# Calibration versus Performance Evaluation Audits for Gaseous Instruments

PQAO Training 2019

Karl Tupper, San Luis Obispo APCD

Michael Hamdan, South Coast AQMD

# Calibrations

# Overview of Calibrations

- **Calibration** checks (and possibly corrects) an instrument's response against a standard of known accuracy
  - Typically, before using instrument to collect data
  - (**Audit** is QA function.)
- Who, When, How
- New criteria and requirements
- Tips and Tricks

# Some Definitions

- "Calibration" is defined as:

  *The comparison of a measurement standard, instrument, or item with a standard or instrument of higher accuracy to detect and quantify inaccuracies and to report or eliminate those inaccuracies by* ***adjustment****.*
  (U.S. EPA QA Handbook Vol II)


- "Verification": comparison done, but no adjustment made


- Today, focus on gas instruments
  - concepts also apply to PM and meteorology

# References

- 40 CFR 50 Appendices
- EPA Quality Assurance Manual Vol II (Jan 2017)
  - https://www3.epa.gov/ttn/amtic/qalist.html
- CARB QAPP for Gaseous Pollutants (Sept 2018)
  - https://ww2.arb.ca.gov/our-work/programs/quality-assurance/qm-document-repository/quality-management-plans-and-quality
- All Districts need to adopt CARB QAPP or updated their addenda by summer 2019!

# How

- Calibrations should be carried out
  - at the field monitoring site
  - by allowing the analyzer to measure test samples of known pollutant concentrations
- Analyzer and calibrator should be warmed up
  - T400 ozone: ≥1 hour (CARB SOP)
  - T200 $NO_2$: ≥1 hour, longer better (CARB SOP)
  - Trace CO: 10 hours (recommendation)
  - T700 Calibrator: ≥1 hour (CARB SOP)

# How
(continued)

- During the calibration the analyzer should be operating in its normal sampling mode, including:
  - Filters / scrubbers /conditioners
  - Through as much of the ambient air inlet system as is **practicable**. → **Ideally, through the probe.**
- Keep this in mind when:
  - Designing new station
  - Purchasing calibration equipment

# When

Upon:

- Installation
- Relocation
- Repairs or Service
- Interruption
- Upon any indication of potential malfunction
- At least every 6 or 12 months (see below)
- Station shutdown

Minimum frequency of calibration:

- CARB: At least every six months
- EPA: Can be annually w/ daily zero/span checks

If possible, avoid calibrating during:

- High pollution episodes
- Adverse weather

Keep track of when calibrations are happening!

# How Many Points?

EPA/CARB requirements

- Ozone, $SO_2$, Carbon Monoxide:
  - Zero
  - 4 upscale points
- NO, $NO_2$, $NO_x$:
  - Zero
  - 4 upscale points for NO & $NO_x$
  - 3 $NO_2$ titration points

