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

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, who has since retired:

> "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".

EPA's *Part 75 Emissions Monitoring Policy Manual* (see https://www.epa.gov/sites/production/files/2015-05/documents/part_75_emissions_monitoring_policy_manual.pdf) states:

> "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 an 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 data 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 https://www.nist.gov/nist-policy-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 https://www.epa.gov/airmarkets/protocol-gas-verification-program-pgvp 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 https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards

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 https://www.epa.gov/airmarkets/protocol-gas-verification-program-pgvp

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. See http://www.macpoll.eu/zero-gas

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 (https://www.epa.gov/airmarkets/protocol-gas-verification-program-pgvp) 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 https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards) 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 (see https://www.vsl.nl/sites/default/files/rtf/DoE%202016-2018%20signed%20by%20NIST%20and%20VSL_0.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 https://www3.epa.gov/ttn/emc/guidlnd/gd-022.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. https://www3.epa.gov/ttn/emc/guidlnd/gd-022.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) in the Emissions Monitoring Branch of CAMD for his 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, who has since retired, 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% CO_2/N_2 as an example; even though the top range listed in Table 2-3 is at 20%, one could use pure CO_2 dynamically diluted to 25% to extend the curve, then use 20% SRM as span gas to certify this 22% CO_2 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 CO_2 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 its 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.

Question 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.

Question 45- 1.For assay of GMISs…. If we identify and correct a specific problem with an instrument that made the third assay invalid, may we discard that third assay and perform a 4th assay after another 7 days?

Answer 45- The situation is analogous to that of a candidate standard which has been found to be unstable by TOST after two assays. The paragraph at the top of Page 24 in the protocol covers this situation:

> "If a candidate standard's concentration is not found to be stable (i.e., not within the TOST acceptance criterion), the analyst may elect to discard the candidate standard or may elect to conduct a third assay of the candidate standard to assess whether stability has been achieved. The analyst must add the additional data to the Appendix C spreadsheet. The analyst must wait an additional 7 days or more and conduct the third assay. If the data for the third assay is found to be equivalent to the data for either of the two previous assays, the candidate standard can be certified using the data from the two equivalent assays, which will be used to calculate the overall estimated concentration and the total uncertainty. Data from a nonequivalent assay should be discarded. The analyst must disqualify the candidate standard if none of the three sets of data are found to be equivalent. The analyst is expected to investigate and document the cause of the lack of agreement among the three assays and is expected to correct any problems that are discovered. Record the equivalent data and any discarded data in the laboratory's records."

If the fourth assay of the GMIS agrees with two of the three previous assays, probably the oddball assay was a blunder for some reason. Discard the data for the blunder and report the data for the three good assays. That being said, I would tear apart the assay apparatus and the experimental procedures to determine how the blunder occurred. If a blunder happens once, it may happen again if something isn't corrected.

Question 46- 2.On the bottom of Page 24, we read the following, "A value of one-half of U for the reference standard should be used in calculating U of candidate standards that are certified under this protocol (see Appendix C).". But, when we go to Spreadsheet C, cell A104, we see the following, "Expanded uncertainty (the two-sigma uncertainty) of the reference standard". Am I reading this right? Should we report U (k=2) or u (k=1) for the reference uncertainty in cell A104 of spreadsheet C?

Answer 46- Report U. The protocol should not be your only source of information regarding uncertainty calculations. NIST Technical Note 1297 (https://www.nist.gov/pml/nist-technical-note-1297) is the basis of the ISO Guide to the Expression of Uncertainty in Measurement (GUM) (See https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf), which is the international standard for metrology uncertainty calculations. There are also several text books that explain error propagation calculations. Two of these books on my bookshelf are John R. Taylor's "An Introduction to Error Analysis. The Study of Uncertainties in Physical Measurements (1997)" and Coleman and Steele's "Experimentation and Uncertainty Analysis for Engineers (1999)". I bought both books on Amazon.

You need to become familiar with the standard uncertainty (u, small u) for one measurement variable, the combined uncertainty (Uc, small U-sub-c) for multiple measurement variables, the coverage factor (k, usually equal to 2), and the expanded uncertainty (U, big U). As NIST's David Duewer et al. (2006) http://cenam.mx/memsimp06/Trabajos%20Aceptados%20para%20CD/Octubre%2027/Bloque%20E/E2-QUIMICA%20IV-Incertidumbre/E2-1.pdf state:

"Most results were derived using the propagation of uncertainty (PoU) approach recommended in the Guide to the expression of uncertainty in measurement (GUM). For the product of a series of quantities such as Result = A × B × C, the PoU model for the combined uncertainty is

$$u_c(\text{Result}) = \text{Result} \times \sqrt{\left(\frac{u(A)}{A}\right)^2 + \left(\frac{u(B)}{B}\right)^2 + \left(\frac{u(C)}{C}\right)^2}$$

"where u(A), u(B), and u(C) are the standard uncertainties for the quantities A, B, and C."

Now go back to the Appendix C spreadsheet and play around with some numbers. Then check your calculations with a calculator. For example, if your NIST reference standard has an expanded uncertainty (Urs) of +/- 1 percent and your assay of the candidate standard has a combined uncertainty (uc) of +/- 0.5 percent, then the expanded uncertainty of the certified concentration of the EPA Protocol Gas should be (calculating in relative percentages):

U = 2 x $\sqrt{}$((1 percent/2)^2 + (0.5 percent)^2)) = 2 x $\sqrt{}$ (0.5) = 2 x 0.707 = 1.4 percent, which would go on the certificate of analysis. Urs was divided by the coverage factor before it was used in the error propagation calculation.

I hope that this discussion will help you put the correct values into the Appendix C spreadsheet. Let me know if you still have questions about the uncertainty calculations. I will check Page 24 and see if the explanation of the uncertainty calculations has to be clarified. Thanks for bringing the problem to my attention.

Question 47- A specialty gas producer approached EPA with a question about assaying and certifying high-concentration EPA Protocol Gases. Its customers requested EPA Protocol Gases with concentrations that are higher than NIST reference standards. The producer proposed to use a variation of Procedure G2, which allows for dilution of reference standards and candidate standards as presented below:

> "Most importantly, the use of Procedure G2 using an ISO17025 annually certified NIST-traceable gas dilution system for analytical testing of compositions above available NTRMs. Example:
> 1) Customer orders 40% CO_2/N_2 Protocol
> 2) We monthly generate the 10+ point curve on a CO_2 NDIR covering 5% to 25% CO_2 through use of the gas dilution system and a nominal 25% CO_2/N_2 NTRM, and then drop undiluted nominal 20% CO_2/N_2 and 10% CO_2/N_2 NTRMs to validate and develop the characterization statistics,
> 3) Then dilute a 25% NTRM down to 20.0% and the candidate Protocol mix (at nominal 40% CO_2/N_2) also down to 20.0% through the gas dilution system
> 4) Run using the normal 3 triads (zero/NTRM/sample)

5) Calculate total uncertainty incorporating: measurement uncertainty, curve uncertainty, NTRM uncertainty, and dilution system uncertainty at 95% CI using propagated uncertainties

"We field a significant number of requests and orders for mixes at higher concentrations than listed in revised Table 2-3. We've produced NTRMs up to 25% CO_2/N_2, 23% O_2/N_2, 2.0% propane/N_2, 1.0% methane/N_2 to capture most requests while using Procedure G1. Plus have PRMs up to 300ppm NH_3/N_2 that permit Procedure G1."

