

NIST Special Publication 260-222

Certification of NIST Gas Mixture Standard Reference Materials®



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Foreword

The National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards, was established by the U.S. Congress in 1901 and charged with establishing a measurement foundation to facilitate U.S. and international commerce. NIST develops reference materials and reference instruments that are used to ensure the accuracy, metrological traceability, and comparability of measurement results in many diverse fields of science, industry, and technology.

The NIST Material Measurement Laboratory (MML) serves as the U.S. national reference laboratory for measurements in the chemical, biological, and material sciences. The MML Office of Reference Materials (ORM) supports the production and dissemination of all NIST reference materials and reference instruments.

NIST's ORM maintains over 1300 Standard Reference Materials (SRMs)[®]. These materials are used to perform instrument calibrations, verify the accuracy of specific measurements, and support the development of new measurement methods. All available SRMs are listed in the NIST SRM Catalog at <https://www.nist.gov/srm>.

Scope

This document provides details on the production and evaluation of gas mixture SRMs, which are certified and sold by NIST. It is meant to serve as a resource for NIST customers, who use gas mixture SRMs as calibrants to establish traceability of their own measurement results, and as a supplement to the Certificates of Analysis (COAs) issued by NIST, which accompany the units of these gas mixtures. This document describes the general procedures employed for the certification of gas mixture SRMs, including mixture production, value assignment, and quality assurance testing.

Abstract

The Gas Sensing Metrology Group at NIST provides accurate, stable gaseous standards for use in various types of emissions testing and environmental monitoring. The group develops and maintains the highest level of primary gas standards, which provide direct traceability to the International System of Units (SI). This traceability is then realized through the certification and dissemination of reference gas standards, such as NIST Standard Reference Materials[®] (SRMs). Gas mixture SRMs are produced by a specialty gas company, analyzed by NIST against primary gas standards, and sold to customers to provide traceability for their gas measurements. This document provides an overview of the gas metrology program at NIST, and describes the general procedures which are used to develop and certify gas mixture SRMs.

Key words

Amount-of-substance fraction; certification; gas mixture; quality assurance; reference material; SRM; traceability.

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Acronyms and Abbreviations

AIC	Akaike's Information Criterion
AICc	AIC corrected for small sample sizes
BIC	Bayesian Information Criterion
COA	Certificate of Analysis
COGAS	computer operated gas analysis system
GSMG	Gas Sensing Metrology Group
LS	lot standard
MML	Material Measurement Laboratory
MSB	magnetic suspension balance
NIST	National Institute of Standards and Technology
NTRM	NIST Traceable Reference Material
ORM	Office of Reference Materials
PSM	primary standard gas mixture
QA	quality assurance
RGM	Research Gas Mixture
SI	International System of Units
SRM	Standard Reference Material

1. Introduction

The Gas Sensing Metrology Group (GSMG) at the National Institute of Standards and Technology (NIST) is responsible for developing, critically evaluating, and applying techniques for the identification and measurement of gaseous species in atmospheres (urban, rural, and pristine) and process streams (automobile and stack).

Since the 1970s, following the enactment of the Clean Air Act [1], the GSMG and its precursor organizations have been providing accurate gas standards, in the U.S. and worldwide, in support of industries responding to federal and state regulations, environmental concerns, fairness in trade issues, and global climate change.

The GSMG works with regulatory bodies, gas suppliers, and international partners to provide the infrastructure for high-quality, traceable gas measurements, thus allowing better decision-making by industry, regulators, government officials, research scientists, and the public.

Traceability for gas analysis is realized through the development and certification of gas mixture reference materials, such as Standard Reference Materials (SRMs), NIST Traceable Reference Materials (NTRMs) [2], and Research Gas Mixtures (RGMs) [2]. These reference gas mixtures provide metrological traceability [3] for the amount-of-substance fractions [4, Sec. 8.6.2] (hereafter abbreviated as “amount fractions”) of a variety of compounds, including greenhouse gases, criteria air pollutants, toxic organics, and volatile organic compounds.

This document focuses primarily on NIST’s gas mixture SRMs, and describes the processes by which they are produced and certified. Information on the other types of gas reference materials and measurement services offered by NIST can be found on the GSMG website at <https://www.nist.gov/mml/csd/gas-sensing-metrology-group>.

2. Procurement of Candidate SRMs

2.1 Production of Gas Mixtures

The units which comprise a gas mixture SRM are typically produced by a contracted specialty gas supplier, according to the technical specifications listed in the SRM contract, and under the guidance of the NIST GSMG.

Most gas mixture SRMs are prepared in aluminum gas cylinders with an internal volume

of 6 L. The mixtures are dynamically blended and filled in batches (i.e., “lots”) to ensure that the SRM is homogeneous, i.e., that each cylinder in the lot contains nominally the same gaseous composition.

At least one additional mixture, of the same composition as the SRM lot, is produced in a larger cylinder with an internal volume of 30 L. This cylinder is designated as the SRM “lot standard” or “LS”, and serves as the analytical control against which all other cylinders in the lot are measured.

The specialty gas supplier is required to analyze every cylinder in the lot, by direct comparison to the lot standard, and to send all data to NIST for review. The data are used not only to confirm whether the lot is homogeneous, but also as a starting point for assessing mixture stability, as described in Sec. 4.3. If NIST approves the data, then the mixtures are sent to NIST as a “candidate SRM” [5] intended for certification.

