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REPORT OF ANALYSIS

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Environmental Protection Agency Blind Audit 2018

Submitted to:

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The U.S. Environmental Protection Agency (EPA) conducted a blind audit of EPA protocol calibration gas mixtures produced by specialty gas manufactures. The objective was to determine the amount-of-substance fraction (concentration) of the analytes in the mixtures, and to compare the quantified values with those stated in the producers' certificates. The mixtures included in this audit consisted of carbon dioxide (CO_2) at 8 % mol/mol to 18 % mol/mol; nitric oxide (NO) at 50 µmol/mol to 800 µmol/mol (ppm) [with total oxides of nitrogen (NO_x) within 1 % relative of NO]; and sulfur dioxide (SO_2) at 75 µmol/mol to 900 µmol/mol (ppm). The quality of these calibration mixtures is critical for the accurate determination and reporting of regulated gaseous emissions.

For this audit, the National Institute of Standards and Technology (NIST) was chosen to conduct the analysis of the selected cylinder mixtures. RTI International was chosen to purchase the cylinders from the gas manufacturers, and to coordinate their transportation to and from NIST.

Candidate Samples Ordered

Following the approach of previous audits [1,2,3,4], a contractor was hired to coordinate the purchase and delivery of samples to NIST. This approach achieved a blind audit, satisfying the following criteria:

1. All gas vendors and their sites that sell EPA protocol gas mixtures in the U.S. are to be represented.
2. Samples are to be new and unused.
3. Samples are to be delivered to NIST in a timely and efficient manner.

RTI International, the designated contractor for this audit, purchased 66 gas mixtures over three ranges; the nominal concentrations (by mole) for each range are listed below. These ranges differed from previous audits in 2013 [3] and 2015 [4].

Nominal concentration ranges for the 2018 EPA audit.

# of Samples	Range Type	CO_2 (%[1])	NO (ppm[2])	SO_2 (ppm[2])
22	High	18	800	900
22	Mid	12	500	600
22	Low	8	50	75

[1] All concentrations labeled "%" in this report are equivalent to the SI unit of % mol/mol. The designation "%" is a standard industry practice.

[2] All concentrations labeled "ppm" in this report are equivalent to the SI unit of µmol/mol. The designation "ppm" (parts per million) is a standard industry practice.

The objective of this audit was to purchase one sample of each range (three samples in total) per manufacturing site of participating first-party vendors (see Table 1 for a list of the vendors that provided samples). However, after taking delivery of the samples, it was discovered that Concorde Specialty Gases (NJ) had their gas mixtures certified by a third party, Matheson (TN). Consequently, the cylinders provided by Concorde were not considered for this audit.

It is NIST's understanding that these 11 vendors and their 22 manufacturing sites, including Concorde Specialty Gases (NJ), fully represent the first-party manufacturing of EPA protocol calibration gas mixtures in the U.S. Nothing can be said regarding the performance of any production site not included in this audit. The results of this audit represent an instantaneous snapshot of the process being measured, and should not be regarded as a final statement on the accuracy of EPA protocol gases; nor should they definitively indicate the analytical capabilities of the individual producers. The information in this audit is presented without assigning any rating to the gas vendors, (e.g., who is the best, who is/is not approved, etc.). Further, any mention of commercial products within this report is for information purposes only, and does not imply recommendation or endorsement by NIST or the EPA.

<u>Candidate Samples Received and Inspected</u>

RTI International began the purchase of the 66 candidate samples in November 2017. By January 2018, all samples were delivered to RTI, and the vendors were notified by the EPA of their participation in this audit.

NIST received the samples in three batches of 22 (High, Mid, and Low range), between January and May 2018. Every sample was received with the cylinder valve shrink wrapped by the vendor and/or with a dust cap (see Tables 2a–2c). This showed that the cylinders had not been used since leaving the gas manufacturing facility.

All samples were within their cylinder Hydro test date (or Ultra test date) and were packaged as:

Cylinder: DOT 3AL2015, Aluminum 6061 alloy; internal volume – 30 L
Valve: Packless, stainless steel, CGA 660

<u>Review of Vendor Certificates of Analysis</u>

It was expected that every vendor certificate of analysis (COA) be in compliance with the requirements outlined by EPA-600/R-12/531 section 2.1.7 [5]. The following list comprises the minimum requirements by which all certificates were evaluated:

1. Cylinder identification number
2. Certified concentrations in parts per million (ppm) or percent (%), generally reported to three or more significant digits
3. Total expanded uncertainty of each certified component
4. Assayed component(s) in the mixture
5. Balance gas of the mixture
6. Cylinder pressure at certification
7. Statement that the standard should not be used when gas pressure falls below 100 psig
8. All assay dates
9. Date of the certification (i.e., date of the last assay)
10. Certificate expiration date
11. Identification of the reference standard(s) used in each component assay
12. Reference standard must be one of the following: (i) Standard Reference Material (SRM), (ii) SRM equivalent Primary Reference Material (PRM), (iii) NIST Traceable Reference Material (NTRM), (iv) Research Gas Mixture (RGM), or (v) Gas Manufacturer's Intermediate Standard (GMIS).
13. Information about the reference standard used: NIST sample number (for SRMs only), cylinder identification number and associated expanded uncertainty, and certification expiration date.
14. For a GMIS: information about the reference standard used (as in item 13) to assay the GMIS.
15. Statement that the certification was performed according to the EPA protocol
16. Statement of the assay procedure (G1 or G2)
17. Identification of the laboratory that performed the assay
18. Statement that a correction factor was used to account for analytical interference (if applicable)

Some nonconformities were observed in the vendor COAs, which are detailed in Table 3. This table also includes comments on other aspects of the COA, which may not qualify as nonconformities but are worth noting. Other than the exceptions stated in Table 3, the following held for all the COAs reviewed:

1. The concentration of the total oxides of nitrogen (NO_x) or nitrogen dioxide (NO_2) was within 1 % of the certified NO concentration.
2. Other than Linde (Canada), Global Calibration Gases (FL) and Airgas (all facilities), the reported values for NO_x (or NO_2) were listed as "Reference Only" or without an analytical uncertainty.
3. Analytical accuracy was ± 1 % or better (unexpanded uncertainty).
4. The balance gas was nitrogen.
5. Except for Industrial Welding Supply (LA) and Praxair (CA), there was no noted correction for analytical interference, even for the chemiluminescence analysis of NO in the presence of CO_2.

Instrumentation and Analytical Method

Previous audits have shown that nondispersive infrared (NDIR) provides the best compromise between low analytical uncertainty (≤ 0.5 %) and simultaneous measurement of CO_2, NO and SO_2 [1,2,3]. Therefore, NDIR was used for all analyses in this audit, with the exception of Low range NO, which was analyzed by chemiluminescence (chemi). Table 4 provides a detailed summary of the instrumentation used by NIST for this audit.

Standards Used

The standards used to determine the CO_2, NO and SO_2 concentrations in the sample cylinders are detailed in Tables 5a, 5b and 5c, respectively. The standards consisted of either NIST Primary Standard Mixtures (PSMs) or Standard Reference Materials (SRMs), which were prepared in a balance of nitrogen and are SI traceable.

The SRM lot standards (LSs) and working standards (WSs) used to determine analytical interference, along with the pure CO_2 with which they were blended, are detailed in Table 6.

Overall Experimental Design

1. NIST standards containing CO_2, NO, or SO_2 in nitrogen were used to generate calibration curves for each range on each instrument used.
2. Interference experiments were performed, using a gas blending system to generate mixtures of NO (or SO_2) with varying amounts of CO_2.
3. One protocol gas sample was selected from the midpoint of each mixture range. This sample was designated “Reference”. Samples were also selected at the minimum and maximum levels per component per range. These samples were designated “Test”.
4. For each Reference and Test cylinder, the CO_2, NO and SO_2 were quantified using calibration curves produced by NIST standards (step 1), and corrected for any CO_2 interference (step 2).
5. The remaining protocol mixtures at each range (including the Test samples) were analyzed by direct comparison to the corresponding Reference.
6. The Test cylinder values calculated in step 4 were compared to those from step 5, to determine any bias in the final analyses of the protocol gases.

Determination of Interference

The same instrumentation and measurement methods were used as in the previous audits. Only certain combinations of components/analytical techniques were previously shown to exhibit an interference that required correction [1,2,3]. Consequently, only these combinations were investigated to determine the correction factors for this audit.

NDIR Analysis of NO or SO_2 in the presence of CO_2

It has previously been established that CO_2 interferes with NO and, to a lesser extent, SO_2 [1,2,3]. This interference is caused by a combination of CO_2 absorption, which increases response, and pressure broadening, which decreases response [6,7]. This interference cannot be mathematically modeled; however, since the effect is not overly dependent on the concentrations of CO_2 and NO (or SO_2), the same multiplicative correction factor can be used for each range.

High, Mid, and Low range gas mixtures were created by blending NIST standards with pure CO_2 and house nitrogen (see Table 6). The correction factors, CFs, for NO (or SO_2) were calculated using Equation 1. The NO and SO_2 CFs as determined for this audit are listed in Table 7.

$$CF = \frac{instrument\ response\ without\ CO_2}{instrument\ response\ with\ CO_2} \tag{1}$$

Chemi Analysis of NO in the presence of CO_2

Previous audits have demonstrated that the CO_2 interference with the chemi is (a) independent of NO concentration in the range of 10 ppm to 1000 ppm, and (b) linear with CO_2 concentrations of up to 20 % [1,2,3]. The chemi CF for low NO in the presence of CO_2 was determined in the same manner as for the NDIR, using Equation 1, and is also listed in Table 7.

Determination of the Reference Cylinder

For each audit range, one protocol gas mixture was designated as a Reference, and was assigned a concentration value for CO_2, NO and SO_2 by direct comparison to NIST standards (Tables 5a–5c). For each analysis, the Reference was used as the control, and response ratios of each standard to the control were determined. Six ratios of each NIST standard to the Reference were obtained over a minimum two-day period. These ratios were then used to produce calibration curves, from which the Reference concentrations were determined (see Table 8).