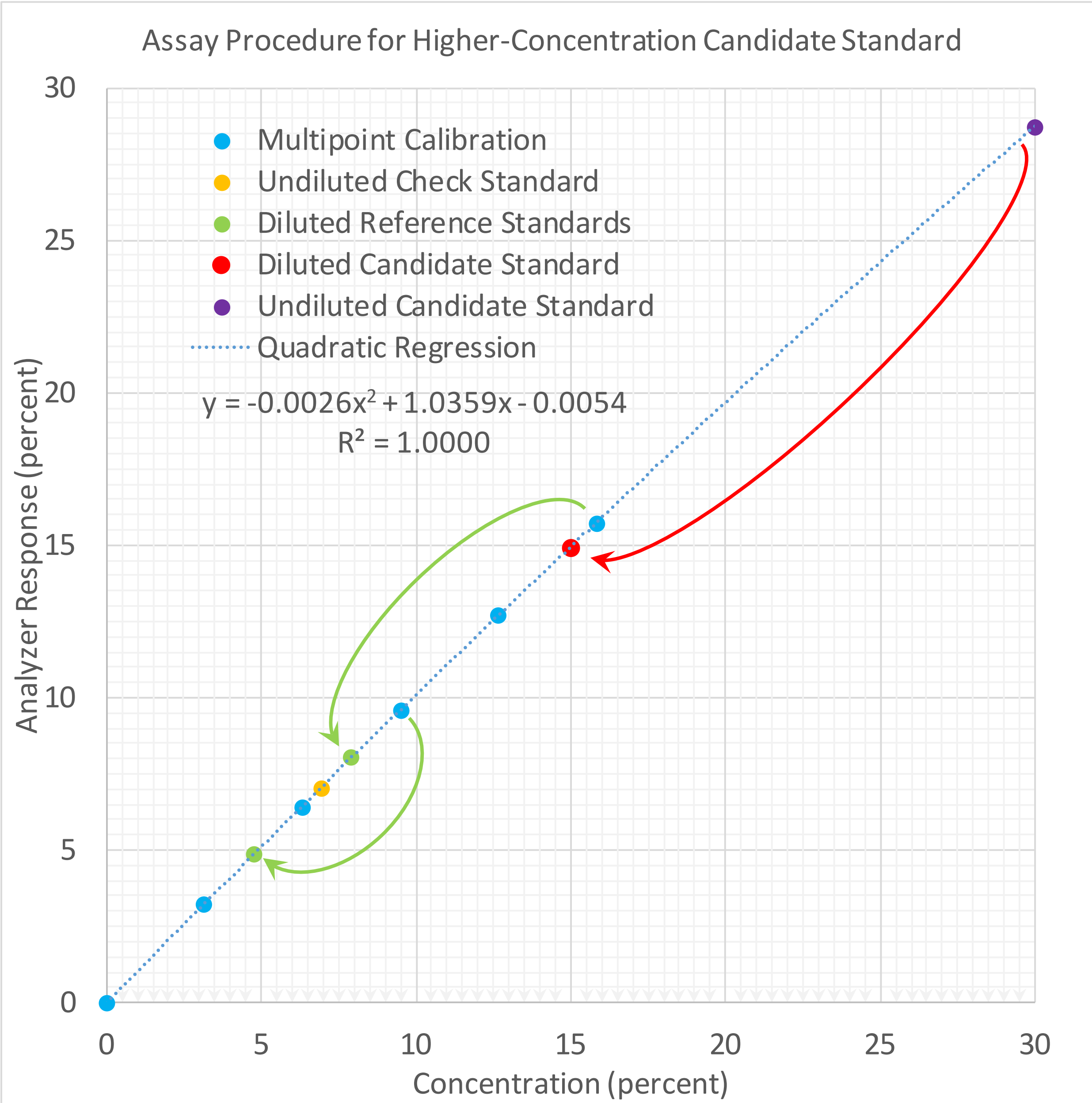
Answer 47- In response to EPA's inquiry, NIST's Frank Guenther addressed this question:

"I think the procedure is sound as long as the gas dilution system is shown to have linear dilution characteristics, and the uncertainty of the dilution is properly considered. Extending outside the validated region as outlined below, (diluting a 25% into the range thus validating the dilution, and then diluting a 40% into the range which effectively is outside the validated range) is the problematic part of the procedure. It would need proper uncertainty estimation, and perhaps a larger uncertainty. For normally stable compounds, I do not see stability issues unless it condenses at high concentrations. Some compounds, NO for instance, is less stable at high concentrations due to the complex nitrogen chemistry, so some caution and chemical knowledge is required. I would think these concentrations would be of less interest to EPA."

EPA unsuccessfully tried to develop an analytical procedure that was similar to the proposed procedure. The main difference would have been that the reference standard and the candidate standard would be diluted equally. This procedure would have been a modification of the G2 procedure as outlined below:

1- Measure your highest-concentration NIST-traceable reference standard 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 would have been that the uncertainty of the gas dilution system would not need to be considered in determining the uncertainty of the undiluted candidate standard concentration. The procedure is shown graphically below. The analyst is using 15.85- and 9.51-percent carbon dioxide reference standards to assay a 30-percent carbon dioxide candidate standard. All three standards are diluted by a factor of two to bring their diluted concentrations into the well-characterized region of the pollutant gas analyzer's quadratic calibration curve.



This proposed procedure failed to account for the fact that the physical and thermal characteristics of high-concentration carbon dioxide gas mixtures vary significantly as the concentration varies significantly. This variation has significant effects on the k-factors for mass flow controllers and viscosity effects for gas dividers, which prevent mass flow controllers and gas dividers from diluting the gas mixtures accurately.

The measurement principle for thermal mass flow controllers involves measuring the temperature difference across two temperature sensors that are mounted on a capillary equidistant upstream and downstream of a constant-power heater. When no gas is flowing through the capillary, the temperatures of the two sensors are equal. When gas is flowing, the upstream sensor will be cooler, and the downstream sensor will be warmer. For very low gas flow rates, the heat transfer equation is given by

$$QmCp = Ctemp\Delta T$$

where

Qm = mass flow rate of the gas through the capillary;
Cp = specific heat capacity of the gas at constant pressure;
$Ctemp$ = constant depending on the geometry and design of the capillary; and
ΔT = temperature difference across the two sensors.

For a specific pure gas, Qm can be determined by measuring ΔT. Different pure gases have different values of Cp at standard temperature and pressure [STP (i.e., 0°C, 1 atmosphere)]. As a consequence, a mass flow controller that is calibrated to deliver a specific mass flow rate of nitrogen will deliver another flow rate for another pure gas at the same setting. To obtain the correct flow rate, the measured value must be multiplied by the gas correction factor (or K-factor) for the pure gas, which is the ratio of the specific heats of the pure gas and nitrogen.

$$\text{Gas correction factor} = Cp(\text{pure gas})/Cp(\text{nitrogen})$$

Because most of the gas passing through a mass flow controller goes through a bypass laminar flow element rather than through the capillary, real controllers may not follow theoretical models. Gas correction factors for individual controllers may vary significantly across brands, models, devices, and flow rates. To avoid errors associated with diluting different pure gases or high-concentration gas mixtures, the user manual for the mass flow controller being used must be consulted for the device-specific gas correction factors to be used. Published gas correction factors are approximations possessing an unknown level of uncertainty. For example, gas correction factors for various gases were measured for three identical mass flow meters at The Department of Energy's Oak Ridge National Laboratory. In the case of carbon dioxide, the published gas correction factor was 0.74. The experimentally determined factors ranged between approximately 0.705 and 0.73 over flow rates between 0 and 2 liters per minute (L/min). At one flow rate, the factors for the three flowmeters ranged between approximately 0.705 and 0.725.

The measurement principle for capillary-tube gas dividers involves passing the pollutant gas and diluent gas through variable numbers of capillary tubes with identical pressure drops. Different dilution ratios are obtained by changing the numbers of capillaries passing pollutant gas and diluent gas. To a first approximation, the laminar flow through a capillary is determined by the Hagen-Poiseuille equation:

$$m = (\pi \rho r^4 (P_1 - P_2))/8\eta L$$

where

m = mass flow of a compressible fluid through the capillary;
ρ = density of the fluid;
r = radius of the capillary;
P_1 = upstream pressure;
P_2 = downstream pressure;
η = dynamic viscosity of the fluid; and
L = length of the capillary.

The flow rate of gas through a capillary is a function of the viscosity of the gas, which is a measure of the resistance of a fluid to the transport of momentum. It is a characteristic of the internal motion of individual gaseous molecules and their collisions with other molecules and the walls of the channel. The viscosities of pure gases are a function of the molecule itself, temperature, and pressure.

