



# Technical Aspects of EPA Protocol Gas Production

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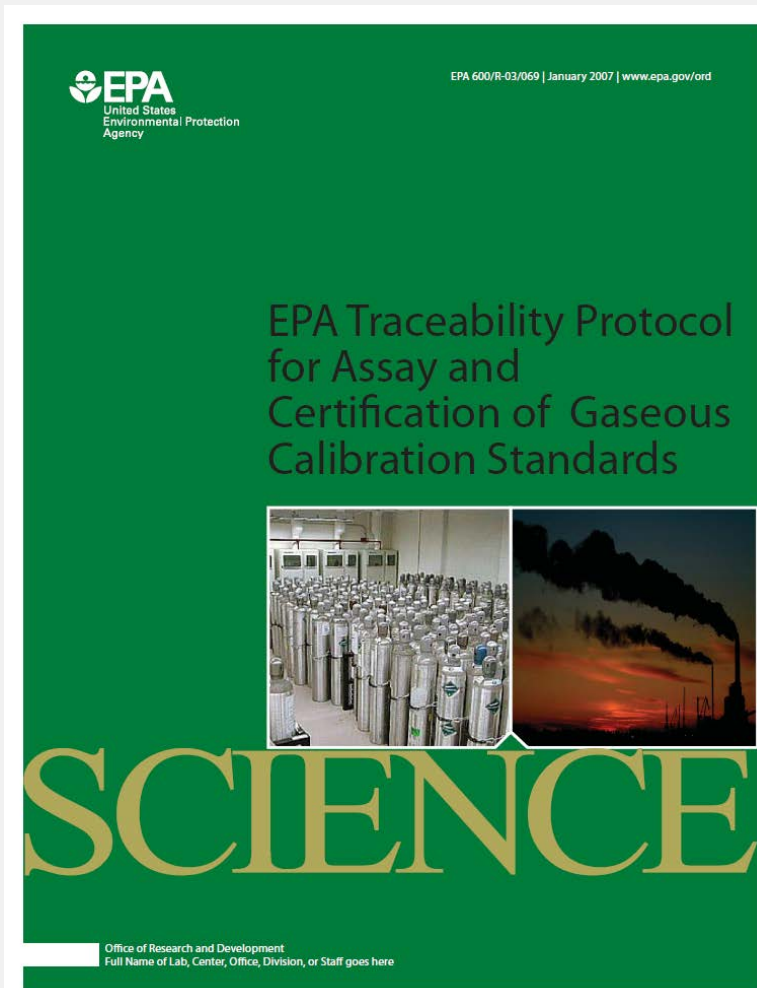
# Outline of Presentation

- General Information
- EPA traceability protocol
- Analytical instrumentation and plumbing
- Reference standards for assays
- Monthly multipoint calibration
- Measurement sequence
- Statistical spreadsheets for uncertainty
- Stability test and calculations
- Documentation requirements

