



# Building a Bigger, Better Zero Air Generator Certification Process

By:

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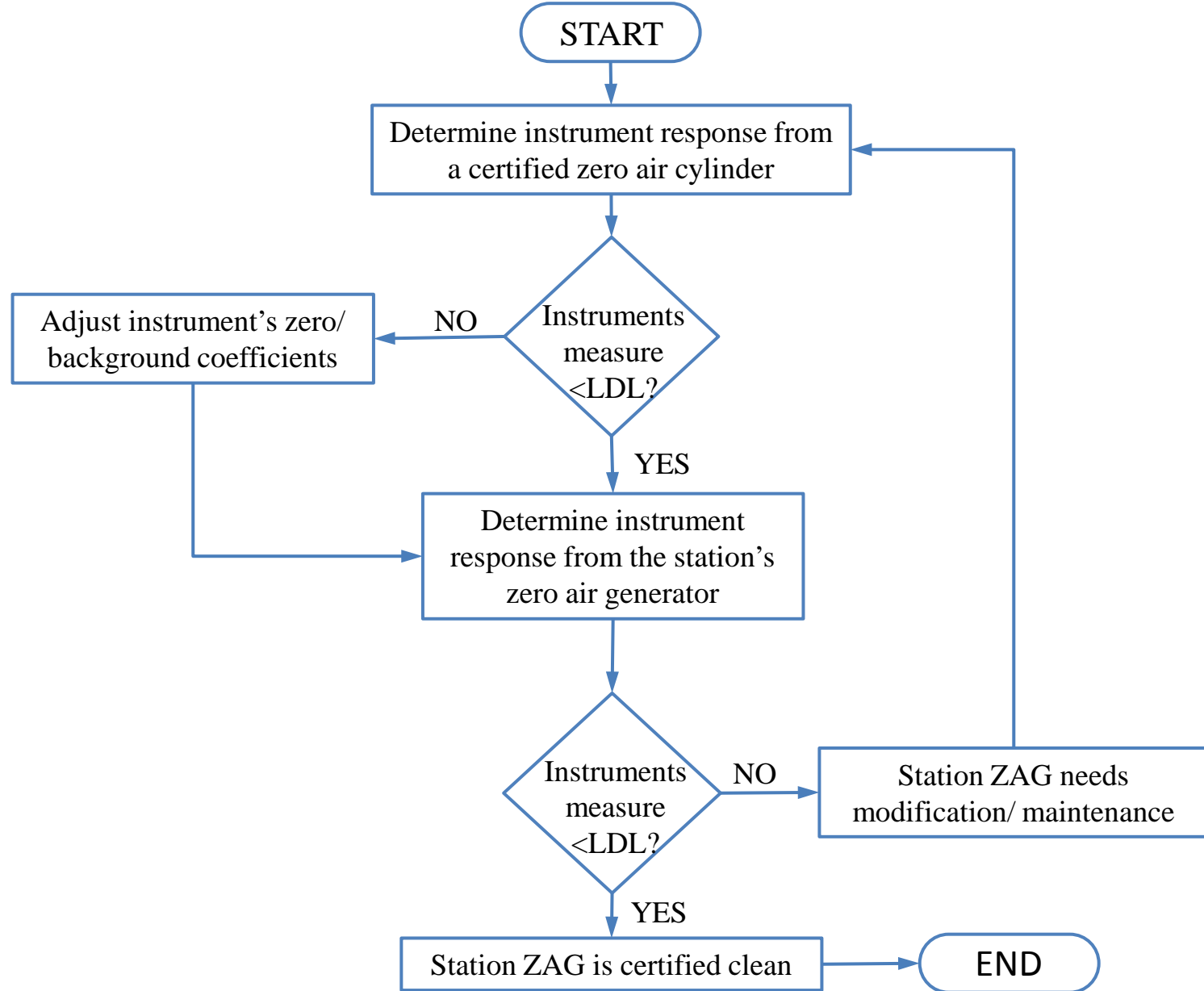
San Diego Air Pollution Control  
District

# The Needs for a Zero Air Generator Certification

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- Per the QA Handbook Vol. 2, the station zero air generators need to be certified annually
- Lowest CARB audit point for O<sub>3</sub> is ~ 55 ppb
- Lowest CARB audit point for NO<sub>2</sub> is ~80 ppb
  - This requires agencies to adjust their QA/QC points to be lower than CARB's.
  - Difference between the zero air sources can adversely affect the outcome of the audit at low concentrations
    - 1 ppb at 55 ppb = 1.8%
    - 1 ppb at 80 ppb = 1.2%

# Ideal Certification Procedure



# Problem with Ideal Procedure

- Ultrapure Air Cylinder levels exceed the instrument's LDLs, except for carbon monoxide

Make and Model	Pollutant	Instrument LDL (ppb) <sup>1</sup>	Ultrapure Air Cylinder (ppb) <sup>2</sup>
TAPI T400	O <sub>3</sub>	0.4	Not specified
Thermo 42C/ 42i / TAPI 200E	NO, NO <sub>2</sub>	0.4	< 1
Thermo 48i, TAPI T300	CO	40	< 10
TAPI T100	SO <sub>2</sub>	0.4	< 1
Thermo 42i-TLE, TAPI T200U	NO <sub>x</sub> (trace level)	0.05	< 1
TAPI 300U	CO (trace level)	20	< 10
Thermo 43i-TLE, TAPI T100U	SO <sub>2</sub> (trace level)	0.05	< 1
Thermo 42i-Y, TAPI T200U/NOY	NO <sub>y</sub>	0.05	< 1

<sup>1</sup> Manufacturer specifications

<sup>2</sup> Scott-Marrin Cylinder

# San Diego APCD Zero Air Generator Certification Procedure

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- Connect the station analyzers directly to a clean sampling manifold
- Analyze output of Reference Zero Air Generator
- Analyze output of Station Zero Air Generator
- Analyze output of Station Zero Air Generator connected to the External Scrubbers