# Standards

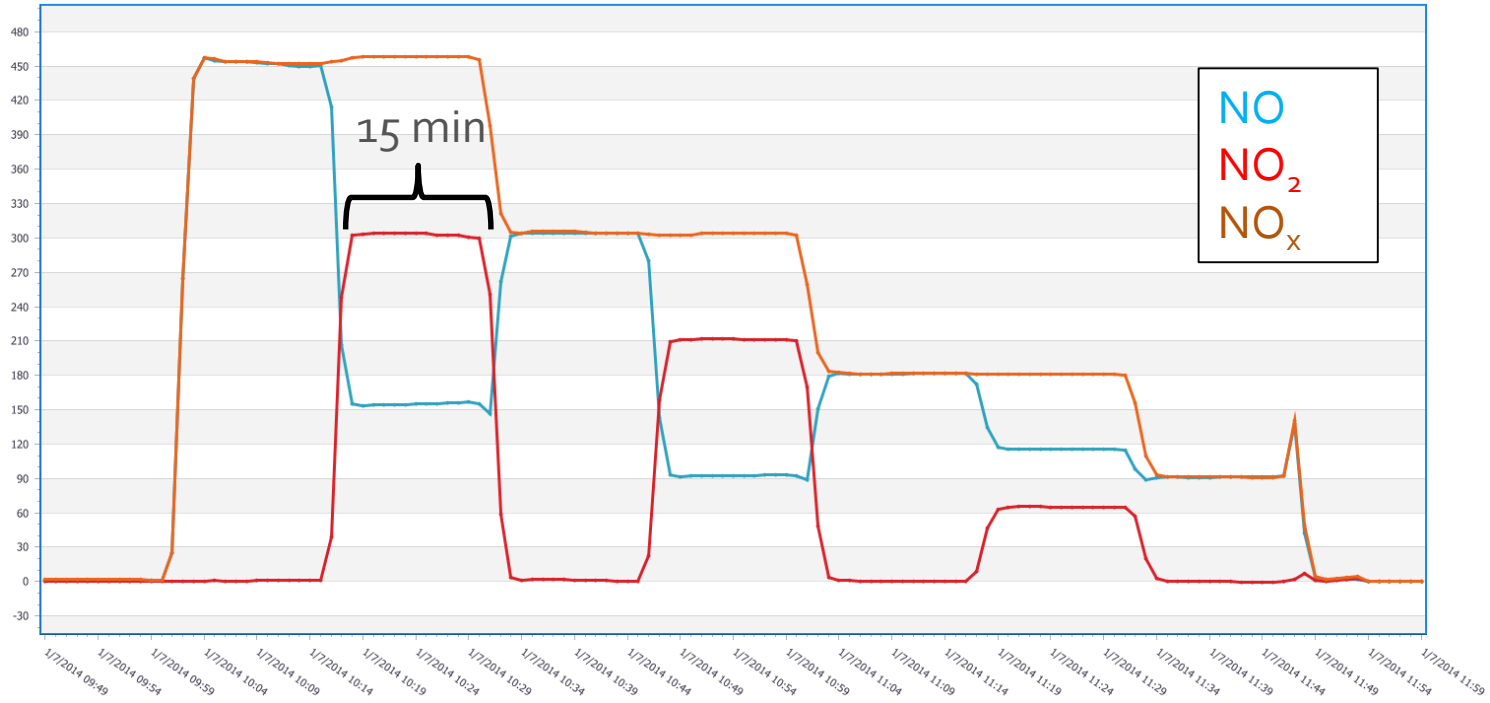
- Must be certified and traceable
  - U.S. EPA QA Vol II, Section 12.1.2
  - CARB Standards Lab:
    - http://www.arb.ca.gov/aaqm/qa/stdslab/stdslab.htm
- Check expiration dates
  - Calibration gas tanks
  - Mass flow controllers
  - Ozone transfer standard (6 months for Level 3/4)
  - Flow standards (1 year)
- Properly warm-up/equilibrate:
  - Flow standards
  - Ozone transfer standard

# Zero Air

- Zero Air Generator (ZAG) is part of calibration system
- Per CARB QAPP, we should:
  - Verify **annually** that our zero air is clean
  - Document ZAG maintenance
- See EPA QA Manual Appendix K

# Response Plateauing

- General practice is to allow concentrations to stabilize (plateau) for at least 10-15 minutes
- Teledyne API Analyzers:
  Stability should be <0.5 ppb (non-trace level)



# Documentation

- Usual stuff: name, date, initials/signature
- Information for standard(s):
  - Serial number(s)
  - Calibration/certification date(s)
  - Concentrations, correction factors, etc.
- Information for instrument:
  - Serial number
  - **As-Is and Final slope/intercept**
- Calibration info:
  - Calibration points
  - Instrument response

# Calibration Acceptance Criteria

**Old CARB criteria:**

- Ozone: ± 2% or 3 ppb "Overall % Accuracy"
- $NO_2$: ± 5% "Overall % Accuracy"
- $SO_2$ and CO: slope of 0.95 to 1.05

**New Criteria:**

- **EPA** Guidance* says:
  - All points within 2.1% or ≤ ±1.5 ppb (≤ ±0.030 ppm for CO) of best-fit straight line, whichever is greater
  - Slope is 1 ± 0.05 (*recommendation only*)
  - For $NO_2$: converter efficiency ≥ 96% (96% - 104.1% recommended)
- **CARB** QAPP for Gaseous Pollutants (2018) says:
  - All points < ±2.1% or ≤ ±1.5 ppb (≤ ±0.030 ppm for CO) of best-fit straight line, whichever is greater
  - Slope is 1 ± 0.05
  - For $NO_2$: converter efficiency 96% - 104.1% for heated Mo converter
  - Or, more stringent criteria in specific SOP may be applied
- Check & update your SOPs and QAPPs!!

