Compilation of Various Questions and Answers about EPA Traceability Protocol for Gaseous Calibration Standards

Question 1- As expected, we've already had a "grey area" occur as we implement the 2012 Green Book. Recertification of a 16ppm SO_2/N_2 EPA Protocol Mix. If the recertification passes the TOST 1-percent test for stability, does it get a new certification period of 4 years or 8 years? I expect it is 4 years, but not sure if it should be moved up to the next higher level such as is typical for upgrading the 6 month mixes.

Answer 1- The "grey area" arises because a 16 ppm SO_2/N_2 mixture was classified in the 1997 protocol as a lower-concentration mixture with a 6-month certification period. Under the 2012 protocol (see Table 2-3) , the same gas mixture falls into the 1 to 50 ppm SO_2 range with a 4-year certification period. When an EPA Protocol Gas gets recertified, the 2012 certification period applies if the recertification data pass the TOST stability test. Do not use an 8-year certification period, which applies for SO_2/N_2 mixtures (either new or recertified) greater than 50 ppm. The 2012 certification periods are based on NIST data. In future years, the certification periods could be revised if longer-period and lower-concentration stability data become available. If available, please send me the recertification data for this EPA Protocol Gas.

Question 2- What is the certification period for an EPA Protocol Gas that is currently in the field and that was certified under the 1997 revision of the protocol? What if the certification has expired?

Answer 2- First, the maximum certification periods that are given in Table 2-3 are based on concentration stability data from NIST and specialty gas producers rather than on the results of the TOST stability test. Both TOST and Student's t-test concern short-term, catastrophic stability problems, rather than long-term ones. The maximum certification periods are based on historical NTRM concentration stability data from NIST and other stability data that have been submitted by specialty gas producers for EPA review. If we make the assumption that the cylinder passivation techniques being used by specialty gas producers for EPA Protocol Gases are similar to those used for NTRMs, then the stability for EPA Protocol Gases should be similar to that for NTRMs. Because the stability data were obtained from NTRMs that were produced in the past, they should be representative of existing EPA Protocol Gases. Consequently, the new maximum certification periods are applicable to existing EPA Protocol Gases and to those now being produced and whose short-term stability is still being tested using Student's t-test. The longer certification periods are applicable independent of the statistical test that is used to evaluate stability. If the protocol's certification period for a gas mixture had been 2 years and is now 4 years, then an existing EPA Protocol Gas that had been certified for 2 years can be used for 4 years and remain in certification.

Second, producers may exercise their own discretion to certify EPA Protocol Gases for less than these maximum periods if they believe that their standards may not be as stable as EPA believes.

Third, producers may elect to notify their customers that the certification periods for existing EPA Protocol Gases (both those in certification and those that are expired) have been extended with the beginning of the now-longer certification period remaining the date of the last assay. For example, an EPA Protocol Gas containing 50 ppm propane in air was originally certified on January 1, 2009 under the 1997 revision of the protocol. Its certification ended three years later on January 2, 2012. Because the new maximum certification period for this gas mixture is eight years as a result of the 2012 revision, the new certification expiration date would be January 2, 2017. The EPA Protocol Gas would not have to be recertified by its producer to receive the longer certification period, but would have to be recertified after January 2, 2017. The TOST stability test would have to be used during the recertification assay to show that the certified concentration has remained stable.

For those end users who are required by EPA regulations to use EPA Protocol Gases as calibration gases, some form of written documentation probably will be needed for the end users' records. For example, the producer could send a blanket letter or E-mail message to its end users and could offer to send a new certificate to those users who need written documentation and/or are required to report about their calibration gases to EPA. I understand that the longer certification periods would have to be reported electronically to EPA. I appreciate that the notification process will place some burden on producers and hope that giving them some discretion in this matter will reduce this burden.

Finally, the longer certification period does not protect against concentration shifts due to back diffusion of oxygen from the regulator into a cylinder through an open hand valve. End users still have to be cautious

to prevent such concentration shifts over time and to properly purge regulators before use and to close hand valves after use. Given the longer certification periods, they must be more cautious than previously.

Question 3- In the field, an end user has an EPA Protocol Gas which is about to expire. They can contact their supplier and request a recertification of the calibration gas. How the supplier achieves the recertification is up to them, either requiring a reanalysis or not, but in any event a new certificate is required to be in the possession of the end user prior to being able to use the gas beyond its original certification period. Actual reanalysis is not a requisite for recertification.

Answer 3- First, the producer can exercise its discretion in this matter. The EPA Protocol Gas would not have to have a recertification assay to receive the longer certification period under the original certification, but the end user could elect to pay for such an assay if it wanted to be completely sure that the concentration has not shifted. Producers are not required to send new certificates to all end users because many end users may not retain the calibration gases for longer than the 1997 certification periods. That being said, a producer may wish to maintain good customer relations by sending new certificates to those end users who request them and who need them for regulatory reporting purposes.

Question 4- What about an EPA Protocol Gas that has already expired. I assume the same route as above but how long can a gas be expired before it is no longer recertifiable?

Answer 4- First, there are DOT requirements for hydrostatic testing of cylinders that may have a bearing on this topic, but I'm not competent to discuss them. Using the example from Question 1, the end user could request a new certificate for the propane in air cylinder at any point up to January 2, 2017 (producer discretion still applicable), but the new certificate would still have an expiration date of January 2, 2017. However, would one expect that an end user pay continuing demurrage for an "expired" EPA Protocol Gas if the longer certification period were not known by the end user? In all likelihood, the end user will return the "expired" EPA Protocol Gas to its producer.

Question 5- Would it be permissible for a third party (e.g., another specialty gas producer) to recertify the expired, or about-to-expire, EPA Protocol Gas without an analysis, even though they were not the producer? Absent the actual reanalysis, can the non-producer recertify another producer's EPA Protocol Gases? The potential third-party recertifier would have PGVP registration and, in fact, be an EPA Protocol Gas producer, but they just did not producer the calibration gas in question in the example.

Answer 5- The original producer can be the only organization that can send out any new certificates for expired/expiring EPA Protocol Gases that are not reassayed. An end user can't shop around for another producer who is willing to send out another certificate. The original producer's discretion in this matter has to be respected.

Questions 6, 7, and 8- The quality assurance laboratory of (deleted country) conducts certifications of EPA Protocol Gases using NIST SRMs following the previous EPA traceability protocol. I would like to know more about the new EPA protocol. In the revised version, EPA has introduced the TOST statistical test for checking whether the first and second assayed measurements are equivalent, and would determine the better models (linear, quadratic, etc.) for the multi-point calibration of the analyzers. For us, we would accept the two assayed measurements if the two concentrations are within 1%. If we also assume the multi-point calibrations of SO_2/NO_X/CO analyzers are linear, then we calculate the uncertainty for the regression-predicted concentration based on Student's t-distribution which should be less than 1% of the largest concentration used in the multi-point calibration. In this regard, I would like to know

1 What is the advantage for using TOST acceptance criteria?
2 Should we assume the multi-point calibrations of SO_2/NO_2/CO analyzers are linear as we find these characteristics for analyzers deployed in the (deleted government) air monitoring network?
3 Should I assume now that the certification periods of all EPA Protocol Gases (50 ppm in our stock) can be extended from 2 years to 4 years, though the gas certificates show otherwise? Or only after we recertify it upon expiration, then the certification period would be extended for another 4 years. If so, the certification period can be up to 6 years!!!

Answers 6, 7, and 8- The main advantage of using Schuirmann's TOST is that the analyst is not rewarded for making measurements with poor precision. Student's t-test determines if there is a statistically significant difference between two values and large analytical uncertainties can mask a smaller concentration difference. On the other hand, TOST determines if two values agree to within a specified acceptance criterion and large uncertainties make it harder to show that the values are equivalent. Read the statistical papers referenced in the protocol for a statistical discussion of TOST. Note that the Appendix C statistical spreadsheet in the protocol calculates the uncertainty of the EPA Protocol Gas based on the uncertainties of the two assays of the candidate standard.

The Appendix A statistical spreadsheet produces polynomial regression equations from linear (i.e., first-order) up to fourth-order. It also makes a recommendation about which regression best fits (i.e., yields smallest uncertainty) the assay data from statistical principles alone. The uncertainty of the calibration equation may be reduced by using higher-order equations, but EPA discourages the use of higher-order equations unless there are sound theoretical grounds for doing so. The analyst should be the one who makes the decision about the most proper equation to use. See Section 2.1.4.2 of the protocol for a discussion of this topic. I surmise from your questions that ambient air quality analyzers are being used for the assays. If so, I would agree that a linear calibration equation is the best assumption. But look at the data to be sure.

Please consult with your specialty gas producer regarding extending the certification periods for existing EPA Protocol Gases without a recertification assay. If the producer elects to do so, new four-year certificates could be issued for existing EPA Protocol Gases, but the new certification period still begins on the date of the last assay and ends four years later. The total certification period without a recertification assay cannot be six years.

Question 9- If a mixture is certified at exactly 50.0 ppm nitric oxide should it receive a 3-year or 8-year shelf life? Same for 50.0 ppm SO_2.

