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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

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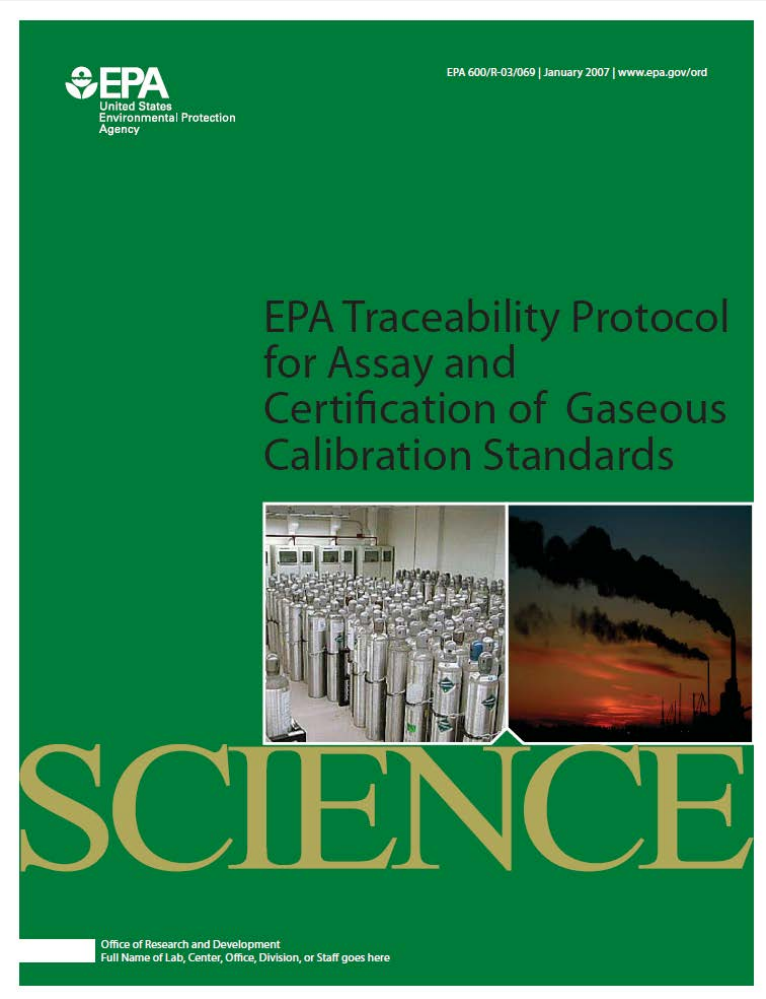
General Information