2.2 Acceptance Testing

Upon receiving any candidate SRM lot, NIST performs preliminary testing on a subset of mixtures, to ensure that the lot is in accordance with NIST technical specifications, and that the mixtures are of sufficient quality to be certified as SRMs. This preliminary testing is referred to as acceptance testing, and includes:

- (i) verification that the nominal amount fraction(s) of the analyte(s) are within the specified limits;
- (ii) analysis of the composition of the balance gas (e.g., oxygen, argon, carbon dioxide), if the mixtures were prepared in air; and
- (iii) verification that any trace impurities are within their maximum allowable limits, per NIST specifications.

If the candidate mixtures are found to have satisfied the above criteria, then the lot is accepted by NIST for certification. Otherwise, the lot may be returned to the gas supplier to be remade.

3. Analysis of SRM Cylinders

3.1 Primary Standards

The value assignment of a candidate SRM, including the LS and the samples which comprise the lot, is determined by comparison to NIST primary standard gas mixtures (PSMs), which are prepared gravimetrically and are directly traceable to the International System of Units (SI).

Gravimetric preparation of gas mixtures involves the transfer of an aliquot of gas (or gases) to an evacuated cylinder, followed by the addition of a dilution (i.e., balance) gas. Prior to and after each addition, the cylinder is weighed relative to a standard control mass. The measured masses and molecular weights of the components are then used to determine the amount fractions of the gas mixture, also taking into account any known impurities. The calculated amount fractions are traceable to the SI unit of mass (kg). Detailed information on the preparation of standards by gravimetry can be found in ISO Guide 6142 [6].

In the event that PSMs are unavailable, SRMs can be value assigned using two independent, critically evaluated methods: (i) the dilution of a gravimetrically calibrated permeation device(s) with a carrier gas of precisely measured flow(s), and (ii) the dynamic dilution of a certified standard.

Permeation devices are typically small tubes containing a pure liquid analyte, which emits a vapor (i.e., permeates) at a constant rate when held at a fixed temperature. The device is placed inside a temperature-controlled chamber, and is suspended from a magnetic suspension balance (MSB), which continuously measures its mass loss over time. The permeation gas is then diluted with a measured stream of dilution gas, typically nitrogen or air. Based on the known flow of the dilution gas, and the mass loss of the permeation device, a gas stream is generated with a known amount fraction, which is traceable to the SI unit of mass. More detailed information on permeation methods can be found in [7] and [8].

3.2 Measurement Methods

A broad range of analytical methods is employed to measure the components in a variety of gas mixture SRMs. Table 1 lists some of the most commonly used instruments and their associated applications.

The readings from the instruments used for analysis are never used directly, either in their

Table 1. Analytical instrumentation used for the analysis and certification of gas mixture SRMs.

Instrument/Measurement Technique	Component(s) Analyzed
Gas chromatography with flame ionization detection (GC-FID)	Propane, methane, carbon monoxide ^a , carbon dioxide ^a , halocarbons
Gas chromatography with thermal conductivity detection (GC-TCD)	Carbon dioxide, carbon monoxide, propane (high-level)
Gas chromatography with mass-selective detection (GC-MSD)	Halocarbons
Nondispersive infrared spectroscopy (NDIR)	Carbon monoxide
Cavity enhanced absorption spectroscopy (CEAS)	Nitrous oxide, carbon monoxide
Cavity ring-down spectroscopy (CRDS)	Hydrogen sulfide, carbon dioxide, carbon monoxide, methane
Pulsed fluorescence	Sulfur dioxide
Electrochemical	Hydrogen sulfide
Paramagnetism	Oxygen
Chemiluminescence	Nitric oxide
Nondispersive ultraviolet spectroscopy (NDUV)	Nitric oxide, sulfur dioxide

^aRequires sample methanation.

raw form or as calibrated amount fractions. Rather, all measurements are taken relative to an analytical control, in this case the SRM LS, which is sampled repeatedly throughout the analysis to compensate for any instrument drift during a measurement sequence.

Typically, in a sequence, one to three cylinders (*C*) are sampled in a random order determined by a computer operated gas analysis system (COGAS) between subsequent samples of the LS (e.g., LS, C1, C2, LS). Ratios, r_C , are then formed using the cylinder's instrumental indication, i_C , as numerator, and the drift-corrected indication of the LS, i_{LS} , as denominator:

$$r_C = \frac{i_C}{i_{LS}}, \quad (1)$$

where

$$i_{LS} = i_{LS1} + \frac{i_{LS2} - i_{LS1}}{N - 1} \times (n - 1) \quad (2)$$

is an interpolated estimate of the instrumental indication of the LS that is approximately contemporaneous with i_C . The i_{LS1} and i_{LS2} are the measured indications of the LS taken before and after the cylinder measurements; N is the total number of measurements in the sequence; and n is the order number of the cylinder measurement within the sequence.

For example, let's say two cylinders (C1 and C2) are sampled with the LS in the following sequence: LS, C1, C2, LS. Their corresponding instrumental indications measured as a voltage output (V) are: 8.43420, 8.43356, 8.44954, and 8.42831, respectively.