# Zero Air Generator Comparison

Parameter	Instrument LDL (ppb) <sup>1</sup>	Ultrapure Air Cylinder <sup>2</sup> (ppb)	Envionics 7000 (ppb) <sup>3</sup>	Thermo 1160 (ppb) <sup>3</sup>	TAPI 701H (ppb) <sup>3</sup>
O <sub>3</sub>	0.4	Not specified	< 0.5	< 0.4	< 0.3
NO / NO <sub>2</sub>	0.4	< 1.0	< 0.5	< 0.1	< 0.025
CO	40	< 10	< 25 <sup>4</sup>	< 20 <sup>4</sup>	< 10
CO TLE	20	< 10	< 25 <sup>4</sup>	< 20 <sup>4</sup>	< 10
SO <sub>2</sub>	0.4	< 1	< 0.5	< 0.1	< 0.025
SO <sub>2</sub> TLE	0.05	< 1	< 0.5	< 0.1	< 0.025
NO <sub>y</sub>	0.050	< 1.0	< 0.5	< 0.1	< 0.025
Hydrocarbon	50	< 10	< 20	< 5	< 0.25
Dew Point at Max Flow Rate	N/A	Not specified	-10 °C	+5 or -40 °C <sup>5</sup>	-40 °C
Max Flow Rate	N/A	30+ slpm	20 lpm @ 30 psig	20 lpm	30 slpm @ 35 psig

<sup>1</sup> Manufacturer specifications: chose the best LDL between TAPI and Thermo