## General Information

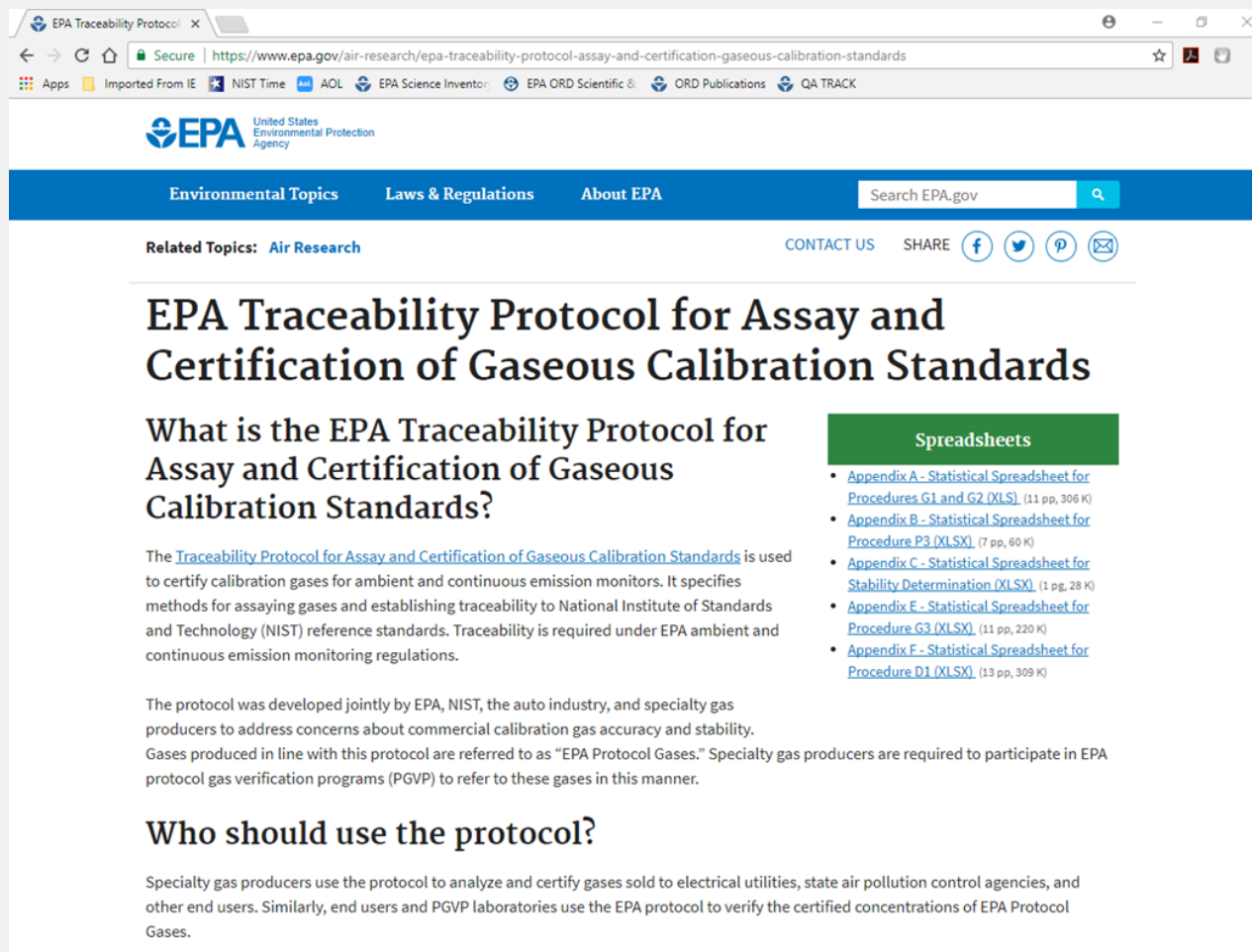
- This protocol may be used by specialty gas producers, end users, or others to assay candidate standards
- The protocol is used to assay individual cylinders, but multiple cylinders can be assayed simultaneously
- No multi-cylinder batch certifications
- Candidate standards must have the same components and concentration ranges as the reference standards
- Standards must remain in the cylinders in which they were assayed... No bulk assays or transfilling
- No producer certification or government oversight to keep production costs as low as possible
- Producers of EPA Protocol Gases must participate in Protocol Gas Verification Program (PGVP) audits

# Protocol also known as “the green book”







- Protocol is a general analytical recipe with statistical calculations for uncertainty and stability
- First published in 1978
- Periodic revisions over the years with gradual changes in requirements
- 2012 revision in effect

# <https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards>



The screenshot shows a web browser window displaying the EPA website. The address bar shows the URL: <https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards>. The page features the EPA logo and navigation menus for Environmental Topics, Laws & Regulations, and About EPA. A search bar is present with the text "Search EPA.gov". Below the navigation, there are social media sharing icons for Facebook, Twitter, LinkedIn, and Email. The main heading is "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards". A sub-heading asks "What is the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards?". The text explains that the protocol is used to certify calibration gases for ambient and continuous emission monitors. A "Spreadsheets" section lists five statistical spreadsheets for various procedures (G1, G2, P3, G3, D1). The "Who should use the protocol?" section states that specialty gas producers and end users use the protocol.

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## EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards

### What is the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards?

The [Traceability Protocol for Assay and Certification of Gaseous Calibration Standards](#) is used to certify calibration gases for ambient and continuous emission monitors. It specifies methods for assaying gases and establishing traceability to National Institute of Standards and Technology (NIST) reference standards. Traceability is required under EPA ambient and continuous emission monitoring regulations.

The protocol was developed jointly by EPA, NIST, the auto industry, and specialty gas producers to address concerns about commercial calibration gas accuracy and stability. Gases produced in line with this protocol are referred to as "EPA Protocol Gases." Specialty gas producers are required to participate in EPA protocol gas verification programs (PGVP) to refer to these gases in this manner.

### Who should use the protocol?

Specialty gas producers use the protocol to analyze and certify gases sold to electrical utilities, state air pollution control agencies, and other end users. Similarly, end users and PGVP laboratories use the EPA protocol to verify the certified concentrations of EPA Protocol Gases.