*EPA Technical Notes (next slide)

# Additional EPA Guidance on Calibrations

EPA Memoranda & Tools on AMTIC website:

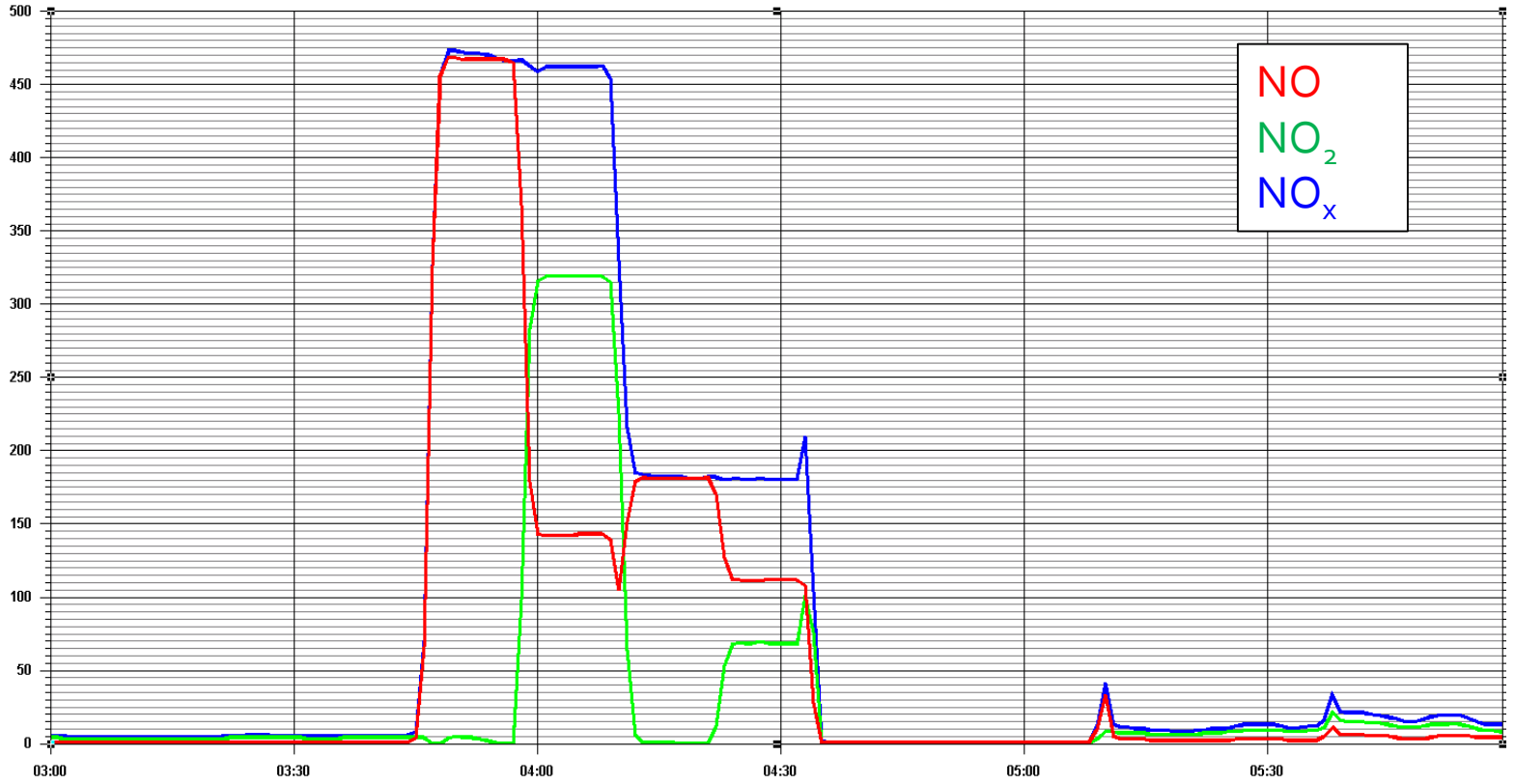
- https://www.epa.gov/amtic/policy-memoranda-and-technical-guidance
- "Technical Note- Alternative to Calibration Procedures Described in NO2, SO2 and CO Methods." (May 4, 2018.)
  - OK to use *Calibration Scale* rather than *Full Scale*
- "Technical Note- Clarifications and Guidance on Gaseous Pollutant Methods" (Jan 30, 2018.)
  - Clarifies "All points within 2.1% or ≤ ±1.5 ppb (≤ ±0.030 ppm for CO) of best-fit straight line, whichever is greater"
- DASC Tool (Excel workbook) for calculations
  - https://www3.epa.gov/ttn/amtic/qareport.html