The flow rate must be corrected if the gas being used differs from the gas used in the calibration of the capillary. In the case of pure gases, the flow rate correction is straightforward using the Hagen-Poiseuille equation. The uncorrected flow rate through all diluent capillaries and the corrected flow rate through all pure gas capillaries yield the correct pollutant concentration (in units of percent) using the following equation:

$$\text{Concentration} = \frac{100\ (\text{corrected pollutant flow rate})}{(\text{corrected pollutant plus diluent flow rates})}$$

Different pure gases have different values of density and dynamic viscosity at normal temperature and pressure [NTP (i.e., 20°C, 1 atmosphere)].

For high-concentration gas mixtures that are diluted by capillary-tube gas dividers, obtaining the same dilution ratio may be complicated by differences in the viscosities of the reference and candidate standards. If the two standards have nearly the same concentrations, there is little need to correct the flow rates for viscosity differences. However, these differences must be considered for high-accuracy assays of standards with significantly different high concentrations. For example, EPA evaluated the characteristics of a gas divider used to generate calibration data for exhaust emission gas analyzers. Calibration curves that were generated by gravimetric calibration gases [i.e., C_3H_8 (0 to 100 ppm), CO_2 (0 to 15 percent), CO (0 to 2500 ppm), and O_2 (0 to 24 percent)] were compared with gas mixtures using the gas divider. The gas divider was found to provide acceptable results for C_3H_8 and CO. However, the viscosity of the CO_2 and O_2 at the higher concentrations affected the gas flow, which caused a 1 to 2 percent error relative to the gravimetric calibration curve.

The technical literature contains numerous publications about theoretical calculations and experimental measurements of the viscosity of gas mixtures. Various theories are used to predict the viscosities, which become more complex as one departs from room temperature and atmospheric pressure to higher levels. Considerable variation exists in the predicted values.

Question 48- I have a request from one of my customers for both carbon monoxide in nitrogen and oxygen in nitrogen EPA protocols in steel cylinders. I looked through my copy of the EPA protocol 2012 revision and didn't see any guidance regarding this. I know from personal experience we can do the oxygen ones (not that we have), but the carbon monoxide ones might be a little tricky in steel because of stability issues. Can you provide me some guidance regarding EPA protocols in steel cylinders?

Answer 48- The relevant sentence in the protocol can be found in Section 2.1.9 on Page 30:

> "In general, the certification period for standards that are contained in nonaluminum cylinders is 6 months."

If your customer can live with a 6-month certification period, you can prepare the CO in N_2 cylinder and certify it as an EPA Protocol Gas.

The late Robert Denyszyn worked for Scott Specialty Gases and later Praxair. In 1985, he got a PhD from Drexel University. His thesis, *Stability Studies of Low Part Per Million Carbon Monoxide Standards in Steel Cylinders* may be of interest to you. The abstract states:

> "This stability study was based on the potential reaction of low ppm carbon monoxide with the various oxides found on steel cylinder surfaces. Analytical and sampling methods were developed to measure the stability of low ppmv CO standards so that CO measurements at the 20 ppmv level could be made with a precision of 0.1% at the 0.95 confidence interval. To confirm the changes in CO concentration, a cryogenic sampling system was developed to concentrate the CO_2 formed during the reaction. The concentrated samples were analyzed on a GC methanization FID system. Oxygen, water and other variables which were known to play a significant role in the overall reaction were also monitored."
>
> "Carbon monoxide stability was evaluated under five different surface cylinder treatments. One treatment was found to significantly improve the stability of carbon monoxide from a batch concentration change of -1. 0% relative/year to -0.1% relative/year. Twenty-one additional CO stability experiments were performed to evaluate the influence of the three predominant iron oxides found on steel surfaces, FeO, Fe_2O_3, Fe_3O_4. At 14,000 kPa, all three oxides were also found to be active at room temperature. Oxygen was found to play a significant role in the rate of CO change. In some cases, increasing the O2 content from <0.02 ppmv to only 5 ppmv changed the rate of CO change/year by an order of magnitude. Gas phase H_2O concentration significantly decreased the reactivity of all oxides."

You be the judge, but I think that there would be fewer stability hassles if your customer used aluminum cylinders, which would have a longer certification period than steel cylinders.

Question 49- In Appendix A, we input the data for zero/span in cell C264 to F273. Shall we enter the same zero/span values in B307 to C326? The table shows it is for "Reference Standards" only. Are the assay data input to H307 to H316?

Answer 49- Section 2.2.6.4 on Page 41 of the EPA traceability protocol for gaseous calibration standards states: "The gas mixtures to be used during the zero and span gas checks need not be, but can be, the reference standards used for the assay of the candidate standard or for the multipoint calibration." The protocol gives the analyst considerable latitude in the gas mixtures that are used for the multipoint calibration, for the zero and span gas checks, and for the assay of the candidate standard. There are two purposes of the zero and span gas checks. The first purpose is to verify that the analyzer's precision is acceptable and to determine how many replicate measurements are needed during the assay of the candidate standard. The second purpose is to verify that excessive calibration drift in the analyzer has not occurred since the multipoint calibration.

The same measurements of the zero and span gases can be used for determining the estimated concentration of the candidate standards. Measurements of different zero and span gases may also be used. The analyst may chose the alternative that makes the most sense for the assay of the candidate standard. If the same measurements are used, then the values that are entered in Cells C264 to F273 should also be entered in Cells B307 to C326. Measurements of the candidate standard are entered in Cells H307 to H316.

Question 50- We have to conduct two assays for new reactive gases (SO_2, NO) and thus we have two sets of results for Appendix C. How about the non-reactive gas such as CO? From the guideline, we only need to conduct one assay for the new gas cylinder. In our old practice, we used to compare the set of assay result with the certificate from manufacturers. If so, we do not have multipoint/zero/ span data to the Appendix A and thus not able to apply the TOST method. Could you please advise?

Answer 50- In the assay of a nonreactive gas mixture that is purchased from a specialty gas producer, the producer's value for the candidate standard should not be used for determining the certified concentration of the candidate standard. I presume that the gas mixture was not purchased as an EPA Protocol Gas from the producer and that the producer did not use NIST-traceable reference standards in the assay of this gas mixture. I also presume that the producer's certificate of analysis for the gas mixture does not have a statistically-valid estimate of the uncertainty of the certified concentration of the gas mixture. If so, it would be an apples-to-oranges comparison to try to compare the producer's value to the concentration that is determined by the protocol. The former value is not traceable in a metrological sense, but the latter value is NIST-traceable traceable.

You may wish to compare the two values for informational purposes. Because you have some statistical estimates from the protocol assay, but none from the producer's assay, Student's t-test for means or TOST are not applicable. I suspect that you will want to do some statistical test having to do with conformance to specification, which is a topic that I have only limited knowledge. The simplest approach would be to see whether the producer's value falls within the expanded uncertainty of the protocol's value. If so, there's probably no problem. If no, there may be some problem with the producer's measurements, the protocol's measurements, or unexpected decay in the cylinder. I suggest that you consult with a local statistician for a more sophistical approach to address the conformance question.

Question 51- We have a low CO cylinder, approximately 100 ppb, that we just received. We were able to certify it and will use it for a CO trace audit. I looked in the green book for recert info and it has CO in air 40 to 500 ppb has TBD for cert period. Do we just say what the recert period will be in our QAPP or has there been some determination on when this low concentration cylinder needs recertified?

Answer 51- Here is the reply from the Van Swinden Laboratorium (VSL), the Dutch national metrology institute, about the appropriate certification period for sub-ppm CO in air standards. VSL is a European equivalent of NIST. They agree with NIST that a six-month certification period is most appropriate for these standards. In the future, longer certification periods may be reasonable provided better treatments or cylinder materials become available. Luxfer in England has developed a new SGS cylinder treatment that looks promising (see http://www.luxfercylinders.com/press-releases/luxfer-exclusive-sgs-aluminum-cylinder-internal-surface-for-specialty-gas-applications), but I am not aware of any long-term stability data for sub-ppm CO in air mixtures in the SGS cylinders.