The drift-corrected reading of the LS, contemporaneous with the reading of C1 ($n = 2$), is then calculated as:

$$i_{LS,C1} = 8.43420 + \frac{8.42831 - 8.43420}{4 - 1} \times (2 - 1) = 8.43224, \quad (3)$$

and the resulting ratio for C1 is:

$$r_{C1} = \frac{8.43356}{8.43224} = 1.00016. \quad (4)$$

The above calculations are based on the assumption that any instrumental drift occurring between successive readings of the LS is linear (i.e., that any potential error associated with non-linearity of the drift is negligible).

The collection of raw data used for the value assignment of gas mixture SRMs comprises all the ratios of instrumental indications obtained from multiple samplings of the PSMS and of each cylinder in the SRM lot.

4. Value Assignment and Uncertainty Evaluation

This section summarizes the procedures used by NIST to assign certified values to gas mixture SRMs and to evaluate their associated uncertainties, which are described in further detail in [9].

4.1 Analysis Function

During calibration, we select a number of PSMS (typically 4 to 6) of similar composition to the candidate SRM, whose range of amount fractions brackets the nominal amount fraction of the SRM mixture.

Each PSM is analyzed in comparison to the LS, and corresponding ratios of instrumental indications are determined. A minimum of six ratios per PSM is obtained over a period of at least two days.

These ratios are then translated into a value of the measurand using an analysis function, G , as defined in ISO Guide 6143 [10]:

$$x = G(\bar{r}), \quad (5)$$

where $\bar{r}$ is an average of replicated ratios of instrumental indications, and x is the amount fraction of the analyte in the SRM mixture. The choice of the degree of the polynomial to represent G involves two criteria: (i) graphical diagnostics and (ii) numerical model selection criteria.

The graphical diagnostics are plots of residuals corresponding to polynomials of several degrees, typically from first to fourth. These plots are examined to compare the magnitudes of the residuals, as well as any patterns in the relationship between the residuals and fitted values.

Figure 1 shows an example of the residual plots for SRM 1665b Propane in Air. The least structured the residuals (e.g., showing no marked parabolic trend), and the smaller their absolute values, the better. However, this must be counterbalanced by consideration of model parsimony (the lower the degree the more parsimonious the polynomial).

The numerical criteria are conventional statistical model selection criteria: Akaike's Information Criterion (AIC), the AIC corrected for small sample sizes (AICC), and the Bayesian Information Criterion (BIC) [11].

Table 2 lists the model selection criteria for each degree of the candidate polynomial for SRM 1665b Propane in Air. The lower these values are, the better the model. Generally, it is recommended that the model corresponding to the lowest value of BIC is the most appropriate candidate. In all cases, the plots of residuals should support the final selection.

Taken together, Table 2 and Figure 1 suggest either a polynomial of the first or second degree. For this example of SRM 1665b Propane in Air, a first degree (linear) polynomial was ultimately selected, supported in part by the known linearity of the instrumentation used for analysis.

Both the model selection criteria, and the computation of the maximum likelihood estimate of the analysis function, depend on a specific statistical model for the calibration data. The

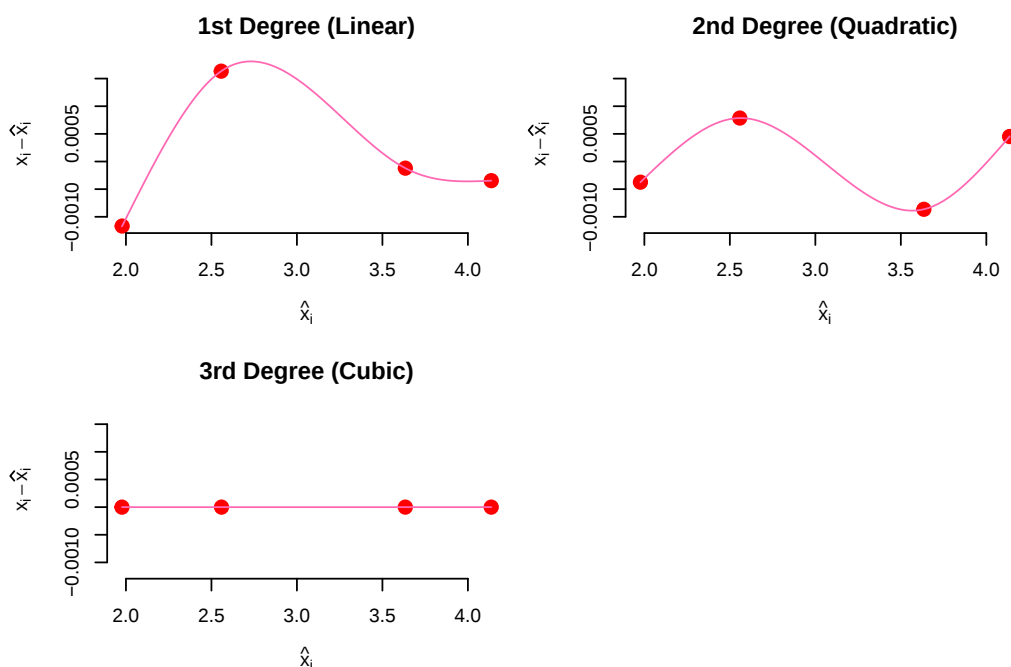


Fig. 1. Plots of residuals versus fitted values for candidate polynomials, for SRM 1665b Propane in Air. Trends are highlighted by interpolating splines (thin red curves).