# Failed Calibration?

- Whatever happens: *Document, Document, Document!!*
- Double check calibration equipment, data logger, and calculations
- Corrective action:
  - Re-zero and/or re-span
  - Fix or replace instrument
  - Perform calibration/verification prior to placing monitor back online
- Inform upstream data users
- How might data be affected?
  - In general, if 1-pt QC check still passes, data invalidation not necessarily needed
  - Note: "post-processing" of data no longer accepted

# Purging a Regulator

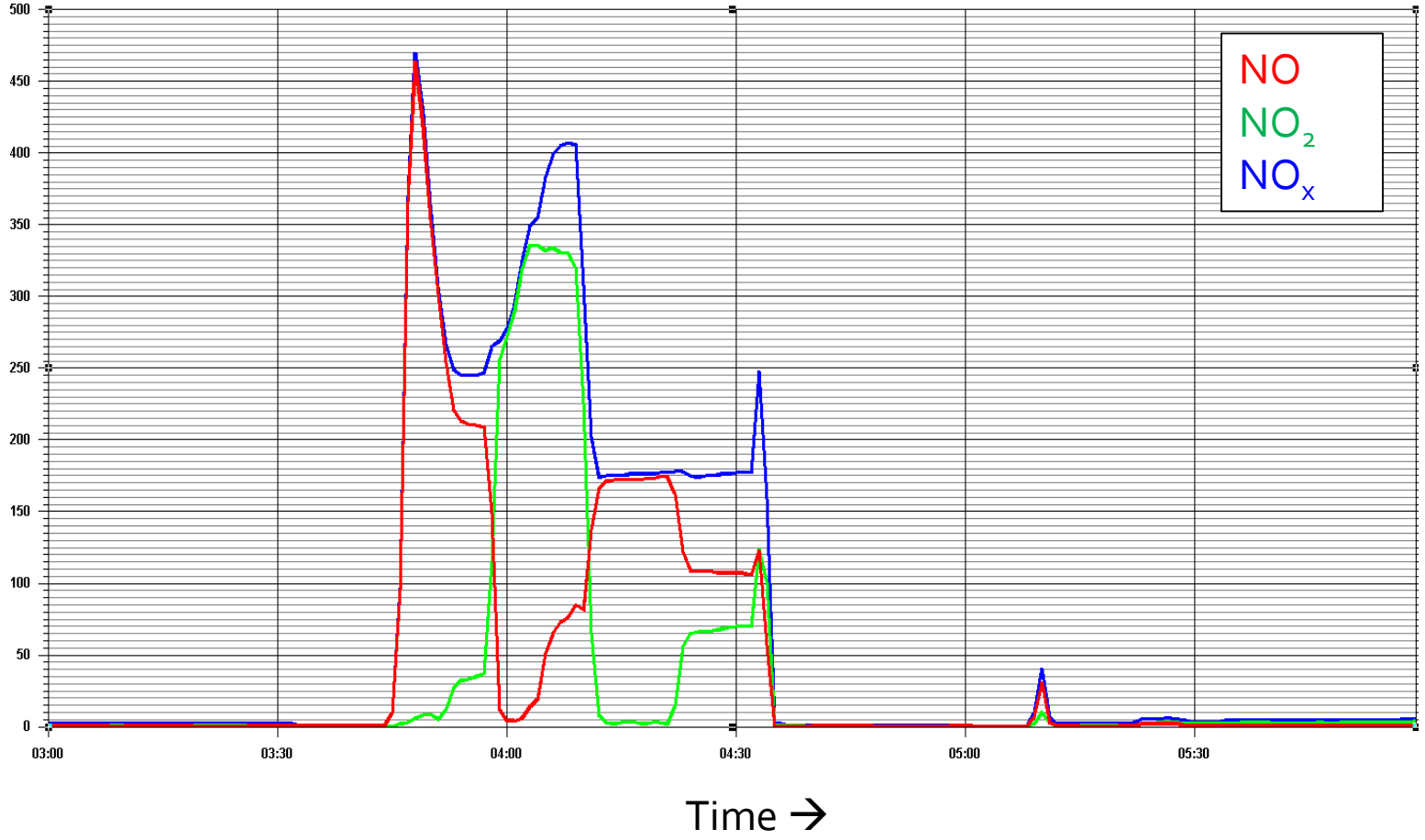
## Z/S/P with Properly Purged Reg




Time →

# Purging a Regulator

## Autocal with Improperly Purged Reg



# Calibration: Purging a Regulator Demo

# Misc.

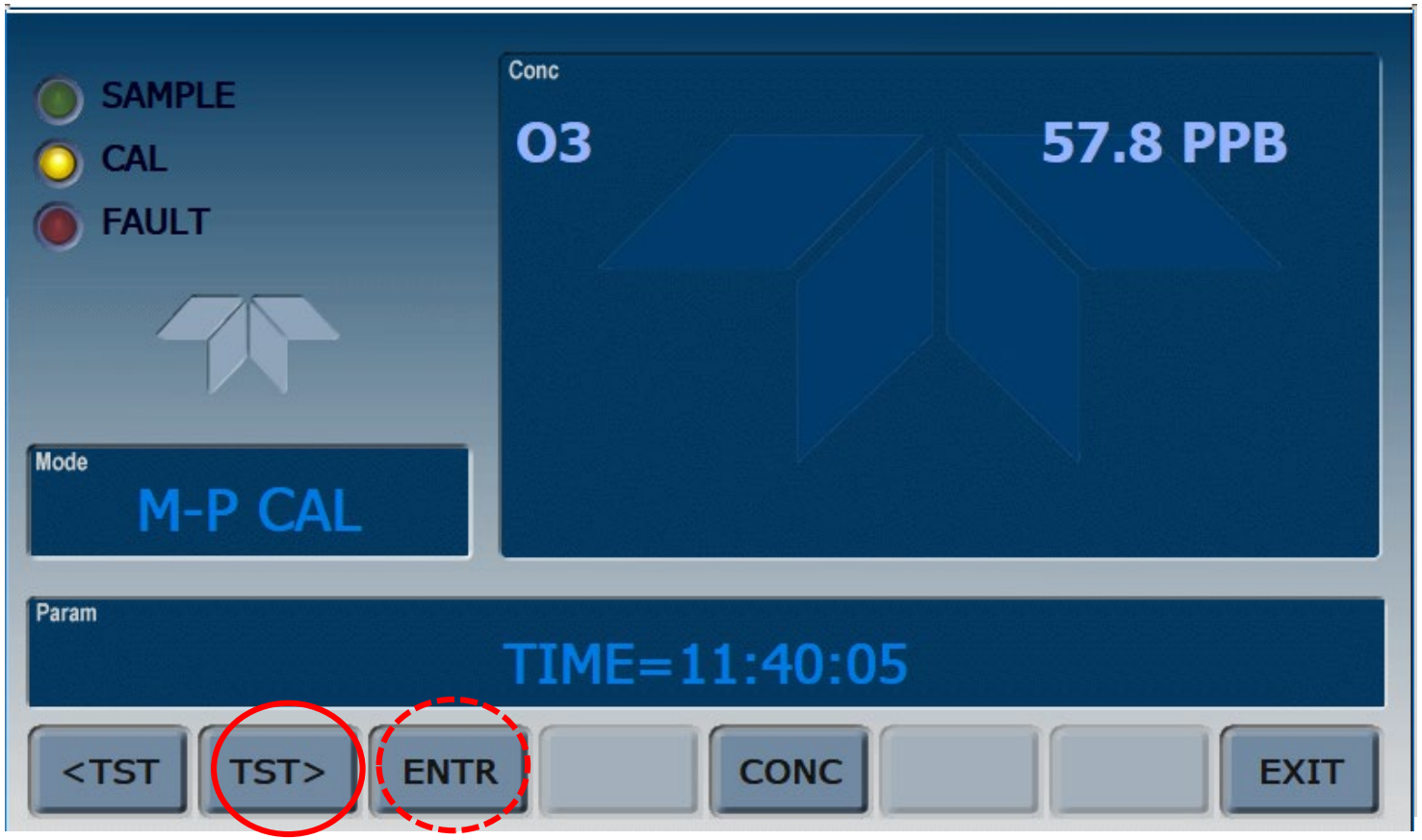
- Instrument Display vs Data Acquisition System
  - Is the DAS calibrated?
- Dynamic Dilution Calibrators (NO, $SO_2$)
  - Regularly calibrate mass flow controllers (MFCs)
  - Calculate "TRUE" audit concentration from MFC calibration curve