Question 52- 2.On the bottom of page 24, we read the following, "A value of one-half of U for the reference standard should be used in calculating U of candidate standards that are certified under this protocol (see Appendix C).". But, when we go to Spreadsheet C, cell A104, we see the following, "Expanded uncertainty (the two-sigma uncertainty) of the reference standard". Am I reading this right? Should we report U (k=2) or u (k=1) for the reference uncertainty in cell A104 of spreadsheet C?

Answer 52- First, take a look at Appendix C on Page 139 in the protocol. The portion of the expanded unceriainty^2 (i.e., variance) due to calibration is shown as a decimal number between 0 and 1 (in this case 0.5) showing that one-half of the variance is due to the multipoint calibration. Second, take a look at Cells K234 and S234 in the spreadsheet associated with Appendix A. It's best to get an unaltered copy of the spreadsheet from the protocol's web page (https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards). These cells also show decimal numbers. One or another of these numbers is reproduced in Cell D 251 as a percentage. Third, take a look at Cells A14, A21, and A29 in the spreadsheet associated with Appendix C. Again, the portion of the expanded unceriainty2 due to calibration is represented as a decimal number (in this case 0.5 again).

So the units to use in Cells A14, A21, and A29 are not in the same units as the measurand because they are not associated with the assay of the candidate standard. Rather, they are associated with the uncertainty of the linear regression parameters arising from the multipoint calibration(s). If you are trying to assess the stability of a candidate standard from two assays that were made within the same multipoint calibration, you don't have to take the uncertainty associated with the multipoint calibration into consideration. However, if the two assays were made during separate multipoint calibrations, then the calibration uncertainty has to be taken into consideration. The portion of expanded uncertainty associated with calibration is used in the former case, but not in the latter case. That is the reason why you have to input the dates of the multipoint calibration in the Appendix C spreadsheet. If the expanded uncertainties are small, the dates of the multipoint calibration won't be much of a factor in determining whether the candidate standard is stable. However, if the expanded uncertainties are larger the dates of the calibration may be a deciding factor in the stability determination.

Question 53- 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 N.I.S.T., 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 53- 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.

Question 54- I am getting requests for HCl mixes as EPA Protocols. I am sure this is related to the issuance of EPA's PS-18. I am not sure how to respond. HCl mixes appeared in the 2014 Letter of Equivalency in the 10-300 ppm range from VSL. However, the relative difference was +/- 5%. I assume that this is the accuracy of the primary standard from VSL. If we were to use that standard per G1 methodology there is no way to satisfy the 2% maximum expanded uncertainty requirement in the

Protocol. So am I correct in thinking that we cannot certify as EPA Protocol? I want to be clear on this issue before I respond to my customers.

Answer 54- I just spoke with Ray Merrill (919-541-5225, merrill.raymond@epa.gov) of EPA's Office of Air Quality Planning and Standards. He suggested that you check https://www3.epa.gov/ttn/emc/approalt.html for (ALT-114) *Approval of Alternative Method for Preparation of HCl Gas Standards for PS 18 and Procedure 6*, which I have also attached. This alternative method will allow you prepare and certify alternative HCl calibration gases until such time as NIST-traceable reference standards become available and HCl EPA Protocol Gases can be assayed and certified. After reading these documents, contact Ray Merrill if you have further questions about the alternative HCl calibration gases.

Question 55- I'm building a EPA spreadsheet for a mix that I'm trying to produce and on my TOST page it says "Case 18", what does that mean? I have also seen "Case 12" what does that mean?

Answer 55- When you are doing the TOST calculations in Appendix C of the EPA traceability protocol, you must properly handle the uncertainty associated with the assay itself and the uncertainty associated with the corresponding multipoint calibration. If two assays of a candidate standard are performed under the same calibration, you don't have to double-count that portion of both expanded uncertaintyies[2] that is due to the same calibration. However, if the two assays have two different calibrations, you do have to consider those portions of both expanded uncertaintyies[2] that are due to the different calibrations. Appendix C determines which case applies depending on the dates that are entered in Cells A15, A23, and A31. The case that is shown in Cell G69 tells you which situation exists for the data that you have entered in Cells A11 through A31. If you go to Page 140 of the protocol, you will see the following table of the various possible combinations of assays and calibrations:

Case		Cal. No.	Cal. No.	Cal. No.
4*	=	1	1	---
6*	=	1	2	---
9	=	1	1	1
12	=	1	1	2
15	=	1	2	2
18	=	1	2	3

So Case 18 means that each of the three assays is associated with a different calibration. Case 12 means that the first two assays are associated with the same calibration and the third assay is associated with a different calibration. This Excel spreadsheet was put together by a PhD statistician who is cleverer than me in statistical bookkeeping and who deserves all the credit for making the spreadsheet simple enough for non-statisticians like the two of us to use and to get the correct uncertainty estimates.

Question 56- One of our cement kiln customers has requested the same 14 ppm ammonia, balance N_2 EPA Protocol Gas, but this time he wants an SF_6 tracer added. My question to you is whether a standard protocol made using a NIST standard remains a protocol if you add something for which there is no NIST standard.

Answer 56- Your basic question is whether an EPA Protocol Gas can contain a noncertified component. I think so. It strikes me that this situation is the same as a NIST NO_X SRM 2660a for which the NO_2 concentration is provided for informational purposes only, not as a NIST-certified value. One question that still nags me is the possibility that the SF_6 component might interfere with the ammonia measurement. If you are using FTIR to measure ammonia, be sure that the SF_6 infrared absorption peaks don't overlap with the NH_3 peaks. If you do have more information about your customer's application, I think that the EPA regulatory folks would appreciate learning whether the NH_3 and SF_6 measurements are being required by a state or local air pollution control agency.

Question 57- I downloaded the Appendix A spreadsheet from the protocol web site. However, the 1997 version of the protocol is cited in its reference section. Is this citation correct?

Answer 57- You have sharp eyes to have noticed this minor error in the Appendix A spreadsheet, which was originally constructed for the 1997 version of the EPA traceability protocol. The spreadsheet was slightly modified by a statistician for the 2012 version of the protocol, but we did not notice that the now-obsolete reference citation was retained. The citation should have been changed to the 2012 version of the protocol at that time. The Appendix A spreadsheet as is found on the protocol website is correct and can be used to calculate the certified concentrations of candidate standards. At some point, I will need to fix this error. Thank you for pointing it out to me.

Question 58- I have a question regarding assaying a previously-certified GMIS on a different day from that of the initial multipoint calibration. Step 6 of the Appendix A spreadsheet deals with the expanded uncertainty of the estimated concentration. There are lower and upper limits for the uncertainty. Does the previously-certified value of my GMIS have to fit in between these limits?

Answer 58- The estimated concentration of the candidate standard (Cell B333 in the Appendix A spreadsheet) does not have to match the previously-certified value of the GMIS. This value always will, by definition, lay within lower and upper limits for the expanded uncertainty (Cells B340 and C340). I suspect what you are doing is remeasuring your GMIS to confirm that its just-assayed value matches the originally-certified value of the GMIS. That's a good thing and confirms that your measurement system is under control. In essence, what you are doing is a recertification of your GMIS whether or not the GMIS is out of its certification period. The relevant section of the traceability protocol is Section 2.1.11 (on Page 32 of the protocol), which covers the recertification of standards. This section states:

"Use the spreadsheet described in Appendix C (or an EPA-approved equivalent statistical technique) to compare the measured concentrations from the recertification assay with the measured concentrations from the previous assays. If the TOST acceptance criterion is attained, the standard can be recertified. The recertification period is the same as that given in Table 2-3. If the measured concentrations are shown to be not equivalent, the standard must undergo a full certification (e.g., Procedure G1) before it can be used again."

I would not use the Appendix A spreadsheet to verify the concentration of your GMIS. Use the Appendix C spreadsheet for this purpose.