Determination of the Vendor Cylinders

For each audit range, the vendor cylinders (treated as unknowns) were analyzed against the corresponding Reference cylinder (Table 8), using the Reference as the analytical control. At least five ratios per sample were obtained by dividing the instrument response of the unknown by the instrument response of the Reference (corrected for instrument drift). The concentrations of the vendor cylinders were then calculated by multiplying the average response ratio by the concentration of the Reference (as determined using NIST standards). The NIST determined concentrations for the High, Mid and Low range components, along with a comparison to the vendor certified values, are listed in Tables 9a, 9b and 9c respectively. The analytical methods and standards used by the vendors to certify their cylinders are provided in Table 10.

To validate the approach of assigning concentrations by direct comparison to the Reference, several Test cylinders were also analyzed using the calibration curves described in the previous section. A comparison of the results (Table 11) showed that the two approaches agreed within the analytical uncertainty (see Table 12), and were therefore statistically equivalent.

Determination of the Pass or Fail 2 % Tag Rule

The NIST concentrations and vendor certified values were compared using the "Paired t Test" [8]. The statistical parameters were:

NULL hypothesis:	NIST and vendor values are equivalent
Level of confidence:	95 % (k = 2)
NIST relative uncertainty:	0.90 % (at k = 2), the largest uncertainty (see Table 12)
Vendor relative uncertainty:	2.00 % (at k =2), i.e., the % Tag Rule

With these parameters, NIST was able to determine that an absolute relative difference of greater than 2.19 % (in practice rounded to 2.2 %) between the NIST analyzed value and the vendor certified value meant that the sample component has failed the 2 % Tag Rule. Figure 1 shows the relative percent differences between the NIST and vendor values for each concentration range. These differences are also listed in Tables 9a–9c, with Tag Rule failures marked by bold, underlined italics. A summary of the number of failures is given below.

Number of failures in the 2018 EPA audit.

Range Type	CO_2	NO	SO_2	**All Components**
High	0	1	1	**2**
Mid	0	0	1	**1**
Low	1	2	1	**4**
Total	**1**	**3**	**3**	**7**
% Total[1]	**1.6 %**	**4.8 %**	**4.8 %**	**11.1 %**

[1] Expressed as a relative percentage of the total number of cylinders (63 cylinders).

Most participating vendors reported certified uncertainties that were smaller than the 2 % Tag Rule. Therefore, it was also determined whether the difference between the NIST concentration and the vendor certified value was covered by the uncertainty stated in the vendor COA. Figures 2a– 2c compare the NIST and vendor values, and their associated uncertainties, for the High, Mid and Low range samples. There are several instances in which the vendor certified value passes the 2 % Tag Rule, but fails to agree with the NIST concentration within its certified expanded uncertainty. For these cases, it is recommended that the vendor reevaluate and amend their reported uncertainties, to better align with their current capabilities.

<u>Comparison to Previous EPA Audits</u>

In order to validate the methodology and provide an analytical link to the previous audits, working standards (WSs) retained from the 2008 audit [1] were analyzed during this current audit, and the CO_2, NO and SO_2 concentrations were determined. These concentrations were then compared to those determined in 2013 [3,9] and 2015 [4] (Table 13).

For nearly all of the WSs, the current and previous analyses agreed within their expanded uncertainties, demonstrating a consistency between the audits. One WS that did not agree with its previous values was WS-EPA8-L2. As shown in Figure 3, this sample has demonstrated a history of degradation over time. Therefore, the observed difference is believed to be the result of cylinder instability, and not an inconsistency in the analytical methods.

<u>Uncertainty Analysis</u>

For each component in the audit mixtures, the uncertainty in the NIST concentration, u_c, was determined from the uncertainties in the Reference concentration (u_{ref}), the ratios to the Reference (u_{ratio}), and the corresponding correction factor employed (u_{cf}). This uncertainty is given by:

$$u_c = \sqrt{u^2{}_{ref} + u^2{}_{ratio} + u^2{}_{cf}} \quad (2)$$

where u_{ref} was determined from the uncertainties in the calibration curve, the standards used for calibration, and the analytical ratios obtained. The final uncertainty, U, is expressed as:

$$U = ku_c \quad (3)$$

where the coverage factor, *k*, is equal to 2. The true concentration is asserted to lie within the interval expressed by the NIST concentration value ± *U* with a level of confidence of approximately 95 % [10].

Disposition of Cylinders

All 66 audit cylinders were returned to their respective vendors.

Vendor Responses and Corrective Actions

Upon receiving the results of this audit, all vendors were given the opportunity to reanalyze their samples and submit a formal response. Several vendors provided statements about their reanalyses (if one or more components failed the 2 % Tag Rule), as well as any corrective actions taken. A summary of the vendor responses is provided below. The results of the vendor reanalyses are included in Table 14.

***Airgas*:** After review of the redacted 2018 PGVP report for Airgas, the percent difference for the nitric oxide component in Table 9c (EPA low range) showed the NIST value to be 2.36 % lower than the initial certification by Airgas Troy, MI. Airgas Troy, MI followed SOP protocol and began an investigation into the original analysis as to why the NO value was higher than the NIST certified concentration. The inquiry determined that an analyst chose the incorrect curve for analysis and the nominal value of 50 ppm was outside the working range of the curve. Cylinder EB0010190 was returned to the producing facility and re-analyzed on 9/24/20 with a value of 51.57 ppm and under the 2 % pass/fail criteria.

***Industrial Welding Supply*:** NIST reported that one sample's certificate was crumpled up and torn inside the cylinder's cap. Industrial Welding Supply indicated that this happened after it left their premises. Their standard procedure for all samples is that the certificate is included in a clear plastic hanger around the cylinder's neck.

On the certificates of analysis, the reported uncertainty shows a different magnitude than the reported value of the sample. This has been addressed for all future certificates to show the same degree of precision in the uncertainty of the standard and the reported value of the sample. The "type of reference" for carbon dioxide not being specified was caused by a template formatting error. The template was referencing the cylinder number twice, rather than in the appropriate field showing the NIST number, or "GMIS" (gas manufacturer intermediate standard).

***Linde*:** Linde performed a reanalysis of SG9164471B, which yielded a result that was consistent with the original certified value. When examining the NTRMs (and GMISs) used as a reference for this blend, Linde noted that one of the lower-end NTRMs used for the certification of the GMISs expired in March 2020 (cylinder CC273230, NTRM batch 091001, certified value 19.39 ppm). Considering the reported values are consistently low and being past its shelf life, this NTRM likely affected the measurements around that concentration (and lower). As an action item, Linde will procure a new NTRM standard in the concentration of around 20 ppm.

***Matheson*:** Uncertainties and expiration dates for reference standards have been added to the Twinsburg certificates since 2018. To avoid any misunderstanding on their COAs, Matheson will replace "last analysis date" with "certification date" once the internal document of change request is approved. Matheson did not observe a statistically significant CO_2 interference with the instrument used for the chemiluminescence analysis of NO. Therefore, no correction factor was employed.

NorLab**:** NorLab has modified its certificate of analysis templates to include the following statement: "EPA uncertainty is equivalent to a 95% confidence with a coverage factor *k* of 2." After review of the Low range certificate, it was determined that the missing SRM sample number was the result of human error. Regarding the Mid and High range certificates, the certified date was not the last date tested; rather it was the date the final paperwork was finished. This error has been eliminated by reviewing the EPA protocol green book for future clarification as to what is needed for the certified date.

All certificate of analysis templates for the EPA protocols that are produced by NorLab have been completely rebuilt to allow for ease of use. All formatting issues have been eliminated; units are included with the concentration rather than by component names. Dates listed are clearly marked as either assay dates or calibration dates. Tables are marked with headers to allow the users to determine concentrations, analytical equipment used, reference standard data, and replicated analysis data.

Praxair**:** Praxair has overhauled its EPA COA program and, since Nov 12, 2020, all EPA COAs include the statement of coverage factor and 95 % confidence; absolute uncertainties are provided in place of relative uncertainties. Uncertainties and expiration dates are listed for both reference standards and standards used to assay GMISs. A correction was factored into the reported NO value. Going forward, a statement regarding the correction will be included on the certificate of analysis when a correction is applied. Location operators will be trained.

The low range cylinder, CC231954 was returned to the Praxair PA facility on 10/29/20. Reanalysis was performed on 11/3/20 and the CO_2 concentration was found to be 8.04 %, approximately 0.05 % difference from the NIST analyzed value. An in depth investigation of the production and analytical processes showed no deviations from the requirements of "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards". However, this low range CO_2 sample cylinder was gravimetrically filled at 8.00 % and analyzed together with the high and mid range sample cylinders at 0–50 % CO_2 analyzer range; where 2 % bias was possible. As a result of this investigation, Praxair PA will be reviewing gravimetric and analytical values of nonreactive EPA Protocol blends; more importantly, EPA protocol blends will be analyzed at the appropriate analyzer range.

Red Ball**:** The certificate of analysis for the low range blend received for the EPA Blind Audit had a typo on the Lot # for the SRM Sample Number. RBO Certificate reflected 95-J-XX instead of 95-J-8. Red Ball conducted refresher training for Reference Standard Receipt, and reviewed the SRM Certificate to confirm where the SRM sample # can be found.

Tier 5**:** The Tier 5 facility has enacted a review of SO_2 certification procedures upon receiving the redacted results of the audit. It is anticipated that the root cause lies in the correction factors for NDIR and FTIR analysis of SO_2 in the presence of CO_2. A study is being conducted utilizing gas dilution systems with our IR systems, as well as gravimetric comparisons. Analytical chemists have received refresher training regarding this interference as well.

The first of the correction factor studies was conducted in November 2020. Six new Luxfer SGS pretreated cylinders were selected and vacuum baked overnight at 130 °F to approximately 128 mTorr. Both sets of cylinders received the analyte together. Afterward, one set was top filled with only nitrogen and the other with an 8 % carbon dioxide balance nitrogen matrix. Resulting analytical comparisons in NDIR yielded a correction factor of 0.9763. The comparative closeness to NIST's own correction factor was encouraging and brought our corrected value to a delta of 1.4 % relative to the NIST finding.