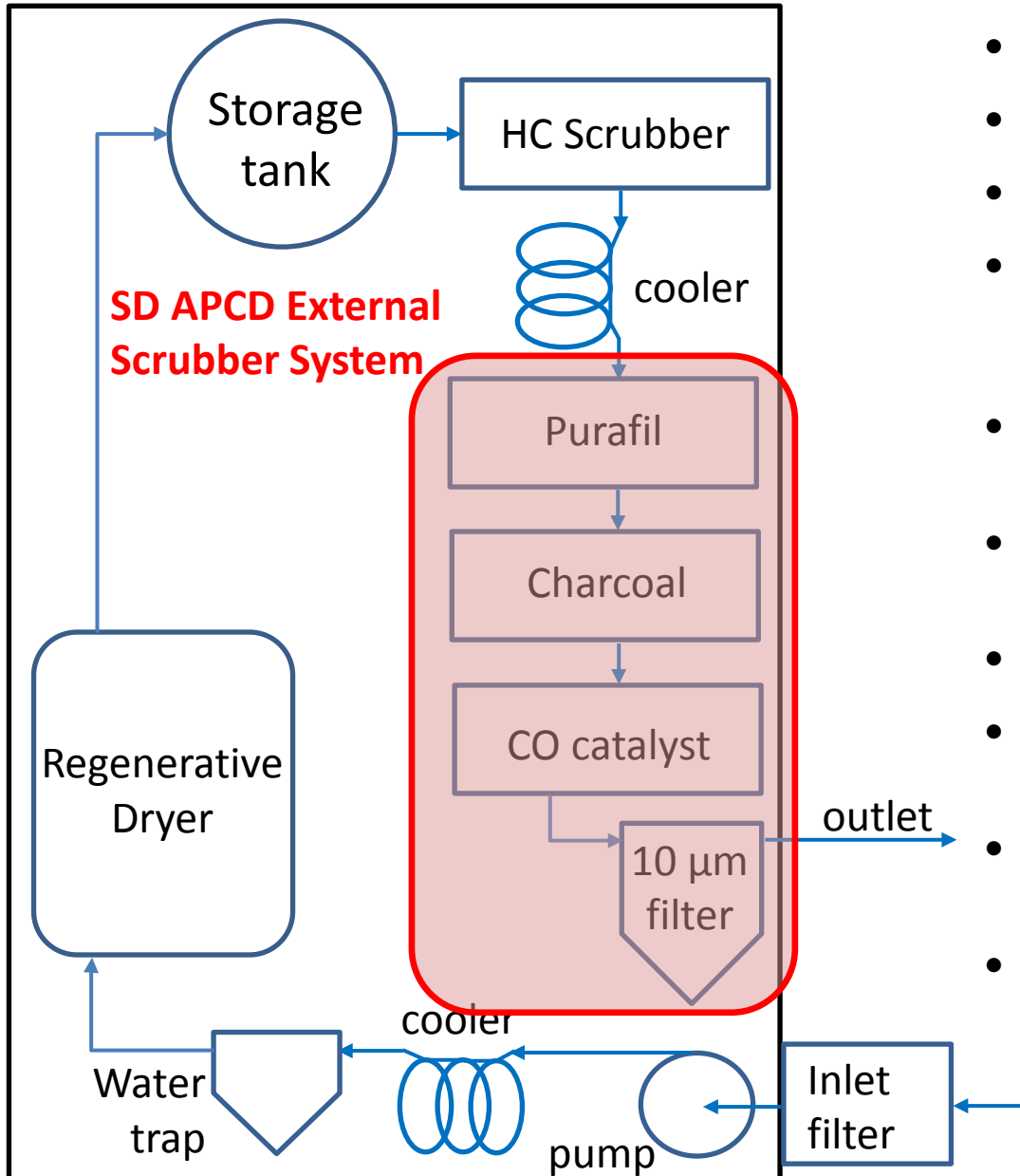
<sup>2</sup> Scott-Marrin Cylinder

<sup>3</sup> Manufacturer specifications

<sup>4</sup> Requires optional scrubber

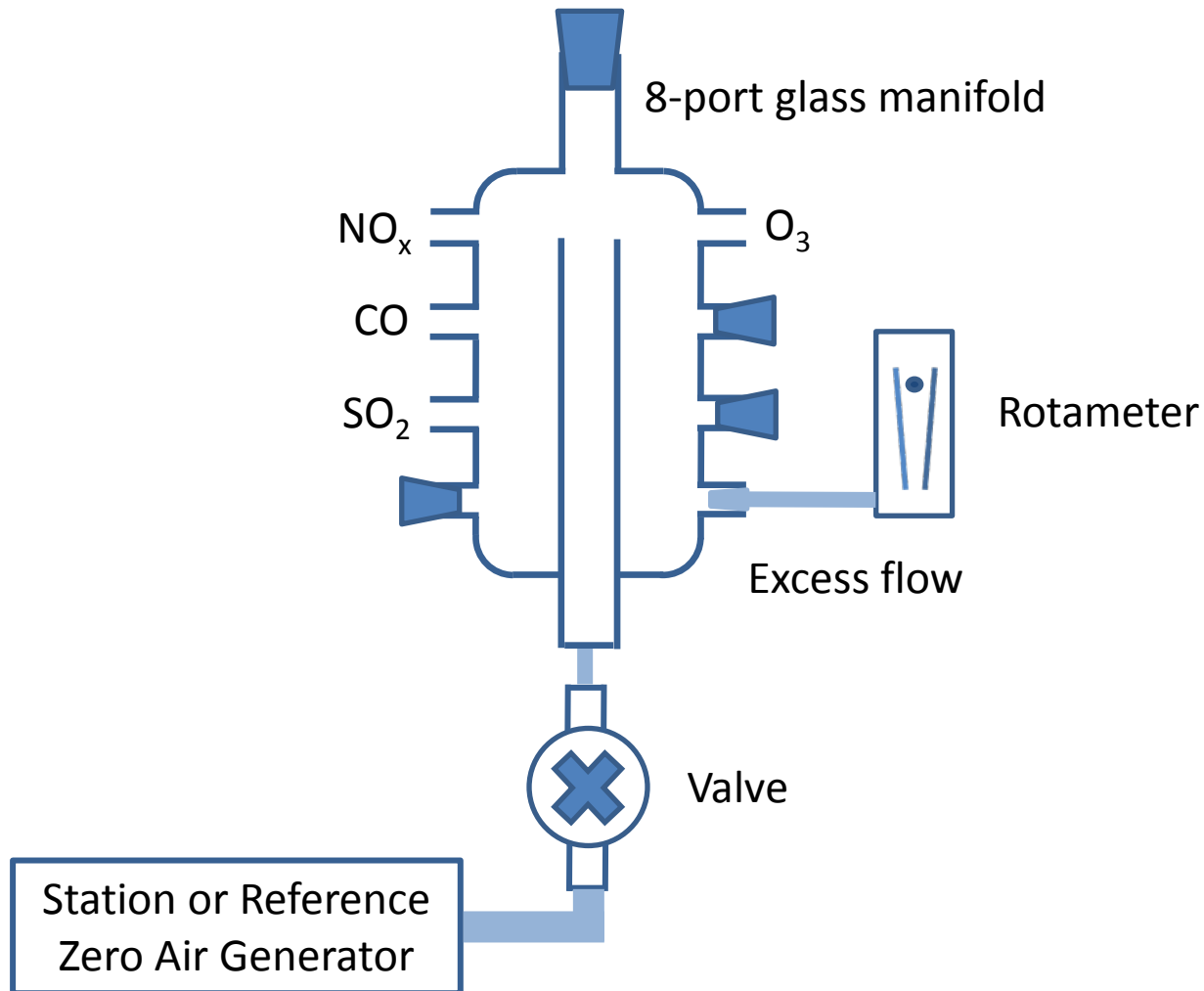
<sup>5</sup> Two different drying options

# Diagram of the TAPI 701H Zero Air Generator



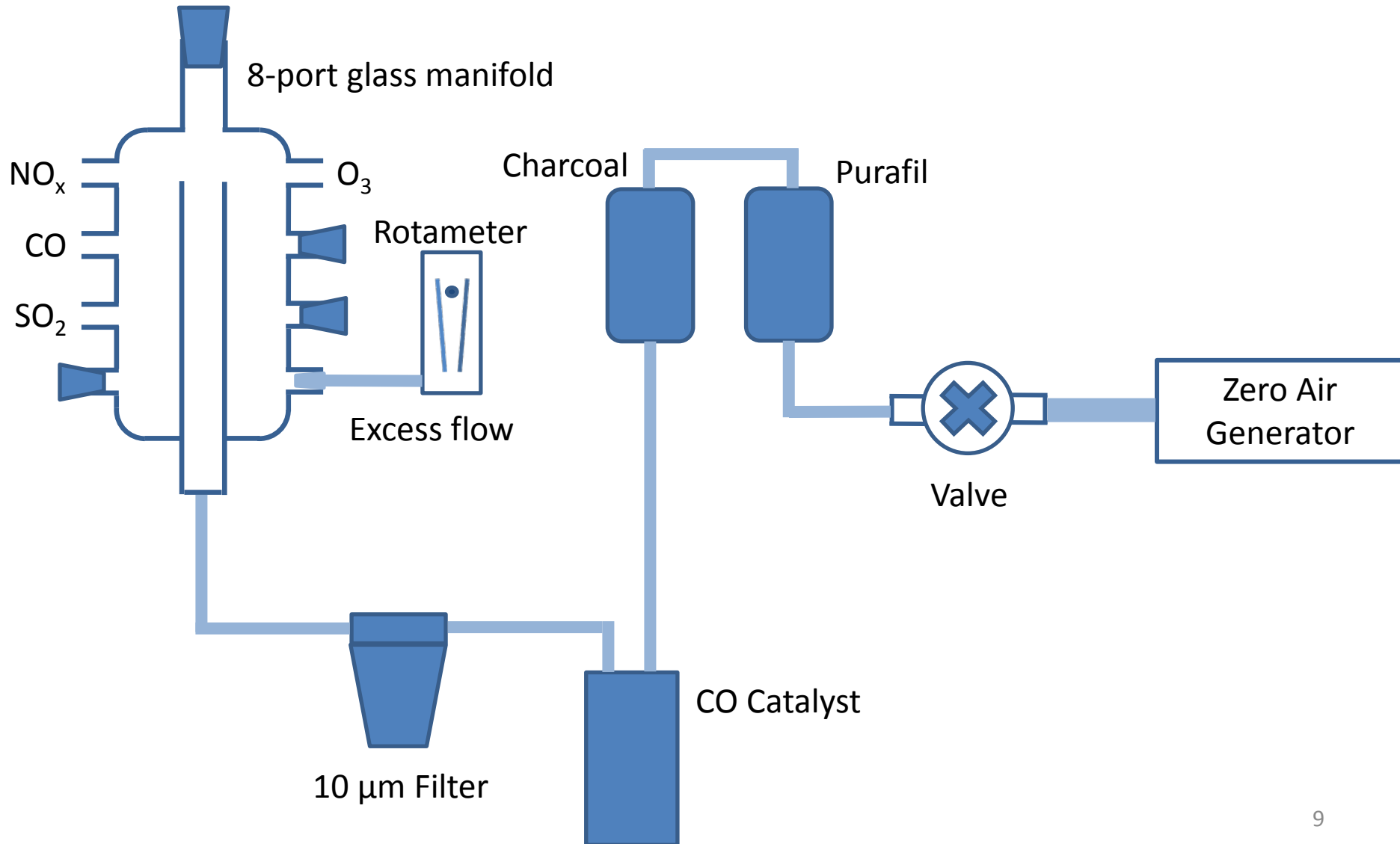
- Pump: Compresses ambient air
- Cooler: Cools the compressed air
- Water Trap: Removes bulk of water
- Regenerative Dryer: Removes residual water vapor and a portion of other contaminant(s)
- Storage Tank: Stores dry air until needed
- HC Scrubber: Catalytically converts (at 300 °C) hydrocarbons to CO<sub>2</sub> and water
- Purafil: Oxidizes NO to NO<sub>2</sub>
- Activated Charcoal: Absorbs NO<sub>2</sub>, O<sub>3</sub>, SO<sub>2</sub> and H<sub>2</sub>S
- CO Catalyst: Catalytically oxidizes CO to CO<sub>2</sub>
- 10 µm Filter: Filters out any particulates 10 µm or greater generated in the zero air generator