Question 59- Recently, we are getting many requests for nitric oxide and nitrogen dioxide at certified concentrations in the same mix per the EPA Protocol. We have always had a policy of not mixing those two species in the same mix. My first question is, "does the Protocol allow this"? And second, "what are your thoughts on this combination as relates to stability and shelf life"?

Answer 59- Dave Worton of the National Physical Laboratory (NPL), which is NIST's equivalent in the United Kingdom, addressed this question:

> "I oversee our reference materials of NO and NO_2 and am currently coordinating a large consortium project to improve the underpinning metrology for ambient measurements of nitrogen dioxide, for more information see http://empir.npl.co.uk/metno2/.
>
> "Due to the reactivity of NO_2, we prepare our NO_2 primary reference materials (PRMs) from NO and reaction with O_2 in cylinder at high amount fractions to form NO_2 (as opposed to starting with pure NO_2) which we then dilute to lower amount fractions. This reaction ($2NO+O_2 \leftrightarrow 2NO_2$) is reversible so to drive the equilibrium towards NO_2 providing the required stability we maintain an excess of O_2, typically more than 1000 umol/mol, in our NO_2 PRMs making them incompatible with the presence of additional NO. As a result, we do not provide PRMs that contain both NO and NO_2 and therefore provide NO PRMs in N_2 and NO_2 PRMS in N_2 or air.

"Our experience based on a previous project (CERMATAIR 2001-2004, https://cordis.europa.eu/project/rcn/58201_en.html) some years ago discussed preparing high pressure cylinders containing 300 nmol/mol (ppb) of NO and 100 nmol/mol of NO_2 in a balance of N_2. A provisional aim was to see if the amount fraction would at least stabilize enough to be useful for field checks. However, there were reportedly difficulties in the initial preparation but eventually 6 mixtures were prepared but further analyses revealed that these mixtures were unstable. The results indicated that there were substantial and variable losses of NO_2 within the cylinders, which would be consist with our current understanding of the need for excess O2 to ensure stability for NO_2.

"Additionally, previously (producer name deleted) offered NO/NO_2 mixtures for sale and colleagues had attempted to purchase them. However, those cylinders never passed the internal stability testing and were thus never delivered."

Given that the concentrations are quite low and given that the work was done in 2002-2003, I can't completely slam the door shut on preparing EPA Protocol Gases containing NO and NO_2. However, I would remain skeptical in the absence of newer data showing that such mixtures are stable, particularly at higher concentrations. The burden of proof would be on specialty gas producers to demonstrate that such mixtures could be assayed accurately and that they remain stable in the long term.

I suggest that you take two steps that you can take that could help to clarify the situation. First, contact your customers to see if their end users' regulatory counterparts are willing to accept environmental monitoring data from analyzers that were calibrated with such calibration gases. If the end users are just trying to save money by obtaining multi-component calibration gases, they may wiser to purchase multiple binary mixtures. If the end users believe that their governmental regulators will accept NO/NO_2/N_2 calibration gases, sell them certified standards that are not EPA Protocol Gases. Tell your customers that EPA does not have confidence in such mixtures based on currently available information.

Second, if you really believe that there is a market for such multi-component calibration standards, prepare several in-house standards and study their long-term stability. I have heard that NO_2 gas mixtures are stable in Luxfer SGS cylinders for VSL. If these standards can be shown to be stable for a reasonable period of time, I would be happy alter the protocol to allow such gas mixtures. In the past, EPA has followed NIST's practice regarding the certification periods for EPA Protocol Gases because EPA doesn't have the facilities to do such stability studies itself. This case is analogous to the situation with NO_2 EPA Protocol Gases for which EPA is seeking long-term stability data.

Question 60- I have a question about the use of interference corrections for analysis of a multi-component EPA Protocol Gas. Could you define what a "statistician" is in Section 2.1.5.3 of the protocol?

Answer 60- Over the 25-odd years during which I have been involved with the EPA traceability protocol for gaseous calibration standards, I have had the privilege to work with several PhD statisticians with degrees from North Carolina State University and the University of North Carolina at Chapel Hill. They possess the statistical skills that were needed to construct and modify the Excel spreadsheets that are used to calculate the certified concentrations and expanded uncertainties of gas mixtures that are assayed and certified under the protocol. Their abilities far exceed my meager statistical skills.

Perhaps the best way to assess the statistical skills that are needed is to review the Excel spreadsheets that are used with the protocol. See https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards. Whoever is going to construct the interference correction equation should have sufficient statistical skills to understand the uncertainty calculations that are performed in these spreadsheets. More complicated calculations are needed for the interference correction calculations. Whereas the existing spreadsheets use bivariant regression analysis of pollutant concentration versus analyzer response, multivariant regression analysis of pollutant concentration versus analyzer response versus interferent concentration would be needed for the interferent correction calculations. The uncertainty that is associated with the interferent correction must be added to the uncertainties of the assay itself, of the multipoint calibration, and of the reference standards. That uncertainty may change with pollutant concentration and with interferent concentration. Some experimental design work will be needed to determine the proper number and concentration ranges for the pollutant and interference measurements that are needed to keep the added uncertainty within acceptable limits.

To make things even more complicated, one also needs to consider the statistical software that would be involved in the interference correction calculations. Proper statisticians prefer to use proper statistical software like R. However, mastering and using such sophisticated software for routine production analysis may be beyond the computing and data handling capabilities of most specialty gas producers. EPA made the decision a long time ago to use Excel to perform the statistical calculations that are associated with the protocol because Excel is a software package for which a producer could be reasonably expected to have some mastery. I am ever grateful that the statisticians were willing to humor me and to get their hands dirty by using Excel. Excel has a number of problems with doing statistical calculations correctly and gets by with approximations that generally doesn't cause problems, but may do so for low-uncertainty calculations such as are used for the protocol. I expect that the integration of the interference correction calculations with the existing protocol uncertainty calculations will not be a trivial exercise.

All this long discussion is meant to convey to you that (producer name deleted) would need a high level of statistical talent to implement the interference correction calculations in a production environment. It certainly can be done, but it won't be easy or cheap

Question 61- We are in the process of acquiring a new SRM to replace the one that we could not receive an extended shelf life from NIST. I was wondering what we need to do with our GMISs that we certified using this SRM. Are they still good to use because we need to reference the expiration date of the SRM that we used to certified them?

Answer 61- Section 2.1.3.1 of the EPA traceability protocol covers gas manufacturer's intermediate standards (GMISs) and Section 2.1.11 covers the recertification of standards. Your GMIS is OK to use to the end of its original certification period regardless of whether the reference standard that was used in its assay is still in its certification period. At the end of the GMIS' certification period, it can be recertified using your new SRM as the reference standard. The results of the GMIS' recertification assay should be compared to the results of its original assay. If Schuirmann's two one-sided test (TOST) show that the estimated concentrations from the two assays differ by less than 1.0 percent, the GMIS can be recertified for the same period as its original certification. If the TOST acceptance criterion is not attained, a second recertification assay may be conducted to establish the new concentration for the GMIS. Hopefully, a second recertification assay would not be needed.

Your question is not off-the-wall. Recently, I fielded a question from (user name deleted) concerning a multi-component EPA Protocol Gas' certificate of analysis that listed an in-certification propane GMIS and an out-of-certification propane SRM. This certificate listed the concentrations and the expiration dates for the GMISs that were used for the EPA Protocol Gas' assay and for the SRMs that were used in the GMIS assay. I explained that this calibration standard was OK because the propane assay was performed with an in-certification reference standard. Perhaps, the certificate could have more explicitly identified which reference standards were used for the assay of the EPA Protocol Gas and which were used for the assay of the GMISs. The end user would then have a clearer picture of the traceability chain from NIST to their calibration standard.

Question 62- I have a question with G1 vs G2 and labeling. Let say I have a mix that has two components, one component I do by G1 analysis and the other by G2 analysis. On my COA and label I already have a statement that says "analysis preformed in accordance with G1 or G2 analysis of the EPA…." Do I need to specifically state which component I did by G1 and what component I did by G2?

