

U.S. Department of Commerce
National Institute of Standards and Technology
Material Measurement Laboratory
Chemical Sciences Division
Gaithersburg, MD 20899

REPORT OF ANALYSIS

April 21, 2015

Environmental Protection Agency Blind Audit 2013

Submitted to:

Travis Johnson
U.S. Environmental Protection Agency
Clean Air Markets Division
1200 Pennsylvania Ave., NW (6204M)
Washington, DC 20460

The U.S. Environmental Protection Agency (EPA) conducted a blind audit of EPA protocol calibration gas cylinder mixtures produced by specialty gas manufacturers. The objective was to determine the concentration of the analytes in cylinder mixtures and to compare the quantified values with those stated in the certificates of the supplying producer. The mixtures are tri-blends of Carbon Dioxide (CO₂; range: 5 % mol/mol-20 % mol/mol); Nitric Oxide (NO; range: 25 µmol/mol - 1000 µmol/mol (ppm) and Total Oxides of Nitrogen, NO_x, within 1 % relative of NO) and Sulfur Dioxide (SO₂; range: 50 µmol/mol - 1000 µmol/mol (ppm)). The quality of these calibration mixtures is critical for the accurate determination and reporting of regulated gaseous emissions.

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

Candidate Samples Ordered

The basic criterion of the audit is that the gas manufacturers are unaware that they are participating in the audit i.e. that the audit is blind. A similar audit was conducted in 2006. For the 2006 audit, Electric Power Research Institute (EPRI) coordinated the shipment of the candidate cylinders from the end users, typically power companies, to NIST [1]. This approach certainly achieved a blind audit, but did not satisfy 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.

A similar, but unrelated audit was conducted in 2008 for the EPA Office of Inspector General [2] and a blind audit was conducted in 2010 [3]. In these audits, a contractor coordinated the purchase and delivery of samples to NIST. This approach achieved a blind audit and satisfied the above criteria. Consequently, the same approach was adopted for the current, 2013 audit where AMEC was chosen to purchase the samples directly from the gas vendors, and then coordinate their shipment to NIST. Again, this approach was successful, satisfying a blind audit, but the low concentration of SO₂ in the Low range caused a severe scheduling problem and time delay (see “Candidate Samples Received” section below).

AMEC purchased 108 gas mixture samples over three ranges. The nominal concentration (by mole) per component for each range was:

# of Samples	Range Type	CO ₂ (% ¹)	NO (ppm ²)	SO ₂ (ppm ²)
20	High	15.0	750	800
20	Mid	9.00	210	320
40	Low	5.00	40.0	35.0

These ranges were different than in previous audits (2008 and 2010):

Range Type	CO ₂ (% ¹)	NO (ppm ²)	SO ₂ (ppm ²)
High (Prev.)	18.0	900	1000
Mid (Prev.)	12.0	400	500
Low (Prev.)	5.00	50.0	50.0

¹ All concentrations labeled “%” in this report are equivalent to % mol/mol in SI units. The designation “%” is used as an equivalent unit and is standard industry practice.

² All concentrations labeled “ppm” in this report are equivalent to μmol/mol in SI units. The designation “ppm” is used as an equivalent unit and is standard industry usage.

The original objective was to purchase one sample of the High and Mid ranges, and two samples of the Low range (four samples in total) per manufacturing site of first-party vendors. However, due to a variety of reasons, this was not possible (see table 1 for a list of the vendors that provided samples). Firstly, the Matheson (TX) and Praxair (PA) facilities no longer produce EPA protocol gas mixtures. Attempted ordering to these facilities resulted in deliveries from Matheson (OH) and Praxair (CA) respectively. Secondly, all vendors claimed to be first-party. However, after taking delivery it was discovered that three vendors: Coastal Specialty Gas; Norco / Norlab; and Specialty Air Technology (underlined in table 1) had purchased their gas mixtures from third parties: Specialty Gases of America [for Coastal and Norco]; and Praxair (CA) respectively (bolded in table 1). Thirdly, the order that was attempted to be placed with Air Liquide (CO) was actually filled by Air Liquide (TX). Lastly, Applied Gas could not provide the gas mixtures and cancelled the order; Linde (Canada) could not provide the Low range gas mixture and transferred this part of the order to Linde (NJ). Consequently, there were the following deviations from the original objective:

- 1) The following manufacturing sites provided more than four samples:
 Air Liquide (TX) provided eight samples
 Linde (NJ) provided six samples

- Matheson (OH) provided eight samples
 Praxair (CA) provided twelve samples
 Specialty Gases of America provided twelve samples
- 2) Two known, first-party manufacturing sites were not represented: Air Liquide (CO) and Linde (Canada).
 - 3) There are 11 known first-party vendors, not the apparent 15. (See table 1.) It is not known if Applied Gas is a first-party vendor.