Tier 5's reanalysis of their cylinders in November 2020 yielded SO_2 results that were closer to the NIST analyzed values. The reanalyzed value of the high cylinder was 886 ppm SO_2 compared to the original value of 864 ppm. The mid range cylinder was closer than the original value of 578 ppm, with the finding being 586 ppm. The low range cylinder finding was 70.4 ppm compared to the original value of 70.5 ppm. Once Tier 5 applied the new correction factor to the low cylinder, the resulting value was closer to NIST – 72.1 ppm.

References

[1] Environmental Protection Agency Protocol Gas Analysis 2008, ROA 839.03-09-010, 4 Dec 2008.

[2] Environmental Protection Agency Blind Audit 2010, ROA 639.03-11-026a, 13 Jan 2011.

[3] Environmental Protection Agency Blind Audit 2013, ROA 646.03-14-071b, 21 Apr 2015.

[4] Environmental Protection Agency Blind Audit 2015, ROA 646.03-15-048, 16 Apr 2015.

[5] EPA 600/R-12/531 EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, Environmental Protection Agency, May 2012.

[6] D. Robert and J. Bonamy, Short range force effects in semiclassical molecular line broadening calculations, Journal de Physique, 40(10), pp. 923–943, 1979.

[7] R. S. Pope and P. J. Wolf, Rare Gas Pressure Broadening of the NO Fundamental Vibration Band, Journal of Molecular Spectroscopy, 208(2), pp. 153–160, 2001.

[8] D. B. Hibbert, Quality Assurance in the Analytical Chemistry Laboratory, pp. 48–49, 2007.

[9] Recertification of SO_2, CO_2 and NO in EPA Audit Working Standards, ROA 646.03-15-051, 2015.

[10] Guide to the expression of uncertainty in measurement, JCGM 100:2008, GUM 1995 with minor corrections, BIPM, Sèvres, France, 2008.

Notebook Reference: Protocol Gas Verification Program # 2 [ACD 3694], pp. 37–66

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Table 1. Participating first-party vendors and their 2017 Protocol Gas Verification Program identifications (PGVP IDs).

Producer/Vendor	PGVP ID	Samples Provided	Audit Participation?	Production Address
Airgas (Los Angeles, CA)	B32017	3	Yes	11711 S Alameda St, Los Angeles, CA 90059
Airgas (Santa Fe Springs, CA)	A52017	3	Yes	8832 Dice Rd, Santa Fe Springs, CA 90670
Airgas (IL)	B12017	3	Yes	12722 S. Wentworth Ave, Chicago, IL 60628
Airgas (MI)	B62017	3	Yes	1290 Combermere Dr, Troy, MI 48083
Airgas (NC)	B22017	3	Yes	630 United Dr, Durham , NC 27713
Airgas (NJ)	B52017	3	Yes	600 Union Landing Rd, Cinnaminson, NJ 08077
Airgas (PA)	A12017	3	Yes	6141 Easton Rd, Bldg 1, Plumsteadville, PA 18949
Airgas (TX)	A32017	3	Yes	9810 Bay Area Blvd, Pasadena, TX 77507
Airgas (UT)	B72017	3	Yes	252 North Industrial Loop Rd, Tooele, UT 84074
Concorde Specialty Gases (NJ)	S12017	3	No[1]	36 Eaton Rd, Eatontown, NJ 07724
Global Calibration Gases (FL)	N22017	3	Yes	1090 Commerce Blvd N, Sarasota, FL 34243
Industrial Welding Supply (LA)	K12017	3	Yes	111 Buras Dr, Belle Chasse, LA 70037
Linde Canada Limited (Canada)	L12017	3	Yes	530 Watson St East, Whitby, Ontario, Canada, L1N 5R9
Matheson (OH)	D42017	3	Yes	1650 Enterprise Pkwy, Twinsburg, OH 44087
Matheson (TN)	D62017	3	Yes	1700 Scepter Rd, Waverly, TN 37185
NorLab (ID)	P12017	3	Yes	898 W Gowen Rd, Boise, ID 83705
Praxair (CA)	F22017	3	Yes	5700 S Alameda St, Los Angeles, CA 90058
Praxair (OH)	F12017	3	Yes	6055 Brent Dr, Toledo, OH 43611
Praxair (PA)	F32017	3	Yes	One Steel Rd East, Morrisville, PA 19067
Red Ball (LA)	G12017	3	Yes	555 Craig Kennedy Way, Shreveport, LA 71107
Specialty Air Technologies (CA)	J12017	3	Yes	6544 1/2 Cherry Ave, Long Beach, CA 90805
Tier 5 Labs (IN)	R12017	3	Yes	5353 W Southern Ave, Indianapolis, IN 46241

[1] Concorde Specialty Gases did not provide its cylinders as a first-party vendor, and was therefore not considered for participation in this audit.

Table 2a. High range cylinder package inspection. Cylinders received at NIST on 15 January 2018.

Producer/Vendor	Cylinder Number	Vendor Certification Date	Valve Shrink Wrapped?	Dust Plug?	Cylinder Pressure (psig)			Package Comments
					Vendor Reported	NIST Start	NIST End	
Airgas (Los Angeles, CA)	CC460224	12/07/2017	Yes	No	1975	2000	1925	
Airgas (Santa Fe Springs, CA)	CC68571	12/07/2017	Yes	No	1974	1950	1925	Rusty valve handle.
Airgas (IL)	CC701504	12/13/2017	Yes	Yes	1950	1900	1875	
Airgas (MI)	CC473278	12/12/2017	Yes	Yes	1950	1950	1925	
Airgas (NC)	CC705292	12/12/2017	Yes	No	2050	2075	2050	
Airgas (NJ)	CC278044	12/15/2017	Yes	Yes	2000	2000	1600	Cylinder stamp very faint, difficult to read.
Airgas (PA)	ALM043891	12/11/2017	Yes	No	1950	1975	1950	Rusty cap, valve handle. Valve threads cross-threaded.
Airgas (TX)	CC701970	12/18/2017	Yes	Yes	2000	2050	1950	
Airgas (UT)	CC705024	12/08/2017	Yes	Yes	1950	1950	1925	
Global Calibration Gases (FL)	EB0098120	12/15/2017	No	Plastic	2000	2025	2000	
Industrial Welding Supply (LA)	EB0097892	12/22/2017	Yes	No	2015	2000	2000	COA provided with cylinder was loose inside cap and torn.
Linde Canada Limited (Canada)	CC19894	11/25/2017	Yes	Yes	2000	2000	1950	Cylinder stamp faint, difficult to read.
Matheson (OH)	SX87551	12/13/2017	Yes	Yes	1800	1800	1775	
Matheson (TN)	SX54031	12/07/2017	Yes	Yes	1900	1750	1750	Pressure lower than reported.
NorLab (ID)	CC83798	12/13/2017	Yes	Plastic	2000	1850	1850	Pressure lower than reported.
Praxair (CA)	CC700544	12/09/2017	Yes	Yes	2000	1850	1825	Pressure lower than reported.
Praxair (OH)	DT0021621	12/21/2017	Yes	Yes	2000	1900	1875	
Praxair (PA)	CC246665	12/13/2017	Yes	Yes	2000	2000	1975	
Red Ball (LA)	EB0096486	12/04/2017	Yes	No	1850	1875	1850	
Specialty Air Technologies (CA)	CC505397	12/12/2017	Yes	No	1950	2000	1975	
Tier 5 Labs (IN)	EB0052818	12/12/2017	Yes	No	2015	1850	1800	Rusty cap threads. Greenish white dust inside valve. Valve difficult to turn. Pressure lower than reported.

Table 2b. Mid range cylinder package inspection. Cylinders received at NIST on 12 March 2018.

Producer/Vendor	Cylinder Number	Vendor Certification Date	Valve Shrink Wrapped?	Dust Plug?	Cylinder Pressure (psig)			Package Comments
					Vendor Reported	NIST Start	NIST End	
Airgas (Los Angeles, CA)	CC435038	12/07/2017	Yes	No	2000	2000	1975	
Airgas (Santa Fe Springs, CA)	CC58292	12/14/2017	Yes	No	1975	1975	1950	Valve handle overtightened. Grime on cylinder threads.
Airgas (IL)	CC701577	12/13/2017	Yes	Yes	1900	1875	1550	
Airgas (MI)	EB0083766	12/13/2017	Yes	Yes	1950	1900	1900	
Airgas (NC)	CC705375	12/05/2017	Yes	No	1950	1950	1925	
Airgas (NJ)	CC339808	12/13/2017	Yes	Yes	1975	1925	1900	Cylinder stamp nearly illegible. Valve handle very difficult to turn.
Airgas (PA)	ALM016436	12/11/2017	Yes	No	1940	1875	1850	Cylinder stamp very faint, difficult to read. Rusty cap.
Airgas (TX)	CC482042	12/09/2017	Yes	Yes	1850	1900	1900	Cylinder stamp faint.
Airgas (UT)	CC705017	12/08/2017	Yes	Yes	1950	1975	1950	
Global Calibration Gases (FL)	EB0098113	12/15/2017	No	Plastic	2000	1900	1875	COA loose inside cap.
Industrial Welding Supply (LA)	EB0097880	12/22/2017	Yes	No	2015	1925	1900	Rusty valve threads. Handle difficult to turn.
Linde Canada Limited (Canada)	CC96405	11/25/2017	Yes	Yes	2000	1875	1850	Rusty cap threads. Pressure lower than reported.
Matheson (OH)	SX39426	12/13/2017	Yes	Yes	1800	1825	1825	Some cylinder markings messy/hard to read.
Matheson (TN)	CC108425	12/07/2017	Yes	Yes	1900	1825	1800	Valve handle very difficult to turn.
NorLab (ID)	CC175063	12/04/2017	Yes	Plastic	2000	1850	1825	Pressure lower than reported.
Praxair (CA)	CC700619	12/09/2017	Yes	Yes	2000	1875	1850	Pressure lower than reported.
Praxair (OH)	DT0021526	12/21/2017	Yes	Yes	2000	1875	1850	Pressure lower than reported.
Praxair (PA)	SA18531	12/13/2017	Yes	Yes	2000	1900	1875	Rusty valve handle and cap threads.
Red Ball (LA)	EB0097462	12/12/2017	Yes	No	1800	1800	1800	
Specialty Air Technologies (CA)	CC501471	12/14/2017	Yes	No	1950	1850	1850	Rusty cap threads.
Tier 5 Labs (IN)	CC473749	12/12/2017	Yes	No	2015	1575	1525	Rusty cap threads. Dust inside valve. Pressure lower than reported.