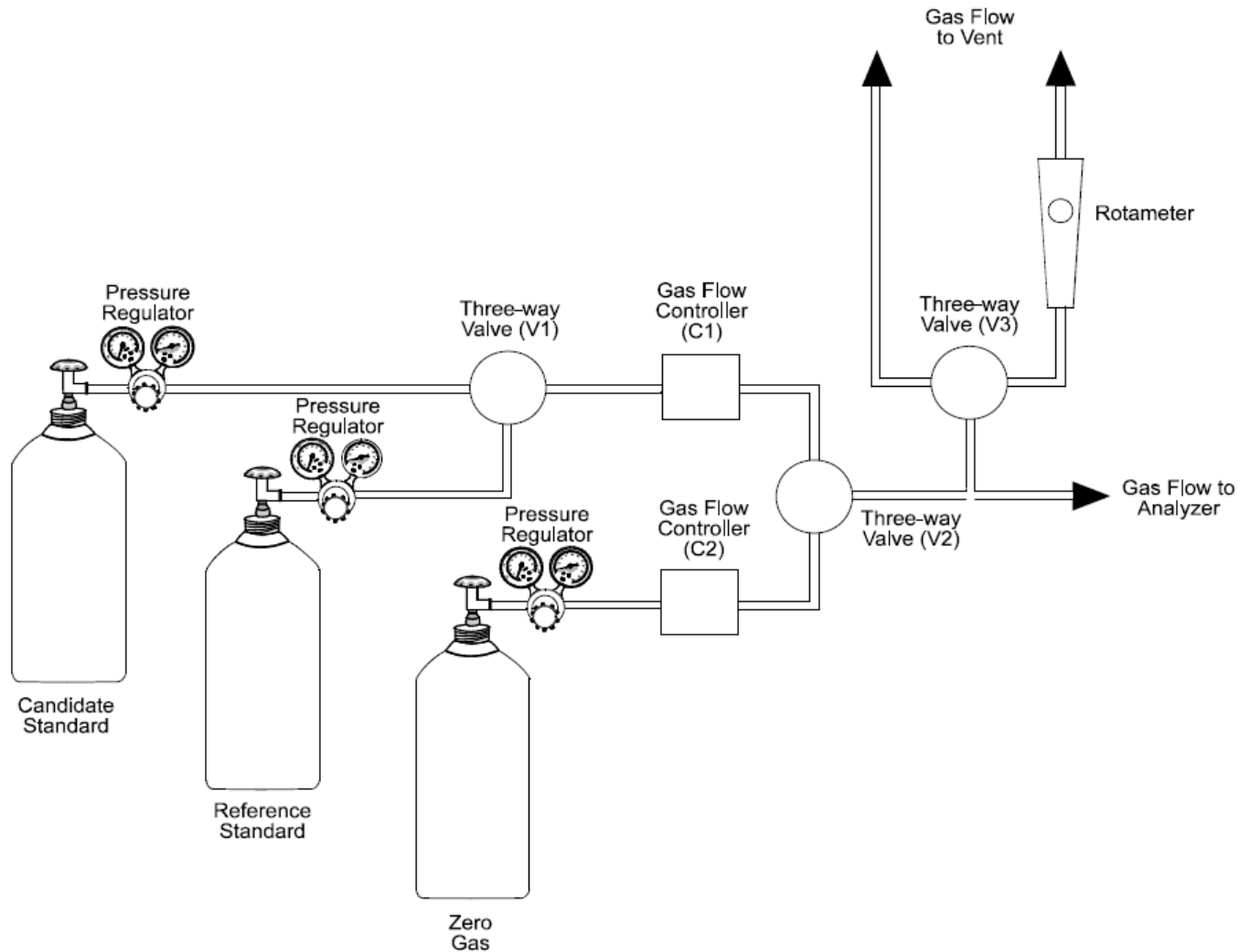
#### Spreadsheets

- [Appendix A - Statistical Spreadsheet for Procedures G1 and G2 \(XLS\)](#) (11 pp, 306 K)
- [Appendix B - Statistical Spreadsheet for Procedure P3 \(XLSX\)](#) (7 pp, 60 K)
- [Appendix C - Statistical Spreadsheet for Stability Determination \(XLSX\)](#) (1 pg, 28 K)
- [Appendix E - Statistical Spreadsheet for Procedure G3 \(XLSX\)](#) (11 pp, 220 K)
- [Appendix F - Statistical Spreadsheet for Procedure D1 \(XLSX\)](#) (13 pp, 309 K)

# Analytical Procedures in Protocol

- **Procedure G1:** Assay and Certification of a Compressed Gas Calibration Standard without Dilution
- **Procedure G2:** Assay and Certification of a Compressed Gas Calibration Standard using Dilution
- **Procedure G3:** Assay and Certification of a Zero Air Material as Conforming to 40 CFR Part 72.2
- **Procedure P2:** Assay and Certification of Permeation Device Calibration Standards based on a Compressed Gas Reference Standard
- **Procedure P3:** Assay and Certification of Permeation Device Calibration Standards based on a Mass Reference Standard
- **Procedure D1:** Assay and Certification of a Dynamic Gas Dilution System