# Misc.

- Ozone Calibrators:
  - Apply current photometer certification to calculate "TRUE" concentrations
  - Provide adequate vent for excess flow
  - Teledyne 700/703 A/E/T specific:
    - Run Backpressure Compensation **EVERY** time there is change in the pneumatic configuration **OR** if PHOTO SPRESS / PH PRESS is not stable
      - See video by Teledyne-API: https://www.youtube.com/watch?v=SyBoaKtrvYo
    - Run Ozone Generator Cal whenever calibrator takes a while to find target concentrations

# Finally…

- Touch Screens:




SETUP > MORE > VARS > 929: manually fix slope and offset

Teledyne Service Note 10-021C: T-Series Touch Screen Calibration (2013)

# Overview of Performance Evaluation Audits

- Why audit?
- Audit types
- How to prepare?
- How to select PE Audit levels and values?
- PE Audit Criteria and Summary Report
- Corrective Action Request (CAR)

## Why do we audit?

- U.S. EPA requirement: 40 CFR Part 58 App. A Sec. 3.2.2
- Data integrity and defensibility.
- Independent review to agency quality control checks and procedures
- Consistency across multiple stations/instruments
- Identifies systematic issues and implements corrective actions (if needed)

# What are the types of Audits?

| Audit Type | Frequency | Done by |
|---|---|---|
| **Performance Evaluation (PE) Program** | Annually for gaseous instruments<br>25% per quarter<br>Semi-annually for PM samplers<br>5-7 month separation | PQAO, Monitoring agency or outside contractors |
| **National Performance Audit Program (NPAP) and PEP** | 20% of ambient air network annually<br>Full coverage in 5 years | U.S. EPA contractors, U.S. EPA, or CARB in California |
| **Technical Systems Audit (TSA)** | Once every 3-5 years | U.S. EPA Regions (for California: Region 9) |
| **Pb Audit Strip Program** | Monthly | U.S. EPA contractor and agency lab |

# What is a Performance Evaluation Audit?

- **Today's focus**: Through-the-Probe (TTP) Performance Evaluation (PE) audit for criteria ($O_3$, $SO_2$, CO, $NO_2$) gaseous instruments

- PE audit minimum requirement is 1/Year and 25% of the network every quarter.

- The audit and site response values are reported to AQS and assessed in the AQS reports.