Table 2c. Low range cylinder package inspection. Cylinders received at NIST on 14 May 2018.

Producer/Vendor	**Cylinder Number**	**Vendor Certification Date**	**Valve Shrink Wrapped?**	**Dust Plug?**	**Cylinder Pressure (psig)**			**Package Comments**
					Vendor Reported	**NIST Start**	**NIST End**	
Airgas (Los Angeles, CA)	CC427859	12/07/2017	Yes	No	2000	2000	1900	Cylinder stamp faint.
Airgas (Santa Fe Springs, CA)	CC400512	12/07/2017	Yes	No	1984	1950	1925	Cylinder stamp faint. Dirty cap threads.
Airgas (IL)	CC701571	12/14/2017	Yes	Yes	1850	1800	1800	
Airgas (MI)	EB0010190	12/13/2017	Yes	Yes	1950	2000	1950	CGA 660 had visible chip in it.
Airgas (NC)	CC705062	12/19/2017	Yes	No	2050	2000	1925	
Airgas (NJ)	CC428602	12/13/2017	Yes	Yes	1925	1900	1900	Cylinder stamp very faint. Valve difficult to turn.
Airgas (PA)	CC501281	12/12/2017	Yes	No	1950	1925	1900	
Airgas (TX)	CC701834	12/18/2017	Yes	Yes	1950	1975	1950	
Airgas (UT)	CC704957	12/12/2017	Yes	Yes	1920	1925	1925	
Global Calibration Gases (FL)	EB0098128	12/15/2017	No	Plastic	2000	1975	1950	
Industrial Welding Supply (LA)	EB0097999	12/22/2017	Yes	No	2015	2000	2000	Dust on valve threads.
Linde Canada Limited (Canada)	SG9164471B	11/25/2017	Yes	Yes	2000	1975	1975	
Matheson (OH)	SX47464	12/14/2017	Yes	Yes	1800	1875	1850	CC276968 also engraved on cylinder. This should be stamped out to avoid confusion. COA inside cap.
Matheson (TN)	SX53344	12/11/2017	Yes	Yes	1900	1825	1150	CC344960 also engraved on cylinder. This should be stamped out to avoid confusion.
NorLab (ID)	CC195636	12/05/2017	Yes	Plastic	2000	1975	1850	
Praxair (CA)	CC700563	12/21/2017	Yes	Yes	2000	1900	1900	
Praxair (OH)	DT0021616	12/21/2017	Yes	Yes	2000	1925	1900	
Praxair (PA)	CC231954	12/13/2017	Yes	Yes	2000	1950	1800	
Red Ball (LA)	EB0074043	12/14/2017	Yes	No	1800	1875	1825	
Specialty Air Technologies (CA)	EB0033968	12/13/2017	Yes	No	1950	1950	1950	Rusty valve, cap threads
Tier 5 Labs (IN)	CC453135	12/15/2017	Yes	No	2015	1650	1525	

Table 3. Vendor Certificate of Analysis (COA): nonconformities and comments. References to the pertaining item in section 2.1.7.1 of the EPA Green Book [5] are listed in parentheses.

Producer/Vendor	**Protocol Nonconformities**[1]	**COA Comments**[1]
Airgas (Los Angeles, CA)	Absolute uncertainties not provided[2] (#3).	Suggest adding that a coverage factor of 2 was used (#3). Same NO_2 PRM used as other Airgas sites, but the information is not consistent throughout[3].
Airgas (Santa Fe Springs, CA)	Absolute uncertainties not provided[2] (#3).	Suggest adding that a coverage factor of 2 was used (#3). Same NO_2 PRM used as other Airgas sites, but the information is not consistent throughout[3].
Airgas (IL)	Absolute uncertainties not provided[2] (#3).	Suggest adding that a coverage factor of 2 was used (#3). Same NO_2 PRM used as other Airgas sites, but the information is not consistent throughout[3].
Airgas (MI)	Absolute uncertainties not provided[2] (#3).	Suggest adding that a coverage factor of 2 was used (#3).
Airgas (NC)	Absolute uncertainties not provided[2] (#3).	Suggest adding that a coverage factor of 2 was used (#3). Same NO_2 PRM used as other Airgas sites, but the information is not consistent throughout[3].
Airgas (NJ)	Absolute uncertainties not provided[2] (#3).	Suggest adding that a coverage factor of 2 was used (#3). Same NO_2 PRM used as other Airgas sites, but the information is not consistent throughout[3].
Airgas (PA)	Absolute uncertainties not provided[2] (#3).	Suggest adding that a coverage factor of 2 was used (#3).
Airgas (TX)	Absolute uncertainties not provided[2] (#3).	Suggest adding that a coverage factor of 2 was used (#3).
Airgas (UT)	Absolute uncertainties not provided[2] (#3).	Suggest adding that a coverage factor of 2 was used (#3). Same NO_2 PRM used as other Airgas sites, but the information is not consistent throughout[3].
Global Calibration Gases (FL)	SRM numbers and sample numbers not listed (#8). Absolute uncertainties not provided[2] (#3).	Was a correction for CO_2 interference on NO included (#2)?
Industrial Welding Supply (LA)	For one or more components, the last significant figure of the reported concentration is not the same order of magnitude as the uncertainty (#2). Type of reference for CO_2 not specified; SRM number for CO_2 not included (#8).	Suggest adding that a coverage factor of 2 was used (#3). Suggest mentioning Industrial Welding Supply on the certificate to add clarity.
Linde Canada Limited (Canada)	Mid and High range: For one or more components, the last significant figure of the reported concentration is not the same order of magnitude as the uncertainty (#2).	Suggest adding that a coverage factor of 2 was used (#3). Mid and High range: Nitric oxide NTRM uncertainty listed as 60 ppm; assuming this is a typo.
Matheson (OH)	Uncertainties and expiration dates not listed for reference standards (#8).	Suggest "certification date" rather than "last analysis date" (#6). Was a correction for CO_2 interference on NO included (#2)?

Producer/Vendor	Protocol Nonconformities[1]	COA Comments[1]
Matheson (TN)		Suggest "certification date" rather than "last analysis date" (#6). Was a correction for CO_2 interference on NO included (#2)?
NorLab (ID)	Statement of coverage factor or 95 % confidence not included (#3). <u>Low range</u>: SRM sample number for SO_2 not included (#8). <u>Mid and High range</u>: Certification date does not match last assay date (#6); as a result, Mid range expiration date is incorrect (#7).	First table is disorganized and difficult to follow. Units should be included with the concentrations rather than by the component names. It is not clear whether the dates listed are assay dates or calibration dates. Sub-headers are awkwardly spaced and confusing. Strange formatting, missing information and Excel errors throughout.
Praxair (CA)	Statement of coverage factor and 95 % confidence not included; absolute uncertainties not provided[2] (#3). Uncertainties and expiration dates not listed for reference standards; missing concentrations, uncertainties and expiration dates of standards used to assay GMISs (#8).	
Praxair (OH)	Absolute uncertainties not provided[2] (#3). Uncertainties not listed for reference standards; missing concentrations and uncertainties for standards used to assay GMISs; CO_2 GMIS reference unclear (#8).	Suggest adding that the uncertainty is expressed at 95 % confidence (#3).
Praxair (PA)	Statement of coverage factor or 95 % confidence not included; absolute uncertainties not provided[2] (#3). Uncertainties and expiration dates not listed for reference standards; missing concentrations, uncertainties and expiration dates for standards used to assay GMISs (#8).	<u>Low range</u>: Was a correction for CO_2 interference on NO included (#2)? <u>Mid range</u>: Suggest adding a decimal point to the SO_2 value, to clarify that the trailing zeros are significant.
Red Ball (LA)	<u>Low range</u>: SRM sample number needed, currently listed as 95-J-XX (#8).	Reference standard table would be clearer if organized by component. Was a correction for CO_2 interference on NO included (#2)?
Specialty Air Technologies (CA)	Expiration dates not listed for reference standards (#8).	Address in certificate does not match PGVP vendor list (#11).
Tier 5 Labs (IN)	<u>Mid and High range</u>: For one or more components, the last significant figure of the reported concentration is not the same order of magnitude as the uncertainty (#2). Missing sample number and expiration date for standard used to assay GMIS (#8).	Was a correction for CO_2 interference on NO included (#2)?

[1] Applies to all COAs provided (High, Mid and Low ranges), unless otherwise specified.
[2] Protocol states that relative uncertainties may be used to supplement absolute uncertainties, but does not specify that they can be used as a replacement (#3).
[3] Inconsistent PRM information reported different Airgas sites, including the concentration, uncertainty and expiration date.

Table 4. Instrumentation and analytical techniques used.

Manufacturer	Description/Analytical Technique	NIST #	Purpose
Horiba	VA-3000 NDIR	631375	CO_2 analysis: High, Mid and Low ranges NO analysis: High and Mid ranges SO_2 analysis: High, Mid and Low ranges
Eco Physics	CLD 62S chemiluminescence	N113582	NO analysis: Low range
Environics	Series 2040 Gas Blending/Dilution System	594333	Correction factor determination to account for CO_2 interference on NO and SO_2
DryCal	ML-800 gas flow calibrator	626779	Correction factor determination to account for CO_2 interference on NO and SO_2

Table 5a. NIST standards (in balance nitrogen) used to determine the CO_2 concentrations.

Audit Range	Standard Type	Cylinder Number	Sample ID (SRM Number)	Concentration (%)	Uncertainty[1] (%)	Report of Analysis
High	PSM	SV13148	N/A	21.17814	0.00052	646.03-16-156
	PSM	FF18060	N/A	17.27488	0.00045	646.03-16-156
	SRM	CC358393	9-DL-02 (2745)	16.0815	0.0094	646.03-13-074
	PSM	FF19031	N/A	15.15124	0.00038	646.03-16-156
Mid	PSM	FF19100	N/A	12.281	0.015	839.03-04-116
	PSM	FA02549	N/A	11.04711	0.00030	646.03-16-156
Low	PSM	X16145	N/A	9.172	0.006	839.03-04-119
	PSM	CAL11249	N/A	7.111	0.012	839.03-04-116
	SRM	CC339403	7-HL-02 (1674b)	6.9440	0.0031	646.03-18-028a
	SRM	CC321328	36-DL-01 (2625a)	3.4625	0.0022	646.03-17-039
	SRM	CC476068	33-FL-02 (2622a)	1.9829	0.0004	646.03-17-072

[1] Uncertainties listed as standard uncertainties ($k = 1$).