# Example G1 Analytical Apparatus



# Pollutant Gas Analyzer

- Specific analytical methods are not specified
- Well-characterized calibration curve required
- Good resolution and precision, stable response
- Good specificity for pollutant of interest
- Correction for any analytical interferences
- Not sensitive to balance gas composition differences or same balance gas for all assays
- High-precision data acquisition system required



# Reference Standards for Assays

- NIST Standard Reference Material (SRM)
- NIST-Traceable Reference Material (NTRM)
- NIST Research Gas Material (RGM)
- VSL (Dutch) Primary Reference Material (PRM)
- Gas Manufacturer's Intermediate Standard (GMIS), which are analyzed using NIST reference standards
  
- The availability of reference standards remains the biggest obstacle to producing EPA Protocol Gases

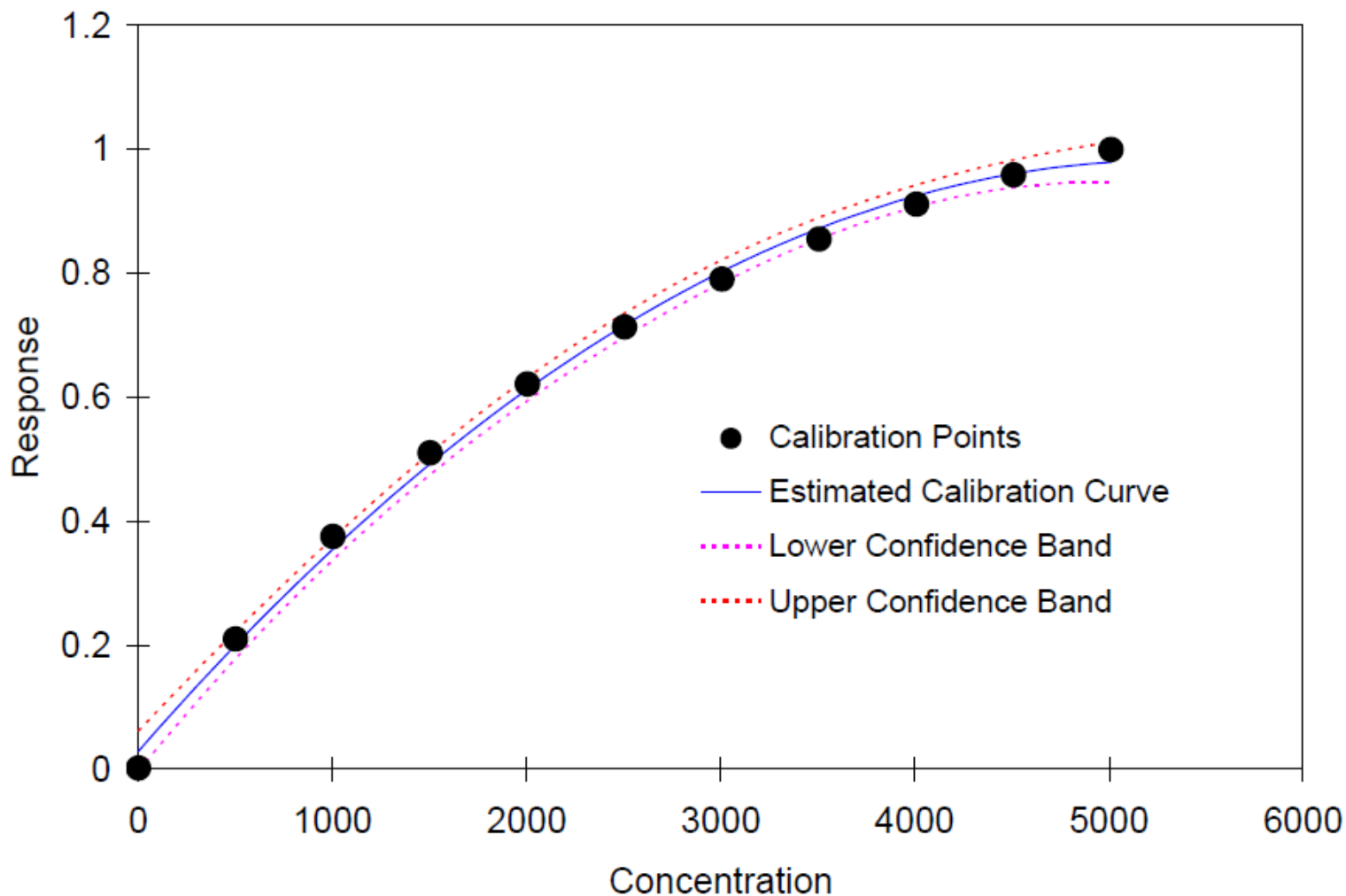
## Compressed Gas SRMs, NTRMs, and RGMs that are available from NIST

