Air Pollution Control Division

Technical Services Program

APPENDIX GM6

Standard Operating Procedure for Gas Cylinder Verification

Page intentionally left blank

TALBE OF CONTENTS

TABLE OF FIGURES

TABLE OF EQUATIONS

Standard Operating Procedure for Gas Cylinder Certification

1 Scope and Applicability

1.1 Introduction

This standard operating procedure (SOP) document describes the procedures used by members of the Air Pollution Control Division (APCD) to complete gas cylinder certification. The procedures given in this SOP are a supplement to APCD's Quality Assurance Project Plan (QAPP) and the latest information published in the Code of Federal Regulations.

1.2 Method Overview

Gas cylinder certification is done to ensure that the candidate standard concentration is within the allowable tolerance of accuracy and to track concentration trends over time. Gas cylinders received from the manufacturer are initially recorded in the ZSPTracking database in the Bottles data entry form and then certified in APCD's laboratory, using laboratory specific analyzers and dilution system. These candidate gas cylinders are compared to the APCD's laboratory reference gas standards. This method leverages aspects from the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards (US EPA, 2012), but is meant to be a relatively quick and easy way to determine whether the gas cylinders produced by the manufacturer are accurate. Upon passing certification the candidate gas cylinders are ready for use in the field. However, if the candidate does not pass the certification and all instrumentation has been determined to be accurate, a corrective action process is started with the gas cylinder manufacturer. Typically this involves the manufacturer taking the cylinder and testing it to determine the cause of the issue.

1.3 Format and Purpose

The sequence of topics covered in this gas acceptance method follows 2007 EPA guidance on preparing standard operating procedures (SOPs) (US EPA, 2007). This method was also written to help understand how and why key procedures are performed.

2 Summary of Method

2.1 Annual Gas Standard Certification

Gas standards distributed across the CDPHE air monitoring network must undergo annual certification using the method described in this SOP. At local sites the field technicians will remove the cylinders from the site and transport them to the lab for certification. Up to four site gas standards will be brought in for a day of certification and then returned to the site after passing certification. The site cylinder regulator will be left on the cylinder for certification. Long range sites, the gas standards will be replaced with an up to date certified replacement cylinder. Once certification of the long range site gas cylinder is completed and passes, the site operator will return the gas standard to the site for continued use.

2.1.1 Site gas standard removal for certification procedure

1. Close the cylinder valve and the regulator output valve.
2. Remove the tubing from the regulator.
3. Unstrap cylinder from cylinder restraint.
4. Transport cylinder to CDPHE lab for certification and place in gas cylinder room.

2.1.2 Perform gas certification

2.1.3 Install site gas cylinder post certification procedure

1. Install gas cylinder in site and affix restraint strap around cylinder.
2. Re install the tubing on the regulator.
3. At the calibrator remove the tubing.
4. Purge the gas standard's gas tubing line.
5. Re install the tubing to the calibrator.

2.2 Gas Standard Certification Method

The certification of low concentration (<10 ppm) candidate CO gas cylinders is done directly (without dilution), while high concentration CO (>10 ppm), all of the SO2 and NO candidates are done indirectly (with dilution). Due to the stability of CO as a gas, the CO cylinders are not routinely certified by APCD at this time. CO is assayed if a cylinder concentration is determined to be suspect. CO gas cylinder certification follows the same procedure as the other analytes, with the exception of direct injection instead of dilution. A candidate standard with a lower or higher concentration than that of the reference laboratory standard may be certified as long as the concentrations (or diluted concentrations) fall within the well characterized region of the analyzer's calibration curve.

Prior to certification an analyzer calibration check must be performed to assess the calibration drift and to determine whether a multi-point calibration is necessary. For the candidate standards that are certified using dilution, the calibrator's flows must be measured with a NIST-traceable flow meter to determine if a recalibration of the mass flow controllers (MFCs) is necessary. See the MFC section 5 in the Standards SOP – Appendix QA2 for further information.

