NPAP-SOP-016
Date: June 8, 1998
Revision: 1
Reviewed:

ANALYSIS OF CYLINDERS CONTAINING CO, SO_2, AND NO

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CAUTION

Disclaimer: This Standard Operating Procedure has been developed for use by ManTech Environmental Technology, Inc. in support of the National Performance Audit Program (NPAP) under contract to the U.S. Environmental Protection Agency and may not be applicable to the activities of other organizations.

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1.0 SCOPE AND APPLICATION

The standard operating procedure (SOP) describes how ManTech Environmental analyzes compressed gas cylinders containing carbon monoxide (CO) with 3500 parts per million (ppm) or less, and sulfur dioxide (SO_2), or nitric oxide (NO) with 50 ppm or less. These gas cylinders are used with audit devices in the National Performance Audit Program (NPAP) and for analyzer calibrations and verifications. The analyses are performed in-house to maintain consistency, accuracy, and traceability. In-house analyses of the cylinders using instruments similar to those being audited reduces the possibility of analysis biasing. After analysis, the cylinder is assigned to a dilution system which is used to reduce the concentration to a level suitable for the ambient monitors. This Standard Operating Procedure (SOP) also covers internal laboratory analyses of cylinders used as working calibration standards. Procedures for the operation and calibration of analyzers and dilution systems are found in the instrument manuals, field instructions, and related SOPs.

2.0 SUMMARY OF METHOD

Commercially available gas mixtures are currently used. The gas cylinders contain 30 to 150 cubic feet of gas mixture with a balance gas of nitrogen, at a maximum pressure of 2000 pounds per square inch (psi). All analyses are National Institute of Standards and Technology (NIST) traceable either directly or through the use of traceable working standard gas cylinders.

A pressure reducing, dual-stage gas regulator is attached to each cylinder to deliver the gas to a dilution system at approximately 40 psi. The audit device mixes the cylinder gas with zero air and reduces the pollutant concentration to an ambient level. CO, SO_2, and NO analyzers sample the flow from the audit device and analyzer outputs are observed for stability.

3.0 DEFINITIONS

175 or T-175:	Thermo Environmental Inc. model 175 dilution system audit device used to audit CO, SO_2, and NO, NO_2, and O_3 analyzers.
Dilution System:	Device for blending gases with zero air. Three configurations are currently being used. Each has an adjustable blend ratio.
GDS:	Dilution system audit device used to audit CO, SO_2, and NO analyzers.

Bench-top dilution system:	A dilution system consisting of mass flow controllers, glass manifolds, and scrubber cartridges.
Standard Cylinder:	The NIST cylinder or NIST traceable cylinder ($Standard_{cyl}$) used to determine the concentration of gas in the Subject Cylinder.
Standard Gas:	The gas contained in the Standard Cylinder ($Standard_{gas}$).
Subject Cylinder:	The gas cylinder to be verified using this SOP ($Subject_{cyl}$) .
Subject Gas:	The gas contained in the Subject Cylinder ($Subject_{gas}$).
Working Standard:	A compressed gas cylinder which has been certified against a NIST SRM. It is used on a daily basis for routine calibrations and verifications.
Zero Air:	Ambient air, scrubbed to remove ozone, oxides of nitrogen, sulfur dioxide, hydrocarbons, particulates, and moisture.

4.0 SAFETY PRECAUTIONS

Observe standard precautions when working with compressed air, compressed gas cylinders, and electrical equipment. The ManTech Environmental safety manual addresses these topics and should be reviewed.

5.0 FACILITY REQUIREMENTS

This SOP requires a laboratory equipped with electricity, adequate bench space for the equipment, a continuous source of zero air, and a cylinder storage area.

6.0 INTERFERENCES

Possible interferences include particulate matter and/or leaks in the sampling system, air flow fluctuations, and power fluctuations.

7.0 APPARATUS

- Ambient air analyzers for CO, SO_2, and NO capable of measuring 0 to 50 ppm CO, and 0 to 1000 ppb SO_2 and NO

- Gas Standards: NIST 5000 ppm CO: SRM 2638a
  NIST 50 ppm SO_2: SRM 1693a
  NIST 50 ppm NO: SRM 1683

- NIST traceable working standards (purchased or generated in-house)

- Stainless steel, dual stage, gas cylinder regulators, with CGA 660 fittings

- Dilution systems, generally composed of Perma-Pure® dryers, mass flow controllers, glass manifolds, and zero air scrubber cartridges

- Data acquisition device

- Teflon tubing, 1/4" and 1/8" OD diameter

- Plastic tubing, 1/4" OD diameter

- Tube fittings, nuts, and ferrules, 1/4" and 1/8"