Certified component	Balance gas	SRM range	NTRM range	RGM range	Certification period (years)
Ammonia	Nitrogen	Not available yet	Not available yet	5 to 50 ppm	2
Carbon dioxide	Air	390 to 400 ppm	360 to 420 ppm	360 to 420 ppm	8
Carbon dioxide	Nitrogen	500 ppm to 16 %	5 ppm to 20 %	Contact NIST	8
Carbon monoxide	Air	60 to 160 ppb	50 to 500 ppb	40 to 500 ppb	TBD
Carbon monoxide	Air	10 to 45 ppm	10 to 45 ppm	Contact NIST	8
Carbon monoxide	Nitrogen	10ppm to 13%	101 ppm to 15%	Contact NIST	8
Formaldehyde	Nitrogen	Not available yet	Not available yet	0.5 to 10 ppm	1
Hydrogen chloride	Nitrogen	Not available yet	Not available yet	Contact NIST	TBD
Hydrogen sulfide	Nitrogen	5 to 20 ppm	1 to 400 ppm	Contact NIST	3
Methane	Air	1 to 100 ppm	1 to 1000 ppm	1.7 to 2.2 ppm	8
Methane	Nitrogen	Not available yet	0.5 ppm to 10%	Contact NIST	8
Methanol or ethanol	Nitrogen or Air	Not available yet	Not available yet	75 to 500 ppm	4
Natural gas components	Natural gas	Not Available yet	Contact NIST	Contact NIST	4
Nitric oxide	Nitrogen	0.5 to 50 ppm	0.5 to 50 ppm	Contact NIST	3
Nitric oxide	Nitrogen	50 to 3,000 ppm	50 to 3,000 ppm	Contact NIST	8
Nitrous oxide	Air	TBD	300 ppb to 5%	300 to 350 ppb	8
Total oxides of nitrogen (NO <sub>x</sub> )	Air	100 ppm	10 to 100 ppm	3 to 100 ppm	3 (SRM 6)
Oxygen	Nitrogen	2 to 21 %	0.4 to 25 %	Contact NIST	8
Propane	Air	0.1 to 500 ppm	0.1 to 500 ppm	Contact NIST	8
Propane	Nitrogen	100 to 2000 ppm	5 ppb to 2%	Contact NIST	8
Sulfur dioxide	Nitrogen	5 ppm	5 to 50 ppm	Contact NIST	4
Sulfur dioxide	Nitrogen	50 to 3,500 ppm	50 to 5,000 ppm	Contact NIST	8
Volatile organics	Nitrogen	5 ppb	Contact NIST	Contact NIST	4
Zero air material	Air	Not available yet	Not available yet	Contact NIST	TBD
<b>Nitrogen dioxide</b>	<b>Nitrogen or Air</b>	<b>TBD</b>	<b>TBD</b>	<b>TBD</b>	<b>TBD</b>

NIST and VSL Primary Standard Gas Mixtures that are declared to be Equivalent  
(declaration expires July 1, 2018)

Certified component	Balance gas	Concentration range for gas mixture suite	Maximum allowable difference	Date of Next Assessment
Ammonia	N <sub>2</sub>	10 to 300 ppm	0.3 % relative	2018
Carbon dioxide	N <sub>2</sub>	10 ppm to 20 %	0.3 % relative	2017
Carbon dioxide	Air	100 to 1000 ppm	0.2 % relative	2017
Carbon monoxide	N <sub>2</sub> or Air	1 ppm to 10 %	0.3 % relative	2018
Ethanol	N <sub>2</sub> or Air	75 to 1000 ppm	0.5 % relative	2016
Hydrogen chloride	N <sub>2</sub>	10 ppm to 300 ppm	5 % relative	2017
Hydrogen sulfide	N <sub>2</sub>	1 to 1000 ppm	1 % relative	2019
Methane	N <sub>2</sub> or Air	1.7 ppm to 10 %	0.1 % relative	2017
Natural gas		Typical	0.5 % relative (0.3 % for CH <sub>4</sub> )	2019
Nitric oxide	N <sub>2</sub>	0.5 ppm to 1 %	0.5 % relative	2017
Nitrogen dioxide	N <sub>2</sub> or Air	10 ppm to 1 %	0.5 % relative	2016
Nitrous oxide	N <sub>2</sub>	0.3 to 1000 ppm	1 % relative	2017
Oxygen	N <sub>2</sub>	10 to 100 ppm	1 % relative	2017
Oxygen	N <sub>2</sub>	100 ppm to 25 %	0.2 % relative	2017
Propane	N <sub>2</sub> or Air	1 ppm to 1 %	0.3 % relative	2016
Stack gas	N <sub>2</sub>	Typical	1 % relative (0.3 % for CO, CO <sub>2</sub> , and CH <sub>4</sub> )	2017
Sulfur dioxide	Air	1 ppm to 1 %	0.5 % relative	2019
Sulfur dioxide	N <sub>2</sub>	1 ppm to 1 %	0.5 % relative	2017
VOCs	N <sub>2</sub>	1 ppb to 1 ppm	2 % relative	2018