# Setup: Reference or Station Zero Air Generator connected to manifold

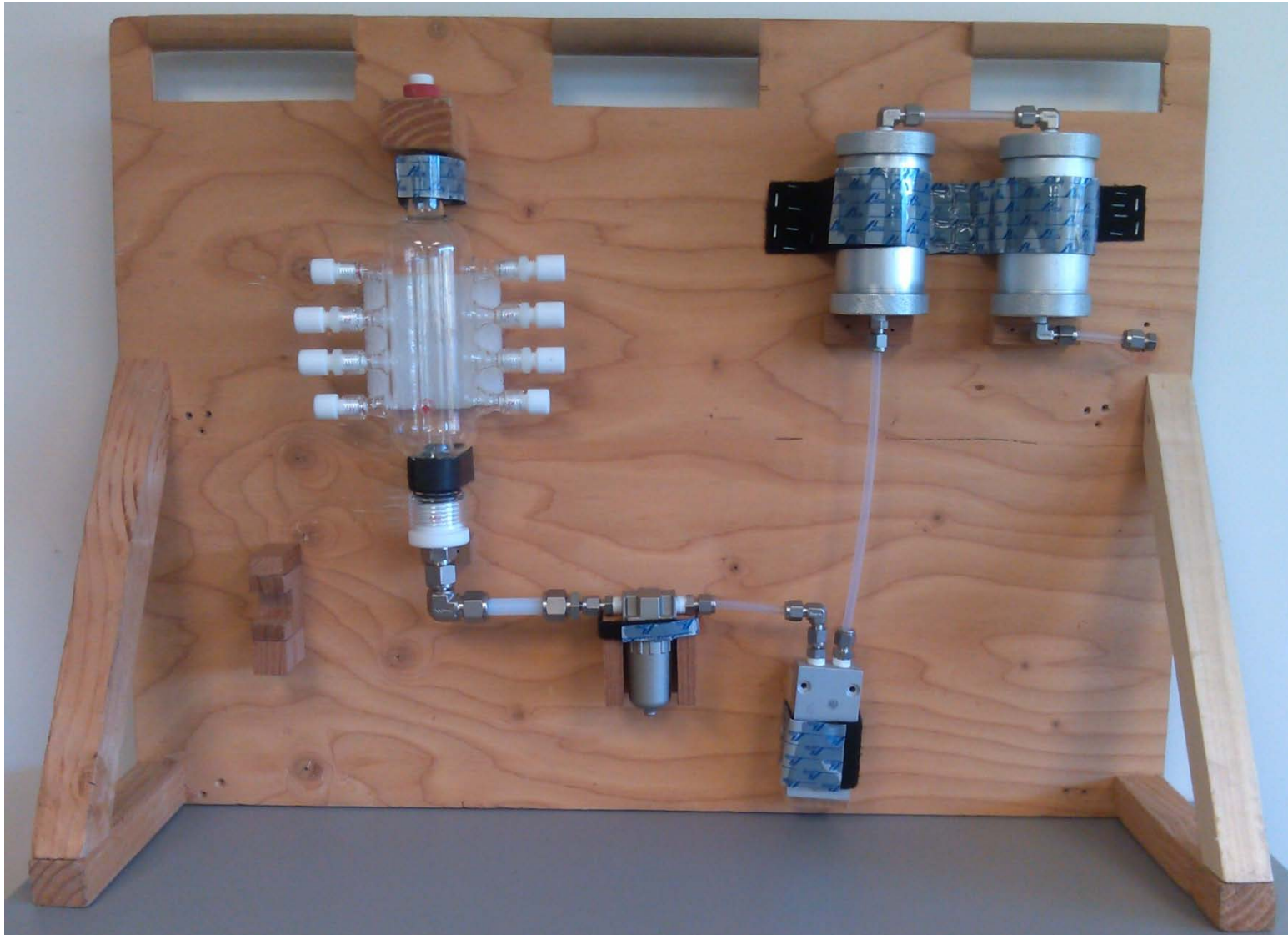




# Setup: Station Zero Air Generator connected to External Scrubber System



# Picture of the Manifold System



# Zero Air Generator Scrubber Change Frequency

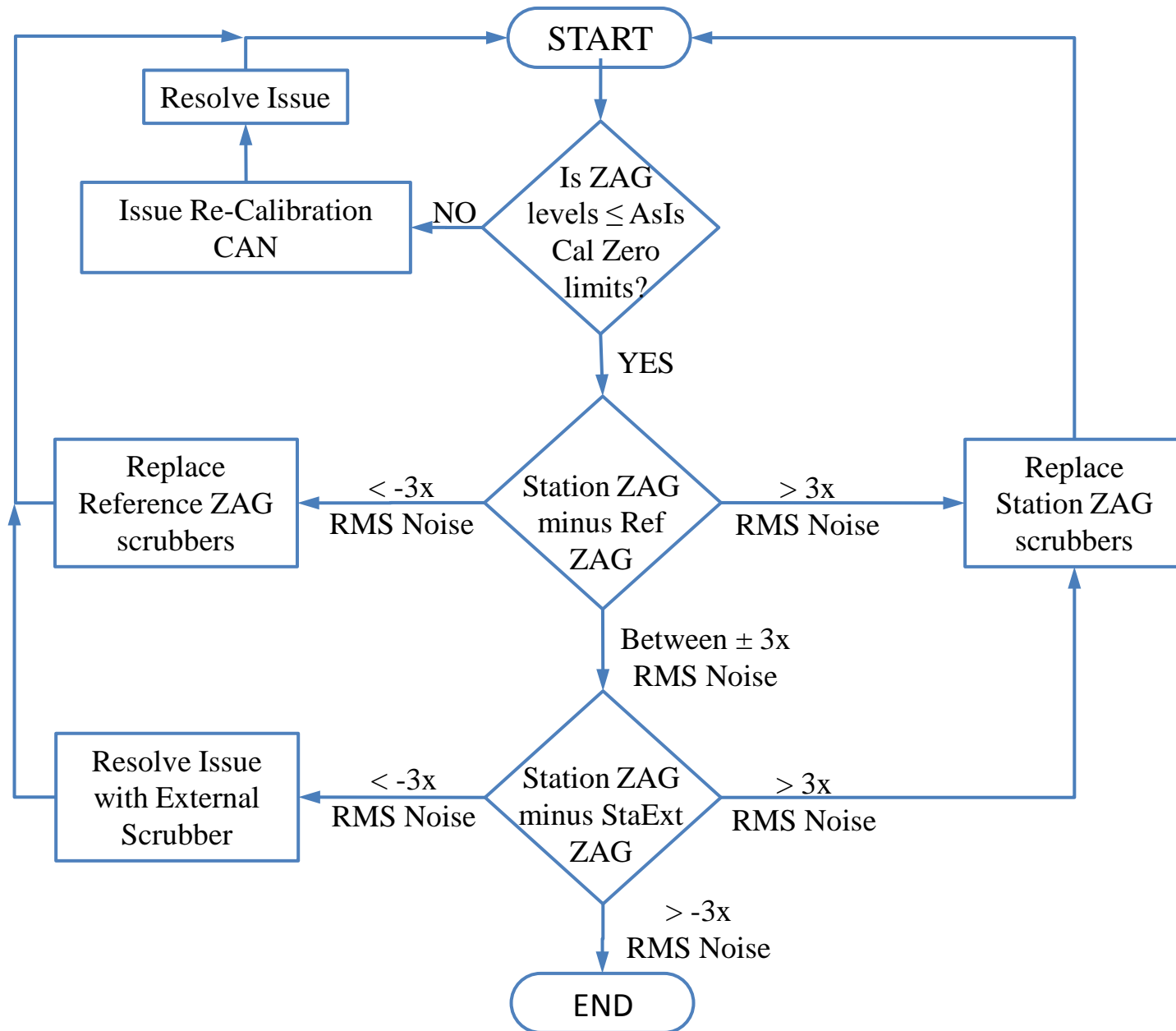
Scrubber	Ambient Station	Reference ZAG	External Scrubber System
Inlet Filter	Yearly	Yearly	N/A
Molecular Sieve	Every 2 years	Yearly	N/A
Purafil	Yearly	Yearly	Every 2 years
Activated Charcoal	Yearly	Yearly	Every 2 years
CO Catalyst	Every 2 years	Yearly	Every 4 years
10 µm Filter (outlet)	Yearly	Yearly	Every 2 years
Comments	ZAG in use continuously	Also used for Audits	Used only for ZAG Certification