- LFEs, types 3, 5, and 11

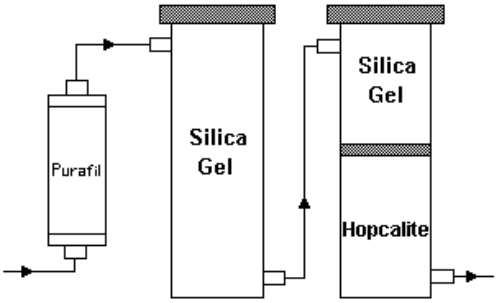
- Electronic manometer

- NIST traceable thermometer

- Computer with the program "LFE Flow Calc"

- Scrubber cartridges containing:

  Purafil®: to remove sulfur, organic compounds, and other reactive low molecular weight compounds
  Silica gel: to monitor Perma-Pure dryer
  Hopcalite®: to convert CO to CO_2 and remove ozone



8.0 CALIBRATIONS AND ZERO/SPAN CHECKS OF ANALYZERS

Leave each analyzer in standby mode, sampling zero air when not in use. This continuous sampling of zero air reduces sample conditioning time.

8.1 Multi-point Calibration

This section gives a general overview of a typical multi-point calibration. A multi-point calibration should be performed on each analyzer every six months or after internal repairs. Consult the analyzer's operation manual for procedures specific to that analyzer.

The multi-point calibration is a six-point calibration consisting of a zero and five upscale points using NIST SRMs or NIST traceable working standards. Cylinder gases are reduced in concentration to levels usable by the analyzers using a bench-top dilution system.

Start the calibration with the zero point. Then go to the highest upscale point and work down. Space the points evenly across the operating range of the analyzer. An example of upscale points for a 500 ppb full scale analyzer would be: 400, 300, 250, 150, 75.

After the points have been run, plot a calibration curve for each analyzer calibrated by using the analyzer's response as the (x) and the actual concentration as the (y). See **Section 10.0 Calculations**.

Accept the calibration if

- 0.98 # m #1.02, where m = slope.
- the y-intercept (b) lies between ±0.3.
- the correlation is $ 0.9999

Reject the calibration if the above criteria are not met. Consult the manufacturer's instrument manual for troubleshooting assistance.

8.1.1 Zero

8.1.1.1 Connect zero air to the gas dilution system. Allow the analyzer to sample the flow, and vent the excess.

8.1.1.2 Determine the zero air flow using an LFE, an electronic manometer, thermometer, and the computer program "LFE Flow Calc".

8.1.1.3 Record the certified flow in the Calibration and Zero/Span logbook.

8.1.2 Upscale Points

8.1.2.1 Connect the regulator output from the standard cylinder to the dilution system.

8.1.2.2 Before connecting the Standard Cylinder's regulator to the dilution system, open the regulator outlet valve and certify the flow of the pollutant gas Mass Flow Controller setting using an LFE, an electronic manometer, thermometer, and the computer program "LFE Flow Calc".

8.1.2.3 Calculate the dilution ratio (**Equation 1** in **Section 10.0 Calculations)** and multiply the certified cylinder concentrations by this ratio (**Equation 2)**. This is the calculated concentration delivered to the analyzer. If the calculated concentration falls outside the required value for the upscale point, readjust the Mass Flow Controller, remeasure the flows, and recalculate the point.

8.1.2.4 Connect the Standard Cylinder's regulator to the dilution system.

8.1.2.5 Check the analyzer's response. Make any span adjustments needed only at the highest upscale point. Allow the analyzer to stabilize as indicated by a straight line on the strip recorder.

8.1.2.6 Record the measured flows, concentrations, and analyzer responses in the Calibration and Zero/Span logbook.

8.1.2.7 Repeat the above procedures for all upscale points.

8.2 Zero / Span Check

8.2.1 Run a zero/span check on the analyzer(s) daily or before each use. Follow the same procedures outlined above for the zero and the highest upscale point. Make no adjustments during this check.

8.2.2 Record the measured flows, concentrations, and analyzer responses in the Calibration and Zero/Span logbook.

8.2.3 Accept the check if the zero difference is within:

- ±2 ppb for SO_2 and NO
- ±0.2 ppm for the Teco 48 CO analyzer
- ±0.5 ppm for the Teco 48H CO analyzer

and the upscale value is within:

- ±1.0% of the calculated concentration for CO
- ± 2 ppb of the calculated concentration for SO_2 and NO.

After the check is performed and all parameter are recorded, adjust the zero and span value to meet specifications, if necessary.

8.1.2.4 If the instrument fails to adjust within specifications, evaluate the problem. Consult the in-house repair facility or the manufacturer's instrument manual for troubleshooting assistance. Conduct a multi-point calibration before returning the instrument to service.

9.0 PROCEDURE FOR GAS CONCENTRATION DETERMINATION

9.0.1 Connect the NIST Standard or NIST Traceable Working Standard gas to the dilution system. Adjust the gas flow Mass Flow Controller until the analyzer's response is approximately equal to the value used during a daily zero/span check.