# Monthly Multipoint Calibration



# G1 Assay Procedure

- Verify multipoint calibration occurred within past month
- Daily zero and span gas check to determine if shift in calibration < 5 percent from multipoint calibration
- Reference standards within well-characterized region of analyzer's calibration curve
- Triplicate measurements of zero gas, reference standard, and candidate standard(s) with changed order of the measurements (e.g., z-r-c-r-z-c-r-c-z)
- Stability test for reactive gas mixtures- repeat assay after at least seven days
- Data analysis to determine certified concentrations, uncertainty, and stability

# Appendix A Spreadsheet

## STEP 1

### Enter Calibration Data

Enter the calibration data in the shaded spaces below. The first column (i) simply counts the calibration points that you enter. The second column (X) is for the certified concentrations of the calibration gas standards. The third column (Y) is for the instrument responses corresponding to the calibration standards. The number of points cannot exceed 50.

i	X <sub>i</sub>	Y <sub>i</sub>
1	0.0000	0.2194
2	0.5000	0.7141
3	1.0000	1.2885
4	1.5000	1.9132
5	2.0000	2.5910
6	2.5000	3.2866
7	3.0000	4.1078
8	3.5000	4.9446
9	4.0000	5.8145
10	4.5000	6.7230
11	5.0000	7.7284
12	5.5000	8.7566
13	6.0000	9.8013
14	6.5000	10.8818
15	7.0000	12.0982
16	7.5000	13.3122
17	8.0000	14.5840
18	8.5000	15.9238
19	9.0000	17.3271

#### Color Code

red = derived value (protected)

blue = entered value (unprotected)

black = fixed text (protected)

Review the estimates of the parameters ( $b_0, b_1, \dots$ )  
for the linear and quadratic models, their expanded  
uncertainties and the overall uncertainty of the fit ( $u^2$ ).

Linear Model		Expanded Uncertainty	
parameter	estimate	lower	upper
$b_0 =$	-1.0778	-1.7351	-0.4204
$b_1 =$	1.9005	1.7757	2.0253
$s^2 =$	0.4986	0.2807	1.1205
$s =$	0.7061	0.5298	1.0585
df =	17		
t =	2.1098		

Quadratic Model		Expanded Uncertainty	
parameter	estimate	lower	upper
$b_0 =$	0.1964	0.1960	0.1968
$b_1 =$	1.0011	1.0010	1.0012
$b_2 =$	0.0999	0.0999	0.0999
$s^2 =$	0.0005	0.0003	0.0011
$s =$	0.0220	0.0164	0.0335
df =	16		
t =	2.1199		

Comparing the two models:

F ratio = 1026.76

F critical = 2.3167 (5% significance level)

The quadratic model produces a significantly smaller overall uncertainty of fit.

The quadratic model appears to be the better choice.