Table 2. Model selection criteria for the analysis function used for value assignment of SRM 1665b Propane in Air.

DEGREE	AIC	AICc	BIC
1	−85.75	−113.7	−89.43
2	−84.39	−112.4	−88.69
3	−82.58	−111.4	−87.49

model currently in use is the same that was introduced by [9], which utilizes a modified Nelder-Mead optimization algorithm [12].

The amount fractions of the analyte in the PSMS are modeled as outcomes of independent Gaussian random variables, and the averages of the ratios of instrumental indications are modeled as outcomes of Student’s t random variables, taking into account their small numbers of degrees of freedom.

The uncertainty is evaluated by application of the parametric statistical bootstrap [13], which is a Monte Carlo method. This approach involves applying stochastic perturbations to the values of the participating quantities repeatedly, and computing the corresponding

estimates of the analysis function and the resulting “replicates” of the amount fraction in the mixture.

The maximum likelihood estimates of the analysis function are repeated for $k = 1, \dots, K$, where K is a suitably large integer ($K = 5000$ is used routinely). The resulting K versions of the analysis function are a sample from the probability distribution that represents the uncertainty surrounding G , and they are used for uncertainty evaluation of the value assigned to the measurand. Figure 2 shows the analysis function used for the value assignment of SRM 1665b Propane in Air. It also depicts magnified versions of the uncertainties associated with the PSMs, and of the 95 % coverage band surrounding the analysis function.

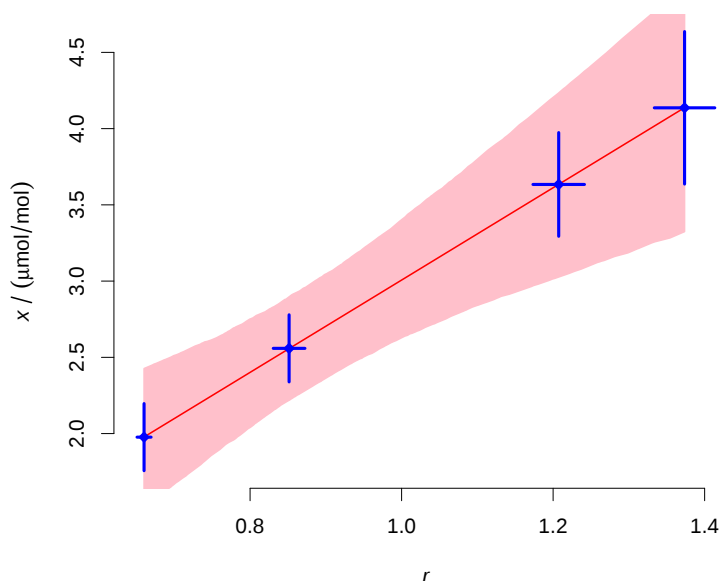


Fig. 2. The analysis function for SRM 1665b Propane in Air is a polynomial of the first degree, depicted by the thin red line. The pink band is a simultaneous, 95 % coverage band for the true analysis function derived from $K = 5000$ replicates of G , whose vertical thickness has been magnified 150-fold to facilitate visualization. The blue points represent the ratios (r) and amount fractions (x) of the PSMs used for calibration, along with their associated standard uncertainties (all similarly magnified).

4.2 Homogeneity

To assess the homogeneity of an SRM, the dispersion of the amount fractions between-cylinders is compared with their within-cylinder dispersion, using graphical diagnostics and statistical tests.

Every cylinder in the lot is evaluated by direct comparison to the LS, and ratios of instrumental indications are determined using Eq. 1. At minimum, six ratios are obtained for each cylinder over two independent analytical periods; these periods are referred to as “homogeneity sets”. The length of time between each homogeneity set is dependent upon the composition of the gas mixture, as described in Sec. 4.3.

The averages of the replicated ratios, r , are evaluated using the analysis function described in Sec. 4.1, to determine the amount fraction values and associated uncertainties of the individual cylinders.

The replicated amount fraction values for the individual cylinders are examined from different viewpoints, also considering their associated uncertainties, to ascertain whether the lot is sufficiently homogeneous to warrant assignment of a single value to the whole lot.

Potential causes for heterogeneity are assessed using a conventional, linear, Gaussian mixed-effects model [14], which is fitted to the replicates of the cylinder values using the method of restricted maximum likelihood (REML) [15]. These causes include:

- the “Cylinder” to which the replicates belong;
- the “Port” of the COGAS manifold used to sample the cylinder;
- the “Day” on which the instrumental indication was obtained;
- the “Break-Set”, i.e., the replicates corresponding to instrumental indications obtained between consecutive changes (“breaks”) of cylinder port connections to the COGAS manifold; and
- the “LS-Set”, i.e., the set of replicates corresponding to instrumental indications obtained between consecutive indications obtained for the LS.

The factor LS-Set is nested within Break-Set, which in turn is nested within Day. Cylinder, Port, Day, Break-Set, and LS-Set all are modeled as random effects. The sole fixed effect in the model is the lot’s overall mean amount fraction.

If the variability between the cylinders is not significantly greater than the variability of the replicated values within-cylinders, then the lot is considered to be homogeneous, and one value is assigned to the entire lot. Otherwise, if significant differences between the cylinders are found, then the lot may be split into sufficiently homogeneous sub-lots (if the distribution indicates bimodality), or each cylinder in the lot may be individually value assigned.