Answer 62- It's OK to put "Analysis was performed in accordance with Procedure G1 or G2 of the EPA Traceability Protocol for Gaseous Calibration Standards" on the certification documentation. The fact that the assay was performed according to the protocol is more important than the specific procedure that was used. EPA monitoring regulations specify that calibration gases be traceable to NIST or be EPA Protocol Gases, but they do not mention the assay procedures.

Question 63- I am looking into the options for recertifying EPA Protocol Gases that have expired in our inventory. Instead of sending them back to the manufacturer and paying about the same cost as a new to recertify, I want to take advantage of (name deleted) in-house FTIRs to potentially recertify our recently expired gases.

Is it acceptable to reference the EPA Traceability Protocol document Section 2.1.11 to perform the recertification process using the Appendix B spreadsheet and include a copy of the spreadsheet (assuming it meets criteria) in an emissions test report with the original "expired" gas certificate? Is this satisfactory for a source emissions test report?

If there is some other alternative to sending the gas back to the original manufacturer for recertification, can you please point me in the right direction? As I mentioned, (name deleted) has several in-house FTIR analyzers and hundreds of EPA Protocol Gases to reference in house. I am sure we can follow the technical aspects of the procedures. I just want to make sure that it will be acceptable in the eyes of EPA.

Answer 63- The EPA traceability protocol is a general analytical procedure that any competent laboratory can use to assay and certify gaseous calibration standards as being traceable to NIST reference standards. If your laboratory has the appropriate analytical instrumentation (such as FTIRs), it is theoretically possible to recertify expired EPA Protocol Gases. However, the key to the recertification assay is having the NIST-certified reference standards (see Section 2.1.3) or gas manufacturers intermediate standards [GMISs (see Section 2.1.3.1)] on hand to serve as the analytical reference standards for the assay. Other EPA Protocol Gases cannot serve as the analytical reference standards for the recertification assay. As stated at the beginning of Section 2.1.3, "The EPA monitoring regulations define a "traceable" standard as one that has been compared and certified, either directly or via not more than one intermediate standard, to a primary standard such as an SRM or a Certified Reference Materials (CRM)". Because each link in a calibration chain adds more uncertainty to the certified value of the last standard in the chain, the chain must be kept as short as possible relative to the uncertainty requirements of the measurement being calibrated.

NIST-certified reference standards are very expensive and are in high demand when they are even available for sale from NIST. Specialty gas producers prepare batches of NIST-Traceable Reference Materials (NTRMs), which are then assayed and certified by NIST as a means of increasing the availability of NIST-certified reference standards (see https://www.nist.gov/programs-projects/nist-traceable-reference-material-program-gas-standards). Even NTRMs are closely guarded by their producers and are unavailable for sale (to the best of my knowledge).

In my estimation, sending your EPA Protocol Gases back to their original producer is probably the cheapest way to get them recertified. I have no doubts that your laboratory would have the technical capability to perform the recertification assay. The trick is having the analytical reference standards to perform the assay.

Question 64- Can a specialty gas company use the EPA Protocol, Section 2.4 to produce air and use suitable detector tubes to certify that the SO_2 and NOx is below 0.1 ppm? If so, do they really need calibration gases for the SO_2 and NOx?

Answer 64- The acid rain monitoring regulations in Section 5.1.6 of Appendix A of 40 CFR Part 75 state:

> "5.1.6 Zero Air Material. Zero air material is defined in § 72.2 of this chapter."

Section 72.2 (Definitions) of 40 CFR Part 72 states:

> "Zero air material means either:

(1) A calibration gas certified by the gas vendor not to contain concentrations of SO2, NOX, or total hydrocarbons above 0.1 parts per million (ppm), a concentration of CO above 1 ppm, or a concentration of CO2 above 400 ppm;
(2) Ambient air conditioned and purified by a CEMS for which the CEMS manufacturer or vendor certifies that the particular CEMS model produces conditioned gas that does not contain concentrations of SO2, NOX, or total hydrocarbons above 0.1 ppm, a concentration of CO above 1 ppm, or a concentration of CO2 above 400 ppm;
(3) For dilution-type CEMS, conditioned and purified ambient air provided by a conditioning system concurrently supplying dilution air to the CEMS; or
(4) A multicomponent mixture certified by the supplier of the mixture that the concentration of the component being zeroed is less than or equal to the applicable concentration specified in paragraph (1) of this definition, and that the mixture's other components do not interfere with the CEM readings."

See also Questions 9.1 and 9.31 of EPA's Part 75 Emissions Monitoring Policy Manual: https://www.epa.gov/sites/production/files/2019-10/documents/part_75_emissions_monitoring_policy_manual_10-18-2019.pdf

There is no requirement in these regulations that the zero air material must be assayed and certified according to the EPA traceability protocol. Specialty gas producers do not appear to have to do very much at all to produce an acceptable zero air material as far as 40 CFR Part 75 is concerned. Your idea to use SO_2 and NOx detector tubes to assay zero air materials seems to be fairly reasonable given the modest requirements of Section 72.2. However, the total hydrocarbons, CO, and CO_2 concentrations in the zero gas would also have to be measured.

Back in 2012, I wrote Procedure G3 of the protocol in anticipation that NIST would be producing zero air Standard Reference Materials (SRMs) and that there would be some regulatory demand for NIST-traceable zero air materials. NIST has never produced a zero air SRM, no regulatory demand emerged, and Procedure G3 has never been used to my knowledge. Lacking a NIST-traceable zero air reference standard, there is no current way to assay and certify zero air EPA Protocol Gases.

NIST's European counterparts are working on standards for zero gas (see https://www.macpoll.eu/zero-gas). This information may not be of any direct help to you, but it may give you some idea about the current state of zero gas technology. If NIST and the European national metrology institutes (like VSL) ever include zero gas under a declaration of equivalence (DoE), then there would be a pathway for assaying and certifying zero gas EPA Protocol Gases.

Question 65- I get frequent calls from labs asking me what is required to produce both zero air and zero grade nitrogen and specifically ask about "CEMs Grade" nitrogen or air. Section 2.4 addresses the procedure's for producing "Zero Air Materials". The text is vague in my opinion as it raises a few questions for clarification.

1) Does the Document term "Zero Air Materials" become synonymous with what the regulated industry refers to as "CEMs Grade"?
2) Is the regulated industry required to procure these materials from PGVP vendors?
3) Must the products be labeled as "EPA Protocol Zero Air Materials"?

There are many non-PGVP producers simply selling UHP nitrogen and standard grades of Zero Air into the regulated industry. As a point of SOPs at (name deleted), when our customers ask for CEMs Grade nitrogen or air, we certify the gases to meet the requirements of 40CFR 1065 750. These requirements were designed to meet vehicle emission standards, but seem to best represent the criteria for NIST Traceability for zero gases. I value your opinion and interpretation on these issues and will welcome your reply.

Answer 65- Procedure G3 of the protocol has been a disappointment to me because It never got off the ground. I've always seen the EPA traceability protocol as being one leg of a three-legged stool to generate NIST-traceable calibration gases. The other two legs are the availability of NIST reference standards and the existence of EPA regulatory drivers to require the use of NIST-traceable calibration gases. Neither of these two other legs currently exist. Back in 2012 when I was revising the protocol, Frank Guenther of NIST made some noises about preparing NIST zero air, but nothing ever came of it. The EPA regulations for the Acid Rain Program (40 CFR Part 75) never required that the zero air be NIST traceable. The attached definition of "zero air material" in 40 CFR Part 72.2 states:

> "Zero air material means either:
> (1) A calibration gas certified by the gas vendor not to contain concentrations of SO2, NOX, or total hydrocarbons above 0.1 parts per million (ppm), a concentration of CO above 1 ppm, or a concentration of CO2 above 400 ppm;
> (2) Ambient air conditioned and purified by a CEMS for which the CEMS manufacturer or vendor certifies that the particular CEMS model produces conditioned gas that does not contain concentrations of SO2, NOX, or total hydrocarbons above 0.1 ppm, a concentration of CO above 1 ppm, or a concentration of CO2 above 400 ppm;
> (3) For dilution-type CEMS, conditioned and purified ambient air provided by a conditioning system concurrently supplying dilution air to the CEMS; or
> (4) A multicomponent mixture certified by the supplier of the mixture that the concentration of the component being zeroed is less than or equal to the applicable concentration specified in paragraph (1) of this definition, and that the mixture's other components do not interfere with the CEM readings."