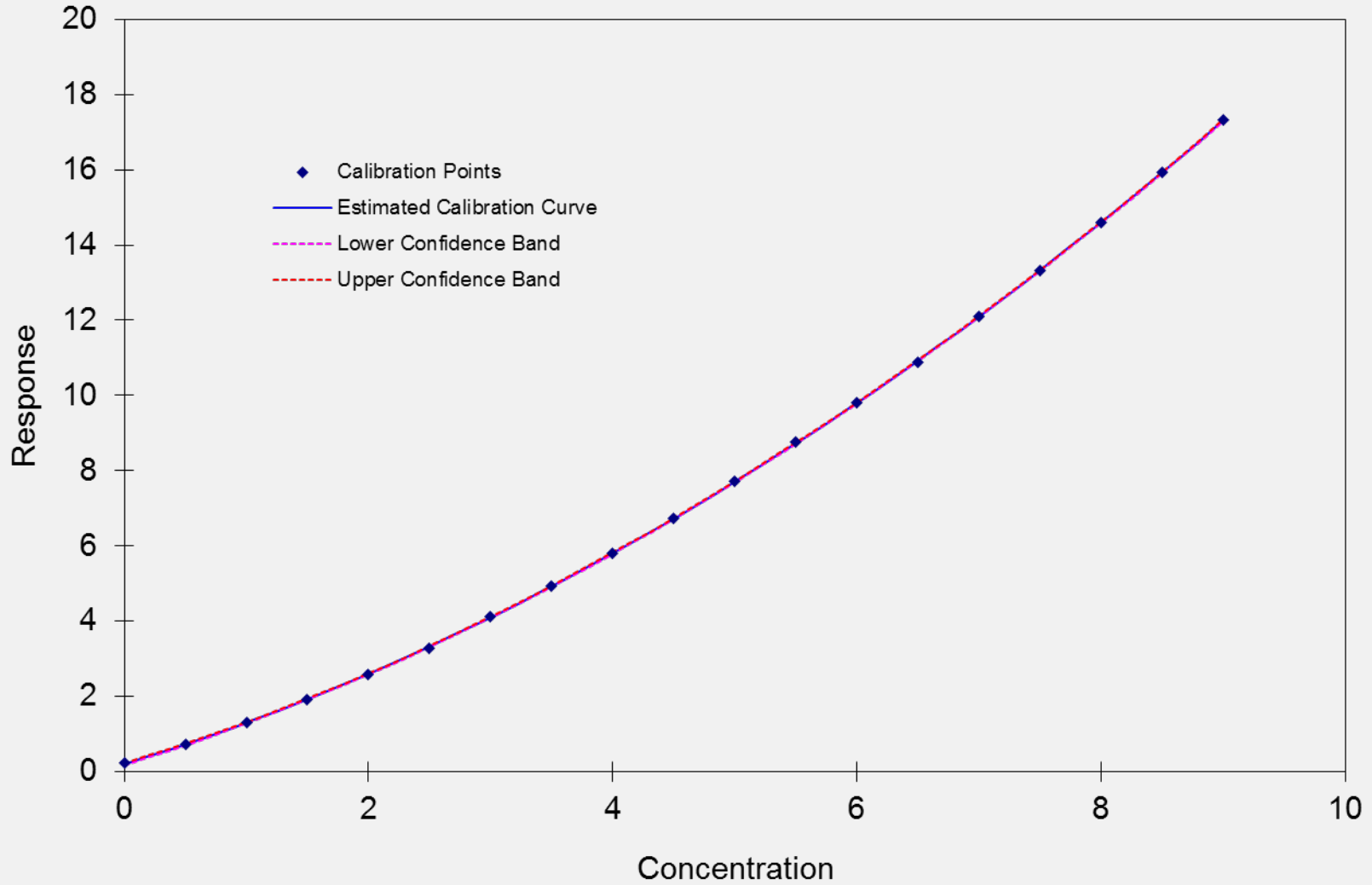
The approximate level of confidence associated with the expanded uncertainties is 95%.

The corresponding intervals take the form estimate  $\pm t^*u$ , where:  
estimate is the quantity of interest,  
 $u$  is its uncertainty, and  
 $t$  is a coverage factor.

For each model,  
the coverage factor,  $t$ , is determined from the t-distribution with appropriate degrees of freedom (df).

Note that the uncertainties are not displayed, but can easily be derived from the estimate, expanded uncertainty, and the coverage factor.

## Initial Calibration, Quadratic Model





# Appendix A Spreadsheet

## STEP 6

### Assay Candidate Standard on Different Day from Initial Calibration

This step applies to candidate standards that are assayed on a different day than the initial calibration. Before candidate standards are run, the measurement system is challenged with zero and span checks. Three or more discrete checks of the zero gas and three or more checks of the span gas are made. Enter the results below:

Response to Zero gas		Span Conc.	Response to Span
	0	9.000	16.010
	0.001	9.000	16.000
	-0.001	9.000	15.990
n =	3	n =	3
mean =	0.000	mean =	16.000
s =	0.001	s =	0.010
Cal. Resp. =	0.196	Cal. Response =	17.301

s = experimental standard deviation

	Zero Gas Results	Span Gas Results
Std. Uncertainty = $s/\sqrt{n}$ =	0.0006	0.0058
Rrs/100 =	0.1600	0.1600
	Std. Uncertainty is okay.	Std. Uncertainty is okay.
Relative Difference (RD)=	1.14%	-7.52%
	RD is okay.	RD is excessive.

# Appendix A Spreadsheet

## STEP 6 (Continued)

See table in Step 6 of the Instructions for the minimum number of different nonzero reference standard concentrations required.

Estimates below are based on the quadratic model.

Tab-Right to view estimates based on the other models.