Answer 9- Although I question whether a producer could hit these concentrations exactly, I'll go with the rather arbitrary principle that the concentration ranges in Table 2-3 start just a smidge above the stated lower value and end exactly at the stated upper value. Turning the question inside out like a sock, wouldn't it be better to ask the end user if you could ship a slightly-higher-than-ordered-concentration in exchange for a longer certification period?

Question 10- Does EPA want to review the concentration limit for propane in nitrogen? The 2012 document requires anything less than 100 ppm to receive a 6-month shelf life. Can this concentration limit be lowered to 0.1 ppm similar to the air balance propane?

Answer 10- You are correct. The concentration range for propane in nitrogen EPA Protocol Gases in Table 2-3 should have been changed to 5 ppb to 2 percent because NIST NTRMs are available in that concentration range as is shown in Table 2-1. During the revision of the protocol, the concentration range in Table 2-3 was changed but I somehow failed to make the corresponding change in Table 2-1. Please accept my apologies for this error. Unfortunately, no one found this error when the draft of the protocol was sent for external review in September 2011. A copy of the 2012 protocol with technical corrections is posted at http://www.epa.gov/nrmrl/appcd/mmd/db-traceability-protocol.html

Question 11- How should specialty gas producers handle shelf life for concentrations above the highest indicated concentration in the protocol (Page 31), for example, 1000 ppm propane in air?

Answer 11- This question about the shelf life for high-concentration standards is largely moot because such standards cannot be assayed or certified under the protocol. Section 2.1.1 of the protocol states "A candidate standard having a concentration that is lower or higher than that of the reference standard may be certified under this protocol if both standards' concentrations (or diluted concentrations) fall within the well-characterized region of the analyzer's calibration curve". Section 2.1.4.2 states "All measurements of candidate standards must fall within the well-characterized region of the analyzer's calibration curve, which lies between the largest and smallest measured concentrations of the multi-point

calibration and for which U for the regression-predicted analyzer response is ≤±1 percent of the measured response for the largest concentration in the calibration". The heart of the matter is the lack of a high-concentration NIST-traceable reference standard with which to generate a calibration curve whose well-characterized region would bracket the high-concentration candidate standard. How would one assay the standard-in-question (i.e., 1000 ppm propane in air) if the highest concentration reference standard available from NIST is 500 ppm for that gas mixture? Such a great extrapolation beyond the measured calibration curve would be extremely questionable.

Question 12- As RGMs are now allowed as reference standards the specialty gas community will, over time, become more flexible/ adaptable to adding new components and concentrations to our EPA Protocol portfolio. If we are limited at the top end of the concentration in the document, there will be confusion of how to apply shelf life rules above the indicated concentration. For example, if we develop RGMs with NIST and are capable of analyzing 100 ppm ammonia to the protocol requirements, how will we assign shelf life at this concentration? Does EPA want to consider removing the upper concentration limit on the concentration range (except for the lower segments of NO and SO_2)? Examples:

- nitric oxide	0.5 ppm to 20.0 ppm	3 years
- nitric oxide	> 20.0 ppm	8 years
- propane in air	> 0.1 ppm	8 years

Answer 12- The concentration ranges in Table 2-3 are based on concentration stability data obtained from NIST and from specialty gas producers. If producers wish to extend the ranges, they should contact EPA and provide long-term concentration stability data for the gas mixture that they propose to be certified as an EPA Protocol Gas. NIST will be consulted regarding this proposal. As appropriate, the protocol will be revised and producers will be notified of the extended concentration range. It is EPA's intention that the protocol be based on the best available information and it may be in the interest of producers to generate such concentration stability data.

Question 13- Methane in nitrogen is not listed on page 31, what will the shelf life be for this combination?

Answer 13- You have found another error that I and the external reviewers missed. Sorry about my error. Table 2-3 should have included methane in nitrogen from 0.5 ppm to 4 percent with a maximum certification period of 8 years. A copy of the 2012 protocol with technical corrections is posted at http://www.epa.gov/nrmrl/appcd/mmd/db-traceability-protocol.html

Question 14- How shall we handle SO_2 in air; H_2S in air, nitrous oxide in nitrogen, and oxides of nitrogen in nitrogen?

Answer 14- Table 2-3 has been revised to include SO_2 in air based on the following information from NIST's Frank Guenther (301-975-3939 or franklin.guenther@nist.gov):

"It is true that the DOE (i.e., Declaration of Equivalence) does not state that there is equivalence between VSL and NIST for SO_2 in air balance. However with CCQM-K76 it was declared that the key comparison results were applicable to a concentration range from 50 ppm to 1 % mol/mol in a balance of air or nitrogen. The CCQM Gas Analysis Working group could see no reason to exclude the possibility of using air as a balance gas in reference materials. I have attached the report for CCQM-K76, which was coordinated by NIST. Therefore NIST would recognize equivalence in VSL gas standard in air above 50 ppm to a maximum of 1 % mol/mol. I will seek to include air balance SO_2 in the next DOE with VSL."

Specialty gas producers may use VSL SO_2 in air reference standards to assay SO_2 in air candidate standards. At this point in time, SO_2 in N_2 reference standards may not be used to assay SO_2 in air candidate standards due to possible balance gas interferences (e.g., collisional broadening of absorption lines) with the sulfur dioxide measurements. Frank Guenther replied to an EPA inquiry as follows:

"We cannot say if there is significant bias due to the balance gas in the wide spread of instruments used to analyze SO_2. The band broadening issue is but one mechanism that can cause biases. Some instruments draw sample through a capillary tube to control flow. Due to viscosity differences, air and

nitrogen can behave differently. The magnitude of the resulting bias is unknown to us here at NIST. It would be a relatively easy experiment to set up using one of our diluters. We will see if we can set up a test station, and then test the various instruments we have in our possession. This will take some time, as we have plenty to do and I am not looking for more projects at this time. But we will try to fit it in over the next 6 months. It would be something a contractor could do, and we would be willing to assist with technical advice."

Table 2-3 of the protocol has been revised to show that EPA Protocol Gases containing 10 to 1000 ppm oxides of nitrogen in nitrogen may be certified for up to two years. VSL sells 10 to 1000 ppm nitrogen dioxide in nitrogen primary reference materials (PRMs) and that the DOE between NIST and VSL includes this gas mixture. The 2013 on-line VSL PRM catalog states that the stability period is two years and that mixtures of nitrogen dioxide in nitrogen also contain approximately 1000 ppm oxygen. NIST-certified reference standards containing oxides of nitrogen in air cannot be used as reference standards for the assay of candidate standards containing oxides of nitrogen in nitrogen because of potential biases from balance gas differences.

There are no available NIST reference standards (or equivalent VSL PRMs) for the other gas mixtures and no corresponding EPA Protocol Gases can be produced as a result. At such a time as NIST makes these reference standards available as SRMs, NTRMs, or RGMs, the protocol will be revised and producers will be notified of the revision

Question 15- We have a 40CFR75 electric utility that wants NOx certified as an EPA Protocol Gas, and with a certification accuracy assigned. They want the NOx as nitric oxide in nitrogen mixtures. This electric utility is purchasing single minor component nitric oxide EPA Protocol Gases. I envision that this could be done if we minimize the NO_2 impurity such that the uncertainty in the NO_2 and total NOx is not statistically significant to the nitric oxide certification accuracy.

In doing NOx analysis, I thought that the NOx channel of a chemiluminescent instrument would be better vs. FTIR. On the chemi, we can measure the total NOx of an SRM or NTRM, and correlate it to NIST's reported NO and NO_2 concentrations. Of course on an FTIR, one obtains separate peaks for NO vs. NO_2, but the resolution and accuracy of the ppm to sub-ppm NO_2 comes more into question on an FTIR. Also, the only NO_2 SRM has air balance gas, and we do everything that we can to keep air out of our FTIR delivery train. What I would like your ruling on:

1 Does the 2012 EPA Protocol Document allow a NO_X EPA Protocol with the composition of nitric oxide, and total NOx certification?
2 Would you agree that the calculations in the attached work aid would allow this composition?

Answer 15- You can directly assay the NO and NO_X concentrations of the nitric oxide in nitrogen candidate standard using the certified NO and NO_X concentrations of the NIST nitric oxide in nitrogen reference standard and a chemiluminescent instrument as discussed below.

Mike Kelley of NIST's Gas Metrology Group says "NIST has been certifying both the NO and NO_X content in their SRMs for years. As far as NTRMs are concerned, if the producer analyzes NOx and submits the results to NIST, we will certify that as well. Some producers analyze the NO only".

