM	NO				~ 10	、 」			
2		35	PPM	NOx			(Q 16	o ipm	ר		
2		17	PPM	SO2					•			
3		0	PPM	H2S								
				CONCE	NTRATIC	N MODE						
MFC	P	ort	Target	Flow	% of full	Target	Gas			Expec	ted Gas	
1	20	SLPM	15.89	SLPM	79%							
2	200	SCCM	109.71	SCCM	55%	CO	6.000	PPM		6.0	со	
3	100	SCCM	109.71	SCCM	110%	NO	0.2400	PPM		0.240	NO resi	dual
4	20	SCCM	109.71	SCCM	549%	NOx	0.2400	PPM		0.240	NOx	
Tota	al Flow:	16	.00	SLPM		SO2	0.1166	PPM		0.000	NO2	
						H2S	0.0000	PPM		0.000	H2S	
Ozone	0.	000	PPM									
		1						MFC		FLOW		
O3	со	NO/NOx	NO2	NO res	SO2	H2S	SCCM	% of full	GAS FLOW	ΤΟΤΑ	L FLOW	
0.700	20.0	0.8000	0.7000	0.1000	0.3886	0.0000	220	166%	0.3657	16	SLPM	<u>.</u>
0.660	19.0	0.7600	0.6600	0.1000	0.3691	0.0000	220	158%	0.3474	16	SLPM	Check
0.620	18.0	0.7200	0.6200	0.1000	0.3497	0.0000	220	150%	0.3291	16	SLPM	SO2
0.580	17.0	0.6800	0.5800	0.1000	0.3303	0.0000	220	88%	0.1943	10	SLPM	and
0.500	15.0	0.6000	0.5000	0.1000	0.2914	0.0000	220	86%	0.1886	11	SLPM	NO/NOx
0.420	13.0	0.5200	0.4200	0.1000	0.2526	0.0000	220	81%	0.1783	12	SLPM	to avoid over-
0.380	12.0	0.4800	0.3800	0.1000	0.2331	0.0000	200	89%	0.1783	13	SLPM	range
0.300	10.0	0.4000	0.3000	0.1000	0.1943	0.0000	200	91%	0.1829	16	SLPM	lange
0.220	8.0	0.3200	0.2200	0.1000	0.1554	0.0000	200	73%	0.1463	16	SLPM	
0.105	6.0	0.2400	0.1050	0.1350	0.1166	0.0000	200	55%	0.1097	16	SLPM	
0.100	5.0	0.2000	0.1000	0.1000	0.0971	0.0000	200	46%	0.0914	16	SLPM	
0.080	4.0	0.1600	0.0800	0.0800	0.0777	0.0000	200	37%	0.0731	16	SLPM	
0.030	3.0	0.1200	0.0300	0.0900	0.0583	0.0000	200	27%	0.0549	16	SLPM	
0.015	2.0	0.0800	0.0150	0.0650	0.0389	0.0000	200	18%	0.0366	16	SLPM	
0.007	1.7	0.0680	0.0070	0.0610	0.0330	0.0000	200	16%	0.0311	16	SLPM	
0.005	1.4	0.0560	0.0050	0.0510	0.0272	0.0000	200	13%	0.0256	16	SLPM	
0.005	1.2	0.0480	0.0050	0.0430	0.0233	0.0000	200	11%	0.0219	16	SLPM	
0.005	1.0	0.0400	0.0050	0.0350	0.0194	0.0000	200	9%	0.0183	16	SLPM	
0.005	0.70	0.0280	0.0050	0.0230	0.0136	0.0000	20	64%	0.0128	16	SLPM	
0.005	0.50	0.0200	0.0050	0.0150	0.0097	0.0000	20	46%	0.0091	16	SLPM	
0.005	0.35	0.0140	0.0050	0.0090	0.0068	0.0000	20	32%	0.0064	16	SLPM	
0.005	0.21	0.0084	0.0050	0.0034	0.0041	0.0000	20	19%	0.0038	16	SLPM	
0.005	0.18	0.0072	0.0050	0.0022	0.0035	0.0000	20	16%	0.0033	16	SLPM	
0.005	0.04	0.0016	0.0050	-0.0034	0.0008	0.0000	20	4%	0.0007	16	SLPM	
0.005	0.02	0.0008	0.0050	-0.0042	0.0004	0.0000	20	2%	0.0004	16	SLPM	
0.000	0.02	0.0000	0.0000	-0.0042	0.0004	0.0000	20	∠ /0	0.0004	10		