4.3 Stability Testing

All candidate SRMs are tested to determine whether the cylinder mixtures in the lot are stable. Evaluation of stability can be performed in two ways: (i) by comparing homogeneity data provided by the specialty gas supplier to that obtained at NIST, and (ii) by evaluating two sets of NIST homogeneity data, separated by a sufficiently long wait period (on the order of days to months, depending on the composition of the gas mixture).

For nonreactive gases, stability is evaluated by comparing the supplier's and NIST's homogeneity data, since the length of time between the two sets of measurements is typically several months. If no significant changes are observed between the two datasets, then the mixtures are assumed to be long-term stable, and no additional wait period is required.

For certain reactive species, which have a higher likelihood of becoming unstable over time, additional testing is performed to further ascertain stability of the lot. Upon completion of the first set of homogeneity measurements, all cylinders comprising the candidate SRM lot are set aside, typically for about six months, before the second set of homogeneity measurements is taken. This extended wait period enables determining whether any long-term changes may be occurring in the cylinder mixtures.

Regardless of the composition of the gas mixture, if the measured ratios for any cylinder differ significantly between the two homogeneity sets, then the cylinder will be reevaluated to examine the cause of the change. If there is evidence that one or more cylinders in the lot may be unstable, then the candidate SRM may be placed on hold for additional stability testing, or specific cylinders may be pulled from the lot, or the entire lot may be rejected and returned to the supplier to be remade.

4.4 Historical Uncertainty

Owing to high and sustained demand, some gas mixture SRMs are developed repeatedly over time. For example, SRM 1662a Sulfur Dioxide in Nitrogen is now in its fifth edition, having been issued originally in 1976, and then again in 1997, 2001, and 2007. The unused portions of the corresponding lot standards are typically preserved, and can provide useful information every time a new lot of the same nominal composition is prepared.

Each of these “historical” lot standards has its own assigned value, originating when the corresponding lot was certified, and updated as needed during quality assurance testing. Suppose that this cylinder is analyzed along with the current lot, and its amount fraction

value is predicted based on its ratios to the current LS and the current analysis function. The difference between the certified and analyzed values can provide insight into additional sources of uncertainty, which do not manifest themselves in the repeatability achieved during certification of any particular lot, in the lot's homogeneity, or in the uncertainty of the analysis function.

Such differences are particularly valuable for reactive species, whose amount fractions may change over time owing to chemical reactions with the cylinder walls or with other species in the mixture. The same difference may also be attributable to changes in analytical methods, use of newly prepared PSMS, or decomposition of the mixture components. Although not explicitly manifest in any particular lot, these effects are sources of uncertainty whose contributions should be taken into account, and are thus incorporated when certifying a new SRM lot.

The inclusion of historical data into the current lot evaluation is done under the assumption that the new lot will behave in the same manner as the old lot(s), which is not always the case. For instance, past lots of nitric oxide in nitrogen have been found to be unstable due to a certain pre-treatment that was applied to the cylinder walls. This pre-treatment has been discontinued and replaced with a more stable alternative. For these nitric oxide SRMS, the historical data would not be considered, as it would yield a considerable (and unfounded) overestimation of the uncertainty of the current lot.

Overall, the use of historical information from past lot standards enables better quantification of potential deviations in the amount fraction of an SRM over time. As a result, the uncertainties assigned to gas mixture SRMS are more robust, realistic, and ultimately more reliable.

4.5 Assignment of the SRM Lot

If the lot is sufficiently homogeneous (particularly once the contribution from historical uncertainty is considered), then the value assigned to the SRM is computed as a DerSimonian-Laird consensus of the individual cylinder values, also taking into account their associated uncertainties [16, 17].

The uncertainty evaluation for the value assigned to the SRM is a prediction uncertainty, so that about 95 % of the individual cylinder values will differ from the value assigned to the SRM by less than the corresponding expanded uncertainty.

Figure 3 shows the SRM value for SRM 1665b Propane in Air, the cylinder-specific values

and associated expanded uncertainties, as well as the expanded uncertainty associated with the SRM value, distinguishing what these uncertainties would be both with and without incorporating the historical uncertainty.