Gas certification involves running a minimum of two points, within the well-characterized region of the analyzer's calibration curve, with the laboratory reference standard and then with the candidate gas standard. Most laboratory reference standard and candidate test gases are in the parts per million range and are required to be diluted through the use of a dynamic dilution calibrator to lower the test gas concentrations to a level that can be analyzed by the laboratory analyzers. It is preferred that the same dilution ratio be used in the analysis of both the laboratory reference standard and candidate test gases. The dilution should be adjusted so that both diluted test gas concentrations are analyzed within the well-characterized portion of the calibration curve of the analyzer. If the concentration difference between the laboratory reference standard gas bottle and the candidate test gas bottle is great enough that a common dilution cannot be performed to allow for both test gases to fall within the well defined calibration curve of the analyzer, then separate dilutions of different magnitudes can be perform to allow for a common target concentration that is within the well-characterized portion of the analyzer's calibration curve. If different dilution ratios are used, it is important to try and keep the total flow being produced by the dilution calibrator between the laboratory standard gas test and the candidate gas test the same. Different flow rates will induce different back pressures on the sample inlet; this can induce bias in the analytical measurement. Additionally, if different dilution ratios are required, then effort should be made to minimize adjustments to the mass flow controllers. If the desired dilution ratio can be achieved by adjusting only one mass flow controller, while keeping the total flow consistent between tests, then it would be the preferred adjustment.

The calibrator's flows are either measured or recorded from the front panel of the calibrator. The analyzer's responses are recorded and averaged. These values are then used to compute the relative percent difference of the analyzer's response between the reference and candidate runs. The concentration of the cylinder is also computed from the flows and analyzer response by:

Equation 1. Calculated candidate cylinder concentration

$$C_{CalConc} = \frac{LS_{Conc} * C_r * DR_L}{LS_r * DR_C}$$

Where:

LS_{Conc} = laboratory standard manufacture tag concentration
LS_r = laboratory standard analyzer response
$C_{CalConc}$ = calculated candidate cylinder concentration
C_r = candidate test gas analyzer response
DR_L = dilution ratio for laboratory standard gas (Equation 2)
DR_C = dilution ratio for candidate test gas (Equation 2)

If the same dilution ratio is used for the dilution of the laboratory standard gas and the candidate test gas during analysis, the two dilution ratios will cancel out and can be effectively be removed from the equation. If different dilution ratios are used between the two gases during analysis then they must be accounted for. The dilution ratio is computed using:

Equation 2. Dilution Ratio

$$Dilution\ Ratio = \frac{Calibration\ Gas\ Flow}{Calibration\ Gas\ Flow + Diluent\ Gas\ Flow}$$

The percent difference is then computed from the calculated candidate cylinder concentration and the stated concentration on the candidate cylinder's tag. The percent difference is computed using:

Equation 3. Percent Difference

$$\%Diff = \frac{C_{CalConc} - C_{Conc}}{C_{Conc}} * 100$$

Where:

$C_{CalConc}$ = calculated candidate cylinder concentration
C_{Conc} = candidate test gas manufacture tag concentration

The candidate standard passes gas certification if the above mentioned percent differences are within the accuracy tolerance plus an additional 1.5% ascribed to measurement system errors. These computations are performed with the spreadsheet located at dphe.local\apc\Programs\ZSFILES\Gas Cyl Certification\Gas Cert Form.xlsx (J:Drive).

3 DEFINITIONS

The CDPHE/APCD/TSP QAPP contains acronyms and definitions in Appendix P2. Any commonly used shorthand designations for items such as the sponsoring organization, monitoring site, and the geographical area will be defined and included in this SOP or in the QAPP.