## How to prepare for the Performance Evaluation Audit?

- Ensure that audit standards are within certification (e.g., *ozone standard* and *gas cylinders)*, audit equipment is warmed up and acclimated to the environmental conditions
- Contact station operator to schedule the audit and ensure access to site and equipment
  - Confirm that equipment is available for audit and not down for calibration or repair
- Acquire current information about the station instruments and monitors under audit (in case an instrument is added or shut down)

# Audit Points

Tip: try to select audit points in the middle of the level measurement

- **How many audit points?**
  - Minimum 3 points but a 4th point is recommended
- **How to select audit points?**
  - Point 1: 2-3 times method detection limit*
  - Point 2: less than or equal to 99$^{th}$ percentile of site data
  - Point 3: primary NAAQS or highest 3-year concentration

*Note difference between federal MDL and alternative MDL

Audit levels should be selected from the U.S. EPA expanded audit levels table below.

| Audit Level | Concentration Range, ppm | | | |
|---|---|---|---|---|
| | $O_3$ | $SO_2$ | $NO_2$ | 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 |

Yellow highlight related to NAAQS Concentration

# CO-based vs Flow-based Audits

Tip: make sure that even if CO-based audit is used, the value should be close to the calculated flow-based audit value

- Audit can be either *CO-based* or *flow-based.*
- ***CO-based audit*** is when the actual audit concentration for each point is calculated based on a response of an audit CO instrument that is calibrated pre- and post- audit to generate a slope and intercept and regression curve.
- ***Flow-based audit*** is when the actual audit concentration is calculated using the gas and air MFC flows.

# What to look out for when carrying a PE Audit?

- Adequate flow delivery and vent so the instruments are not pressurized.
- Use the flow mode on the dilution system to generate the audit points.

# An Example of Generated Audit Target Values for Ozone

| Audit Point # | Ozone (ppb) |
|---|---|
| 1 | 105 |
| 2 | 60 |
| 3 | 30 |
| 4 | 12 |

## Example of Generated Audit Target Values for CO, $SO_2$, NO, and $NO_2$ Using a Cylinder with 1200 ppm CO, 9 ppm $SO_2$, and 30 ppm NO

| CO (ppm) | $SO_2$ (ppb) | NO (ppb) | $NO_2$ (ppb) |
|---|---|---|---|
| 8 | 60 | 199 | 105 |
| 4 | 30 | 100 | 60 |
| 2 | 15 | 50 | 30 |
| 1 | 7 | 25 | 12 |

# PE Audit Criteria

| Pollutant | Audit Levels 1 & 2 | Audit Levels 3-10 |
|---|---|---|
| CO | ± 0.03 ppm | < ± 15 % |
| NOx and SO2 | ± 1.5 ppb | < ± 15 % |
| Ozone | ± 1.5 ppb | < ± 10 % |

# Example PE Summary Audit Report

**PRELIMINARY SUMMARY AUDIT REPORT**
**AUDIT AGENCY**

Site Name: Anaheim

Audit Date: 6/19/2018

| Parameter | PE Lab Response (ppm) | Station Response (ppm) | Percent Difference | Absolute Difference (ppm) | Pass/Fail | Warning |
|---|---|---|---|---|---|---|
| **Ozone** | | | | | | |
| Ozone Audit level 5* | 0.1056 | 0.1035 | -2.0 | -0.0021 | Pass | |
| Ozone Audit level 4* | 0.0615 | 0.0600 | -2.4 | -0.0015 | Pass | |
| Ozone Audit level 3* | 0.0309 | 0.0298 | -3.6 | -0.0011 | Pass | |
| Ozone Audit level 2* | 0.0125 | 0.0117 | -6.4 | -0.0008 | Pass | |
| Ozone Audit level 1* | | | | | N/A | |
| **Carbon Monoxide** | | | | | | |
| CO Audit Point #1 | 8.108 | 7.870 | -2.9 | -0.2380 | Pass | |
| CO Audit Point #2 | 4.071 | 3.980 | -2.2 | -0.0910 | Pass | |
| CO Audit Point #3 | 2.143 | 2.080 | -2.9 | -0.0630 | Pass | |
| CO Audit Point #4 | 0.824 | 0.820 | -0.5 | -0.0040 | Pass | |
| CO Audit Point #5 | 0.824 | | | | N/A | |
| **Oxides of Nitrogen** | | | | | | |
| NO Audit Point #1 | 0.1990 | 0.1915 | -3.8 | -0.0075 | Pass | |
| NO Audit Point #2 | 0.0999 | 0.0973 | -2.6 | -0.0026 | Pass | |
| NO Audit Point #3 | 0.0526 | 0.0510 | -3.0 | -0.0016 | Pass | |
| NO Audit Point #4 | 0.0202 | 0.0199 | -1.5 | -0.0003 | Pass | |
| NO Audit Point #5 | 0.0202 | 0.0199 | -1.5 | -0.0003 | Pass | |