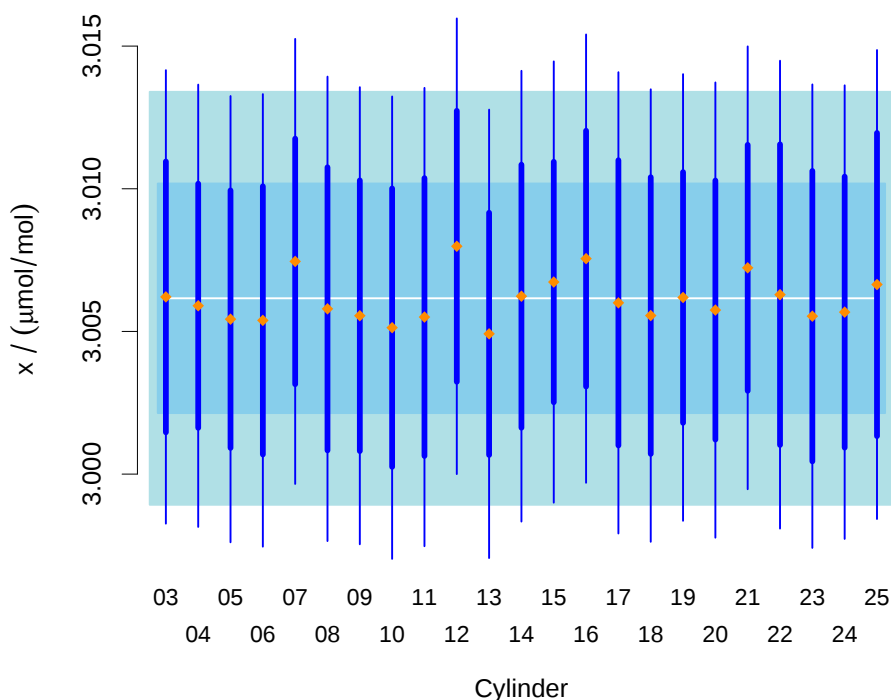


Fig. 3. Value assigned to SRM 1665b Propane in Air (horizontal, white line), and the values assigned to the individual cylinders in the lot (orange diamonds). The thin and thick vertical error bars represent the cylinder-specific expanded uncertainties, with and without incorporating the historical uncertainty. The horizontal, medium blue band, and its wide, light-colored counterpart, distinguish the impact that disregarding or considering the historical uncertainty has upon the expanded uncertainty associated with the SRM value.

In the case that the lot is deemed heterogeneous, such that the cylinder-to-cylinder variability far exceeds the variability within-cylinders, then the SRM may be partitioned into acceptably homogeneous sub-lots, as described by [9], or each cylinder in the lot will be assigned an individual certified value.

Certain gas mixture SRMs are assigned individual certifications regardless of whether the lot is considered homogeneous, such as those containing low-level reactive gas mixtures, and ambient air samples. Table 3 lists the SRMs which are typically given individual cylinder certifications. These cylinders are also individually recertified by NIST when the SRM reaches its expiration.

Table 3. Typical gas mixture SRMs for which the cylinders comprising the lot are assigned individual certifications.

SRM Number	Mixture Composition	Nominal Amount Fraction
1689	Sulfur Dioxide in Nitrogen	5 $\mu\text{mol/mol}$
1693a	Sulfur Dioxide in Nitrogen	50 $\mu\text{mol/mol}$
1720	Northern Hemisphere Air	Ambient level
1721	Southern Hemisphere Air	Ambient level
1722	Halocarbons in Continental Air	Ambient level
2627a	Nitric Oxide in Nitrogen	5 $\mu\text{mol/mol}$
2628a	Nitric Oxide in Nitrogen	10 $\mu\text{mol/mol}$
2629a	Nitric Oxide in Nitrogen	20 $\mu\text{mol/mol}$
2737	Nitric Oxide in Nitrogen	500 nmol/mol
2738	Nitric Oxide in Nitrogen	1000 nmol/mol

5. SRM Certification

Each unit of a gas mixture SRM is issued with a Certificate of Analysis (COA). The COA provides detailed information pertaining to the SRM mixture, including: (i) the cylinder number and corresponding SRM sample number; (ii) certified and non-certified values; (iii) the analytical method(s) used for value assignment; (iv) the conditions under which the certification is valid; and (v) the expiration of certification. The information included in the COA, as well as in this document, is made available to customers who may need it to use a certified value for their own purposes.

Additional information is also made available in the following NIST Special Publications: SP 260-136-2021 [5], which explains the different vocabulary and terms used to define and describe SRMs; and SP 260-202 [18], which provides detailed guidance on how to evaluate and propagate the uncertainties listed in the COA.

The information included in the COA may be revised at any time. Changes may include editorial revision, extension of the period of validity, upgrading non-certified values to certified status, downgrading certified values to non-certified status, and removing values. A revision history is typically provided on the last page of the COA.

5.1 Certified Values

Following the criteria described in [5], certified values provided by gas mixture SRMs are believed by NIST to be:

- stable (for some defined period when properly stored and handled),
- accurate (unbiased within a specified level-of-confidence interval),
- metrologically traceable (to a higher-order reference system), and
- fit for the purpose(s) specified in the documentation supplied to the customer.

Certified values are provided only when the above criteria have been adequately established, and are therefore believed to be suitable for accurately calibrating or validating measurement procedures, which can then be used to obtain values that are metrologically traceable to the SI.

The certification of gas mixture SRMs produces certified values which are method-independent, such that metrological traceability to the SI is independent of the the procedure used to obtain the value.

5.2 Non-Certified Values

Results from additional analyses performed during the certification process, which do not meet the above criteria for certified values, may be provided to the customer as non-certified values.

Non-certified values (previously referred to as “reference values” or “information values”) are considered to be of interest to the SRM user, but are given for informational purposes only, and cannot be used to establish metrological traceability.

Typical non-certified values provided for gas mixture SRMs include the composition of the balance gas (for air balance SRMs), as well as any measured impurities in the gas mixture.

5.3 Period of Validity

The period of validity for a gas mixture SRM is the time during which the certified value is expected to remain correct within the stated uncertainty. The period of validity is estimated from stability testing (see Sec. 4.3), as well as from previous experience with SRMs of

similar nominal composition. A list of the typical periods of validity assigned to different gas mixture SRMs is included in Table 4.

Table 4. Periods of validity based on nominal composition of gas mixture SRMs.