- 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

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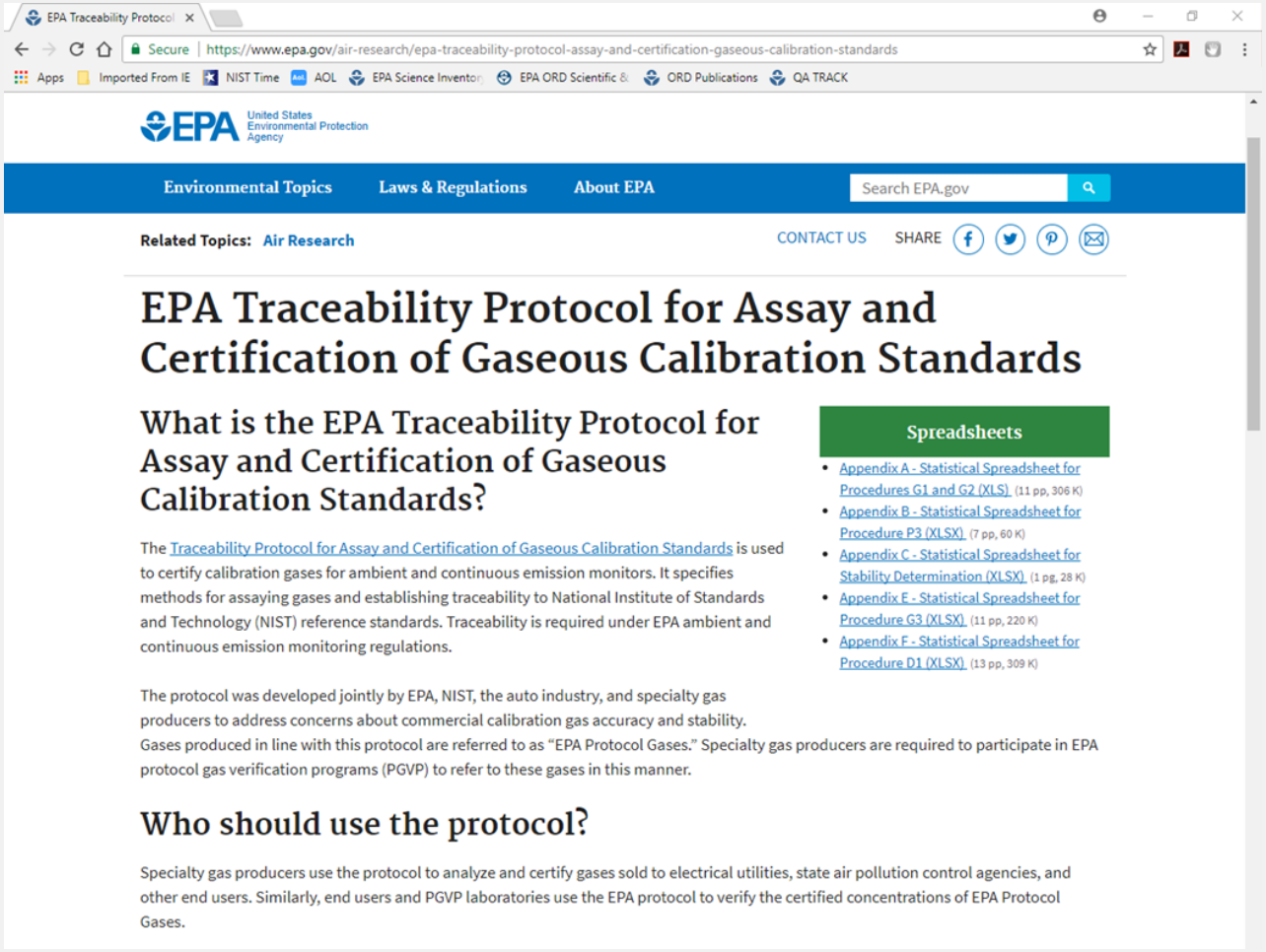
https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards



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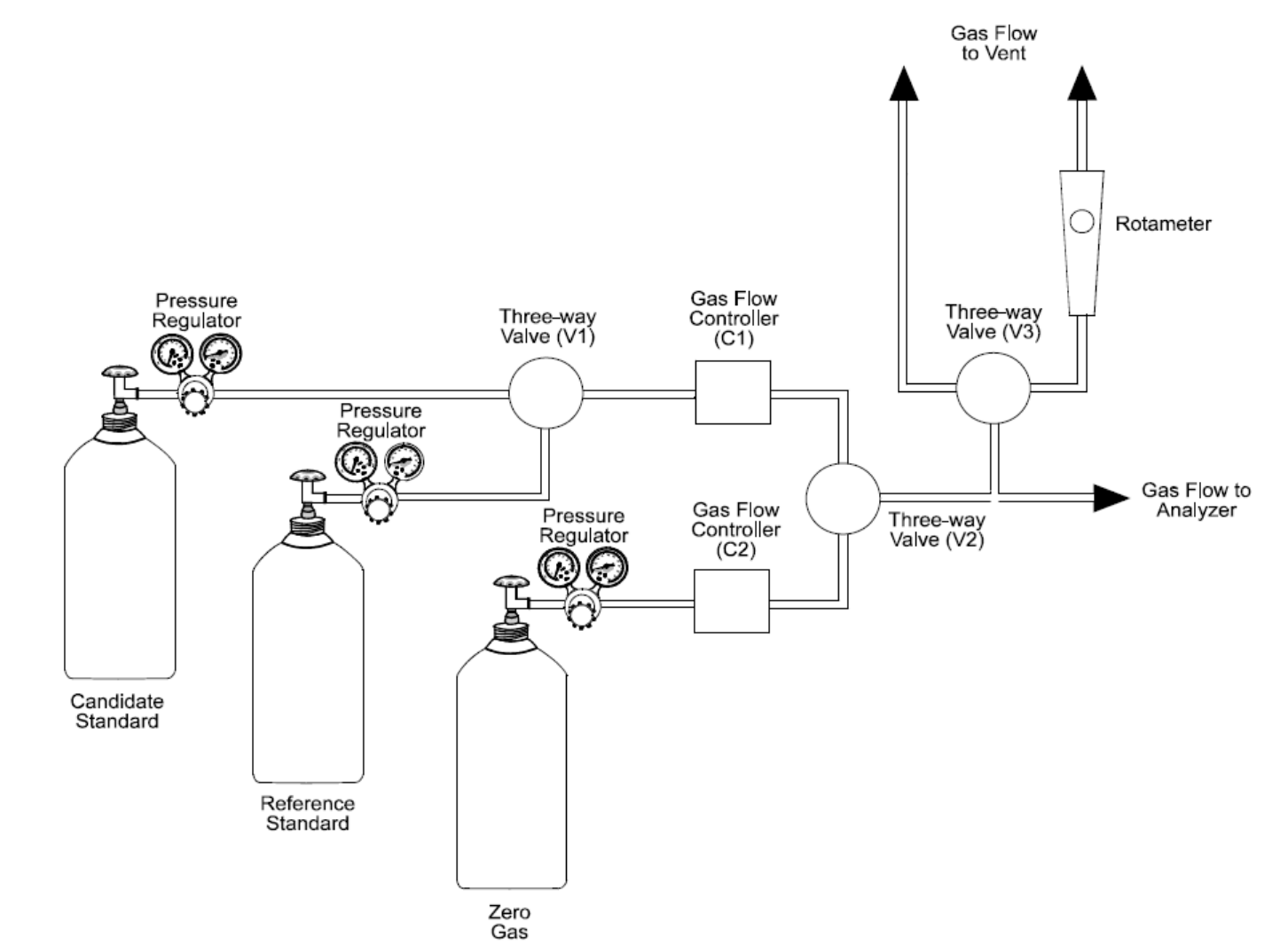
Analytical Procedures in Protocol

- 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



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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

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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

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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_X)	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
Nitrogen dioxide	Nitrogen or Air	TBD	TBD	TBD	TBD

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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_2	10 to 300 ppm	0.3 % relative	2018
Carbon dioxide	N_2	10 ppm to 20 %	0.3 % relative	2017
Carbon dioxide	Air	100 to 1000 ppm	0.2 % relative	2017
Carbon monoxide	N_2 or Air	1 ppm to 10 %	0.3 % relative	2018
Ethanol	N_2 or Air	75 to 1000 ppm	0.5 % relative	2016
Hydrogen chloride	N_2	10 ppm to 300 ppm	5 % relative	2017
Hydrogen sulfide	N_2	1 to 1000 ppm	1 % relative	2019
Methane	N_2 or Air	1.7 ppm to 10 %	0.1 % relative	2017
Natural gas		Typical	0.5 % relative (0.3 % for CH_4)	2019
Nitric oxide	N_2	0.5 ppm to 1 %	0.5 % relative	2017
Nitrogen dioxide	N_2 or Air	10 ppm to 1 %	0.5 % relative	2016
Nitrous oxide	N_2	0.3 to 1000 ppm	1 % relative	2017
Oxygen	N_2	10 to 100 ppm	1 % relative	2017
Oxygen	N_2	100 ppm to 25 %	0.2 % relative	2017
Propane	N_2 or Air	1 ppm to 1 %	0.3 % relative	2016
Stack gas	N_2	Typical	1 % relative (0.3 % for CO, CO_2, and CH_4)	2017
Sulfur dioxide	Air	1 ppm to 1 %	0.5 % relative	2019
Sulfur dioxide	N_2	1 ppm to 1 %	0.5 % relative	2017
VOCs	N_2	1 ppb to 1 ppm	2 % relative	2018