John Schakenbach (now retired) of EPA's Clean Air Markets Division (CAMD) points to CAMD's May 2012 draft policy Q&A regarding use of NO and NOx gases under 40 CFR Part 75 (see http://www.epa.gov/airmarkets/emissions/monitoring.html):

"Question 9.34
Topic: Use of EPA Protocol Gas Components for Calibration
Question: Should the NO or the NO_X concentration on an EPA Protocol gas cylinder be used for NOx analyzer calibrations and linearity checks?
Answer: Prior to 2004, only the NO component of EPA Protocol gas cylinders was certified as traceable to the National Institute of Standards and Technology (NIST); the NO_X concentrations shown on calibration gas certificates were for informational use only. However, since then, NIST has been certifying

both the NO and NO_X concentrations of Standard Reference Materials (SRMs) and NIST Traceable Reference Materials (NTRMs). Therefore, it is now possible for specialty gas companies to produce EPA Protocol gas cylinders in which both the NO and NO_X concentrations are NIST traceable. In view of this:
(1) When both the NO and NO_X concentrations of an EPA Protocol gas cylinder are certified NIST-traceable:
(a) If you have an analyzer that measures total NO_X, you may use either the certified NO concentration[1] or the certified NO_X concentration when conducting calibration error tests or linearity checks, or when calibrating a reference analyzer for a Part 75 NO_X RATA or an App E NO_X test; or
(b) If your analyzer measures only NO, rather than total NO_X, use the certified NO concentration for calibration error tests, and linearity checks.
(2) If only the NO concentration of the EPA Protocol gas cylinder is NIST-traceable but the NO_X concentration is not, use the certified NO concentration for calibration error tests and linearity checks, and for calibrating a reference analyzer[1] for a Part 75 NOX RATA or an App E NO_X test.
[1] Note: An NO2 EPA Protocol gas must also be used when calibrating a reference analyzer that measures NO and NO_2 separately without a converter.
References: Appendix A, § 6.2 and 6.3; Appendix B § 2.1.1 and 2.2.1
Key Words: EPA Protocol gas, calibration gas, calibration error test, linearity check, NO_X monitoring
History: New"

Question 16- A refinery needs an EPA Protocol Gas that is 4.9% methane, 2% propane with balance nitrogen. The highest NIST SRM for methane is 100 ppm; however (deleted producer) has a natural gas NTRM with methane at 90%; and propane at 3%. Plus we can use pure methane for the calibration curve. We want to use a GC/FID for the analysis so dynamic dilution of pure methane is not a good fit into a GC sample valve (per section 2.1.3.2 on page 11). Since method G2 allows static dilution which could be quantitative gravimetric dilution of non-reactive gas components, could we use static, gravimetric dilution of the pure methane to generate the calibration curve?

Answer 16- In response to EPA's inquiry, NIST's Frank Guenther addressed this question:

"To analyze a 5% methane properly you need to construct a calibration curve with standards near 5%. I would use two or more standards that bracket the analyzed cylinder, but no lower than 1% and no higher than 10%. The larger the standard range the more standards needed. If you have a standard you trust that lies extremely near the candidate cylinder in concentration, you can even just use the one trusted standard. NIST can certify methane standards up to 10 % in nitrogen, and thus can issue NTRM certs or RGM certs for this concentration."

Question 17- (deleted producer) uses the following statement on EPA Protocol Certificates of Analysis:

“This certification was performed according to EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards September 1997, using procedure G1 or G2.”

(deleted producer) will continue to practice the 1997 EPA Protocol document while we update the uncertainty calculations. However, we want to implement the new shelf lives immediately. Is the following statement acceptable:

“This certification was performed according to EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards September 1997, using procedure G1 or G2. The certification expiration date is assigned using the May 2012 revision of the EPA Traceability Protocol document.”

Answer 17- The proposed statement is acceptable during the one-year interim period while the producer updates its uncertainty calculations.

Question 18- We currently provide a significant amount of end users with EPA Protocol Gases and we procure these standards from producers on the PGVP. My question is can a distributor who procures EPA Protocol Gases from a producer on the PGVP register and participate in the audit program and have their name added to the PGVP? Any help or clarification in this matter would be greatly appreciated.

Answer 18- This question was forwarded to EPA's John Schakenbach (schakenbach.john@epa.gov) who ran the Emission PGVP and Mike Papp (Papp.michael@epa.gov), who ran the Ambient Air PGVP. John's response is shown below and Mike agreed with John's position on this question:

"40 CFR Part 75 only allows production sites (i.e., sites that actually assay an EPA Protocol gas cylinder) to participate in the Emission PGVP. The main reason is we don't want to end up with duplicate cylinders from the same production site because a distributor happens to sell cylinders from that production site. For our audit, NIST needs to end up with the same number of cylinders from each production site. Our rule allows a distributor to sell unaltered cylinders from an Emission PGVP participant, and those cylinders would have a PGVP Vendor ID associated with them. So the distributor could claim in their advertising that they sell cylinders assayed by an Emission PGVP participant."

Because John and Mike ran the two PGVPs, their decisions are definitive. Please contact me if you have any other questions about the protocol. John Schakenbach has retired and responsibility for the emission PGVP has shifted to Travis Johnson (202-343-9018 or johnson.travis@epa.gov). Responsibility for the ambient air PGVP has shifted from Mike Papp to Solomon Ricks (919-541-5242 or ricks.solomon@epa.gov).

Question 19- Subsection 2.1.5.3 Assay/Certification of Multicomponent Candidate Standards: Data from the interference study must be evaluated using multiple-variable least-squares regression analysis. The analyst should consult with a statistician before beginning the study or evaluating its data. The regression analysis must produce an interference correction equation and an estimate of the standard uncertainty ($u_{CORRECTED}$) associated with the corrected concentrations for the assayed components. The interference correction equation will be valid for the range of concentrations covered in the study for which the uncertainty of the corrected concentration is ≤1 percent of the corrected concentration. The analyst must add the interference correction uncertainty to the total uncertainty of the standard. The certification documentation must include a statement that the certified concentration of a specified component has been corrected for interferences from other specified components. An interference study is not needed if the assay analyzer is interference free. In your opinion, who will be qualified as a statistician? The one with a statistic or math degree or have some kind of statistical training? Does our six-sigma black belt person qualified as a statistician?

Answer 19- The person who needs to analyze the assay data that are needed to develop an interference correction equation needs to have well-developed and appropriate statistical skills, rather than any specific educational degree or professional certification. Many individuals with statistical or mathematical degrees would not have the particular set of statistical skills that are needed for this task. A six-sigma black belt certification does not appear to require any knowledge of statistics as applied to metrology. The preface to Harry and Schroeder's book, *Six Sigma: The Breakthrough Management Strategy Revolutionizing the World's Top Corporations*, states: "What is Six Sigma? It is a business process that allows companies to drastically improve their bottom line by designing and monitoring everyday business activities in ways that minimize waste and resources while increasing customer satisfaction." The individual that you need should have experience in performing multi-variant linear regressions and in calculating the uncertainty associated with a correction factor that is predicted from the resulting regression equation. This individual also should have experience in the statistical design of experiments so that you can be advised of the optimum combination of gas mixtures and concentrations that will yield the smallest uncertainty estimates for the multi-component gas mixtures that you anticipate assaying. These uncertainty estimates must be used in the Appendix C statistical spreadsheet to determine the expanded uncertainty of the candidate standard. It would also be helpful if this individual has a good understanding of BIPM's *Evaluation of measurement data — Guide to the expression of uncertainty in measurement* (see http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf), which is abbreviated as GUM, or NIST's *Technical Note 1297: Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results* (see http://www.nist.gov/pml/pubs/tn1297/index.cfm).

Question 20- The effect of instrument interference could cause a positive influence (response) and contribute the concentration of an analyte such as NDIR due to the overlap of IR regions. It could cause a

negative influence (response) and reflect a lower concentration of the analyte such as the quenching effect of NOx chemiluminescence analyzer. From my own observation, interference in NDIR could be expressed in one equation. However, the interference of NO_X chemi was more complicated and may require multiple equations in different conditions. Does EPA allow us to tabulate the interference correction instead of using just one equation?

Answer 20- Al Dageforde of Horiba Instruments, Inc. wrote a paper in 1980 on the determination of the carbon dioxide quench effect on chemiluminescence NO_X analysis using a standard gas divider. He used a graphical approach to correct for interference based on measurements of two diluted NO calibration gases; one with CO_2 and one without CO_2. In 2010, NIST's Lyn Gameson (lyn.gameson@nist.gov) made a presentation on the accurate quantification of multi-component EPA Protocol Gases. He used linear regression equations to correct for interference based on measurements of NO, SO_2 or CO_2 calibration gases diluted either with balance gas or with interferent gas. He found that the interference correction for chemiluminescence NO_X analyzers can be represented by a single equation that is a function of the CO_2 concentration and that is independent of the NO concentration. Finally, a group of Chinese researchers published a 2012 article on interference correction for a multi-gas (CO_2, CO, and NO) NDIR analyzer. They used linear regression equations for interference correction. The calculation of calibration curves was based on least-square fittings with third-order polynomials. The interference correction equations were approximated by linear curves. They state that after the interference correction, the signal detected at each filter channel only depends on the absorption of the intended gas. The citation for their research is Sun YW et al., "Cross-interference correction and simultaneous multi-gas analysis based on infrared absorption" *Chinese Physics B*, vol. 21, no. 9, pg. 090701, 2012.