Component	Nominal Amount Fraction	Period of Validity
Carbon monoxide	10 $\mu\text{mol/mol}$ to 13 % mol/mol	8 years
Carbon dioxide	365 $\mu\text{mol/mol}$ to 16 % mol/mol	8 years
Methane	1 $\mu\text{mol/mol}$ to 100 $\mu\text{mol/mol}$	8 years
Propane	0.1 $\mu\text{mol/mol}$ to 2500 $\mu\text{mol/mol}$	8 years
Oxygen	2 % mol/mol to 21 % mol/mol	8 years
Total oxides of nitrogen	100 $\mu\text{mol/mol}$ to 2500 $\mu\text{mol/mol}$	8 years
Nitric oxide	0.5 $\mu\text{mol/mol}$ to 20 $\mu\text{mol/mol}$	3 years
Nitric oxide	50 $\mu\text{mol/mol}$ to 100 $\mu\text{mol/mol}$	8 years
Nitric oxide	250 $\mu\text{mol/mol}$ to 3000 $\mu\text{mol/mol}$	8 years
Sulfur dioxide	100 $\mu\text{mol/mol}$ to 3500 $\mu\text{mol/mol}$	8 years
Sulfur dioxide	5 $\mu\text{mol/mol}$ to 50 $\mu\text{mol/mol}$	4 years
Hydrogen sulfide	5 $\mu\text{mol/mol}$ to 20 $\mu\text{mol/mol}$	4 years
Nitrous oxide	323 nmol/mol to 1 $\mu\text{mol/mol}$	6 years
Halocarbons	23 pmol/mol to 530 pmol/mol	4 years

The period of validity stated in the COA begins from the certificate issue date until the specified expiration date, provided the SRM is handled and stored in accordance with the recommended instructions.

NIST monitors all SRM mixtures to the end of their period of validity. If substantive technical changes occur that affect the certified value(s) during this period, NIST will take corrective action and notify the users and purchasers.

For newly developed SRMs, such as for SRM 1718 Nitrous Oxide in Air, the period of validity is initially set to a shorter period, such as four years. Over time, as their stability is monitored and future lots are prepared, the period of validity may be increased per the discretion of the GSMG, typically in increments of two years.

5.4 Quality Assurance Testing

Quality assurance (QA) testing is performed when an existing SRM lot reaches the last year of its period of validity (as listed in Table 4), or when a new candidate SRM lot is certified. QA testing may also be performed in response to customer complaints, which may trigger a review of available data and, if the potential deficiency is found credible, a reanalysis of the SRM lot.

As part of QA testing, SRM cylinders residing in NIST's Office of Reference Materials (ORM) warehouse, as well as those retained by the GSMG, are analyzed using suitable PSMS and appropriate analytical methods. If no changes are observed in the analyzed samples, then the SRM is assumed to be stable and the period of validity for the lot is extended. If a measurable change is observed in the value assignment or uncertainty of the SRM, then NIST will notify SRM users and generate a new COA reflecting the change.

If at any point the validity of a certified value becomes suspect, the SRM is put "on restriction" and sales are ceased until the issue is resolved by direct experimental measurements. During this time, all warehoused SRM mixtures are reanalyzed.

6. Whole Air SRMs

In addition to the SRM mixtures prepared by specialty gas producers, NIST also supports several "whole air" SRMs, which are composed of natural, atmospheric air that has been pumped from stations in either Niwot Ridge, Colorado or Baring Head, New Zealand. These ambient-air SRMs include SRM 1720 Northern Continental Air [19], SRM 1721 Southern Oceanic Air [20], and SRM 1722 Halocarbons in Continental Air.

Since these mixtures are produced in a manner that differs from most other gas mixture SRMs, they do not necessarily follow the same certification procedures as described in this document. For more appropriate detailed information regarding the development and certification of NIST's whole air SRMs, please refer to their corresponding COAs and/or supplementary publications.

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Appendix A: NIST Gas Mixture SRMs

Table A1 lists the gas mixture SRMs maintained by NIST. This table is provided for information purposes only, and may not reflect the most current listing of SRMs supported or available for purchase. The most up-to-date listing of all SRMs and their corresponding status can be found in the NIST SRM Catalog at <https://www.nist.gov/srm>.

Table A1. List of NIST gas mixture SRMs.

SRM Number	Description	Sample Designation ^a
1658a	1 $\mu\text{mol/mol}$ Methane in Air	12-
1659a	10 $\mu\text{mol/mol}$ Methane in Air	11-
1661a	500 $\mu\text{mol/mol}$ Sulfur Dioxide in Nitrogen	94-
1662a	1000 $\mu\text{mol/mol}$ Sulfur Dioxide in Nitrogen	93-
1663a	1500 $\mu\text{mol/mol}$ Sulfur Dioxide in Nitrogen	92-
1664a	2500 $\mu\text{mol/mol}$ Sulfur Dioxide in Nitrogen	91-
1665b	3 $\mu\text{mol/mol}$ Propane in Air	85-
1666b	10 $\mu\text{mol/mol}$ Propane in Air	84-
1667b	50 $\mu\text{mol/mol}$ Propane in Air	83-
1668b	100 $\mu\text{mol/mol}$ Propane in Air	82-
1669b	500 $\mu\text{mol/mol}$ Propane in Air	81-
1674b	7 % mol/mol Carbon Dioxide in Nitrogen	7-
1677c	10 $\mu\text{mol/mol}$ Carbon Monoxide in Nitrogen	5-
1678c	50 $\mu\text{mol/mol}$ Carbon Monoxide in Nitrogen	4-
1679c	100 $\mu\text{mol/mol}$ Carbon Monoxide in Nitrogen	3-
1680b	500 $\mu\text{mol/mol}$ Carbon Monoxide in Nitrogen	2-
1681b	1000 $\mu\text{mol/mol}$ Carbon Monoxide in Nitrogen	1-
1683b	50 $\mu\text{mol/mol}$ Nitric Oxide in Nitrogen	45-
1684b	100 $\mu\text{mol/mol}$ Nitric Oxide in Nitrogen	44-
1685b	250 $\mu\text{mol/mol}$ Nitric Oxide in Nitrogen	43-
1686b	500 $\mu\text{mol/mol}$ Nitric Oxide in Nitrogen	42-
1687b	1000 $\mu\text{mol/mol}$ Nitric Oxide in Nitrogen	41-
1689	5 $\mu\text{mol/mol}$ Sulfur Dioxide in Nitrogen	98-
1693a	50 $\mu\text{mol/mol}$ Sulfur Dioxide in Nitrogen	96-