Table 5b. NIST standards (in balance nitrogen) used to determine the NO concentrations.

Audit Range	Standard Type	Cylinder Number	Sample ID (SRM Number)	Concentration (ppm)	Uncertainty[1] (ppm)	Report of Analysis
High	PSM	CAL016199	N/A	832.8	1.3	839.03-06-002
	PSM	CAL9151	N/A	798.37	0.54	646.03-17-007
	SRM	AAL070907	141-CL-02 (2735)	783.60	1.00	639.03-12-037
	PSM	CAL015990	N/A	758.19	0.55	646.03-17-007
Mid	PSM	CAL016356	N/A	548.70	0.52	646.03-17-053
	PSM	CAL016189	N/A	486.11	0.46	646.03-17-053
Low	PSM	CAL016331	N/A	54.511	0.037	646.03-17-124a
	PSM	CAL016386	N/A	44.512	0.038	646.03-17-124a

[1] Uncertainties listed as standard uncertainties (k = 1).

Table 5c. NIST standards (in balance nitrogen) used to determine the SO_2 concentrations.

Audit Range	Standard Type	Cylinder Number	Sample ID (SRM Number)	Concentration (ppm)	Uncertainty[1] (ppm)	Report of Analysis
High	SRM	AAL072004	93-HL-02 (1662a)	978.31	0.93	646.03-18-055
	SRM	CAL017070	93-H-04 (1662a)	977.0	2.1	646.03-18-055
	PSM	FF19612	N/A	907.04	0.26	839.03-07-046
	PSM	FF19126	N/A	806.16	0.25	839.03-07-046
Mid	PSM	FF26847	N/A	700.92	0.23	839.03-07-047
	PSM	FF38013	N/A	504.03	0.16	839.03-07-047
Low	PSM	SG080108A	N/A	81.476	0.035	639.03-12-075
	PSM	FF38019	N/A	69.28	0.06	839.03-07-218

[1] Uncertainties listed as standard uncertainties (k = 1).

Table 6. NIST standards (in balance nitrogen) used to determine analytical interference.

Component	Standard Type	Cylinder Number	Sample ID (SRM Number)	Concentration (ppm)	Uncertainty[1] (ppm)	Report of Analysis
NO	SRM	AAL071141	47-FL-02 (2631a)	2952.3	1.6	839.03-06-076
NO	SRM	CC419640	43-ML-01 (1685b)	251.17	0.15	646.03-15-075
SO_2	SRM	AAL071145	90-DL-03 (1696a)	3395.3	0.4	646.03-17-025
SO_2	WS	KAL003797	SO2-WS-2	255.57	0.14	646.03-16-072
CO_2	dilution gas	ALM006921	N/A	pure[2]	N/A	N/A

[1] Uncertainties listed as standard uncertainties (k = 1).
[2] SFE Grade (research purity, > 99.99 %), from Scott Specialty Gases.

Table 7. NDIR and chemi correction factors for NO and SO_2 in the presence of CO_2[1].

Range Type	NO CF	SO_2 CF
High	1.0170 ± 0.0043 (NDIR)	1.0019 ± 0.0043 (NDIR)
Mid	1.0019 ± 0.0031 (NDIR)	1.0006 ± 0.0030 (NDIR)
Low	1.0330 ± 0.0038 (chemi)	0.9877 ± 0.0034 (NDIR)

[1] Correction factors are unitless, with uncertainties expressed at k = 1.

Table 8. NIST concentrations of Reference cylinders, determined by direct comparison to NIST standards[1].

Range Type	Vendor	Cylinder Number	CO_2 (%)	NO (ppm)[2]	SO_2 (ppm)[2]
High	Airgas (NJ)	CC278044	18.03 ± 0.02	802.1 ± 3.4	898.9 ± 3.9
Mid	Airgas (IL)	CC701577	12.03 ± 0.01	503.0 ± 1.6	603.7 ± 1.8
Low	Matheson (TN)	SX53344	8.024 ± 0.011	50.57 ± 0.19	75.63 ± 0.28

[1] Uncertainties expressed at k = 1.
[2] Includes corrections for CO_2 interference.

Table 9a. Vendor certified and NIST analyzed concentrations – EPA High range.

Vendor	**Cylinder Number**	**CO_2 (%)**			**NO (ppm)**			**SO_2 (ppm)**		
		Vendor	**NIST**	**%Diff [1]**	**Vendor**	**NIST**	**%Diff [1]**	**Vendor**	**NIST**	**%Diff [1]**
Airgas (Los Angeles, CA)	CC460224	17.8	17.78	−0.04	826.1	823.9	0.26	899.5	897.1	0.26
Airgas (Santa Fe Springs, CA)	CC68571	18.1	18.08	−0.12	801.1	807.2	−0.75	892.8	896.4	−0.40
Airgas (IL)	CC701504	18.0	18.04	0.00	811.4	810.5	0.11	873.5	871.0	0.28
Airgas (MI)	CC473278	18.0	18.07	−0.42	800.8	803.3	−0.31	902.0	897.8	0.47
Airgas (NC)	CC705292	18.0	17.97	0.19	826.1	820.7	0.66	894.6	892.7	0.22
Airgas (NJ)	CC278044	18.1	18.03	0.61	807.2	802.1	0.63	901.0	898.9	0.23
Airgas (PA)	ALM043891	18.3	18.30	0.05	799.8	805.6	−0.72	907.3	911.6	−0.47
Airgas (TX)	CC701970	17.6	17.63	0.00	818.4	823.9	−0.67	888.1	887.2	0.10
Airgas (UT)	CC705024	17.9	18.03	−0.86	810.6	810.9	−0.04	903.6	897.0	0.74
Global Calibration Gases (FL)	EB0098120	18.0	18.01	−0.04	792.0	792.2	−0.02	900.0	899.0	0.11
Industrial Welding Supply (LA)	EB0097892	18.0	18.00	−0.01	801.0	820.8	***−2.42***	879.0	894.9	−1.78
Linde Canada Limited (Canada)	CC19894	18.0	17.99	0.24	812.3	813.0	−0.09	924.6	926.3	−0.18
Matheson (OH)	SX87551	18.2	18.02	0.69	805.0	808.0	−0.37	890.0	888.6	0.15
Matheson (TN)	SX54031	17.9	18.01	−0.47	817.8	818.8	−0.12	898.0	898.4	−0.05
NorLab (ID)	CC83798	18.0	17.98	−0.08	813.5	809.6	0.48	898.6	904.9	−0.70
Praxair (CA)	CC700544	18.1	18.08	−0.07	812.0	817.8	−0.71	904.0	901.7	0.26
Praxair (OH)	DT0021621	18.1	18.07	0.24	825.0	823.9	0.13	897.0	895.7	0.15
Praxair (PA)	CC246665	18.0	18.22	−0.99	812.3	803.6	1.08	907.4	907.7	−0.03
Red Ball (LA)	EB0096486	18.1	18.03	0.38	793.0	803.8	−1.34	895.0	894.6	0.05
Specialty Air Technologies (CA)	CC505397	17.9	18.01	−0.49	792.0	790.8	0.15	895.3	895.1	0.03
Tier 5 Labs (IN)	EB0052818	18.2	18.09	0.61	780.0	792.8	−1.62	864.0	884.9	***−2.36***

[1] %Diff computed as: 100 * (Vendor − NIST) / NIST

Table 9b. Vendor certified and NIST analyzed concentrations – EPA Mid range.

Vendor	Cylinder Number	CO_2 (%)			NO (ppm)			SO_2 (ppm)		
		Vendor	NIST	%Diff [1]	Vendor	NIST	%Diff [1]	Vendor	NIST	%Diff [1]
Airgas (Los Angeles, CA)	CC435038	12.0	11.78	1.63	513.5	514.4	−0.17	600.6	599.2	0.23
Airgas (Santa Fe Springs, CA)	CC58292	12.0	12.01	−0.06	500.0	501.5	−0.30	594.8	595.5	−0.11
Airgas (IL)	CC701577	12.0	12.03	−0.33	501.9	503.0	−0.22	608.0	603.7	0.71
Airgas (MI)	EB0083766	11.8	11.85	−0.26	520.9	522.2	−0.25	590.6	591.4	−0.13
Airgas (NC)	CC705375	12.0	11.97	0.39	509.5	505.7	0.74	606.0	603.6	0.41
Airgas (NJ)	CC339808	12.1	12.02	0.27	506.7	504.0	0.54	598.6	596.1	0.43
Airgas (PA)	ALM016436	11.9	11.90	−0.03	495.2	496.6	−0.28	622.5	624.2	−0.28
Airgas (TX)	CC482042	12.0	12.03	0.05	514.0	513.0	0.19	608.4	603.8	0.76
Airgas (UT)	CC705017	12.0	12.00	−0.23	510.4	507.1	0.65	602.3	596.9	0.91
Global Calibration Gases (FL)	EB0098113	12.0	12.01	−0.12	501.0	494.0	1.42	602.0	600.6	0.23
Industrial Welding Supply (LA)	EB0097880	12.0	12.03	−0.07	501.5	509.8	−1.62	597.1	593.7	0.58
Linde Canada Limited (Canada)	CC96405	12.1	11.97	1.12	522.0	512.7	1.81	616.1	620.3	−0.67
Matheson (OH)	SX39426	12.2	12.01	1.51	501.2	503.0	−0.35	601.0	598.7	0.38
Matheson (TN)	CC108425	12.0	11.99	−0.01	508.3	510.3	−0.38	607.0	604.8	0.37
NorLab (ID)	CC175063	12.0	12.00	−0.23	510.6	507.1	0.69	603.7	605.0	−0.21
Praxair (CA)	CC700619	12.1	12.00	0.41	511.0	510.0	0.19	598.0	599.5	−0.25
Praxair (OH)	DT0021526	12.1	12.09	0.09	515.0	512.0	0.59	604.0	603.8	0.03
Praxair (PA)	SA18531	12.0	12.03	−0.37	495.0	495.9	−0.19	600.0	599.4	0.11
Red Ball (LA)	EB0097462	11.9	12.04	−1.16	495.0	504.4	−1.87	604.0	602.8	0.20
Specialty Air Technologies (CA)	CC501471	12.0	12.01	−0.11	497.6	492.8	0.97	596.7	595.2	0.24
Tier 5 Labs (IN)	CC473749	12.1	12.11	−0.08	491.0	490.3	0.15	578.0	592.0	***−2.36***

[1] %Diff computed as: 100 * (Vendor − NIST) / NIST

Table 9c. Vendor certified and NIST analyzed concentrations – EPA Low range.