# Example PE Summary Audit Report $NO_2$

| | | | | | |
|---|---|---|---|---|---|
| NO2 Audit Point #1 | 0.1076 | 0.1030 | -4.3 | -0.0046 | Pass |
| NO2 Audit Point #2 | 0.0634 | 0.0604 | -4.7 | -0.0030 | Pass |
| NO2 Audit Point #3 | 0.0319 | 0.0302 | -5.3 | -0.0017 | Pass |
| NO2 Audit Point #4 | 0.0120 | 0.0118 | -2.1 | -0.0003 | Pass |

| | | |
|---|---|---|
| Converter Efficiency NO2 Audit Point #1 | 100.2% | Pass |
| Converter Efficiency NO2 Audit Point #2 | 99.8% | Pass |
| Converter Efficiency NO2 Audit Point #3 | 99.7% | Pass |
| Converter Efficiency NO2 Audit Point #4 | 97.5% | Pass |

**Sulfur Dioxide**

| | | |
|---|---|---|
| SO2 Audit Point #1 | 0.0585 | N/A |
| SO2 Audit Point #2 | 0.0294 | N/A |
| SO2 Audit Point #3 | 0.0155 | N/A |
| SO2 Audit Point #4 | 0.0059 | N/A |
| SO2 Audit Point #5 | 0.0059 | N/A |

* = CFR Appendix A Audit Levels

# Corrective Action Request (CAR)

- CARs are issued, documented, and tracked by the SCAQMD QA Branch for:
- PE Audit results that are not within the audit acceptable criteria.
- Any potential quality assurance and safety findings.
- In addition, There will be a break-out session on corrective action processes tomorrow morning if you would like more information.

# Example CAR

## AQMD CORRECTIVE ACTION REQUEST

| | | | | | |
|---|---|---|---|---|---|
| **To:** | David Sawyer | **Date:** | 3/14/2019 | **Assessor:** | Mike Hamdan |
| **Location:** | Los Angeles N. Main | **Assessment Date:** | 3/8/2019 | **CAR #:** | 20190006 |
| **Expected Deadline:** | 3/29/2019 | **Instrument:** | TL CO | **S/N:** | 125 |

**FINDINGS:** The trace level CO instrument at Los Angeles N. Main has been having issues for an extended period that is impacting data completeness and data quality produced by the instrument.

**RECOMMENDATIONS:**

1. Review both instruments' internal parameters and set up to check if are any major discrepancies.
2. Place both CO instrument at one site on the same manifold and let both acclimate to the site conditions.
3. Calibrate both instruments using the same zero and CO concentration.
4. Monitor the performance over a period of time on ambient sampling nightly Zero/Span results.
5. If the result is acceptable put the instrument back in operation, replace the instrument if the issue cannot be resolved.

*Please indicate the corrective action taken below, save, and return this form to:*
**Quality Assurance Senior AQ Chemist or Instrument Specialist**
*and also copy this CAR electronically to your supervisor and manager*

# Site Technical Systems Audit

- Siting criteria
- Material of probe, manifold, sample lines, connections
- Residence time calculation
- Station gas expiration date and pressure
- Calibration/maintenance records
- Annual ZAG maintenance and verification
- General station safety

# Conclusion

- Calibrations and PE audits complement each other; both are distinct and required.
  - Calibrations occur routinely
  - PE audits are a snapshot in time, intended to have redundant checks
- The PE audit result alone does not invalidate the data; however, it may alert us of potential issues to investigate.
- There is a poster displaying key differences between a calibration and an audit.

## Contact Information:

Karl Tupper
A.Q. Specialist, San Luis Obispo County APCD
ktupper@co.slo.ca.us
phone: (805) 781-5912

Mike Hamdan
Sr. AQIS, South Coast AQMD
mhamdan@aqmd.gov
phone: (909) 396-2267