It is NIST's understanding, that these 11 vendors and their 22 manufacturing sites, including Air Liquide (CO) and Linde (Canada), fully represent the first-party manufacturing of EPA protocol calibration gas mixtures for sale in the United States. Nothing can be said regarding the performance of any EPA Protocol gas production site inadvertently not included in the audit. Any accuracy assessment is an instantaneous snapshot of the process being measured. These results should not be regarded as a final statement on the accuracy of EPA Protocol gases. They can be used as an indicator of the current status of the accuracy of EPA Protocol gases as a whole. However, individual results should not be taken as definitive indicators of the analytical capabilities of individual producers. The information in this audit is presented without assigning a rating to the gas vendors, for example, who is the best, who is approved, or not approved. Further, any mention of commercial products within this report is for information only; it does not imply recommendation or endorsement by NIST or EPA.

Candidate Samples Received and Inspected

AMEC began the purchase of the 108 candidate samples in August 2011. They started taking delivery of these samples in September 2011, and all were in their possession in January 2012. At this stage, 28 were returned to their respective vendors (for the reasons described in the "Candidate Samples Ordered" section above). The remaining 80 should have been delivered to NIST over the next few months. However, as per the EPA regulations in place at the time (see "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards", EPA-600/R-97/121), September 1997) the shelf life of the Low range was only 6 months due to the 35 ppm SO₂ concentration. Consequently, these 80 samples were returned to their respective manufacturing sites for re-certification from March 2012 onwards. The re-certification and return of mixtures to AMEC was not completed until January 2013.

Notice of audit participation was sent to the vendors by the EPA in February 2013. By the end of March 2013, as per the Code of Federal Regulations [40 CFR 75.21(g)(6) and (7)], the vendors had reimbursed AMEC, and arranged payment to NIST for the analysis of their audit samples. NIST took delivery of these 80 samples from April to October 2013 in four batches of approximately 20 (High, Mid, and the Low range split in two as: Air Liquide and Airgas only; and all other vendors).

Every sample was received with the cylinder valve shrink wrapped by the vendor and / or with a dust cap. (See tables 2.) This showed that the cylinders had not been used since leaving the gas manufacturing facility.

All samples were inside cylinder Hydro test (or Ultra test) and were packaged as:

Cylinder: DOT 3AL2015, Aluminum 6061 alloy; Internal Volume - 30 liters

Valve: Packless, stainless steel, CGA 660

Tables 2a, 2b, and 2c in the attachments detail the samples received, together with the start and end gas pressures at NIST. Gas pressure was measured using a 0-3000 psi gauge with increments of 50 psi. A discrepancy of more than 200 psi, between the vendors reported certified pressure and NIST start pressure, was considered significant. Three samples fell into this category (see Table 2c): two samples from Global Calibration where the observed pressure was 350 psi higher than that reported; and one

sample from Linde (NJ) where the observed pressure was 1000 psi lower pressure than that reported. The discrepancy for Global Calibration was attributed to a typing mistake on the certificate. The discrepancy for Linde (NJ) warranted further investigation which showed a slow leak at the cylinder / valve connection. However, it was concluded that there was sufficient gas pressure for this sample to remain in the audit. Consequently, all of the samples were in acceptable condition and were considered new since they were within their expiration dates.

Check of Vendor's Certificate of Analysis (CoA)

During the time between the order of gas mixtures (August 2011) and actual delivery to NIST (April to October 2013) the "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards" was updated from EPA-600/R-97/121 (September 1997) to EPA-600/R-12/531 (May 2012). There was a transition period from May 2012 to May 2013 where vendors were allowed to comply with a hybrid of the old and new versions of the EPA protocol. This is of particular importance for checking if the reported expiration dates are in compliance since the shelf life of mixtures increased with the newer protocol (e.g. Low Range: 6 month maximum certification period for September 1997 version, increased to 48 month for the May 2012 version). To avoid any confusion between the two versions of the EPA protocol, only elements that were not changed will be checked for compliance (i.e. the value of certificate expiration date will not be checked):

- 1) Cylinder identification number
- 2) Certified concentrations to be in parts per million (ppm) or percent (%) and be reported to three significant digits.
- 3) Balance gas of the gas mixture.
- 4) Cylinder pressure at certification.
- 5) Date of the certification.
- 6) Identification of the reference standard used in each component assay.
- 7) Reference standard must be Standard Reference Material (SRM) or SRM equivalent PRM (Primary Reference Material) or NIST Traceable Reference Material (NTRM) or Gas Manufacturer's Intermediate Standard (GMIS).
- 8) Statement that the certification was performed according to the EPA protocol.
- 9) Statement of assay procedure – G1 or G2.
- 10) Identification of laboratory that performed the assay.
- 11) If applicable, statement that a correction factor had been used to account for analytical interference.