4 HEALTH AND SAFETY WARNINGS

Gas Hazards

Gas cylinder certification involves the use of several gases such as, carbon monoxide (CO), sulfur dioxide (SO_2), nitric oxide (NO), etc. CO is a colorless, odorless, and tasteless gas. It is a hazardous compound as it combines with hemoglobin and reduces the oxygen carrying ability of the blood. SO_2 is a hazardous compound with a sharp irritating order that causes severe respiratory tract, eye, and skin burns. NO is also a hazardous compound that causes skin and eye irritation, and contains material that can cause target organ damage. NO gas may be fatal if inhaled for a prolonged period or at a high concentration. Gas cylinders balanced with nitrogen also present an asphyxiation hazard.

As several of the source gases are poisonous gases, calibration source tanks and delivery systems, or any other calibration span gas, should be vented to the atmosphere rather than into the laboratory or other sampling area. If this is impossible, limit operator exposure to the gas by getting fresh air every 5 to 10 minutes. The operator must leave the area immediately if he/she experiences lightheadedness, headache or dizziness. Refer to the respective material data safety sheet (MSDS) for more information on hazards and safety.

Electrical Hazards

1. Always use a third ground wire on all instruments.

2. If it is necessary to work inside an analyzer while it is in operation, use extreme caution to avoid contact with high voltage inside the analyzer. The analyzer has high voltages in certain parts of the circuitry, including a 110 volt AC power supply. Refer to the manufacturer's instruction manual and know the precise locations of these components before working on the instrument.

3. Avoid electrical contact with jewelry. Remove rings, watches, bracelets, and necklaces to prevent electrical burns.

4. Always unplug the analyzer whenever possible when servicing or replacing parts.

5 CAUTIONS

To prevent damage to the equipment, the following precautions should be taken:

1. Keep the interior of the instruments and laboratory clean.

2. Inspect the system regularly for structural integrity.

3. Inspect tubing for cracks and leaks.

4. EPA protocol gases are hazardous materials. Long term exposure can cause problems with motor coordination and mental acuity. It is strongly recommended that all agencies have MSDS at all locations where gas cylinders are stored or used. MSDS are located on the gas room door of the APCD laboratory. MSDS can be obtained from the DOT or from your vendor.

6 INTERFERENCES

Interferences are physical or chemical entities that cause measurements to be higher (positive) or lower (negative) than they would be without the entity. The only interference that would cause a reading to be higher or lower would be due to pneumatic leaks in the calibrator, mis-calibrated or otherwise inaccurate pressure or temperature sensors, impurities present in the source gas cylinders, and/or diluent air source. Interferences of the gas analyzers are the purview of their respective SOPs and manuals.

7 Personnel Qualifications

General Personnel Qualifications are discussed in the CDPHE/APCD/TSP QAPP. Personnel qualified to perform this certification must have read this SOP and have received on the job training and sign-off documentation attesting to the completion of the training.

8 Assay Apparatus and Materials

8.1 Assay Equipment

8.1.1 Gaseous Analyzers

See the calibration SOP and operator manuals on the operation and calibration of the gaseous analyzers (NO, SO2, and CO) to be used for candidate assays.

8.1.2 Calibrator

The calibrator used to generate test gas concentrations during the calibration check and dilution check must have certified mass flow controllers. See the Standards SOP Appendix QA2 Section 5 and the calibrator operator's manual on the procedures for certifying the calibrator.

8.1.3 Dilution system

The dilution system is composed of a zero air pack and a calibrator with certified MFCs (Figure 1). The reference gas cylinder and candidate gas cylinder are precisely diluted with zero air to achieve the desired concentration via certified MFCs. The diluted gas concentrations are then sampled by a gaseous analyzer.

8.1.4 Wiring, Tubing and Fittings

Teflon™ and/or borosilicate glass are inert materials that should be used exclusively throughout the ambient air intake system. It is recommended that Polytetrafluoroethylene (PTFE) or Fluoroethylpropylene (FEP) Teflon™ tubing be used. PTFE or FEP Teflon is the best choice for the connection between an intake manifold and the bulkhead fitting. While not preferred, the use of stainless steel tubing and fittings in the sample train is permissible for standard (not trace level) CO analyzers. Examine the tubing and discard if particulate matter has collected on the tube's interior. All fittings and ferrules should be made of Teflon™ or stainless steel.