The advantages of using linear regression equations for interference correction are (1) the ability to obtain a interference correction for any combination of gases and concentrations, (2) the ability to obtain an uncertainty estimate for the interference correction, and (3) the ability to incorporate the equations in the software that is used to calculate the certified concentration and the expanded uncertainty estimate. While one could use a graphical or tabular approach to determine the interference correction, it would be difficult to obtain an uncertainty estimate using either of these approaches. Additionally, the tabular approach would introduce an additional error that is associated with interpolating between the values in the table and that would have to be added to the expanded uncertainty estimate. Unless your procedures for calculating the certified concentration and the expanded uncertainty estimate rely heavily on manual techniques, linear regression is the best and most direct method to perform the interference correction calculations and to estimate the uncertainty of the interference correction. Also note that the range restriction (i.e., uncertainty is ≤1 percent of the corrected concentration) means that the interference study's data must be analyzed using least-squares regression analysis.

Question 21- Subsection 2.1.4.3 Uncertainty of the Calibration Curve: This third component of uncertainty does not exist if the concentrations of the reference and candidate standards are equal. The assumed calibration equation and the true calibration curve will pass through the data for the reference standard regardless of whether they diverge elsewhere and the equation will be accurate for that single concentration. However, the uncertainty does exist if the concentrations of the reference and candidate standards differ. Does EPA allow a point-to-point analysis? If yes, how close the standard and sample concentrations need to be? (0.5%, 1%?)

Answer 21- There are many analytical procedures for assaying gas mixtures and the EPA traceability protocol represents just a few of them. Nevertheless, these few procedures have been developed since 1978 and there is consensus acceptance of them by specialty gas producers and end users. This acceptance is partly due to the external review of the protocol by producers as it has been revised in 1987, 1993, 1997, and 2012. The protocol has evolved incrementally, rather than radically, to minimize disruptions of the specialty gas industry. New procedures have been added to the protocol over the years and they have been reviewed by interested parties. Although a point-to-point comparison procedure might have some utility in some limited circumstances, the current procedures were designed to allow for a lot of analytical flexibility to assay a continuous range of concentrations. Restricting EPA Protocol Gases to only the same concentrations as NIST certifies would not allow end users much choice. A new procedure cannot be established casually, but it would have to be formally added to the

protocol, which might take several years to accomplish. The time to have proposed such a procedure was while the protocol was being revised between 2005 and 2012. You are free to make a more comprehensive technical proposal to add a new procedure to the protocol and to justify the need for the new procedure. Supporting technical would strengthen the case for the new procedure.

Question 22- I have a customer that requires a protocol mix that is at a higher concentration than my SRM. May I dilute my candidate cylinder down to the concentration of my existing SRM and be in compliance with G2? My dilution system is in current calibration, traceable to NIST by a NVLAP accredited ISO 17025 metrology lab.

Answer 22- Three aspects of this question need to be addressed. First, EPA Protocol Gases cannot be prepared at concentrations that exceed the ranges of reference standards that are available from NIST or VSL as are shown in Tables 2-1 and 2-2 of the protocol. If the customer specifies a calibration gas that exceeds these ranges, offer the customer a non-protocol calibration gas that is traceable to your own primary standards. Second, if the concentration of the specified calibration gas is within the range of NIST and VSL reference standards, purchase one of these reference standards from NIST, VSL or an NTRM from another specialty gas producer or offer the customer a non-protocol calibration gas. Third, the lack of a NIST-traceable reference standard of the appropriate concentration does not justify assaying candidate standards using casually-designed modifications of the analytical procedures included in the protocol. As indicated in the previous answer, the trust that the regulated community places in EPA Protocol Gases is partly due to the producers' external review and consensus acceptance of the procedures included in the protocol. The publication of PGVP results also generates trust in EPA Protocol Gases. If other procedures are needed, they must be developed in a formal fashion and must be published in a revised version of the protocol.

The proposed procedure is a combination of elements of Procedures G1 and G2 in that the reference standard would be assayed without dilution and the candidate standard would be assayed with dilution. While it is physically possible to perform this procedure, the big issue is whether assays performed using it would be considered by the regulated community to be traceable to NIST reference standards. The NIST Policy on Metrological Traceability (see http://www.nist.gov/traceability/) states that NIST adopts for its own use and recommends for use by others the definition of metrological traceability provided in the most recent version of the International Vocabulary of Metrology: "property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty." The proposed procedure would need to include measurements and statistical calculations for quantifying the uncertainties associated with the analyzer's calibration curve and with the dilution flow rates and for including them in the expanded uncertainty of the candidate standard. Estimating the expanded uncertainty is a component of the protocol that cannot be ignored.

Questions 23, 24, and 25- (deleted distributor) imports gas mixtures from (deleted producer) and a significant part of these mixtures are EPA Protocol Gases. In the last 2 years, (deleted country) requires an ISO 17025 for environmental mixes. As a result of this, our customers request the same. I would appreciate your help with some questions I have:

1. Is there a list of all the companies who authorized to produce EPA Protocol Gases?
2. Are there any EPA regulation regarding analyzing tests?
3. If the company who produce the mixture is not certified/ have ISO 17025 certification, and they send the mixture to third-party accreditation services for testing it, would the mixture have the ISO 17025 certification?

Answer 23- EPA monitoring regulations require that vendors advertising certification by the protocol and distributing calibration gases as "EPA Protocol Gases" must participate in the EPA Protocol Gas Verification Program (PGVP) or not use "EPA" in any form of advertising. The participants are posted at http://www.epa.gov/ttn/amtic/aapgvp.html and http://www.epa.gov/airmarkets/emissions/pgvp-detail.html along with PGVP results and other information about the PGVP. All that being said, EPA's regulations do

not extend beyond the United States' borders. Your country's requirements are applicable to air pollution monitoring in your country.

Answer 24- The EPA traceability protocol and other information about EPA Protocol Gases are posted at http://www.epa.gov/nrmrl/appcd/mmd/db-traceability-protocol.html

Answer 25- The EPA traceability protocol is somewhat different from ISO Standard 17025 (General requirements for the competence of testing and calibration laboratories) although both documents concern traceability. The EPA document is a general analytical procedure with associated statistical calculations for assaying and certifying gaseous calibration standards. The ISO document establishes technical requirements for calibration and testing laboratories to demonstrate their competence, to document and implement their quality management system, and to produce valid measurement results in technical fields of their own choosing. In other words, the EPA document concerns the gaseous calibration standards while the ISO document concerns the laboratories that might assay and certify these standards. ISO Standard 6143 (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures) more closely parallels the EPA document. Now with all this background discussion finally out of the way, your question can be addressed. A third-party accreditation service would not be capable of assaying and certifying gaseous calibration standards. It can only determine the competence of the laboratories that perform such assays and certifications. The specialty gas producer would have to obtain ISO 17025 accreditation to meet your customers' specifications.

Question 26- I have a few questions about the following paragraph in Section 1: "15. A new procedure has been written and a new spreadsheet has been prepared for the assay and certification of dynamic gas dilution systems (see Section 4). At this time, EPA does not require the regulated community to use NIST-traceable dynamic gas dilution systems for the calibration of ambient air or continuous emission monitors that are required by 40 CFR Parts 50, 58, 60, and 75. However, end users may elect to use these systems for calibrations." Does the regulated community include both end users and EPA Protocol Gas producers?

Answer 26- The regulated community is comprised of those organizations that are required to monitor ambient air quality and air pollution emissions under Parts 50, 58, 60, 72, and 75 of Title 40 of the Code of Federal Regulations (CFR). Examples of such organizations are state and local air pollution control agencies, electrical utilities, and industrial facilities. The term does not include specialty gas producers unless they are covered by these EPA regulations.

EPA does require NIST-traceable calibrations of dynamic gas dilution systems that may be used under Appendices A and C of Part 50 to calibrate ambient air quality monitors for SO_2 and CO. 40 CFR Part 75 only allows use of compressed gas calibration standards when calibrating CEMSs that are being used for purposes of Part 75 and when calibrating Test Methods 3A, 6C, and 7E when these methods are used for Part 75 testing.

Question 27- Appendix F is for the calculation of uncertainty due to a gas dilution system based on mass flow control. Does EPA allow other types of dilution techniques such as gravimetric dilution or gas divider based on capillary tube? If so, will it be acceptable to EPA for Protocol gas producers to calculate the uncertainty of the dilution system ? (Obviously we cannot use prot12appendf.xls)

Answer 27- Section 4 of the protocol is intended to be used for the direct calibration of ambient air quality and air pollution emission monitors by the regulated community, rather than for the preparation of calibration gases by specialty gas producers for such monitors.

Please note that the use of gas dilution systems (e.g., capillary-tube-based gas dividers) for multipoint calibrations in the preparation of EPA Protocol Gases is already allowed under Section 2.1.3.2 of the protocol: "The reference standards for the multipoint calibration must be diluted or undiluted SRMs, RGMs, PRMs, CRMs, NTRMs, or GMISs (see Subsection 2.1.3) or dynamically diluted pure gases. Pure gases may be dynamically diluted to prepare gas mixtures for use in multipoint calibrations, but such

mixtures may not be used as the reference standards for the span gas check or for the assay of the candidate standard. Pure gases may not be diluted by more than a factor of 100."