Reference Standards (Enter 0 for zero Conc.)				
Conc.	Response	Conc.^2	Conc.^3	Conc.^4
0	0.2184	0.000	0.000	0.000
0	0.2194	0.000	0.000	0.000
0	0.2204	0.000	0.000	0.000
4.5	6.6930	20.250	91.125	410.063
4.5	6.7230	20.250	91.125	410.063
4.5	6.7730	20.250	91.125	410.063
9	17.3171	81.000	729.000	6561.000
9	17.3271	81.000	729.000	6561.000
9	17.3371	81.000	729.000	6561.000

nn = 9

Candidate Standard	
Observed Response	Estimated Conc.
4.01	2.9400
4.00	2.9337
3.99	2.9274

nnn = 3

mean = 4 2.9337

Experim. std. dev. = 0.00631

Rel. Std. Uncertainty = 0.12%

df = 2

F = 0.077954

F sig? = FALSE

Pr{>F} = 0.925262

The relative standard uncertainty is okay.

# Appendix A Spreadsheet

Estimated Concentration of Candidate Standard

2.9337

Rel. Expanded Uncertainty

0.76%

Portion of Variance Due to Calibration Uncertainty

45.66%

Expanded Uncertainty for Candidate Standard Concentration

Lower

Upper

The approximate level of confidence is 95%.

2.9114

2.9560

These upper and lower limits are compared with the corresponding limits estimated on different assay dates to establish that the candidate standard has not drifted.

# Appendix C Spreadsheet based on Schuirmann's Two One-Sided Tests (TOST)

## ASSAY RESULTS

In this sheet the results of two or three Assays are entered. Calibration dates are entered so Assays having the same calibration uncertainty may be treated correctly. (Assays having a common calibration share the same calibration uncertainty.)

Enter the results for up to three separate assays in chronological order below.

### ASSAY 1

<b>500</b>	= estimated concentration
<b>0.10%</b>	= Expanded uncertainty (expressed as percentage of estimated concentration)
<b>0.5</b>	= portion of expanded uncertainty <sup>2</sup> due to calibration
<b>5</b>	= number of measurements
<b>5/1/1997</b>	= date of prior calibration

### ASSAY 2

<b>501</b>	= estimated concentration
<b>0.10%</b>	= Expanded uncertainty (expressed as percentage of estimated concentration)
<b>0.5</b>	= portion of expanded uncertainty <sup>2</sup> due to calibration
<b>3</b>	= number of measurements
<b>6/1/1997</b>	= date of prior calibration

### ASSAY 3 (if applicable)

<b>502</b>	= estimated concentration
<b>0.10%</b>	= Expanded uncertainty (expressed as percentage of estimated concentration)
<b>0.5</b>	= portion of expanded uncertainty <sup>2</sup> due to calibration
<b>3</b>	= number of measurements
<b>6/8/1997</b>	= date of prior calibration

Number of different calibrations represented by the above data:

N = **3** (If this value seems to be incorrect, check the dates entered for the three assays. The earliest data should be for Assay 1. Trailing spaces may cause N's formula to interpret identical dates as different.)

# Appendix C Spreadsheet

## OVERALL ESTIMATE

Case = 18 (right click to see comment)

The standard error of the estimate produced in an assay is equal to approximately 1/2 of the "95% uncertainty." The inverse of the square of the standard error is the (raw) weighting factor used in producing an overall estimate of the concentration. The raw weights are adjusted (Adj. Wt.) so their sum is 1.00.

Calibration	Estimate	Exp Uncert.
1	500	0.100%
2	501	0.100%
3	502	0.100%

Raw Wt.	Adj. Wt.	Wt.*Conc.	Variance of Wt.*Est.
1000000	0.333	166.667	0.02778
1000000	0.333	167.000	0.02789
1000000	0.333	167.333	0.02800

501 = overall estimate of the candidate standard's concentration

0.289253 = Expanded uncertainty (concentration units)

0.058% = Expanded relative uncertainty

The standard error and expanded uncertainty displayed above do not account for uncertainty in the reference standards used to calibrate the analytical instrument, or for the uncertainty due to the dilution flow rate. In the first space below, enter the expanded uncertainty (typically 2 times the standard error) of the reference standards. If different calibration standards had different uncertainties, enter the largest.

# Appendix C Spreadsheet

**1.00%** = Expanded uncertainty (the two-sigma uncertainty) of the reference standard

**0.00%** = Expanded uncertainty (the two-sigma uncertainty) of the dilution system flow rate (This only ap

**0.00%** = Expanded uncertainty (the two-sigma uncertainty) for interference corrections when measuring

**1.002%** = Expanded uncertainty of the candidate standard (including the contribution of the reference standard)

# Documentation Requirements on Certificate of Analysis

- Cylinder identification number
- Certified concentration and estimate of uncertainty
- Components of gas mixture and balance gas
- Cylinder pressure at certification
- Dates of assays and certification expiration date
- Reference standard used in the assay
- Statement that assay performed according to protocol
- Assay procedure used (e.g., G1)
- Analytical method
- Laboratory performing the assays
- Any interference corrections made

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