8.1.5 Reagents and Standards

The calibrator requires O_3 as a reagent for GPT with NO source gas. Since O_3 is short lived and highly reactive, it is generated internally by the calibrator. All source gas is obtained from cylinders whose contents must be traceable to NIST Standard Reference Material (SRM) gases via EPA Protocol procedures.

8.1.6 Spare Parts and Incidental Supplies

- Laboratory gas analyzer and calibrator manuals
- Teflon™ crush washers for cylinder regulators
- NIST traceable flow meter
- FEP or PTFE tubing

8.2 Calibration Equipment

See the calibration SOP GM2, and calibrator manuals for calibration equipment, reagents, and standards.

9 CALIBRATION

See the calibration SOP GM2, and calibrator manuals for the Calibration procedures.

10 CANDIDATE STANDARD ASSAY

10.1 Introduction

10.2 Equipment and Supplies

For a complete listing of supplies and equipment please see Section 8 of this standard operating procedure.

10.3 Logs and Form

All actions made on the laboratory standard analyzers and calibrators are noted in the laboratory notebook. This includes maintenance and calibrations. The Gas Certification form is used to record data during an assay (Figure 2). After the assay the bottle concentrations, tag and computed, are recorded in the bottle action data entry form in the Site & ZSP Tracking database.

10.4 Assay Procedure

Prior to performing the candidate assay a dilution system and an analyzer calibration check must be completed. A dilution system check is performed to determine whether the MFCs are performing well or are in need of a verification/calibration. In addition, the respective analyzer must have been calibrated within the last month. If not, then a calibration must be completed. If the analyzer has been calibrated within the last month, then a calibration check is required to assess the instrument's drift and to determine if it is acceptable or if a new calibration should be performed. A calibration check is done using the span target for the respective gas. The current span level targets for NO and SO_2 are given in Table 1. During an assay session, multiple candidate cylinders may be assayed against the reference standard.

Table 1. Span level targets for NO and SO_2

NO Span	600 ppb
SO_2 Span	80 ppb

10.4.1 Dilution System Check

The dilution system flow check is done to verify that the calibrations of the MFCs have not drifted significantly since the last verification/certification. See the Standards SOP - Appendix QA2 Section 5

1. Measure the diluent and gas stream flows off of the MFCs with a NIST-traceable flow meter for a total of three sets of ten, and average the sets.

2. Compute the relative difference between the indicated flow rate on the calibrator and the actual flow rate as measured by the flow meter, for both MFCs.

3. If the relative difference for either MFC is greater than 1.0% (US EPA, 2012), then a recertification must be performed.

4. If the relative difference for either MFC is less than or equal to 1.0%, then the assay can proceed.

10.4.2 Calibration Check

1. Generate zero gas with the calibrator and allow the analyzer to stabilize.

2. Take ten successive readings of the analyzer response and average, or take the data logger's 5 minute average reading.

3. Generate a span level point with the reference standard and allow the analyzer to stabilize.

4. Take ten successive readings of the analyzer response and average, or take the data logger's 5 minute average reading.

5. Compute the relative difference for both zero and span check points.

6. If the absolute differences for the zero checks are less than 1% full scale of the analyzer, and the absolute relative span checks are less than or equal to 5.0%, then the assay can proceed (US EPA, 2012).

7. However if the absolute differences for the zero and span checks are greater than 1% full scale and 2.0%, respectively, then a multi-point calibration must be performed on the analyzer before proceeding with the candidate assay.

10.4.3 Reference and Candidate Assay

Upon completion and passing the dilution and calibration checks, the candidate assay may begin.