Any significant change to the protocol such as the use gravimetric dilution in the preparation of EPA Protocol Gases or alternative statistical procedures would require a formal revision to the protocol, which could take several years to complete. In addition to the actual writing of the revised document, internal and external reviews are needed before the final revisions are made. New statistical spreadsheets would have to be developed. This revision is not something any one specialty gas producer can undertake independently because the entire specialty gas industry would have to have access to and benefit from this revision. The revision would have to be acceptable to all interested parties, including NIST. Any producer may request that the protocol be revised again. The probability of accepting a suggested revision would be improved by the submission of suggested text and supporting technical data demonstrating the accuracy and precision of the suggested revision. Both technical and statistical revisions will be considered.

Question 28- Question about prot12appendc.xls. I input some test data and wonder if the cell A110 format was wrong. Should the cell A110 be divided by 100?

Answer 28- The Appendix C statistical spreadsheet has been revised to address minor calculation errors. A note has been added stating that all relative uncertainties (in Cells A15, A23, A31, A108, A110, and A112) are in the Excel format for percentages. If the relative uncertainty is 0.5 percent, then it should be keyed in as 0.005 and the cell will display 0.50%. It's a recognized quirk of Excel.

Question 29- Will it be required for a facility that only produces H_2S/N_2 EPA Protocol Gas to get a PGVP vendor ID? H2S was not listed in 40 CFR 75.21(g)(6) and (7).

Answer 29- I spoke with both Mike Papp (ambient air PGVP) and John Schakenbach (emission/acid rain PGVP), who said that the facility would not be required to participate in the PGVP because that facility does not produce the specific EPA Protocol Gases that are verified by their respective PGVPs.

That being said, there may be some business advantage to have the facility listed as participating in the PGVP because this action may reduce customer confusion if that facility sells and ships non-H2S EPA Protocol Gases that are produced at other facilities. That is, the sales reps at that facility wouldn't have to explain to potential customers why the facility doesn't participate and yet still sells EPA Protocol Gases in apparent conflict with EPA regulations. Participation by the facility would not cost your firm any money if the facility's H2S products are never verified by EPA.

Of course, it would be solely your business decision for that facility to participate or not participate in the PGVP. If you decide that you want the facility to participate, the application should include a note to the effect that the facility only produces H_2S EPA Protocol Gases. In this manner, EPA will not attempt to procure ambient air or emission/acid rain EPA Protocol Gases from that facility for verification purposes.

Your contact for the ambient air PGVP is Solomon Ricks (919-541-5242 or ricks.solomon@epa.gov). The ambient air PGVP web page is http://www.epa.gov/ttn/amtic/aapgvp.html. Your contact for the emissions/acid rain PGVP is Travis Johnson (202-343-9018 or johnson.travis@epa.gov). The emission/acid rain PGVP web page is http://www.epa.gov/airmarkets/emissions/pgvp-detail.html.

Question 30- We had a new request come in to provide a 6-pack (6 cylinders connected into a common manifolded pallet with a common outlet) of EPA Protocol Gases. Essentially, the 6 cylinders are to be dynamically blended at one concentration as a homogenous batch and individually certified as EPA Protocol Gases while in the manifolded assembly. The previous supplier to the customer did this with one COA covering the entire 6 cylinders, which I don't believe is correct. The previous supplier argues that they are filled simultaneously, must be identical, and since the cylinder valves are all open that they constitute one "container" and can be covered with one certificate and label. I proposed to the customer via our sales people that we manufacture through dynamic blending, which does not require rolling to homogenize, and individually test each cylinder and individually certify each cylinder.

Answer 30- Your interpretation of the protocol is correct. The protocol has always been intended to be used on a cylinder-by-cylinder basis. As was stated in the 1978 version of the protocol, "analyze each cylinder gas directly against the nearest SRM (or GMPS) by alternate analyses of the SRM and cylinder gas in triplicate (three pairs)". In general, EPA Protocol Gases are prepared, assayed, and certified individually, rather than in multiple-cylinder batches as is the case with SRMs and NTRMs. This approach allows producers to sell individual cylinders containing user-specified gas mixtures at user-specified concentrations on demand. The protocol does not require producers to maintain a large inventory of cylinders having identical compositions, which helps to reduce the cost of these standards. The protocol was never intended for the bulk assay and certification of multiple EPA Protocol Gases, either manifolded together or used individually. Any specialty gas producer who has misunderstood this aspect of the protocol should immediately stop bulk assays and certifications of EPA Protocol Gases and should assay and certify them individually. Any user of bulk-assayed and -certified EPA Protocol Gases should stop using them. The protocol is silent regarding production techniques and producers may employ their own cylinder-filling procedures, such as dynamic blending. Multiple cylinders may be filled simultaneously, but must be assayed individually. A technical correction will be added to Page 5 of the corrected version of the protocol to clarify this point.

Question 31- I just want to make sure that the paragraph at the bottom of Page 33, “Standards having certified…the last assay”, only applies to compositions below the bottom end with an initial 6-month cert period, and does not imply that a 3-year NO mix (or 4-year SO_2 mix) can move up to 8 years.

Answer 31- Thanks for spotting something that I had not considered when revising the protocol. The corrected version of the protocol will include the following technical correction on Page 33: “The maximum certification periods for recertified, low-concentration standards containing nitric oxide and sulfur dioxide are 3 years and 4 years, respectively.”

Question 32- I continue to get challenged by customers as well as other Protocol producers concerning whether or not a SO_2 in air can be labeled as an EPA Protocol mix. I have been referring to your answer to question #13 in your e-mail dated 8/7/12 (“Various Questions and Answers about EPA Traceability Protocol for Gaseous Calibration Standards”). In this answer it seems clear to me that, in the absence of a SRM or NTRM in a balance gas of air there can be no SO_2 in air EPA Protocol mix. It still appears that some producers are making the mix as EPA Protocol and they defend their decision by saying that they can demonstrate that there is no bias in their readings on their instrument between SO2 in air vs. SO2 in nitrogen. Are they correct that this is acceptable? Please let me know if that is the case. Thanks for your help on this.

Answer 32- As is indicated in Answer 14, Table 2-3 has been revised to include SO2 in air. When NIST and VSL sign the next Declaration of Equivalence (DoE) in the summer of 2014, a specialty gas producer will be able to purchase a VSL reference standard containing SO_2 in air to use in assaying candidate standards containing SO_2 in air.

Question 33- Since EPA invested a significant amount of time in writing Procedure G3 for the assay and certification of zero air materials, I was surprised to find out from NIST that no standard exists for air or N_2. I would like to start monitoring our zero gas. What do you recommend that I use as a standard?

Answer 33- I understand that NIST is developing zero air reference standards, which could be used to assay zero air materials using Procedure G3 in the EPA traceability protocol. Until such time as NIST-certified standards become available, I suggest that you use the best available zero air cylinders as your reference standards. Any assay of zero air cylinders using these reference standards would not be NIST-traceable, but they would help you to identify contaminated cylinders. It’s the best that you can do for the moment.

While the protocol was being revised in the past few years, several specialty gas producers had pointed out the need for NIST-traceable, commercially-available zero air cylinders. Three things were needed to allow such cylinders to be produced. First, EPA air pollution monitoring regulations or some other driver

was needed to create wide user demand for such cylinders. Second, an analytical procedure for assaying and certifying the zero air materials using NIST-certified reference standards had to be developed. Third, NIST had to see enough commercial demand for NIST-certified zero air reference standards to justify expending government funds to develop the standards. A different government organization (EPA's regulatory office, EPA's research office, and NIST, respectively) was responsible for each one of the three necessary steps. The inclusion of Procedure G3 in the revised protocol was just one of these steps. NIST's current work is another of these steps.

The International Organization for Standardization (ISO) Technical Committee TC 158 (gas analysis) is currently working on specifications and a standard for zero gas. I suggest that you keep track of TC 158's progress regarding zero gas. Contact VSL's Annarita Baldan (abaldan@vsl.nl) for information about their progress.

Question 34- I have heard folks in our industry referring to what they call an "EPA Protocol Blue List", which evidently refers to those PGVP participants that should be avoided. These comments typically originate from competitors in the field. Is there such a list and where may I find it on the web-site?

Answer 34- I've not heard about this blue list, either as an EPA-written document or an industry-written document. A PGVP participant is a PGVP participant, period. The underlying philosophy behind the protocol and the PGVP has been that EPA does not certify specialty gas producers as EPA Protocol Gas vendors. Rather, EPA publishes the verification results and lets the end users make the decision about what producer to buy from. The 2003 publication ("The Role of the Accuracy Assessment Program in the EPA Traceability Protocol for Gaseous Calibration Standards") about the old audit program states:

"The protocol does not provide a blanket certification of a specialty gas producer and EPA has not established a list of producers who are qualified or certified to produce EPA Protocol Gases. The protocol may be used by any producer, standard user, or other analytical laboratory to establish the traceability of a gaseous calibration standard to NIST SRMs or NTRMs."