# Development of the QA QC Criteria

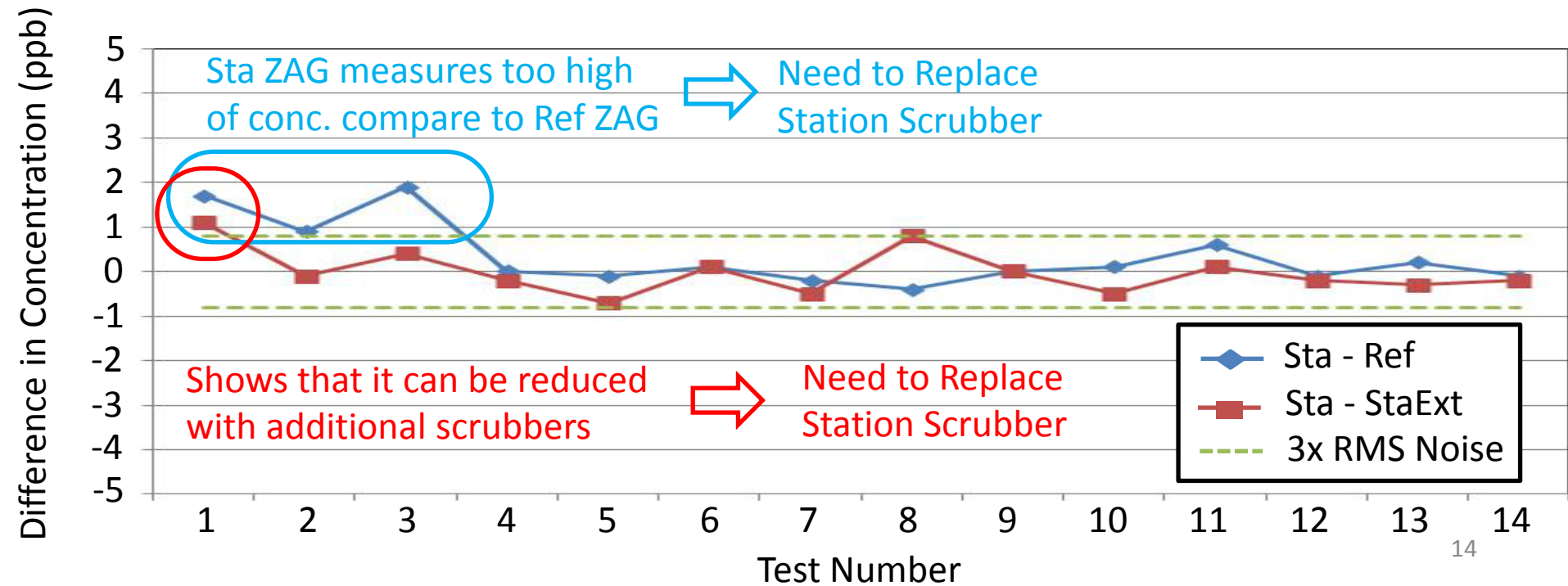
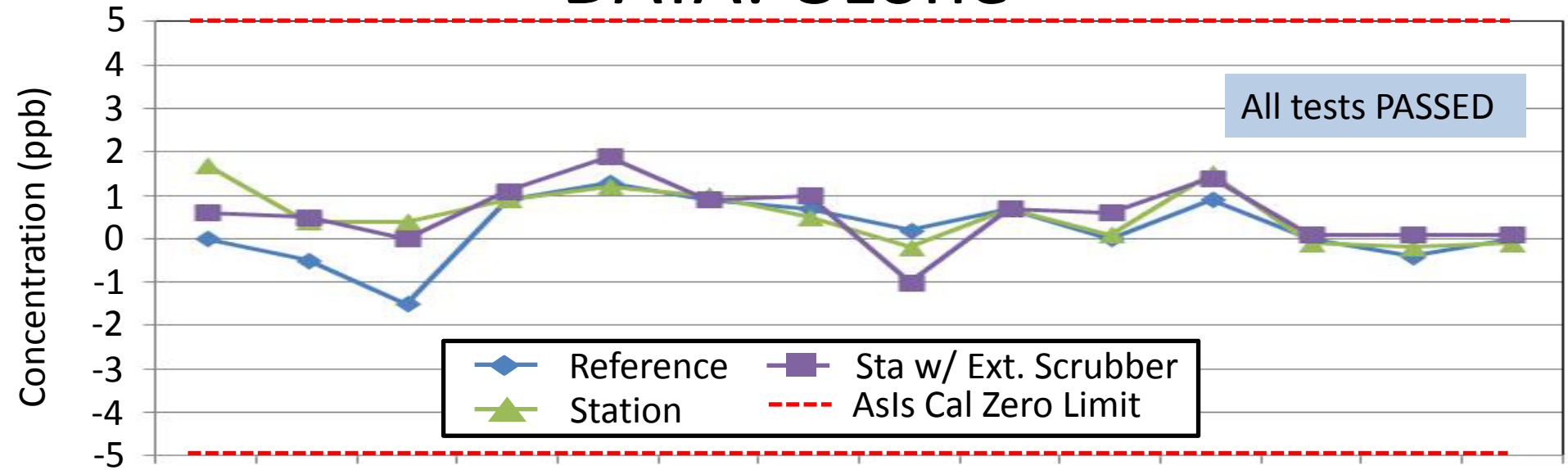
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- Absolute criteria for both Reference ZAG results and Station ZAG results
  - Needs to account for instrument drift
    - As-Is Calibration Zero limit: O<sub>3</sub> & NO<sub>x</sub>: ± 5 ppb
    - As-Is Calibration Zero limit: CO: ± 0.6 ppm
- Criteria for difference between Station ZAG and Reference ZAG
  - Needs to account for instrument noise
    - Three times the RMS noise
- Criteria for difference between Station ZAG and Station ZAG + External scrubber
  - Needs to account for instrument noise
    - Three times the RMS noise