9.0.2 Allow the analyzer to stabilize and record the response on the worksheet.

9.0.3 Use equation 4 in **Section 10.0 Calculations** to calculate the dilution ratio. Make NO FURTHER ADJUSTMENTS to the mass flow controller.

9.0.4 Remove the Standard Cylinder and connect the Subject Cylinder.

9.0.5 Allow the analyzer to stabilize and record the response on the worksheet.

9.0.6 Use the calculated dilution ratio determined in **Section 9.0.3** and calculate the Subject Cylinder's gas concentration.

9.0.7 Run each Subject Gas three times with a Standard Gas run between each Subject Gas run. The runs for the pollutants can be run simultaneously. For each pollutant, the average of the three runs is the certified gas concentration.

9.0.8 This procedure is used initially on new cylinders and whenever a cylinder's gas concentration is called into question.

9.0.9 Use the original concentrations when doing a confirmatory analysis on an in-service cylinder When a repeat analysis is performed, the original concentrations may be used if the averaged repeat values are within ±2% of the original concentrations.

9.0.10 Make entries in the NPAP computer for purposes of tracking the analyses and assigning the cylinder to an audit device.

Note: Whenever cylinders are received from or returned to a vendor, that information **must** be recorded in the cylinder inventory system. Send all copies of packing slips to the person responsible for the inventory system.

10.0 CALCULATIONS

Equation 1:

$$\textit{Dilution Ratio} = \frac{\textit{Pollutant Flow}}{\textit{Pollutant Flow} + \textit{Dilution Air Flow}}$$

where:

Pollutant Flow	=	Measured flow of gas from the cylinder. This can be the Standard gas or the Subject gas.
Dilution Air Flow	=	Measured flow of zero air delivered to the gas dilution system.

Equation 2:

$$\textit{Calculated concentration} = \textit{Dilution Ratio} \times \textit{Standard}_{cyl}$$

where:

Calc. conc.	=	The value to which the analyzer is compared or adjusted.
Dilution Ratio	=	Value determined using Equation 1.
Standard_{cyl}	=	The certified gas concentration of a NIST or NIST traceable cylinder.

Equation 3:

$$y = mx + b$$

where:

y = Calculated concentration (calc. conc.)
m = Slope
x = Analyzer Response
b = y-Intercept

Equation 4:

$$\textit{Dilution Ratio} = \frac{\textit{Analyzer Response}}{\textit{Standard}_{cyl}}$$

where:

Analyzer Response = Analyzer's response to the $Standard_{gas}$.
$Standard_{cyl}$ = Concentration of NIST or NIST traceable cylinder

Equation 5:

$$\textit{Subject Cylinder Gas Concentration} = \frac{\textit{Analyzer Response}}{\textit{Dilution Ratio}}$$

where:

Subject Cylinder Gas Concentration = Calculated concentration of the cylinder being certified.
Analyzer Response = Analyzer's response (concentration) to the Subject Gas.
Dilution Ratio = Value determined in **Equation 4**.

11.0 QUALITY CONTROL

- Use only NIST SRMs or NIST traceable gases as calibration standards.
- Keep Standard Gas and NIST certificates on file in the laboratory.

- Analyze new NIST gases against the standards currently in use; values must agree within ±2%.
- Check Standard Gases against NIST gases at least every six months.
- Perform zero/span checks on analyzers prior to use.
- Adjust zero if it is off by more than ±2 ppb (±0.5 ppm for the Teco 48H carbon monoxide analyzer).
- Adjust span if it is off by more than ±2 ppb (±1% for carbon monoxide).
- Perform repeat analysis on cylinders whenever the concentration is in question.

12.0 CORRECTIVE ACTION

If the calibration criteria are exceeded, consult the in-house repair facility, analyzer's manual, or manufacturer for guidance.

If after three analyses, a new cylinder fails to meet the requested criteria, return the cylinder to the manufacturer.

13.0 DATA STORAGE

Record the cylinder number, pollutant concentration, date, and manufacturer in the General Cylinder Log for the current year in *Quality Analyst*. Keep Cylinder Certification/ Verification Worksheets in the Cylinder Analysis Logbook. Record data in the NPAP computer database in the **Standards Data Entry Section.**

14.0 REFERENCES

Model 43A Pulsed Fluorescent Ambient SO_2 Analyzer INSTRUCTION MANUAL, Thermo Environmental Corp. Inc.

Model 42 Chemiluminescence NO-NO_2-NO_x Analyzer INSTRUCTION MANUAL, Thermo Environmental Corp. Inc.

Model 48(H) GFC Ambient CO Analyzer INSTRUCTION MANUAL, Thermo Environmental Corp. Inc. 5/8/91.