This philosophy has continued with the PGVP. The emission PGVP web site (http://www.epa.gov/airmarkets/emissions/pgvp-purpose.html) states:

"The PGVP has four main objectives: (1) to ensure that EPA Protocol gases meet the accuracy requirements of 40 CFR Part 75; (2) to assist calibration gas consumers in their purchasing decisions; (3) to provide an incentive for gas vendors that perform well in the audits to continue to use good practices; and (4) to encourage gas vendors that perform poorly in the audits to make improvements."

The ambient air PGVP web site contains an annual report for 2012 (http://www.epa.gov/ttn/amtic/files/ambient/qaqc/aagvp2012report.pdf), which states:

"This program is considered a verification program because its current level of evaluation does not allow for a large enough sample of EPA Protocol Gases from any one specialty gas producer to yield a statistically rigorous assessment of the accuracy of the producer's gases. It will not provide end users with a scientifically defensible estimate of whether gases of acceptable quality can be purchased from a specific producer. Rather, the results provide information to end users that the specialty gas producer is participating in the program and with information that may be helpful when selecting a producer."

Question 35- We are a (country deleted)-based company with a production facility in (country deleted). We produce and calibrate ISO 17025 emission gases. Our clients in (country deleted) have a requirement to use EPA Protocol Gases. We would like some information on how to become registered as a provider of EPA Protocol Gases and what criteria we need to meet.

We use the analytical technique of bracketing according to ISO CD 12963, with mass flow controllers for dynamic dilution (ISO 6145: Part 7). We use a robust statistical method that takes into consideration both the uncertainty on the measurement and the uncertainty on the calibration standard. We have traceability back to NPL (UK). We are also accredited to ISO 17025 for this calibration. As part of the accreditation

we are required to do regular linearity checks and participation in annual PT schemes (round-robin). Would it be acceptable to put a note in the description "conforms to EPA Protocol methods" on the certificate?

Answer 35- The EPA traceability protocol does not provide a blanket certification of a specialty gas producer to assay and certify EPA Protocol Gases. EPA has not established a list of producers who are qualified or certified to produce EPA Protocol Gases. The protocol may be used by any producer, standard user, or other analytical laboratory to establish the traceability of a gaseous calibration standard to NIST SRMs or NTRMs. Because you are not selling EPA Protocol Gases in the US, you do not need to participate in EPA's PGVP.

In order for your firm to certify a calibration gas as being an EPA Protocol Gas, the assay procedures, NIST-traceable gaseous reference standards, and statistical analysis procedures that are defined in the EPA traceability Protocol (see http://www.epa.gov/nrmrl/appcd/mmd/db-traceability-protocol.html) must be followed. The certificate of analysis for the calibration gas must contain all the information that is specified in the protocol. Alternative procedures are not acceptable for EPA Protocol Gases. Your traceability must be to US NIST gaseous reference standards. Traceability to other national metrology institutes' reference standards or to NIST mass reference standards is not acceptable for EPA Protocol Gases (see note below). If your firm is not able to follow the EPA traceability protocol, you should contact your client and inform them that your firm cannot supply EPA Protocol Gases. Of course, this is an opportunity to educate your client regarding alternative traceability routes for calibration gases. If the client is required by EPA air pollution monitoring regulations to use EPA Protocol Gases, then the calibration gases must be purchased from a specialty gas producer that can follow the protocol. If the client is not required to use EPA Protocol Gases, you can offer calibration gases having an alternative traceability route (e.g., to NPL) that can meet their needs.

Note that NIST and VSL have signed a Declaration of Equivalence in June 2012 (see http://www.vsl.nl/sites/default/files/rtf/DoE%20-%20NIST%20and%20VSL.pdf), which allows specific VSL gaseous reference standards to be used for the assay of EPA Protocol Gases. VSL gaseous reference standards may be a traceability route that you may wish to consider.

Question 36- My client wants to sell EPA Protocol Gases to countries in (deleted global region), which has adopted 40 CFR Part 75 regulations and which requires EPA Protocol Gases as calibration gases. I want to know how EPA Protocol Gas production relates to participation in the PGVP.

Answer 36- This question was forwarded to EPA's John Schakenbach (schakenbach.john@epa.gov), who ran the Emission PGVP and who is now retired. John's response is shown below:

"Our international law expert said that if the country is a participant in one of our international free trade treaties, we cannot discriminate against them based on foreign nationality. Therefore, we'll need to know first what country is asking to participate. If the country is not planning to sell the cylinders in the U.S., what is the benefit to us and the U.S. in allowing them to participate in the program? If none, then there might be an appropriations problem.

"I just want to be clearer about the possible participation in the Emission PGVP of a non-U.S. EPA Protocol gas production site. 40 CFR 75.21(g)(1)(iii) requires a valid address for an Emission PGVP participant. A valid address must include the country where the production site is located. Therefore, if the production site that you represent does not provide the country where it is located, it cannot participate.

"In the Emission PGVP, the National Institute of Standards and Technology (NIST) analyzes a blind sample of EPA Protocol Gas cylinders collected from specialty gas companies. NIST provides the results to EPA; EPA posts the results on our web site. Calibration gas customers can use our web site to make buying decisions. The Emission PGVP is based on economic incentives - - production sites that do well in the audit will presumably be rewarded by gaining customers; those that do poorly may lose customers.

"However, for the PGVP economic incentives to work, we need to ensure that potential buyers have "equal" access to all participants. If a production site has significantly higher shipping costs, or refuses to sell EPA Protocol gas cylinders to U.S. customers, that production site no longer has the same economic incentives to maintain or improve the quality of its calibration gases as the other PGVP participants have, and would not be a good candidate for the Emission PGVP."

Question 37- (name deleted) facility has an infrared continuous emission monitor system (CEMS) for hydrogen sulfide (H_2S) permitted under 40CFR Part 60. Part 60 Appendix F requires cylinder gas audits using NIST-traceable or EPA Protocol Gases. After reviewing your EPA traceability protocol, I still have several questions concerning the composition of these gases and meeting traceability requirements.

1. (name deleted) has determined that the CEMS produces optimal data if the H_2S cylinder composition matches the digester gas matrix which is predominantly composed of methane (60%) and carbon dioxide (40%). Gas vendors are not able to provide EPA Protocol Gases with this mix but can provide a gravimetric NIST traceable gas mix. Attached is an example certification sheet for a 700ppm H_2S gas with 40% CO_2 and 60% CH_4. Does a gas traceable by weight, such as this example, fulfill the Part 60 requirements?
2. In conjunction with #1 above, (name deleted) has found it difficult to obtain these gases at high H_2S concentrations such as 1600ppm and 2600ppm either in balance nitrogen or in matrix CH_4/CO_2. Again, these are available as gravimetric NIST-traceable gases, are these acceptable?
3. The CEMS is currently set up to perform cylinder gas audits and also sealed cell audits. The CEMS has several sealed cells containing different concentrations of H_2S. Attachment #2 is a copy of a certificate the vendor has supplied for one of the sealed cells which contains 5.1% H_2S and, in this case, balance N_2. In your opinion is this a NIST-traceable standard as the certificate indicates? If not, do you have any guidance as to what criteria are necessary to demonstrate that the sealed cells would meet EPA protocol or NIST traceability?
4. Part 60 does not include a provision for using sealed cell technology. (name deleted) is in the process of evaluating if the sealed cells could be used instead of the cylinder gas audits. We propose performing side-by-side audits of the cylinder gas and sealed cells at a frequency that would produce a statistically robust data set to compare and present to regulators for approval of this technology. Do you have any advice on putting together that study or know of any other utility or business that has done this that I could contact? If not, do you know anyone else at EPA I could contact about this?

Answer 37- This question was forwarded to Ray Merrill (merrill.raymond@epa.gov, 919-541-5225), who works in EPA's Office of Air Quality Planning and Standards. Ray's response is shown below:

"As I understand your procedure involves using an extractive system based on White cell - tunable diode laser (TDL) technology to monitor H_2S on a continuous basis. You did not mention a specific subpart of 40 CFR Part 60 or 63 that applies to the requirement to measure H_2S so my answer will be general. Our Performance Specification 7 is generic for continuous H_2S monitors. The ongoing QA/QC that are required for monitoring should be identified in the specific regulatory requirement in your permit or regulatory rule.

"You are correct that we consistently require EPA Protocol Gases when you are required to perform Cylinder Gas Audit (CGA) as part of the QA/QC from 40 CFR Part 60 Appendix F. (e.g., from Procedure 1 intended for fixed gas analysis:

> "Section 5.1.2, (3) Use Certified Reference Materials (CRM's) (See Citation 1) audit gases that have been certified by comparison to National Institute of Standards and Technology (NIST) or EPA Traceability Protocol Materials (ETPM's) following the most recent edition of EPA's Traceability Protocol No. 1 (See Citation 2). Procedures for preparation of CRM's are described in Citation 1. Procedures for preparation of ETPM's are described in Citation 2. As an alternative to CRM's or ETPM gases, Method 205 (See Citation 3) may be used. The difference between the actual concentration of the audit gas and the concentration indicated by the monitor is used to assess the accuracy of the CEMS.")