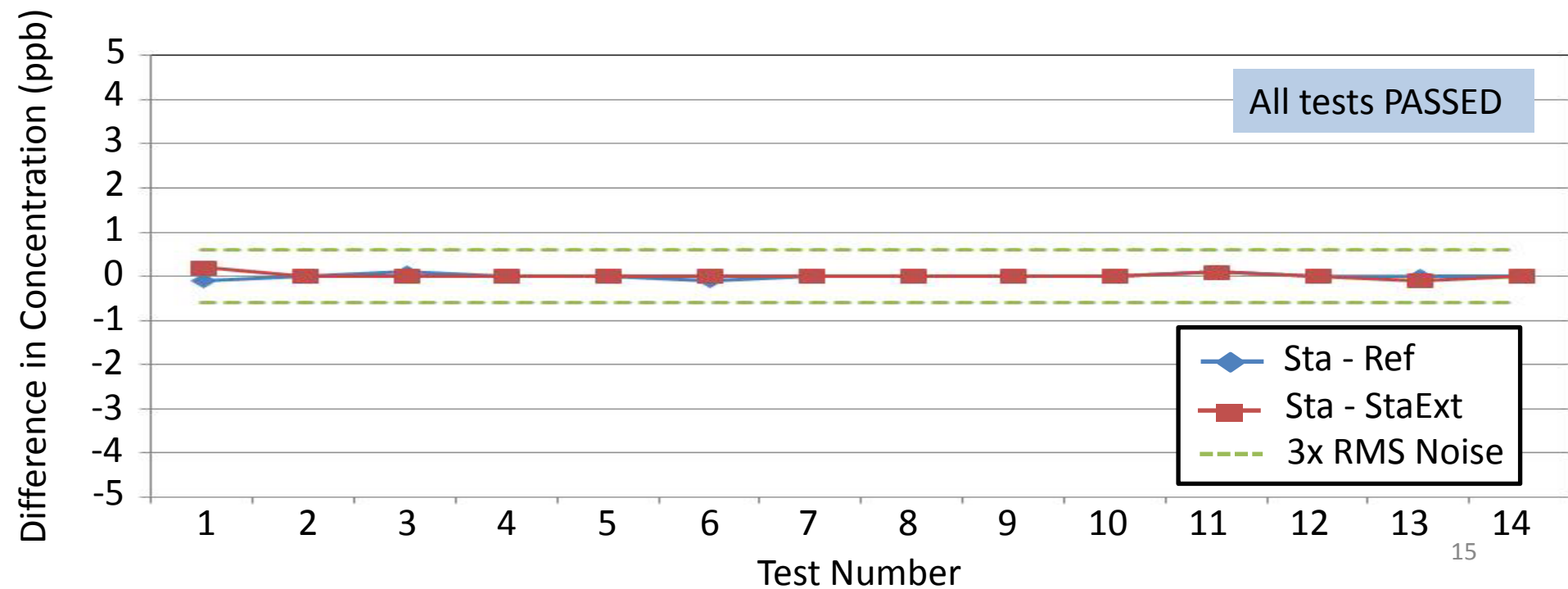
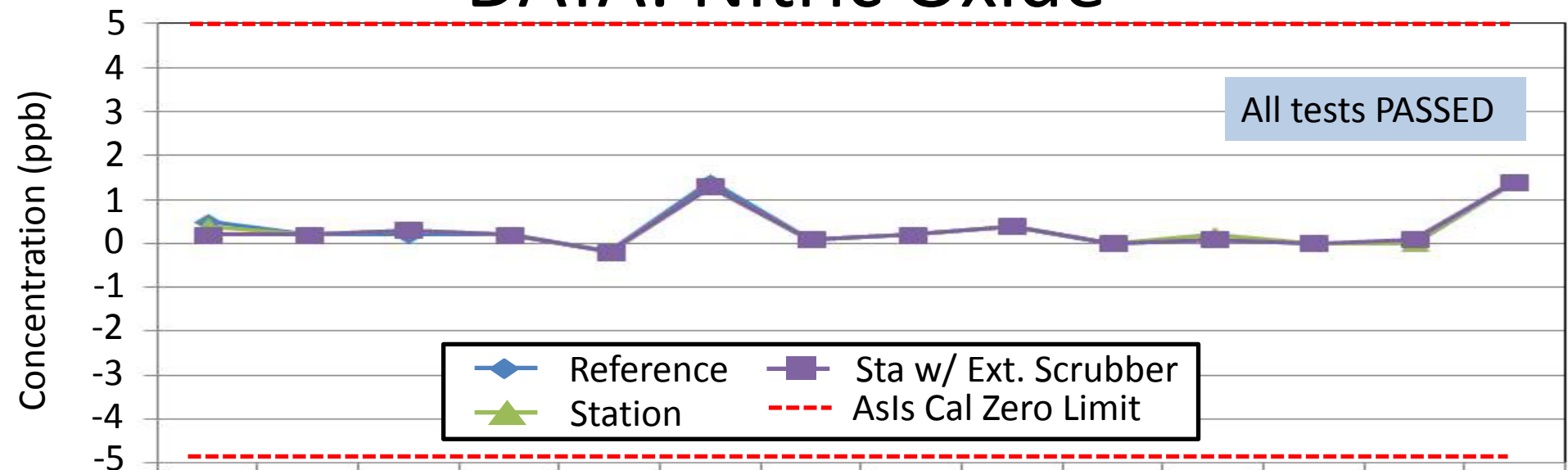
# QA QC criteria