Vendor	Cylinder Number	CO_2 (%)			NO (ppm)			SO_2 (ppm)		
		Vendor	**NIST**	**%Diff [1]**	**Vendor**	**NIST**	**%Diff [1]**	**Vendor**	**NIST**	**%Diff [1]**
Airgas (Los Angeles, CA)	CC427859	7.90	7.911	−0.17	49.9	49.78	0.15	73.17	72.80	0.51
Airgas (Santa Fe Springs, CA)	CC400512	8.06	8.099	−0.45	50.0	50.18	−0.34	74.67	74.78	−0.15
Airgas (IL)	CC701571	7.89	8.044	−1.92	51.1	50.99	0.16	75.40	74.41	1.33
Airgas (MI)	EB0010190	8.11	8.013	1.26	50.9	52.08	***−2.36***	75.30	75.32	−0.03
Airgas (NC)	CC705062	8.07	8.025	0.56	50.3	50.96	−1.35	74.58	74.01	0.77
Airgas (NJ)	CC428602	8.03	8.063	−0.39	50.8	51.14	−0.64	73.90	73.77	0.18
Airgas (PA)	CC501281	7.84	7.852	−0.14	48.9	49.07	−0.30	76.73	76.45	0.37
Airgas (TX)	CC701834	7.94	8.001	−0.76	48.7	48.54	0.33	75.66	74.38	1.72
Airgas (UT)	CC704957	7.99	8.018	−0.41	50.6	50.34	0.48	75.94	74.85	1.46
Global Calibration Gases (FL)	EB0098128	8.01	8.041	−0.38	50.5	50.49	0.02	76.00	75.99	0.01
Industrial Welding Supply (LA)	EB0097999	8.01	8.040	−0.42	50.7	51.18	−0.93	75.47	75.39	0.10
Linde Canada Limited (Canada)	SG9164471B	8.02	8.002	0.23	49.5	50.63	***−2.30***	76.96	75.47	1.98
Matheson (OH)	SX47464	8.03	8.022	0.10	50.9	50.73	0.34	75.30	75.20	0.13
Matheson (TN)	SX53344	8.01	8.024	−0.17	50.2	50.57	−0.83	75.60	75.63	−0.04
NorLab (ID)	CC195636	8.01	8.018	−0.13	51.2	50.82	0.68	77.22	76.79	0.56
Praxair (CA)	CC700563	7.99	8.023	−0.42	50.7	50.89	−0.37	74.80	74.57	0.31
Praxair (OH)	DT0021616	7.99	8.085	−1.18	51.1	50.80	0.59	76.50	75.93	0.75
Praxair (PA)	CC231954	8.23	8.044	***2.31***	49.0	49.14	−0.29	75.80	76.01	−0.27
Red Ball (LA)	EB0074043	8.03	8.034	−0.05	50.7	50.81	−0.22	74.50	74.07	0.58
Specialty Air Technologies (CA)	EB0033968	7.99	8.023	−0.40	49.0	49.18	−0.37	73.53	73.86	−0.44
Tier 5 Labs (IN)	CC453135	8.06	8.097	−0.46	45.7	45.45	0.55	70.50	73.09	***−3.54***

[1] %Diff computed as: 100 * (Vendor − NIST) / NIST

Table 10. Vendor analytical methods and standards used for certification of EPA audit cylinders. Applies to all ranges unless otherwise specified.

Vendor	PGVP ID	CO_2		NO		SO_2	
		Method	**Standard**	**Method**	**Standard**	**Method**	**Standard**
Airgas (Los Angeles, CA)	B32017	FTIR	NTRM	FTIR	NTRM	FTIR	NTRM
Airgas (Santa Fe Springs, CA)	A52017	FTIR	NTRM	FTIR	NTRM	FTIR	NTRM
Airgas (IL)	B12017	FTIR	NTRM	FTIR	NTRM	FTIR	NTRM
Airgas (MI)	B62017	FTIR	NTRM	FTIR	NTRM	FTIR	NTRM
Airgas (NC)	B22017	FTIR	NTRM	FTIR	NTRM	FTIR	NTRM
Airgas (NJ)	B52017	FTIR	NTRM	FTIR	NTRM	FTIR	NTRM
Airgas (PA)	A12017	FTIR	NTRM	FTIR	NTRM	FTIR	NTRM
Airgas (TX)	A32017	FTIR	NTRM	FTIR	NTRM	FTIR	NTRM
Airgas (UT)	B72017	FTIR	NTRM	FTIR	NTRM	FTIR	NTRM
Global Calibration Gases (FL)	N22017	GC-TCD	High: RGM Mid/Low: GMIS	Chemi	GMIS	NDIR	GMIS
Industrial Welding Supply (LA)	K12017	NDIR/ Paramagnetic	not specified	Chemi	GMIS	NDIR	GMIS
Linde Canada Limited (Canada)	L12017	FTIR	GMIS	FTIR	GMIS	FTIR	GMIS
Matheson (OH)	D42017	NDIR	SRM	Chemi	PRM	NDIR	SRM
Matheson (TN)	D62017	NDIR	SRM	Chemi	High/Mid: SRM Low: PRM	NDIR	High/Mid: PRM Low: SRM
NorLab (ID)	P12017	FTIR	GMIS	FTIR	GMIS	FTIR	GMIS
Praxair (CA)	F22017	FTIR	GMIS	Chemi	GMIS	NDIR	High/Mid: GMIS Low: NTRM
Praxair (OH)	F12017	High/Low: NDIR Mid: FTIR	GMIS	FTIR	GMIS	High/Mid: FTIR Low: NDUV	GMIS
Praxair (PA)	F32017	NDIR	GMIS	High/Mid: FTIR Low: Chemi	GMIS	FTIR	GMIS
Red Ball (LA)	G12017	NDIR	PRM	Chemi	GMIS	NDIR	GMIS
Specialty Air Technologies (CA)	J12017	NDIR	GMIS	FTIR	GMIS	FTIR	GMIS
Tier 5 Labs (IN)	R12017	GC-TCD	PRM	Chemi	High/Mid: GMIS Low: PRM	NDIR	SRM

Table 11. Comparison of Test cylinder concentrations, as determined by calibration curves and by direct comparison to the Reference cylinder.

Audit Range	CO_2 (%)				NO (ppm)[1]				SO_2 (ppm)[1]			
	Cylinder	**Curve**	**Reference**	**%Diff**	**Cylinder**	**Curve**	**Reference**	**%Diff**	**Cylinder**	**Curve**	**Reference**	**%Diff**
High	ALM043891	18.29	18.30	0.03	CC460224	824.1	823.9	−0.02	CC19894	926.5	926.3	−0.02
	CC701970	17.63	17.63	−0.01	EB0052818	792.7	792.8	0.01	EB0052818	884.7	884.9	0.02
Mid	SX39426	12.01	12.01	−0.01	CC96405	513.4	512.7	−0.13	ALM016436	624.3	624.2	−0.01
	CC435038	11.78	11.78	0.02	CC473749	489.4	490.3	0.17	CC473749	591.9	592.0	0.01
Low	CC231954	8.046	8.044	−0.03	CC195636	50.81	50.82	0.01	CC195636	76.77	76.79	0.02
	CC501281	7.861	7.852	−0.11	CC453135	45.58	45.45	−0.27	CC453135	73.13	73.09	−0.06

[1] Using correction factors listed in Table 7.

Table 12. Uncertainties of the audit samples as a function of range and component analyzed[1].

Audit Range	Component	u_{ref} (%)	u_{ratio} (%)	u_{cf} (%)	u_c (%)
High	CO_2	0.11	0.09	0.00	0.15
	NO	0.06	0.14	0.42	0.45
	SO_2	0.06	0.08	0.43	0.44
Mid	CO_2	0.08	0.06	0.00	0.10
	NO	0.10	0.13	0.31	0.35
	SO_2	0.04	0.08	0.30	0.31
Low	CO_2	0.14	0.10	0.00	0.17
	NO	0.10	0.21	0.37	0.44
	SO_2	0.12	0.15	0.34	0.40

[1] Uncertainties listed as standard uncertainties ($k = 1$).

Table 13. Concentrations and uncertainties of 2008 EPA audit working standards[1].