"There seem to be two questions in your correspondence that need to be addressed and a third that I bring to your attention:

1 If H_2S cylinder gas audit material that meets NIST traceability or EPA's protocol gas traceability standard, can you use a vendor certified standard that is traceable gravimetrically to NIST?
2 Are sealed cell H_2S standards that you insert into your instruments optical path equivalent to flow through cells?
3 Since your system is an extractive White cell technology, one question you did not ask, but we should consider is: Does a calibration type cell inserted into the optical path meet the requirements of a CGA?

"In my opinion, the intent of the CGA is to test the entire CEMS system not just the measurement path in the instrument. (As a related example, direct measurement of H_2S using Method 15 requires a recovery test executed by spiking a certified H_2S standard gas at the probe.)

"We've received several inquiries regarding CGA requirements when the facility or test firm believed there was no qualifying NIST or EPA Protocol Gas available. I'm consistently recommending that facilities or test firms review and follow the guidance (3 pages) for requesting an alternative method request found on our website at: http://www.epa.gov/ttn/emc/guidlnd/gd22.pdf. By submitting a request that has the information summarized in this document we can review and provide a formal response that you will have for your records. Supporting data that demonstrates the effectiveness of your approach will streamline the process. Once you've had a chance to review the alternative request guidance, call me if you have questions."

Question 38- I received an e-mail from the owner/operator of a cement plant in (location deleted). He indicated that he could no longer purchase EPA Protocol Gas for CO_2 in a concentration over 20%. Our current guidance is that cylinder gases must be in accordance with the requirements specified in the "Reference Gases" section of 40 CFR, Part 75, Appendix A or as specified in an applicable Federal regulation. Could you provide a recommendation on what requirements the vendor should follow for CO_2 gas in concentrations above 20% assuming that EPA Protocol Gas is no longer available in such concentrations?

Answer 38- This question was forwarded to Ray Merrill (merrill.raymond@epa.gov, 919-541-5225), who works in EPA's Office of Air Quality Planning and Standards. Ray's response is shown below:

" To help in this instance, I need to know if the testing requirement comes from 40 CFR Part 75 or from one of the other stationary source requirements like 40 CFR Part 60, or 63 (i.e., NSPS or PSD). For Part 60, and 63 we recognize many of the higher concentration gases are not available as "EPA Protocol Gases" because there is no comparable NIST standard gas (NTRM/RGM etc) for traceability. In some cases we've been asked to approve an alternative to the protocol gas requirement when, for instance, cylinder gas audits are required for our instrumental methods.

"For example, see Alternative 102 on our website which says in part: "We acknowledge that NIST-certified reference gases are not available for TRS gases at the applicable 40 CFR 60 Subpart Ja instrument span values, and that alternative gases must be permitted. We believe that gases certified to 2 percent of the manufacturer's listed concentrations are a reasonable alternative for the CGA in this case.

"If formally asked, we'd most likely follow the same intent in response to similar requests for alternative approvals when protocol gases are not available to meet Part 60 or 63 requirements. Formal requests for alternative methods can be submitted following Guidance document 22 on our website. http://www.epa.gov/ttn/emc/guidlnd/gd22.pdf

"Subpart 75 falls under the jurisdiction of EPA's Clean Air Markets Division (CAMD). You'd have to ask Travis Johnson (202-343-9018, johnson.travis@epa.gov) or his supervisor Rey Forte (202-343-9134,

forte.reynaldo@epa.gov) in the Emissions Monitoring Branch of CAMD for their recommendation or opinion on this issue in regard to Subpart 75."

Question 39- Has there been a determination of the acceptability of CO_2 in air, and C_3H_8 in air gas mixtures above the 500-ppm limits found in Table 2-3 of the 2012 EPA traceability protocol? In addition to the balance air mixtures, our company also continues to receive requests for CO_2 or C_3H_8 or SO_2 mixtures each containing different concentrations of %-level O_2 in a balance of nitrogen. We have been successfully producing these gas mixtures for decades under the older EPA Protocol Gas rules. Are these acceptable under Paragraph 2.1.5.3 of the 2012 EPA traceability protocol? Again, our experience is that all these gas mixtures are no different than any other multi-component candidate standard and they are stable and the O_2 does not alter the stability of either compound.

Answer 39- Calibration gases containing gas mixtures and concentration ranges that are not listed in Table 2-3 cannot be certified as EPA Protocol Gases. As indicated in previous answers, end users can submit an alternative method request to EPA for the use of other calibration gases in the place of EPA Protocol Gases. In addition to concerns about the potential instability of such calibration gases, there are also concerns about potential measurement bias if the candidate standard and the reference standard are not closely-matched. NIST's Frank Guenther (301-975-3939 or franklin.guenther@nist.gov) responded to EPA's question about NIST's definition or specification for the composition of balance air in SRMs, NTRMs, and RGMs as follows:

"The composition of the balance gas is a very important issue that relates to biases in certain instrumentation. Even gas chromatography, where the balance gas is largely separated from the peaks of interest, these issues can cause small biases. The bottom line is that the calibration gas must match the balance gas of the flow being analyzed as much as possible. Air is a fuzzy definition that I do not think solves anything, as the flow being analyzed may differ from normal air composition. Close matching of the balance gases would be my suggestion, and if greater accuracy is required, a study of composition biases in the analytical system should be done. As far as our definition of “air” it is:

Oxygen: (20.95 ± 0.05) % mol/mol
Argon: (0.93 ± 0.01) % mol/mol
Nitrogen: (78.08 ± 0.02) % mol/mol
Carbon dioxide: (490 ± 10) µmol/mol

"This mixture will eliminate composition biases in most instrumentation."

Question 40- EPA Protocol Gases have an initial certification period of 6 months if they fall below the lowest concentration that is listed in Table 2-3 (e.g., 4 ppm ammonia in N_2). If a low-concentration standard is returned, re-assayed, and meets the TOST test for stability, can it then be recertified for the next level above, i.e. 12 months?

Answer 40- Your question is covered by Section 2.1.11 of the protocol, which states:

“Standards having certified concentrations that are lower than those given in Table 2-3 may be recertified for the period given in Table 2-3 provided at least 6 months have elapsed between the initial certification and the recertification. The maximum certification periods for recertified, low-concentration standards containing nitric oxide in nitrogen and sulfur dioxide in nitrogen are 3 years and 4 years, respectively. The corresponding maximum certification period for sulfur dioxide in air standards is 2 years. For example, a 0.5-ppm sulfur dioxide in nitrogen standard will have an initial certification period of 6 months. After a successful recertification, this standard will have a maximum recertification period of 4 years. The certification date is the date of the last assay.”

Question 41- I understand "Calibration gases containing gas mixtures and concentration ranges that are not listed in Table 2-3 cannot be certified as EPA Protocol Gases."; however, according 2.1.3.2, "Pure gases may be dynamically diluted to prepare gas mixtures for use in multipoint calibrations, but such mixtures may not be used as the reference standards for the span gas check or for the assay of the

candidate standard." Taking 22% CO2/N2 as an example; even though the top range listed in Table 2-3 is at 20%, one could use pure CO2 dynamically diluted to 25% to extend the curve, then use 20% SRM as span gas to certify this 22% CO2 EPA protocol gas. Please advise if my understanding of protocol is wrong.

Answer 41- The procedure that you propose would be acceptable under the protocol as is discussed below:

Section 2.1.1 of the protocol states "A candidate standard having a concentration that is lower or higher than that of the reference standard may be certified under this protocol if both standards' concentrations (or diluted concentrations) fall within the well-characterized region of the analyzer's calibration curve."

As you found, Section 2.1.3.2 states "Pure gases may be dynamically diluted to prepare gas mixtures for use in multipoint calibrations, but such mixtures may not be used as the reference standards for the span gas check or for the assay of the candidate standard. Pure gases may not be diluted by more than a factor of 100."

Section 2.1.4.2 states "All measurements of candidate standards must fall within the well-characterized region of the analyzer's calibration curve, which lies between the largest and smallest measured concentrations of the multipoint calibration and for which U for the regression-predicted analyzer response is ≤±1 percent of the measured response for the largest concentration in the calibration.

Section 2.1.4.2 also states: "If a gas dilution system is used in the assay apparatus, it must have a specified accuracy of no worse than 1.0 percent of the undiluted reference standard concentration. Additionally, the gas dilution system must be checked by the analyst at monthly intervals to verify that its calibration has not drifted significantly since its last calibration or recertification. Use an NIST-traceable flow rate reference standard to check at least one flow rate setting for each pollutant and dilution gas stream in the assay apparatus."

Your experimental procedure would be to first check the calibration of the gas dilution system to make sure that it is functioning correctly. Second, dilute the pure CO2 to generate a multipoint calibration curve, whose minimum concentration must be less that the concentration of the reference standard. Don't skimp on the number of measurements and the number of concentrations because more measurements and concentrations will give you a wider and tighter well-characterized region. It may be a good idea to limit the range of the multipoint calibration to the region immediately around the concentrations of the candidate standard and reference standard. Third, measure the reference standard and predict it's concentration using the multipoint calibration curve. If the actual and predicted concentrations for the reference standard match to within the uncertainty of the curve, then you good to go ahead with the assay of the candidate standard. If not, something has gone wrong, probably with the gas dilution system. Stop until you figure out what caused the disagreement in the predicted and actual concentrations.