Figure E.12 Expected Concentration Calculator

NOTE: In the example shown in Figure E.12, the total flow was reduced to achieve the desired CO target without "over-ranging" the MFCs. The API T700U gas dilution calibrator will automatically combine flows through both MFCs when the largest capacity is exceeded. MFCs can be unstable and/or inaccurate outside 5 to 95% of their operating range.

Some of the important equations in the calculator are:

CO ratio = (CO target/CO cylinder concentration)

NO concentration = (CO ratio) * NO cylinder concentration

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NO_x concentration = (CO ratio) * NO_x cylinder concentration

SO₂ concentration = (CO ratio) * SO₂ cylinder concentration

 NO_2 concentration = NO_X concentration - (NO concentration - O_3 concentration)

NO residual = NO concentration – NO₂ concentration

MFC % of full (scale)= (((Total Flow/(CO cylinder concentration/CO target))*1000)/MFC size)*100

Alternative Expected Gas Concentration calculation (not shown)= (Gas Flow Rate * Gas Cylinder Concentration)/Total Flow Rate

E.13.5 UPDATING CHANGES AND REVIEW SCHEDULE

If changes are made from previous audit levels and/or targets, the U.S. EPA should be consulted and approval granted before adopting the new criteria. Changes must be made to supporting documentation, including Audit Worksheets, SOPs, and the Quality Assurance Project Plan (QAPP), and new equipment and/or cylinders may need to be procured. Finally, the Audit Information System will need to be updated to ensure the gaseous audit modules include the new audit levels and flag exceedances or warnings appropriately.

A review of CARB's audit level targets will be conducted every 3 years, at a minimum, by QAS staff and management, or as necessary. Scheduled reviews will be conducted in Q4 of the following years:

- 2020 (for 2021 audits)
- 2023 (for 2024 audits)
- 2026 (for 2027 audits)
- 2029 (for 2030 audits)
- 2032 (for 2033 audits)
- 2035 (for 2036 audits)
- 2038 (for 2039 audits)
- 2041 (for 2042 audits)

E.14.0 <u>REFERENCES</u>

CARB Air Monitoring Quality Assurance Manual-Volume V: Audit Procedures for Air Quality Monitoring, "Appendix AO: Air Quality Data Action Request (AQDA), (June 27, 2017) <u>https://www.arb.ca.gov/aaqm/qa/qa-manual/vol5/v5apxao.pdf</u>

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Technical Memorandum- Guidance on Statistics for Use at Audit Levels 1 and 2 of the Expanded List of Audit Levels for Annual Performance Evaluation for SO₂, NO₂, O₃, and CO as Described in 40 CFR Part 58 Appendix A Section 3.2.2, (February 17, 2011) <u>https://www3.epa.gov/ttn/amtic/files/ambient/pm25/datamang/2011021</u> <u>7lowlevelstatmemo.pdf</u>

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Teledyne API User Manual: "Model T300U CO Analyzer with Auto-Reference (Addendum to T300/T300M Operation Manual, P/N 06864)" 06867C DCN7545, (March 20, 2017) <u>http://eservices.teledyne-api.com/manuals/06867C-</u> <u>Addendum Manual T300U.pdf</u>

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http://eservices.teledyneapi.com/manuals/06876B_T700U_Addendum.pdf