Component	Sample ID	Cylinder Number	2013 Certification[2]	2015 Audit Analysis[3]	Current Analysis	% Difference from Most Recent Value
CO_2 (%)	WS-EPA8-L1	CA08181	5.111 ± 0.015	5.111 ± 0.015	5.097 ± 0.032	−0.28
	WS-EPA8-L2	ALM054809	5.011 ± 0.015	5.005 ± 0.015	4.996 ± 0.030	−0.18
	WS-EPA8-M1	CC51188	12.186 ± 0.036	N/A	12.159 ± 0.034	−0.22
	WS-EPA8-M2	CA08177	12.073 ± 0.050	N/A	12.077 ± 0.038	0.04
	WS-EPA8-H1	CA08268	18.038 ± 0.076	N/A	17.993 ± 0.056	−0.25
	WS-EPA8-H2	SA10582	18.208 ± 0.054	N/A	18.153 ± 0.040	−0.30
NO (ppm)	WS-EPA8-L1	CA08181	50.55 ± 0.43	50.64 ± 0.43	51.17 ± 0.72	1.05
	WS-EPA8-L2	ALM054809	51.08 ± 0.43	51.22 ± 0.43	51.34 ± 0.80	0.23
	WS-EPA8-M1	CC51188	408.4 ± 2.2	N/A	409.2 ± 5.4	0.20
	WS-EPA8-M2	CA08177	399.5 ± 2.8	N/A	401.6 ± 5.4	0.52
	WS-EPA8-H1	CA08268	895.8 ± 6.0	N/A	895.8 ± 11.6	0.00
	WS-EPA8-H2	SA10582	929.8 ± 5.0	N/A	930.8 ± 12.4	0.11
SO_2 (ppm)	WS-EPA8-L1	CA08181	51.35 ± 0.34	51.24 ± 0.34	50.96 ± 0.38	−0.54
	WS-EPA8-L2	ALM054809	51.37 ± 0.34	51.08 ± 0.34	50.21 ± 0.40	−1.71
	WS-EPA8-M1	CC51188	515.1 ± 2.5	N/A	512.5 ± 4.6	−0.50
	WS-EPA8-M2	CA08177	497.2 ± 3.0	N/A	497.5 ± 4.4	0.06
	WS-EPA8-H1	CA08268	998.0 ± 6.0	N/A	999.7 ± 12.8	0.17
	WS-EPA8-H2	SA10582	1003.5 ± 4.6	N/A	1000.8 ± 12.6	−0.27

[1] Uncertainties listed as expanded uncertainties (k = 2).
[2] ROA 646.03-15-051 [9].
[3] ROA 646.03-15-048 [4].

Table 14. Vendor reanalysis of samples that failed the 2 % Tag Rule[1].

Vendor	Cylinder Number	Component	Vendor Concentrations			NIST Results		
			Original	Reanalysis	%Change[2]	NIST	%Diff Original[3]	%Diff Reanalysis[4]
Airgas (MI)	EB0010190	Low NO	50.85 ppm	51.57 ppm	1.42	52.08 ppm	***−2.36***	−0.98
Praxair (PA)	CC231954	Low CO_2	8.23 %	8.04 %	−2.31	8.044 %	***2.31***	−0.05
Tier 5 Labs (IN)	EB0052818	High SO_2	864 ppm	886 ppm	2.55	884.9 ppm	***−2.36***	0.12
	CC473749	Mid SO_2	578 ppm	586 ppm	1.38	592.0 ppm	***−2.36***	−1.01
	CC453135	Low SO_2	70.5 ppm	72.1 ppm	2.27	73.09 ppm	***−3.54***	−1.35

[1] Industrial Welding Supply (LA) and Linde Canada Limited (Canada) did not provide reanalysis values for their components that failed the 2 % Tag Rule.
[2] %Change computed as: 100 * (Reanalysis − Original) / Original
[3] %Diff computed as: 100 * (Original − NIST) / NIST
[4] %Diff computed as: 100 * (Reanalysis − NIST) / NIST

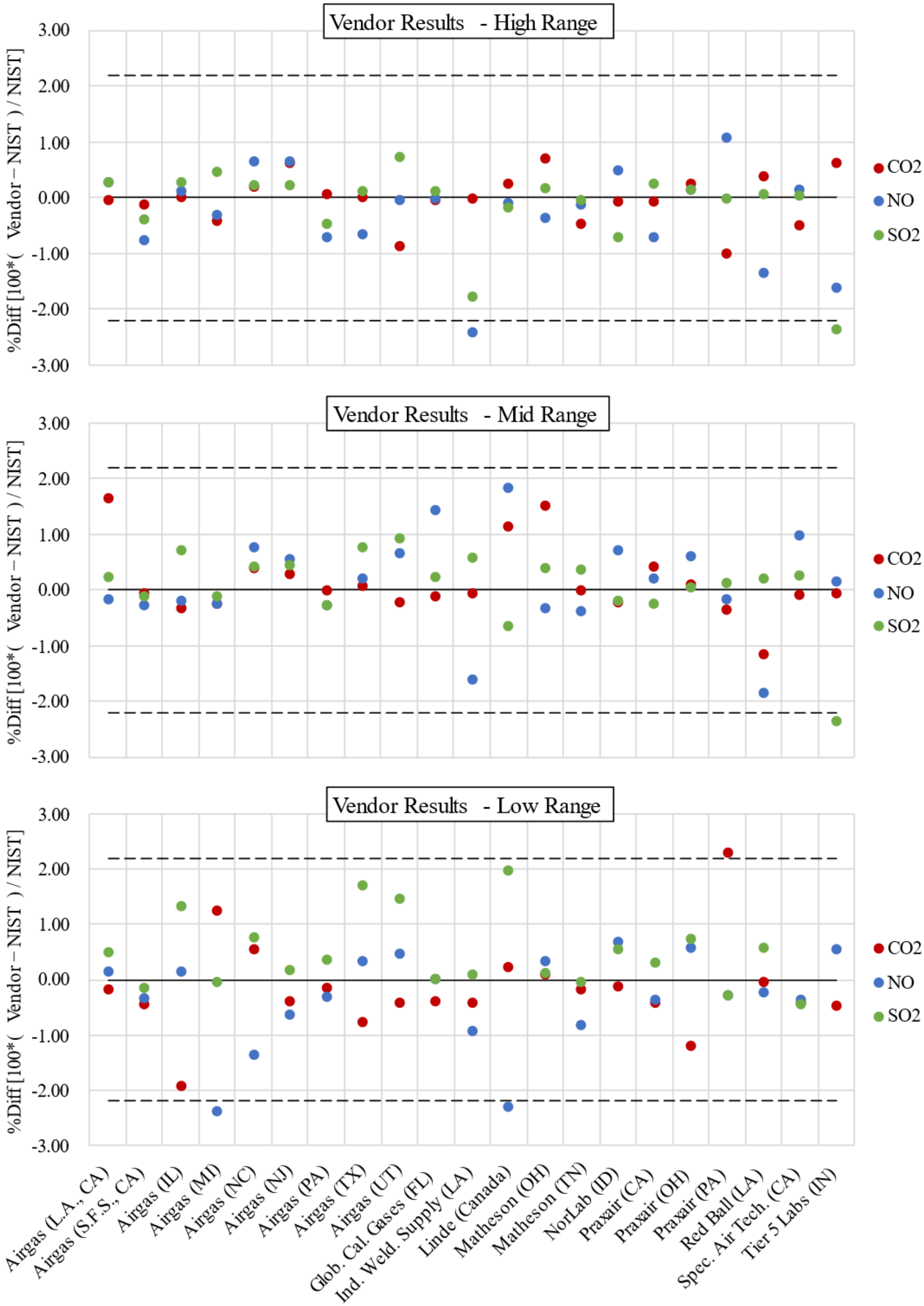

Figure 1. Relative difference between the vendor reported and NIST analyzed value for each component in the High, Mid and Low audit ranges. Points located outside the dashed lines (± 2.2 %) indicate a failure of the 2 % Tag Rule.

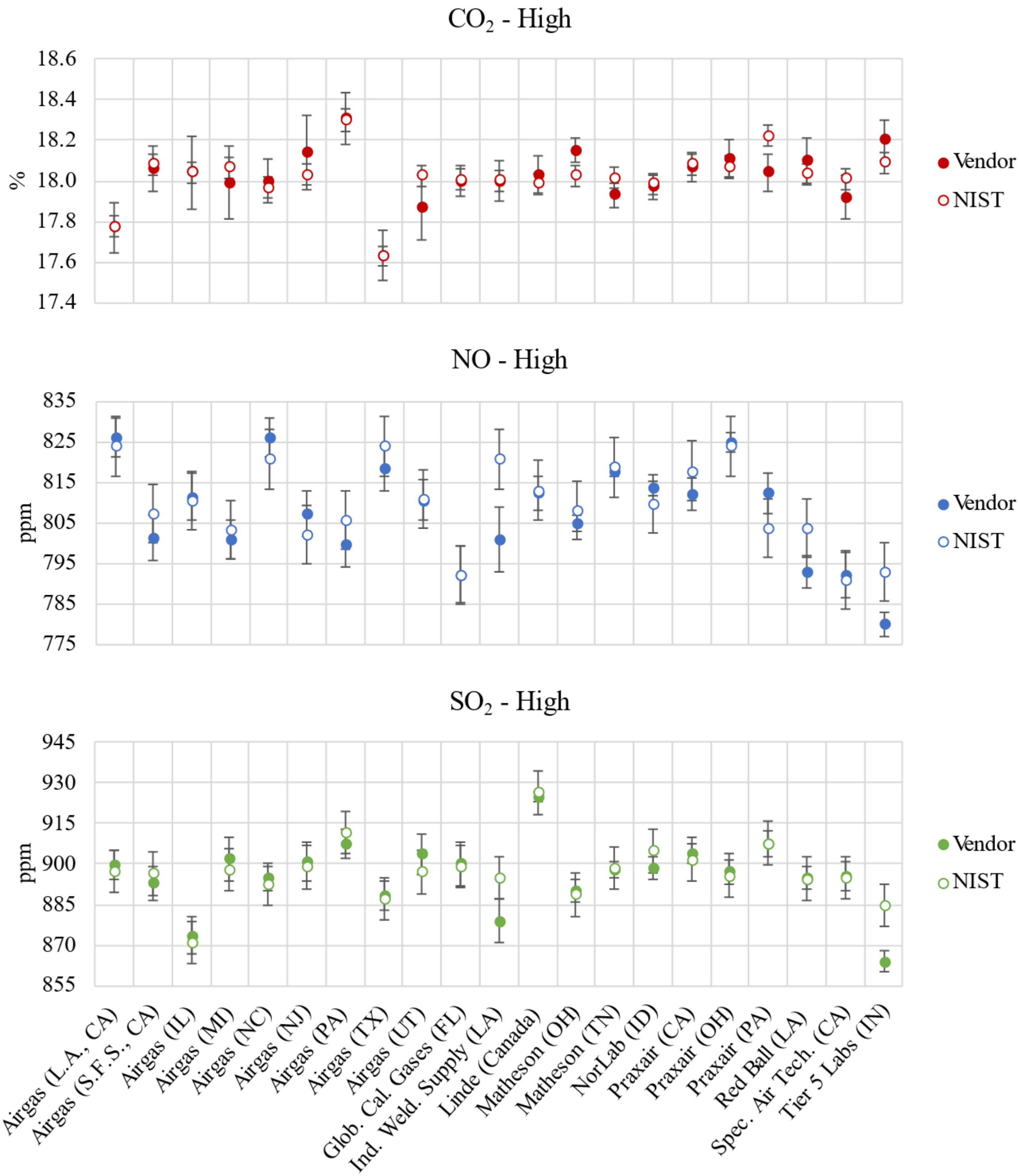

Figure 2a. Vendor certified and NIST determined concentrations for High range audit cylinders. Error bars represent *k* = 2 expanded uncertainties.