This approach should work if the concentration of the candidate standard is not much greater than the reference standard. The protocol's uncertainty constraints will make it difficult to assay if the concentration separation is too great.

Question 42- I just want to confirm my understanding of the EPA Protocol, Section 2.1.3.1 about GMIS:

> "A candidate GMIS must be assayed on at least three separate dates that are uniformly spaced over at least a 3-month period."

One could interpret this to mean that we need three assays which are separated by a month. I don't think that was the intention. The way I read the sentence is that we need three assays (of at least three measurements each) that are spread over 90 days. To clarify…Interpretation A: If I assayed the candidate GMIS on 1/10/2017 and again on 2/10/2017 and again on 3/10/2017. (Three separate months – total elapsed time = ~60 days). Interpretation B: If I assayed the candidate GMIS on 1/10/2017 and

again on 2/25/2017 and again on 4/10/2017. (Three calendar months – total elapsed time = ~90 days). I think Interpretation B is correct. Am I correct???

Answer 42- You are correct. The point of requiring three separate assays over a three-month period is to detect any instability in the gas mixture. The uniform spacing of the assays is not that rigid of a requirement, but would help in the statistical analysis of the data to quantify any trend. There is nothing magical about what specific dates are chosen in that period. Perhaps I should substitute the words "approximately uniformly spaced" to clarify the purpose of this requirement.

Question 43- We are looking into producing methane EPA Protocol blends, but the NIST website is limited as far as the SRM's offered. Currently, there are 10 ppm, 50 ppm, and 100 ppm methane/air SRM's available as well as a 1 ppm methane/air SRM that is out of stock. Since the recommended 5 points for the curve is not available from NISY, would we be able to start with 3 points from the 10 ppm, 50 ppm, and 100 ppm SRM's and build up to a 5-point curve by analyzing 25 ppm and 75 ppm GMIS's against the SRM curve? We want to know if there is a way we can get started with what is available.

Answer 43- Section 2.1.3.2 of the protocol states: "The reference standards for the multipoint calibration must be diluted or undiluted SRMs, RGMs, PRMs, CRMs, NTRMs, or GMISs (see Subsection 2.1.3) or dynamically diluted pure gases." So it is acceptable to do the multipoint calibration using a combination of undiluted SRMs and undiluted GMISs as you have proposed.

Section 2.1.4.2 of the protocol states: "The multipoint calibration must consist of one or more measurements of the analyzer responses to at least five different concentrations. The use of an NIST-traceable zero air material in the calibration is recommended, but is not required (see Section 2.1.3.3)." The correct section about the zero gas is Section 2.1.3.5, which states: "Zero gas used for multipoint calibrations, zero gas checks or for dilution of any candidate or reference standard must be clean, dry, zero-grade air or nitrogen containing no detectable concentration of the pollutant of interest." These sections mean that you can do a multipoint calibration using a zero gas and four undiluted SRMs, RGMs, PRMs, CRMs, NTRMs, or GMISs. You can't do a multipoint calibration with less than five different concentrations.

Que**stion 44-** I was reviewing the EPA Protocol again this morning and found this section:

> "2.1.3.2 Reference Standards for Multipoint Calibrations—
> The reference standards for the multipoint calibration must be diluted or undiluted SRMs, RGMs, PRMs, CRMs, NTRMs, or GMISs (see Subsection 2.1.3) or dynamically diluted pure gases. Pure gases may be dynamically diluted to prepare gas mixtures for use in multipoint calibrations, but such mixtures may not be used as the reference standards for the span gas check or for the assay of the candidate standard. Pure gases may not be diluted by more than a factor of 100. Information concerning this standard (e.g., cylinder identification number, certified concentration, expanded uncertainty, certification expiration date, cylinder pressure, etc.) must be recorded in the laboratory's records."

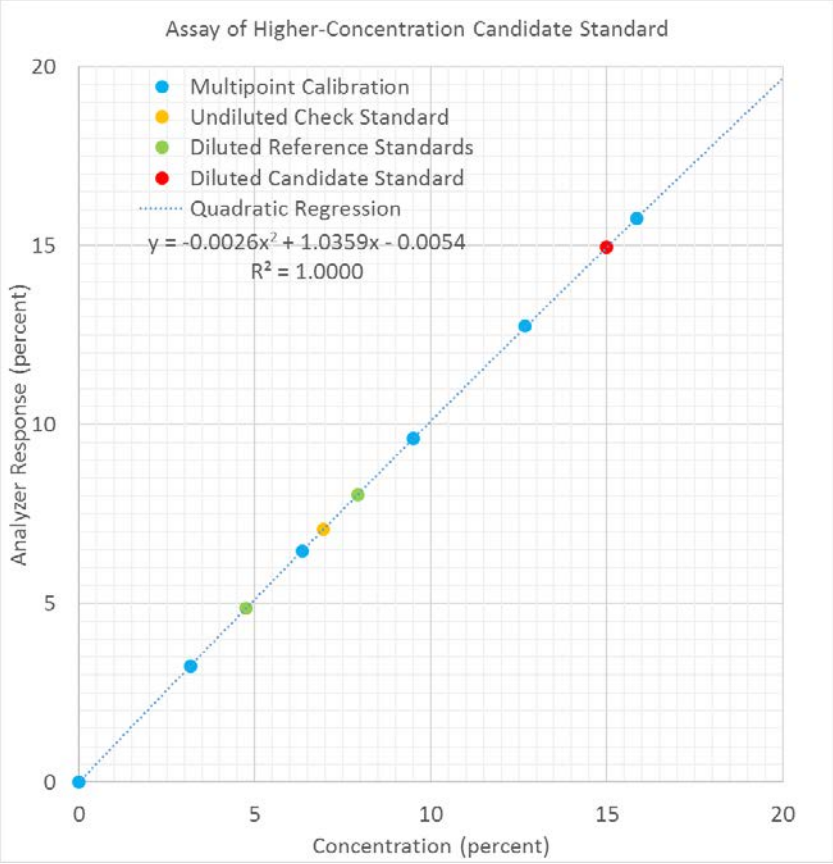
This can help us a lot for those cases where the concentration is in the percent level range and no SRM's exist (e.g. 5% methane in nitrogen). This section would allow us to linearize using pure methane and a suitable dilution system. This allows us to linearize but not for the span check or use for the assay of the candidate standard.

Question: If we use a pure gas and dilutions to linearize and do the assay on the same day of linearization must we also have an SRM, RGM, PRM, CRM, NTRM, or GMIS in the percent range (which does not exist) as a reference standard for the assay of the candidate standard?

Follow-up question: If the answer above is "Yes" – If we must have an additional standard in order to perform the assay on the same day as the linearization by dilution of a pure gas, may we use a standard developed under ISO 6143 as the standard? (FYI – We are ISO 17025 and Guide 34 accredited.)

Answer 44- I don't think that your proposed procedure will work because error of the diluted pure gas is unknown. You will need to use a NIST-traceable reference standard for the assay of high-concentration calibration gases and you cannot use the multipoint calibration of diluted pure gas as the reference standard. That being said, I'm working on another way to assay high-concentration calibration gases. I'll be writing a new procedure for the protocol. This procedure will be a modification of the G2 procedure. The attached Excel spreadsheets show where I'm going with the idea as outlined below:

1- Measure your highest-concentration NIST-traceable without dilution
2- Use a gas dilution system to dilute your highest-concentration NIST-traceable reference standard to generate a multipoint calibration curve;
3- Enter the calibration data (undiluted and diluted) in the Appendix A spreadsheet;
4- Use an undiluted check standard (also an NIST-traceable reference standard) to verify the accuracy of the multipoint calibration curve;
5- Use the same gas dilution system to dilute the highest-concentration NIST-traceable reference standard such that its analyzer response falls somewhere in the well-characterized region of the calibration curve;
6- Calculate the dilution ratio using the analyzer responses for the undiluted and diluted reference standard measurements;
7- Without altering the settings of the gas dilution system, dilute the candidate standard such that its analyzer response also falls somewhere in the well-characterized region of the calibration curve;
8- Enter the data for the diluted reference standard and the diluted candidate standard in the Appendix A spreadsheet;
9- Use the Appendix A spreadsheet to determine the concentration and uncertainty of the diluted candidate standard; and
10- Multiply the concentration and uncertainty by the dilution ratio from Step 6 to obtain the concentration and uncertainty of the undiluted candidate standard.



The beauty of this approach is that the uncertainty of the gas dilution system does not need to be considered in determining the uncertainty of the undiluted candidate standard concentration. The analyst will need to generate a real tight calibration curve so that the multiplied uncertainty doesn't get too big. Probably the concentration of the candidate standard shouldn't be too many times greater than the concentration of the reference standard. The new procedure can't be used until it's published in a new version of the protocol, but at least can see that I'm making some progress in this area. You may want to try the new procedure in the lab to see if it works for you. If you elect to do so, I'd appreciate your sharing with me the analytical results. Having real data would strengthen the case for the new procedure.