Table A1. (continued)

SRM Number	Description	Sample Designation ^a
1694a	100 $\mu\text{mol/mol}$ Sulfur Dioxide in Nitrogen	95-
1696a	3500 $\mu\text{mol/mol}$ Sulfur Dioxide in Nitrogen	90-
1718	1 $\mu\text{mol/mol}$ Nitrous Oxide in Air	1718-
1720	Northern Continental Air	1720-
1721	Southern Continental Air	1721-
1722	Halocarbons in Continental Air	1722-
2613a	18 $\mu\text{mol/mol}$ Carbon Monoxide in Air	22-
2614a	42 $\mu\text{mol/mol}$ Carbon Monoxide in Air	21-
2617	500 $\mu\text{mol/mol}$ Carbon Dioxide in Nitrogen	26-
2619a	0.5 % mol/mol Carbon Dioxide in Nitrogen	30-
2620a	1.0 % mol/mol Carbon Dioxide in Nitrogen	31-
2621a	1.5 % mol/mol Carbon Dioxide in Nitrogen	32-
2622a	2.0 % mol/mol Carbon Dioxide in Nitrogen	33-
2624a	3.0 % mol/mol Carbon Dioxide in Nitrogen	35-
2625a	3.5 % mol/mol Carbon Dioxide in Nitrogen	36-
2627a	5 $\mu\text{mol/mol}$ Nitric Oxide in Nitrogen	48-
2628a	10 $\mu\text{mol/mol}$ Nitric Oxide in Nitrogen	49-
2629a	20 $\mu\text{mol/mol}$ Nitric Oxide in Nitrogen	50-
2630	1500 $\mu\text{mol/mol}$ Nitric Oxide in Nitrogen	46-
2631a	3000 $\mu\text{mol/mol}$ Nitric Oxide in Nitrogen	47-
2635a	25 $\mu\text{mol/mol}$ Carbon Monoxide in Nitrogen	58-
2636a	250 $\mu\text{mol/mol}$ Carbon Monoxide in Nitrogen	57-
2637a	2500 $\mu\text{mol/mol}$ Carbon Monoxide in Nitrogen	56-
2638a	5000 $\mu\text{mol/mol}$ Carbon Monoxide in Nitrogen	55-
2639a	1 % mol/mol Carbon Monoxide in Nitrogen	54-
2640a	2 % mol/mol Carbon Monoxide in Nitrogen	53-
2641a	4 % mol/mol Carbon Monoxide in Nitrogen	52-
2642a	8 % mol/mol Carbon Monoxide in Nitrogen	51-
2644a	250 $\mu\text{mol/mol}$ Propane in Nitrogen	101-
2647a	2500 $\mu\text{mol/mol}$ Propane in Nitrogen	104-

Table A1. (continued)

SRM Number	Description	Sample Designation ^a
2657a	2 % mol/mol Oxygen in Nitrogen	73-
2658a	10 % mol/mol Oxygen in Nitrogen	72-
2659a	21 % mol/mol Oxygen in Nitrogen	71-
2660a	100 µmol/mol Total Oxides of Nitrogen (NO _x) in Air	2660-
2730	5 µmol/mol Hydrogen Sulfide in Nitrogen	65-
2731	20 µmol/mol Hydrogen Sulfide in Nitrogen	66-
2735	800 µmol/mol Nitric Oxide in Nitrogen	141-
2737	0.5 µmol/mol Nitric Oxide in Nitrogen	2737-
2738	1.0 µmol/mol Nitric Oxide in Nitrogen	2738-
2740a	10 % mol/mol Carbon Monoxide in Nitrogen	59-
2741a	13 % mol/mol Carbon Monoxide in Nitrogen	60-
2745	16 % mol/mol Carbon Dioxide in Nitrogen	9-
2750	50 µmol/mol Methane in Air	211-
2751	100 µmol/mol Methane in Air	212-
2764	0.25 µmol/mol Propane in Air	2764-
2765	0.1 µmol/mol Propane in Air	2765-

^a SRM sample designations are unique identifiers which correspond to individual lots of an SRM. For example, the units comprising SRM 1665b lot “K” are designated as 85-K-XX, where XX represents the sample number of a specific cylinder in the lot.