No one is forcing end users to buy NIST-traceable zero air, which would most likely cost more than vendor-certified zero air. Producers can sell self-certified products with their own specifications.

The situation is different in Europe, where there is an ongoing effort to produce zero gas that is traceable to national metrology institutes and where European monitoring directives require the use of such zero gas. See https://www.macpoll.eu/zero-gas. Your best point-of-contact is Annarita Baldan of VSL in the Netherlands (abaldan@vsl.nl).

To directly answer your questions:

1) "Zero air material" is air that has been certified by its producer to meet the requirements of 40 CFR Part 72.2;
2) The regulated industry is not required to procure these materials from PGVP vendors; and
3) There is no current way to produce "EPA protocol zero air materials" until such point that NIST or VSL start to sell zero air reference standards that producers can use to assay the zero air that they would sell to end users.

If your customers are selling zero gas for mobile source testing applications, I suggest that you continue to reference 40 CFR Part 1065.750. However, if they have ambient air or stationary source applications, I suggest that you reference 40 CFR Part 72.2 because this regulation is probably more familiar to them.

Question 66- I have a customer inquiring about EPA Protocol sulfur dioxide balance air. I see in the protocol itself it talks about balance nitrogen and not air, is this something that hasn't come up much and that is why it isn't mentioned in the protocol? The mix is definitely in my wheelhouse for testing, but just wondering why SO_2 balance air doesn't have certification period.

Answer 66- At long last, I can now respond to your request for information about the appropriate certification period for EPA Protocol Gases containing sulfur dioxide in air. I consulted a number of international metrology organizations for any information that they could share about the long-term stability of these gas mixtures. I did receive responses from them, which I will summarize below. Unfortunately, I received only anecdotal stability data and no information about appropriate cylinder passivation techniques. Based on the limited information that is available, I am reluctant to make a pronouncement about a reasonable certification period for these gas mixtures until (name deleted) or another specialty gas producer develops its own stability data that can be shared with EPA.

The first piece of information comes from a 2004 international key comparison among national metrology institutes (NMIs) (see https://www.bipm.org/utils/common/pdf/final_reports/QM/K26/CCQM-K26.b.pdf). Thirteen travelling standards containing approximately 280 ppb of sulfur dioxide in air were analyzed by the NMIs. The standards were obtained from BOC Gases and were contained in their Spectra-Seal cylinders. The coordinating laboratory was the National Physical Laboratory (NPL) in the United Kingdom (UK). Concentration drift was seen in the standards. The median drift corresponds to a decay of 2.2 percent over 6 months (see Page 5 of report).

I next contacted NPL for any additional stability data that it might have and received the following response from NPL's Nick Allen (nick.allen@npl.co.uk):

> "I am pleased to be able to inform you that NPL now has Declaration of Equivalence following on from the memorandum of cooperation with NIST which would cover sulphur dioxide mixtures. We are currently coordinating a CCQM key comparison for 300 nmol mol-1 of sulphur dioxide in an air matrix, which will assess the global state of the art and provide additional stability data. For this comparison we are also trialling a new type of cylinder with a different passivation."
>
> "At NPL we can provide mixtures from 100 – 1000 nmol/mol with a stability of greater than two years above 200 nmol/mol or a stability of greater than three years above 300 nmol/mol (depending on the uncertainty required).
>
> "If you are interested in discussing this further or would like to hear more about NPL's sulphur dioxide mixtures then I am happy to provide further information."

In "A high accuracy dilution system for generating low concentration reference standards of reactive gases" (see *Measurement*, Volume 47, January 2014, Pages 607-612), NPL's Paul Brewer *et al.* state that "the rate of change in amount fraction for each of the mixtures is similar, with gradients ranging from -0.0006 to -0.0117 nmol per mol per day". My own regression calculations indicate that the SO_2 concentrations decayed between 0.03 and 0.62 percent over 6 months, which is less that that seen in the 2004 key comparison. Note that I haven't seen a Declaration of Equivalence (DoE) between NPL and NIST and expect that one is planned (see https://www-new.npl.co.uk/getattachment/products-services/Gas/NPL-NIST-MOC.pdf?lang=en-GB).

I tried to get information from BOC, whose webpage stated: "Parts per billion mixtures of sulphur dioxide in air are now routine and parts per trillion mixtures of some components have been developed". BOC's Andrew Deighton (Andrew.Deighton@boc.com) provided the following response:

> "Many thanks for your enquiry regarding SO_2 in air mixtures. We have been manufacturing ppb level SO_2 in air mixtures in the UK for many years, with a 450-ppb mixture being a UK standard product for the ambient air monitoring sector. Our version of this mixture comes with a 36-month shelf life, which is obtainable due to our patented Spectra-Seal process. The 36-month shelf life is not typically available market wide, as our competition tend to have shorter shelf life based on their different passivation techniques.
>
> "Unfortunately, the Spectra-Seal IP is confidential, so there isn't any data we can share at this time. Presumably what can be achieved in the US will depend on the passivation technologies in use by US gas suppliers and the stability these can provide at low SO_2 levels in air."

I then contacted Ricardo Energy & Environment, which provides quality assurance support for the UK's Automatic Urban and Rural Network (AURN) (see https://ee.ricardo.com/air-quality/case-studies/aurn), including certifying AURN calibration gas mixtures. Ricardo's Stewart Eaton (Stewart.Eaton@ricardo.com) provided the following response:

> "Yes-we have quite a bit of data on SO_2 cylinder stability. I'm not sure how best to collate it, but we have two sources of such information:

> "1. A quality control cylinder, analysed every time we calibrate cylinders for the AURN. This gives regular measurements over a period of a few years
> 2. Concentration checks of site cylinders, giving a six-monthly value over the life of the gas mixture. This will have a higher uncertainty but gives a very useful check of the accuracy of the analyser calibrations.
>
> "I attach the spreadsheets of the last two QC cylinders, the first D337164 is notionally 150ppb, and the second 108007 450ppb. There are step changes when we start using a new reference cylinder, calibrated by NPL. While D337164 seems acceptably stable, we got higher numbers of outliers at intercalibration exercises on the AURN, so we switched to 450ppb.
>
> "Cylinder 107585 was at the Marylebone Road monitoring site in London from mid-2014 to late 2019, and the concentration was reassessed against freshly calibrated audit cylinders every 6 months. I attach the results from that cylinder. It appears our uncertainty on this check is typically 3-5%, although this is not part of our ISO17025 accreditation. There are a couple of missing results where the audit result was not reliable due to site issues.
>
> "All these cylinders are commercially obtained from Air Liquide, calibrated against NPL calibrated gas mixtures of typical uncertainty ±2% I have no knowledge of their cylinder preparation methods. We have certainly seen a few unstable mixtures over the years. In the last year we have switched to BOC for our AURN and QC cylinders, and Air Products for the reference cylinder; we have no useful stability data on these at present."

AURN's 150-ppb QC cylinder D337164 does not show SO_2 decay, but it shows a lot of scatter. I don't think that these data are as good as Brewer's regarding stability. I did not receive any data for the 450-ppb QC cylinder108007.