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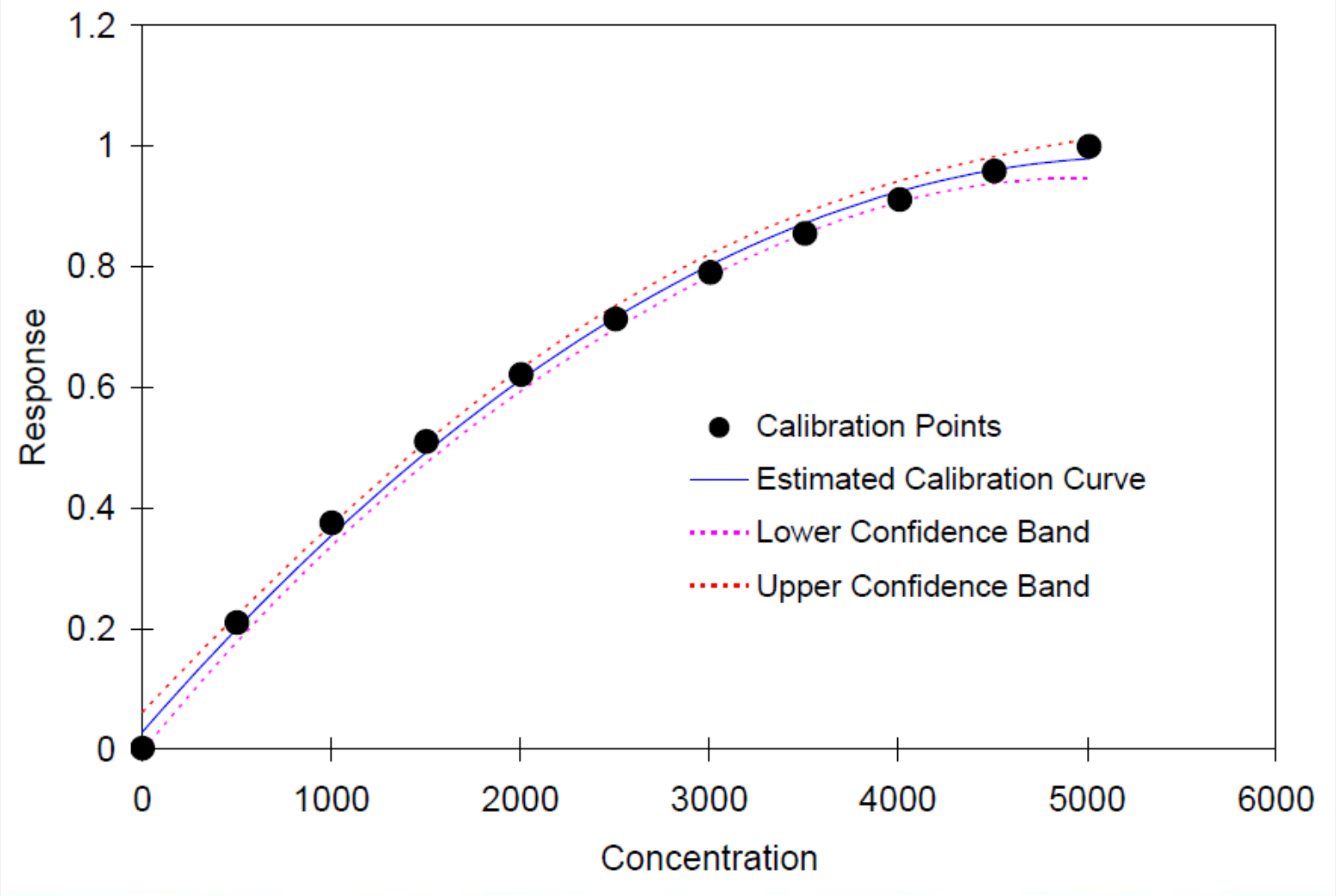
Monthly Multipoint Calibration



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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_i	Y_i
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)

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STEP 2

Review the Parameter Estimates

Review the estimates of the parameters (b_0, b_1, …)

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		

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

The corresponding intervals take the form estimate +/- 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.