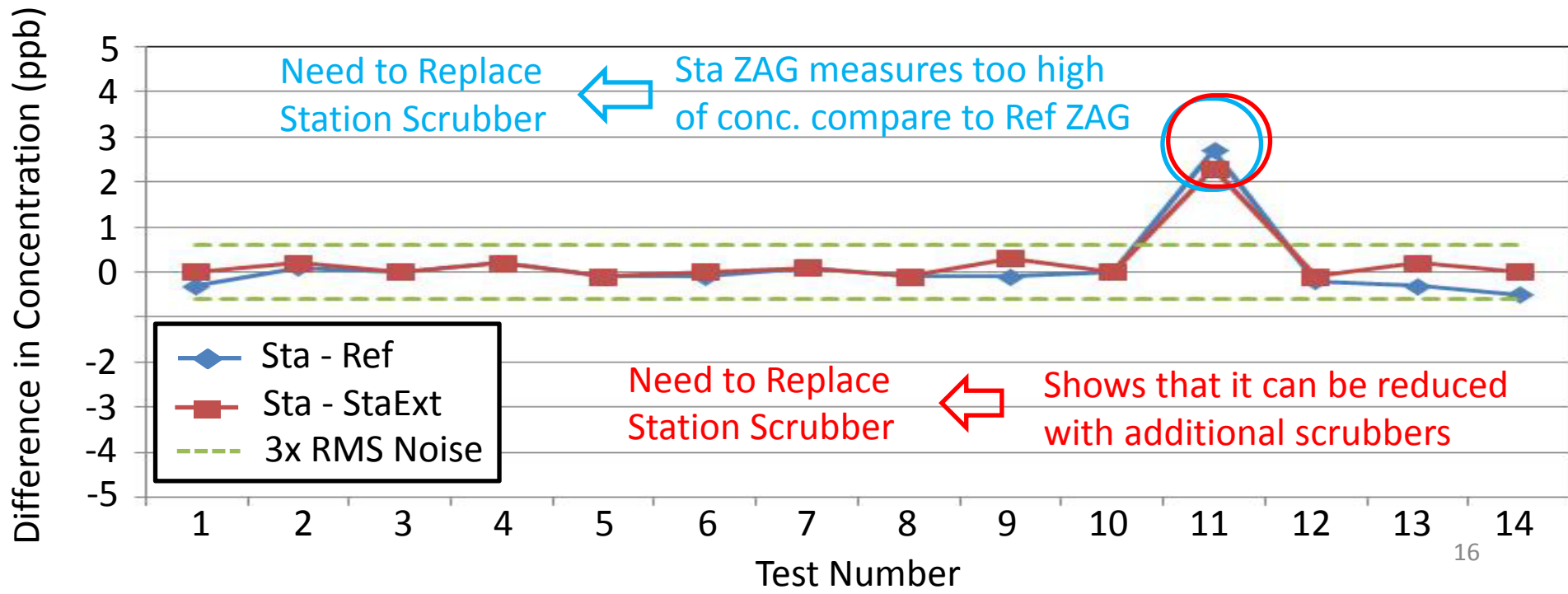
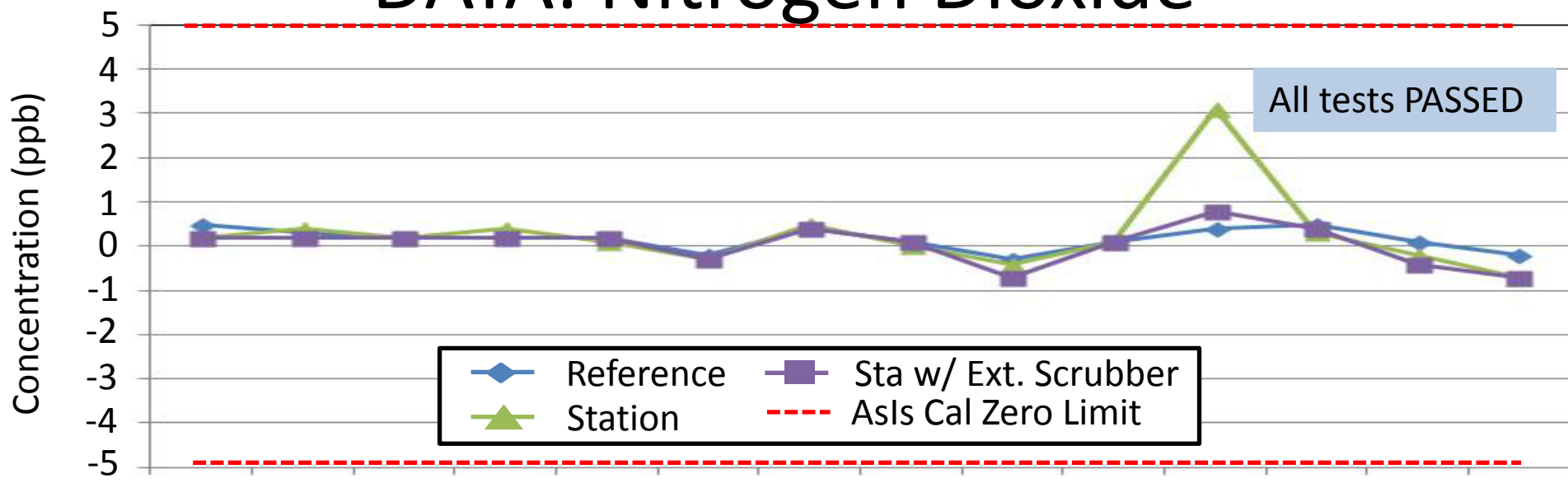
# DATA: Ozone