1. Starting with the reference standard, generate a zero point.

2. Record the laboratory reference standard cylinder tag information on the form:

    - Cylinder SN
    - Tag concentration
    - %Accuracy
    - Certification expiration date.

3. Allow the analyzer to stabilize and take ten successive readings and average, or take the data logger's 5 minute average reading.

4. Record the calibrator's diluent and gas flow rates and output concentration on the Gas Cert. Form.

5. Generate two additional points in the well-characterized region of the analyzer's calibration curve (typically span and precision levels).

6. Allow the analyzer to stabilize and record the analyzers average response (same as step 3).

7. Record the calibrator's diluent and gas flow rates, as well as the actual concentrations.

8. Put the calibrator in PURGE mode.

9. Disconnect the laboratory reference standard from the calibrator and close the regulator.

10. Connect a regulator to the candidate standard to be assayed and purge the regulator (10.4.4).

11. Connect the candidate standard to the calibrator.

12. Generate a zero point.

13. Record the candidate standard cylinder tag information on the form (as in step 2).

14. Take the zero reading after the analyzer has stabilized (as in step 3).

15. Generate two additional points in the well-characterized region of the analyzer's calibration curve (typically span and precision levels).

16. Record the analyzer's average response and calibrator's flows and output (as in steps 6 and 7).

17. After the candidate standard has been assayed, close the cylinder and remove the regulator.

18. Enter the reference standard and candidate standard data into the Gas Certification spreadsheet.

19. A candidate standard cylinder is certified if the percent differences in cylinder concentration, computed in the spread sheet, are less than the tag Accuracy range plus an additional 1.5% for errors. If the candidate standard does not pass certification, a corrective action (CAT) process must be started with the respective vendor. Prior to the CAT ensure that the testing instruments are operating properly, and run additional points to ensure results are consistent.

    If more than one candidate standard is to be assayed, repeat the above steps for the additional candidate standard.

10.4.4 Regulator Purge Procedure

1. Inspect Teflon washer and replace if necessary.

2. Connect the regulator to the new gas bottle.

3. Purge the regulator and line:

    a. Ensure regulator exit valve is closed.

    b. Using a quick connect with a push stop, connect it to the vacuum side of a pump.

    c. Open the regulator exit valve.

    d. Back off the regulator pressure knob and allow the pump to evacuate the regulator.

    e. Close the regulator valve.

    f. Quickly open the gas bottle valve until the bottle-side pressure gauge reads the bottle psi.

    g. Quickly close the gas bottle valve.

h. Open the regulator exit valve and allow the gas line and regulator to go to vacuum as measured by the regulator gauges.

i. Close the regulator valve.

j. Repeat for a total of three times.

k. Either cap or connect the gas line to the quality control test gas system.

11 HANDLING AND PRESERVATION

Refer to the relevant EPA protocol gas MSDS for handling and preservation of compressed gas cylinders.

12 SAMPLE PRESERVATION AND ANALYSIS

EPA protocol gas samples receive no special preparation prior to analysis by APCD for gas certification. Therefore a section for sample preservation and analysis in this SOP is not required.

13 TROUBLESHOOTING

13.1 General Factors

Troubleshooting is necessary if a candidate standard fails the certification. Care must be taken to ensure that the assay system is working properly and not causing issues. Some common issues are:

- Regulator and gas line not purged correctly, causing low response.
- Leaks in the analyzer or dilution system.
- MFCs needing to be re-calibrated.

13.2 Instrument Troubleshooting

See the site operation and calibrator SOP for additional troubleshooting techniques and information.

14 DATA MANAGEMENT AND RECORDS MANAGEMENT

14.1 Data Management

Data are generated from the analyzer(s) at intervals internally set, ranging from an averaging time of 20 seconds to 5 minutes. The data is collected by the on-site data logger as near-real-time data (often every 3 to 10 seconds) and is aggregated into 1and 5 -minute averages.