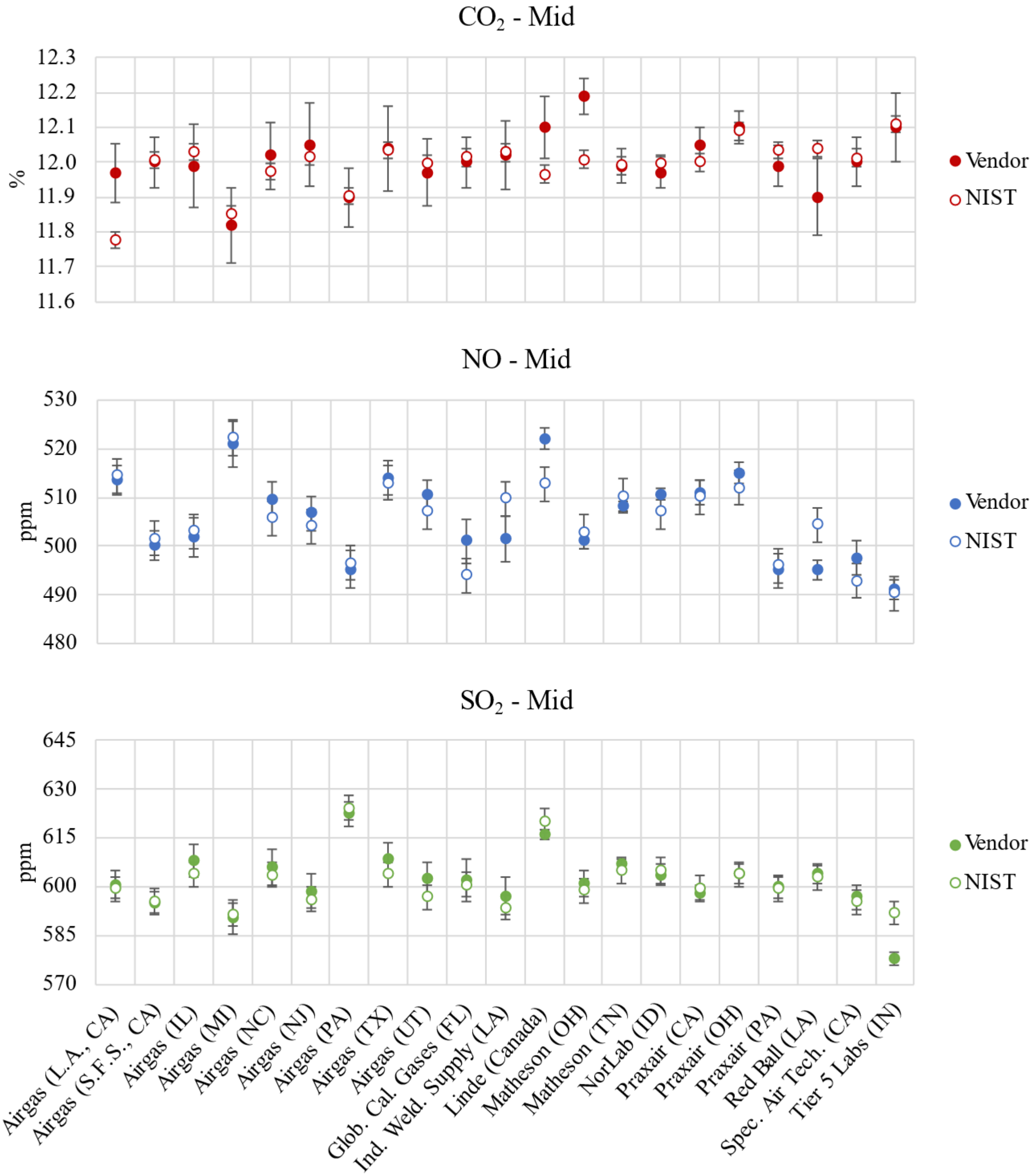

Figure 2b. Vendor certified and NIST determined concentrations for Mid range audit cylinders. Error bars represent *k* = 2 expanded uncertainties.

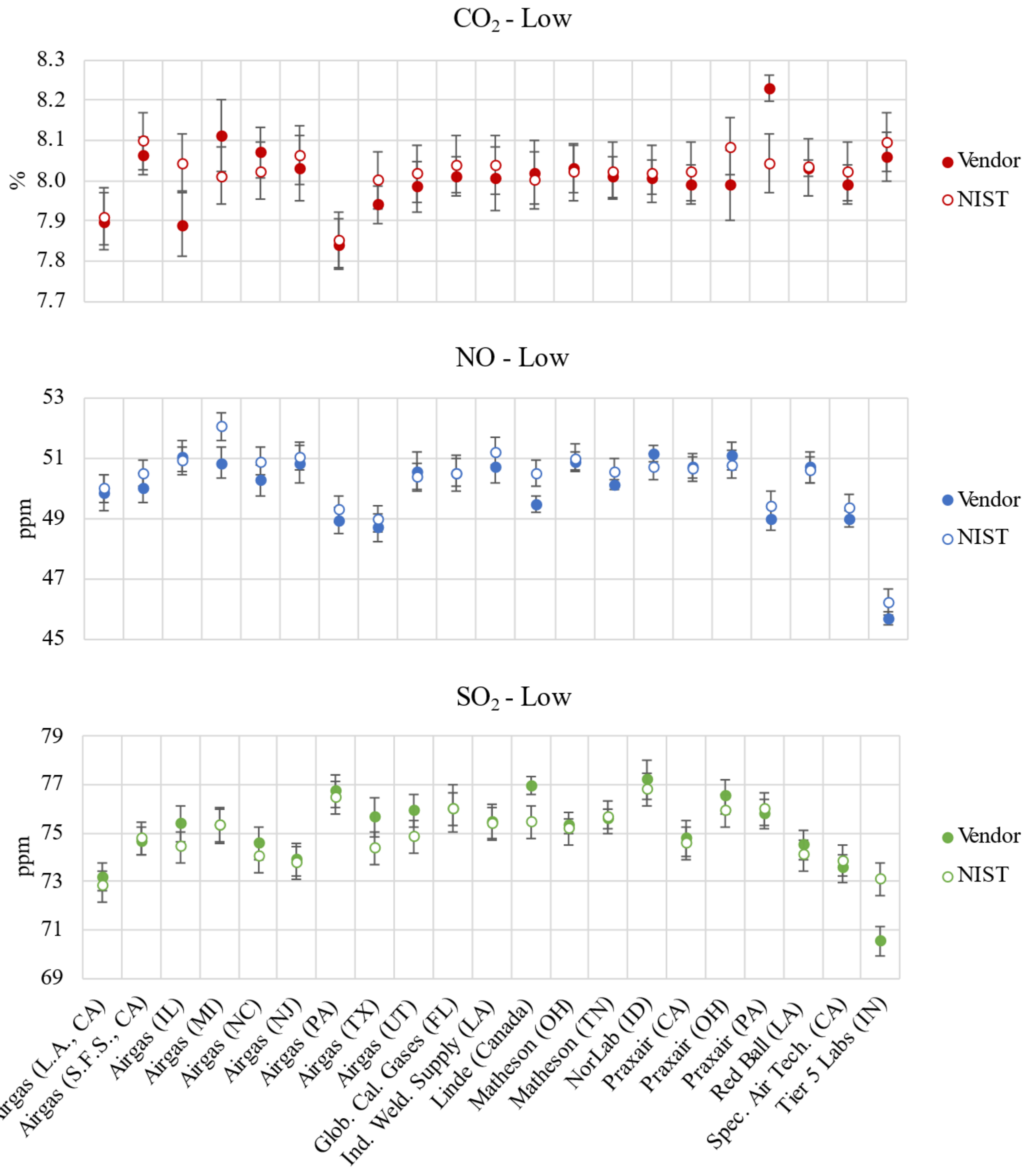

Figure 2c. Vendor certified and NIST determined concentrations for Low range audit cylinders. Error bars represent $k = 2$ expanded uncertainties.

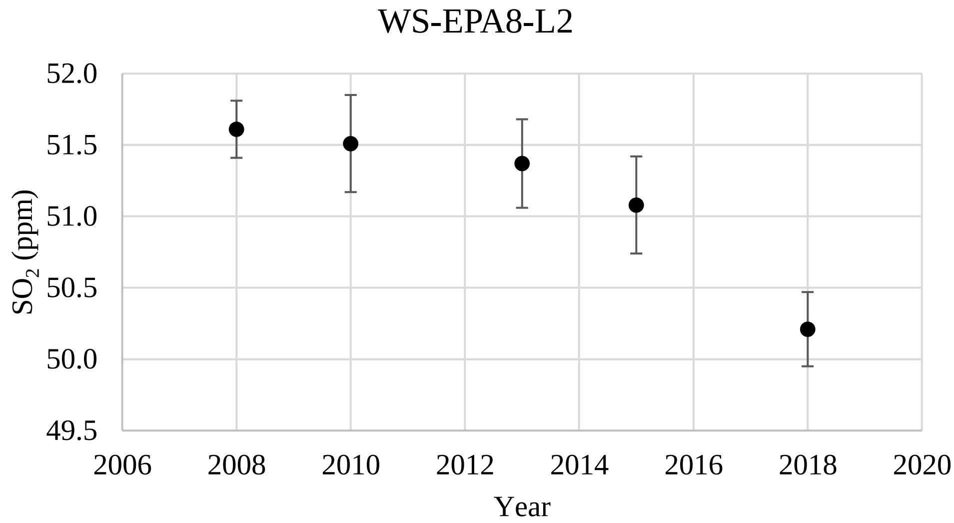

Figure 3. Analysis of the SO_2 concentration in working standard WS-EPA-L2 over time. Error bars represent expanded (k = 2) uncertainties.