# DATA: Nitric Oxide

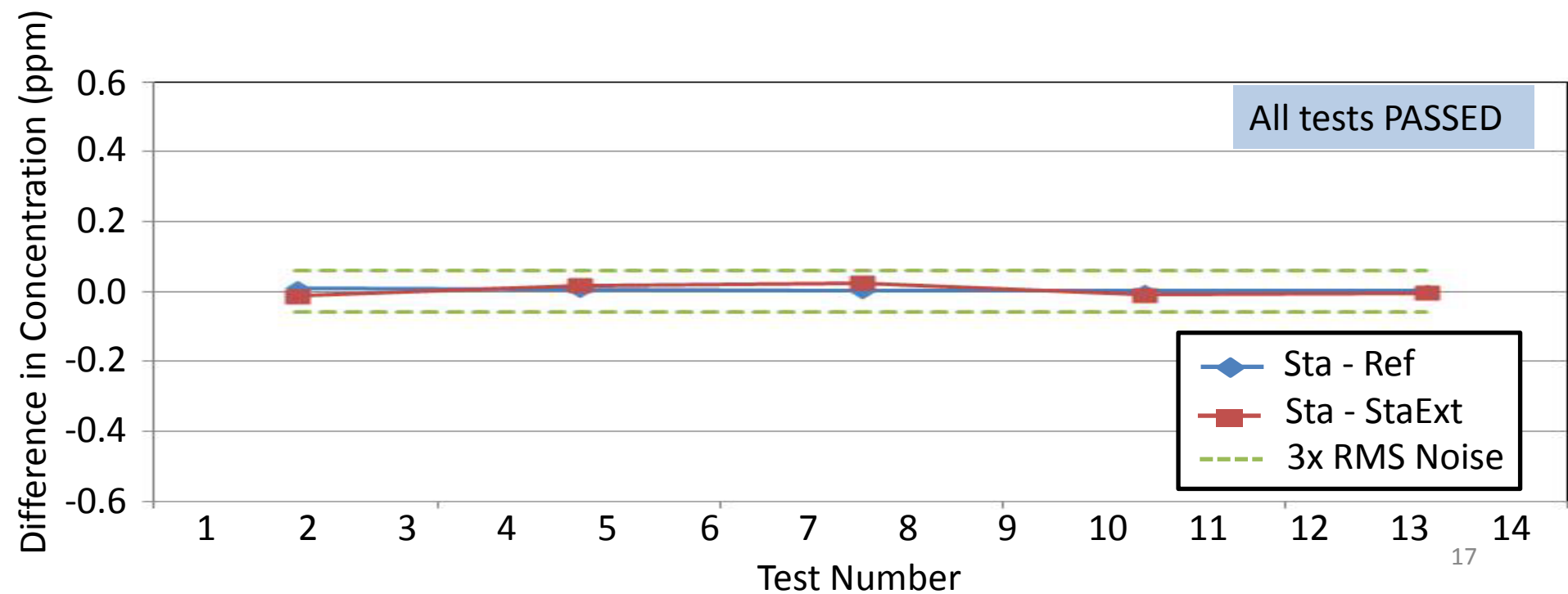
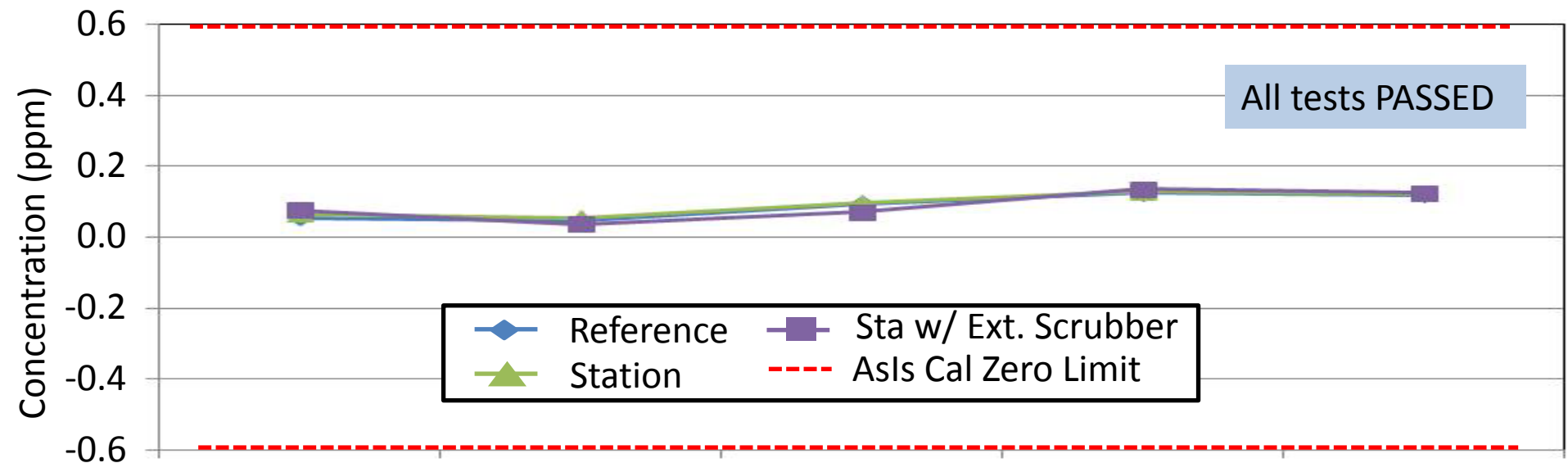


# DATA: Nitrogen Dioxide





# DATA: Carbon Monoxide



# Summary and Recommendations

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- The lower QA levels are requiring lower QC levels
- Newer technology based monitors have made the zero air generator certification using a cylinder of the best available UltraPure air obsolete
- To truly test if a station zero air generator is operating within tolerances, another zero air generator must be used

# Summary and Recommendations

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- Conduct the certification in a clean, dedicated manifold to prevent contamination and or bias
- Do NOT over pressurize manifold system
  - 2 to 3 lpm of excess flow is good
  - Overpressure = long response time for O<sub>3</sub> to stabilize
- **DISCLAIMER:** EPA is aware that SD APCD is using this method but we haven't received any comments (good or bad) about this method