14.2 Records Management

Records of laboratory analyzer multi-point calibration, MFC verifications, and candidate assay data are kept in both electronic and hard-copy formats. These records are kept in the relevant databases and filing locations. The gas certification form is kept in the laboratory notebook. The bottle certification data are recorded in the Site & ZSP Tracking database under the Actions data entry form. For more information on bottle entry and management see Appendix D2, Data Validation, section 6.1.4.

15 WORKS CITED

Teledyne-API. (2012). *Addendum - Model T700U Calibrator.* San Diego, CA: Teledyne-API.

Teledyne-API. (2010). *Addendum - Ultra Sensitivity Model 200EU NO/NO2/NOx Analyzer.* San Diego, CA: Teledyne-API.

Teledyne-API. (2009). *Operation Manual - Model 700E Dynamic Dilution Calibrator.* San Diego, CA: Teledyne-API.

Teledyne-API. (2011). *Operation Manual - Model 701 Zero Air Generator.* San Diego, CA: Teledyne-API.

Teledyne-API. (2010). *Operation Manual - Model 701H High Performance Zero Air Generator.* San Diego, CA: Teledyne-API.

Teledyne-API. (2013). *Operation Manual - Model T100 UV Fluorescence SO2 Analyzer.* San Diego, CA: Teledyne-API.

Teledyne-API. (2013). *Operation Manual - Model T200 Nitrogen Oxide Analyzer.* San Diego, CA: Teledyne-API.

Teledyne-API. (2013). *Operation Manual - Model T700 Dynamic Dilution Calibrator.* San Diego, CA: Teledyne-API.

Teledyne-API. (2014). *Operation Manual - Models T701, T701H, 701, and 701H Zero Air Generators.* San Diego, CA: Teledyne-API.

Thermo Scientific. (2007). *Instruction Manual - 48C Gas Filter Correlation CO Analyzer.* Franklin, MA: Thermo Scientific.

Thermo Scientific. (2007). *Instruction Manual - Model 48i Trace Level-Enhanced Gas Filter Correlation CO Analyzer.* Franklin, MA: Thermo Scientific.

US EPA. (2012). *EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, EPA/600/R-12/531.* Research Triangle Park, NC: US EPA.

US EPA. (2007). *Guidance for Preparing Standard Operating Procedures.* Research Triangle Park, NC: US EPA OAQPS AQAD.