The final piece of information about the stability of sulfur dioxide in air mixtures came from Annarita Baldan (a.baldan@vsl.nl) of VSL, which is the Dutch NMI equivalent to NIST. Her reply is interleaved with my questions as follow:

> Baldan: "I have consulted my colleagues, specialist in production of sulfur dioxide reference standards and I will now try to answer your questions. For your information, note that sulfur in air mixtures were also included in the previous DoE for the same range."
>
> Wright: "First, do your two organizations believe that stable gas mixtures can be prepared by American producers using aluminum cylinders that have been passivated by their normal passivation techniques? Alternatively, are special passivation techniques needed for sulfur dioxide in air mixtures?"
>
> Baldan: "We have no knowledge of the passivation techniques for aluminum cylinders used by American gas producers, so we cannot make assumptions. VSL uses for the production of sulfur dioxide primary standards a special passivation treatment which improve the stability of the gas mixtures (within the stated uncertainties)."
>
> Wright: "Second, what would be an appropriate certification period for such EPA Protocol Gases? VSL's current catalog of primary gas standards shows a stability period of 18 months for 10 umol/mol mixtures, 2 to 3 years for 11 to 100 umol/mol mixtures, 3 years for 101 to 1000 umol/mol mixtures, and 4 years for 0.11 to 1 percent mol/mol mixtures. Are these certification periods reasonable for commercially-produced EPA Protocol Gases or should different periods be specified? As the following message from BOC-UK indicates, their certification period is 36 months for 450 nmol/mol mixtures, which is longer than VSL's period for a PRM that has a 20 times greater concentration. Unfortunately, BOC-UK would not provide any technical data to support their certification period."

> Baldan: "Again, we cannot suggest or advice on an appropriate certification period for the sulfur dioxide in air under the EPA Protocol Gases. Being our preparation method based on gravimetry, we must guarantee that the gravimetric value remains stable along the certified period. Our research results have shown that the stability of gas mixtures at nmol/mol level are strongly depending on the quality of the cylinder batch. We see great variations from batch to batch and even within the same batch. For this reason, our PRMs are sold starting µmol/mol and preferably from 10 µmol/mol. Commercial gas producers use a certified analytical value. This may help improving the certification period, being the largest losses of sulfur dioxide in the first period after preparation."
>
> Wright: "Third, do you know what analytical reference standards that BOC-UK uses to assay their sulfur dioxide in air mixtures? Are NPL gas reference materials now (or will be) recognized as equivalent to NIST reference standards? See attached Memorandum of cooperation. NPL's catalog includes 50 nmol/mol to 10 mmol/mol mixtures containing sulphur dioxide in nitrogen or air (see https://www.npl.co.uk/products-services/gas/air-quality-monitoring)."
>
> Baldan: "We are not informed of the activities carried out under the NIST-NPL cooperation."
>
> Wright: I believe that US EPA will need to explicitly allow sulfur dioxide in air EPA Protocol Gases under the traceability protocol and the new DoE. By doing so, a reasonable certification period for these mixtures can be specified in the protocol (rather than letting producers choose whatever they wish). I'm just at a loss to know what to specify. I would appreciate whatever advice and/or stability data that you could provide."
>
> Baldan: "As stated above, VSL cannot recommend a certification period for sulfur in air reference standards. This is much depending on the passivation technology used by specialty gas producers."

I hope that this long discussion demonstrates that I have taken your question seriously and that the certification period for sulfur dioxide in air mixtures is still a hard question to answer. The big question is finding the passivation techniques that are needed to attain acceptable stability.

Question 67- I have a question related to the Green Book (EPA Traceability Protocol for Gaseous Calibration Standards). In order to recertify an EPA Protocol #1 dual blend cylinder (i.e. NO_X ~2.5 ppm/ CO 5.0 ppm) is there a limitation on the amount the NO_2 may change from the initial certification? Our cylinder vendor indicates their standard procedure limits the NO_2 change to no more than 0.3 ppm. In reviewing the Green Book, I unable to locate this requirement/ limitation. As such, I'm thus seeking your clarification to better my understanding.

Answer 67- My best guess (without looking at the certificates of analysis for the cylinder) is that the vendor has an internal policy against recertifying NO calibration gases as EPA Protocol Gases if there is evidence of excessive NO-to-NO2 conversion between when the cylinder was originally assayed and when the cylinder was reassayed. The EPA traceability protocol (see https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards) does not have any such limitation. My own nonexpert review of 40 CFR Part 60, Appendix F did not reveal any concentration shift limitations for calibration standards that are used for cylinder gas audits.

I suspect that the pressure regulator for your EPA Protocol Gas was not properly purged when it was put into use and that some residual oxygen (and perhaps water) in the regulator diffused into the cylinder and caused the NO-to-NO2 conversion. I would be worried that water might have gotten to the cylinder's interior wall and that nitric acid might have formed and might form more in the future. I would be suspicious of the EPA Protocol Gas. In the long run, it may be less hassle to buy a new EPA Protocol Gas rather than to risk failing the cylinder gas audit because of a bad calibration standard.

Section 2.1.11 of the protocol covers the recertification of standards. The basic procedure is for the specialty gas producer to reassay the EPA Protocol Gas using NIST-traceable reference standards, although not necessarily the same as was used in the original assay. Then Schuirmann's two one-sided tests (TOST, see Section 2.1.5.2 and Appendix C) is used to determine if the measured concentration from the recertification assay is within 1.0 percent of the certified concentration from the original assay. If the TOST acceptance criterion is attained, the EPA Protocol Gas can be recertified. If the criterion is not attained, a second recertification assay may be conducted. If the two recertification assays attain the TOST acceptance criterion, the EPA Protocol Gas can be recertified. If not, the calibration standard must be disqualified for further use under the protocol.

I talked with Ray Merrill (919-541-5225 or merrill.raymond@epa.gov) of EPA's Office of Air Quality Planning and Standards (OAQPS) because he has expertise in source measurement technology. He is not aware of any EPA regulatory limitations on NO-to-NO2 conversion in calibration gases. He also suspects regulator purging problems were the cause of the conversion.

Question 68- A tank technically doesn't have to be EPA Protocol, just traceable to one of the highlighted, correct?

> 2.6 Gaseous and Flow Rate Audit Standards.
> 2.6.1 Gaseous pollutant concentration standards (permeation devices or cylinders of compressed gas) used to obtain test concentrations for CO, SO2, NO, and NO2 must be traceable to either a National Institute of Standards and Technology (NIST) Traceable Reference Material (NTRM) or a NIST-certified Gas Manufacturer's Internal Standard (GMIS), certified in accordance with one of the procedures given in reference 4 of this appendix. Vendors advertising certification with the procedures provided in reference 4 of this appendix and distributing gases as "EPA Protocol Gas" for ambient air monitoring purposes must participate in the EPA Ambient Air Protocol Gas Verification Program or not use "EPA" in any form of advertising. Monitoring organizations must provide information to the EPA on the gas producers they use on an annual basis and those PQAOs purchasing standards will be obligated, at the request of the EPA, to participate in the program at least once every 5 years by sending a new unused standard to a designated verification laboratory.

Answer 68- The traceability requirements are different for different EPA air pollution monitoring methods. For ambient air monitoring, calibration gases must be EPA Protocol Gases. For conventional source sampling methods, calibration gases must be traceable to NIST standards or to a producer-certified standard. OAQPS Guidance Document 039 allows for a less rigorous assay procedure that the protocol for daily CEM calibrations where EPA Protocol Gases are not required. For 40 CFR Part 75 acid rain monitoring, the calibration gases must be EPA Protocol Gases and must also have a vendor-certified uncertainty of +/- 2.0 percent. Mobile source (i.e., motor vehicles and aircraft engines) testing regulations only specify +/- 2 percent uncertainty without any specific traceability requirement. EPA NVFEL has its own separate gas naming procedure for calibration gases. Therefore, you must look at the specific monitoring regulation to understand the applicable traceability requirements for calibration gases.

In the case of 40 CFR Part 58, Appendix A, the calibration gas has to be an EPA Protocol Gas because it has to be certified in accordance with cited Reference 4, which is the 1997 traceability protocol that has been replaced by the 2012 protocol (see https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards).

It's always bothered me that different parts of EPA have different requirements for calibration gases, but in the 26-odd years that I've worked with EPA Protocol Gases no harmonization of the requirements has occurred. Maybe someday.