Comparing the two models:

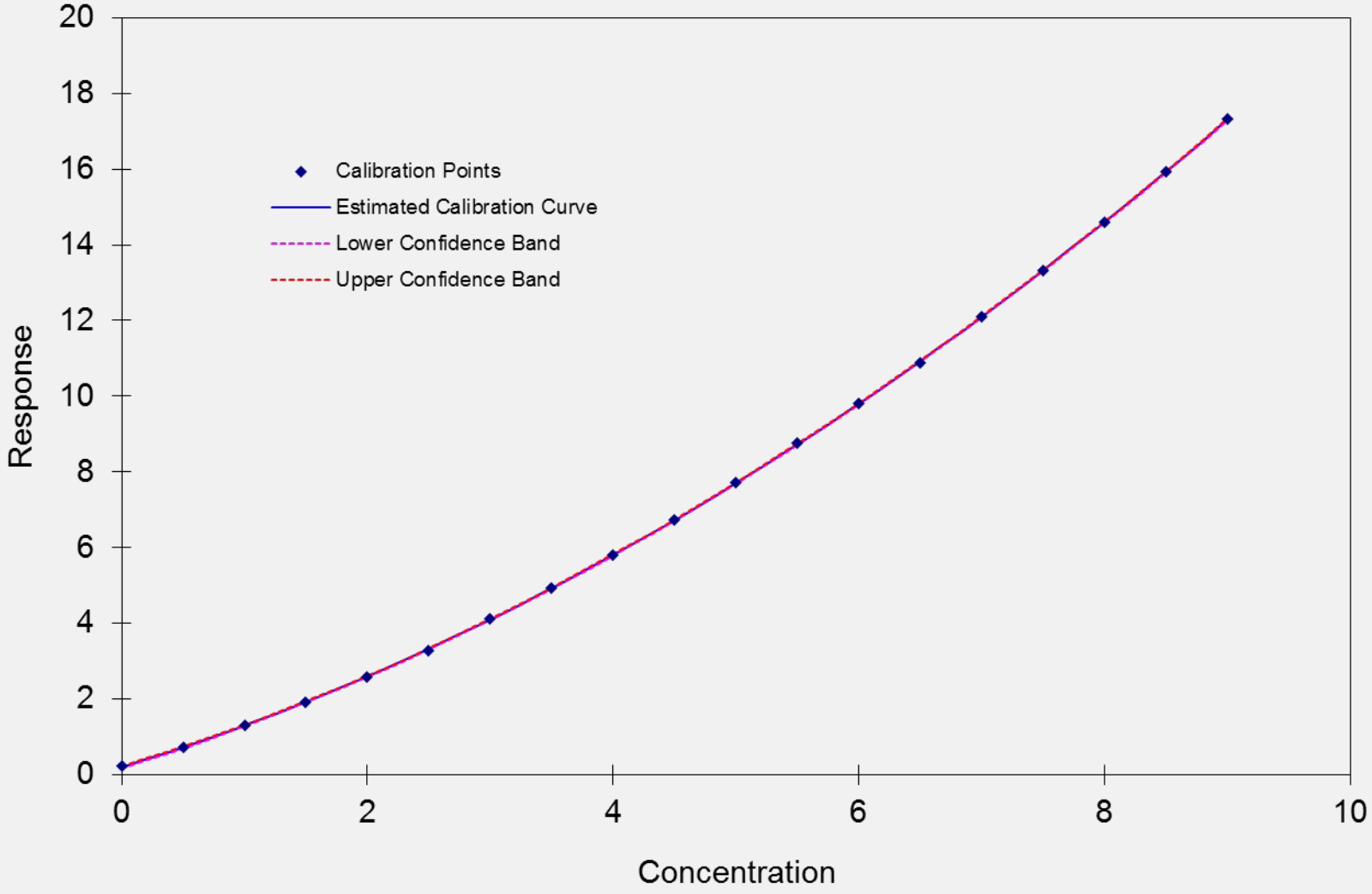
F ratio = 1026.76

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.

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	s = experimental standard deviation
Cal. Resp. =	0.196	Cal. Response =	17.301	

	Zero Gas Results	Span Gas Results
Std. Uncertainty = s/sqrt(n) =	0.0006	0.0058
Rrs/100 =	0.1600	0.1600
	Std. Uncertainy is okay.	Std. Uncertainy 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
2.9114	2.9560

The approximate level of confidence is 95%.

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 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

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

ASSAY 2

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

ASSAY 3 (if applicable)

502	= estimated concentration
0.10%	= Expanded uncertainty (expressed as percentage of estimated concentration)
0.5	= portion of expanded uncertainty^2 due to calibration
3	= number of measurements
6/8/1997	= 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 measurin
1.002%	=Expanded uncertainty of the candidate standard (including the contribution of the reference standard)

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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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