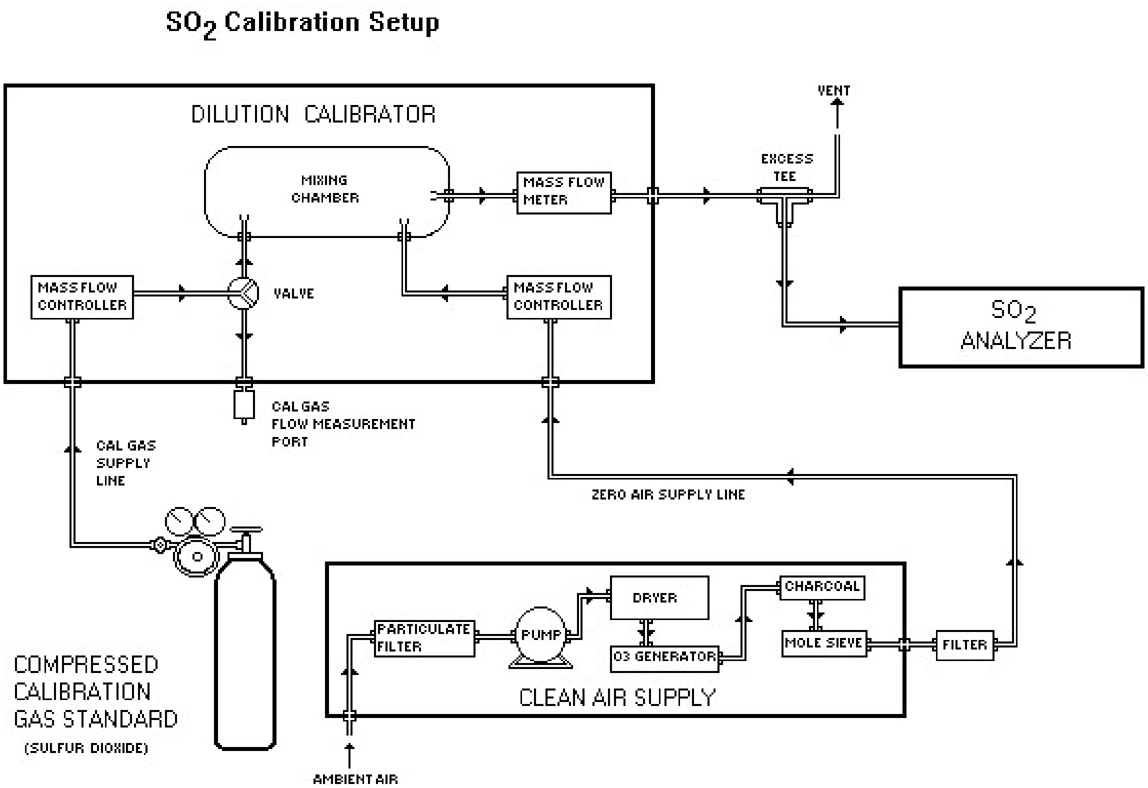

Figure 1. Typical Assay apparatus with dilution.

Figure 2. Gas Cylinder Certification Form (page 1)

Gas Cylinder Certification Form
APCD

Date:		Operator:		Gas:	NO/Nox	Analyzer:		Last Cal Date:	
Dilution System Check		Regression Slope:				Regression Int.:			

Measured Dil Flow		Measured Cal Flow	
1)		1)	
2)		2)	
3)		3)	
Average=	#DIV/0!	Average=	#DIV/0!

Calibrator Dil Flow	Calibrator Cal Flow	
		(LPM)

Relative % Differences (<1%)	
Dil Flow:	#DIV/0!
Cal Flow:	#DIV/0!

Calibration Check

Take three discrete measurments of zero and span

Zero		Span	
NO	Nox	NO	Nox
#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!

NO: Calibrator Output		Absolute % Differences	
Zero:	0	#DIV/0!	<1%F.S.
Span:		#DIV/0!	<2%

Nox: Calibrator Output		Absolute % Differences	
Zero:	0	#DIV/0!	<1%F.S.
Span:		#DIV/0!	<2%

Lab Reference Standard

Cyl SN:		Tag Conc:			Accuracy:		Expiration Date:		
Zero			Level 1			Level 2			Calibrator Data
									Conc:
									Cal:
									Dil:
									Calibrator Data
									Conc:
									Cal:
									Dil:
#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	Average

Candidate Standard

Cyl SN:		Tag Conc:			Accuracy:		Expiration Date:		
Zero			Level 1			Level 2			Calibrator Data
									Conc:
									Cal:
									Dil:
									Calibrator Data
									Conc:
									Cal:
									Dil:
#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	Average

Gas Cylinder Certification Form
APCD

Assay Results

Level 1	NO	Nox
Dilution Ratio Lab Standard	#DIV/0!	
Dilution Ratio Candidate	#DIV/0!	
Computed Cylinder Conc:	#DIV/0!	#DIV/0!
Cylinder Conc. % Diff:	#DIV/0!	#DIV/0!

Candidate Certification Pass? #DIV/0! #DIV/0!

Level 2	NO	Nox
Dilution Ratio Lab Standard	#DIV/0!	
Dilution Ratio Candidate	#DIV/0!	
Computed Cylinder Conc:	#DIV/0!	#DIV/0!
Cylinder Conc. % Diff:	#DIV/0!	#DIV/0!

Candidate Certification Pass? #DIV/0! #DIV/0!

Figure 2 continued. Gas Cylinder Certification Form (page 2)