Title 40 Code of Federal Regulations Part 58, Appendix A - Quality Assurance Requirements for Monitors used in Evaluations of National Ambient Air Quality Standards <u>https://ecfr.io/Title-40/pt40.6.58#ap40.6.58_161.a</u>

U.S. Environmental Protection Agency, National Performance Audit Program (NPAP) Standard Operating Procedures; NPAP TTP Draft Operators Field SOP - Sections 0-11 (updated July 19, 2011) <u>https://www3.epa.gov/ttn/amtic/files/ambient/npapsop/20110719NPAP</u> <u>TTPDraftOperatorsFieldSOP.pdf</u>

U.S. Environmental Protection Agency, Quality Assurance Handbook, Volume II (January 2017) <u>https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/Final%20Handb</u> <u>ook%20Document%201_17.pdf</u>

U.S. Environmental Protection Agency, Quality Assurance Handbook, Volume II, Appendix D - Measurement Quality Objectives and Validation Templates

https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/APP_D%20valid ation%20template%20version%2003_2017_for%20AMTIC%20Rev_1.pdf

E.15.0 <u>REVISION HISTORY</u>

E.15.1 <u>REVISION HISTORY (REVISION 9.0)</u>

Subject	Revision 9.0 (2019)	Revision 8.0 (2015)
New or	Summary of Method	
Revised	Gaseous audit process (Figure	
Sections	E.2)	
	Acronyms and Definitions	
	Interferences	
	Personnel Qualifications	
	(expanded)	
	Health, Safety, and Cautions	
	(expanded)	
New	E.6.0 - Gas calibrator with ozone	Gas calibrator with
Equipment	generator and photometer	ozone generator
Calibration	E.8.2- Revised Figure E.3: QA	
and Audit	Gaseous Audit Worksheet	
Points	(new target values)	

Subject	Revision 9.0 (2019)	Revision 8.0 (2015)
	E.8.3 – Revised Figure E.4: CARB Audit Ranges, Revised 09- 05-2018; new EPA concentration ranges for audit levels or audit points	
	E.8.4 – Revised concentrations of NIST-traceable CO gases	E.1.2.4 - Use of NIST- traceable CO gases at concentrations of approximately 9ppm and 40ppm
	Note: CO analyzer drift at >0.25 ppm may require calibration or adjustment	Note: CO analyzer drift >0.5 ppm may require calibration
	CO analyzer calibration must be within ±0.25 ppm of zero	CO analyzer response to zero air must be ±0.5ppm of zero
Audit Procedures	E.8.5 – Full audit procedures for CO, NO ₂ , and SO ₂ analyzer or H ₂ S analyzer are described in one section	Audit procedures separately described in E.1.2.5 (CO), E.1.2.6 (H ₂ S), E.1.2.7 (Full Audit)
	E.8.7 – New Figure E.5: Audit Action Item Notification	Figure E.1.3.1 AQDA Form not used
	E.9.2 – Ozone line loss test revised with new test points. Figure E.6: O3 Line Loss Worksheet revised	Figure E.1.5.1 revised
	E.12.2 – Rewritten from E.1.5 (Revision 8, 2015) and condensed Revised Figure E.8: Trace-level Gaseous Audit Worksheet	E.1.6.1 revised
References	E.14.0 – References updated and links provided	E.1.0.5 revised

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E.15.2 <u>REVISION HISTORY (REVISION 10.0)</u>

Subject	Revision 10.0 (March 2021)
New Section	Addendum E.13.0 (Selecting Audit Ranges)
Revised Sections	 Section E.8.6 (Step 2) was revised to clarify calculations of actual audit concentrations. Sections E.6.0.1 and E.6.0.2 were replaced with a new Ozone Line Loss procedure (Section E.11.2)
Other Changes	 Revised Section and Figure numbering Updated Figures to include the most recent versions of worksheets and documentation Moved Acronyms and Definitions to a position preceding SOP content
References	• Added references for the new Addendum (E.14.0)