This checklist is the minimum requirement to comply with sections 2.1.4 (September 1997) and 2.1.7 (May 2012) of the two versions of the protocol document. Some non-conformities were observed, as detailed in tables 3a, 3b, and 3c of the attachments. These tables also contain comments about the CoA which are **not** non-conformities. Other than the exceptions stated in table 3, the following held for all of the CoAs:

- 1) Total oxides of nitrogen (NO_x) or Nitrogen Dioxide (NO₂) was < 1 % of the certified NO concentration.
- 2) NO_x (or NO₂) was reported as "Reference Only" or without an analytical uncertainty.
- 3) Analytical accuracy was ± 1 % or better (unexpanded uncertainty).
- 4) The balance gas was nitrogen.
- 5) Other than Scott-Marrin (all Ranges) and Praxair (CA) (for High and Mid ranges), no correction factor to account for analytical interference was noted, even for the chemiluminescence (chemi) analysis of NO in the presence of CO₂.

Instrumentation / Analytical Techniques Used

The choice of analytical technique for each component was carefully considered. There were three aims. In order of priority they were:

- 1) Calculated uncertainty of 0.5 % or better.
- 2) An interference free analysis.
- 3) Simultaneous analysis of NO, SO₂, and CO₂.

It was not possible to achieve these three aims for every component for the three EPA ranges. (See table 4.) The best compromise, which satisfied the ≤ 0.5 % uncertainty aim, was:

- a) NO, SO₂ and CO₂ analyzed by Non Dispersive Infrared (NDIR) for High and Mid range.
- b) SO₂ and CO₂ analyzed by NDIR for Low range. NDIR was too imprecise for Low range NO.
- c) NO and SO₂ analyzed by Non Dispersive Ultra Violet (NDUV) for Low Range. The uncertainty of NO was > 0.5 % at High and Mid range due to severe interference from SO₂.
- d) NO analyzed by chemi luminescence for Low Range.

In addition, for at least three samples per High and Mid range, the NO NDIR analysis would be checked by Chemi and the SO₂ NDIR analysis checked by NDUV.

Details of the instrumentation used are in table 5.

Standards Used

The standards used to determine the CO₂, SO₂, and NO concentrations in the sample cylinders are detailed in tables: 6a, 6b, and 6c. The standards were SRM Lot Standards (LS) or Working Standards (WS), both of these type of standards are certified referencing NIST Primary Standards on a set schedule. The LS and WS standards used were all within their respective certified period. All the standards used are NIST traceable and are in balance N₂.

The LSs used to determine possible analytical interference between the three components of interest are detailed in table 6d. The pure CO₂ used was Research Grade (Purity > 99.99 %) from Airgas.

Tri-component Working Standards (WS-3), retained by NIST from the 2008 audit (see table 7e), were used to validate the analytical methodology and provide a qualitative link to the 2008 and 2010 audits.

Overall Experimental Design

1. Calibration curves consisting of binary mixtures of CO₂ or SO₂ or NO in balance N₂ were generated for each range on each instrument used. This was achieved by using a well characterized dilution system to create some of the curves, and Lot Standards and Working Standards to create others.
2. Interference experiments were then performed where the gas blending system was used to generate mixtures of NO with varying amounts of CO₂; and mixtures of SO₂ with varying amounts of CO₂.
3. One protocol gas sample was selected from the mid-point of each mixture level. This sample was designated "Reference". Next, samples were selected at the minimum and maximum level per component per range. These samples (2 to 6 per range) were designated "Test"
4. For each range, the Reference, some Test cylinders and the two WSs (see table 6e) were quantified for the 3 analytes using the closest NIST binary standard for each of the components and incorporating data from both the calibration curve and the interference experiments
5. The remaining protocol mixtures (and Test samples and WSs) at each range were analyzed using the "Reference".
6. The values determined for the Test cylinders (and WSs) at step 3 were compared with those determined in step 4 to determine any bias in the final analyses of the protocol gases.

Determination of Interferences

The same analytical techniques and instruments were used as in the previous audits. Only certain combinations of components / analytical technique had previously exhibited an interference that required a correction factor [1-3]. Consequently, only these combinations were investigated to determine a current correction factor. (See Table 6.)

NDIR Analysis of NO or SO₂ in the presence of CO₂

It has previously been established that [2,3]:

- 1) There is interference by CO₂ on NO and, to a lesser extent, on SO₂.
- 2) This interference is caused by a combination of CO₂ absorption which increases response, and pressure broadening [4,5], which decreases response.
- 3) This interference cannot be mathematically modeled. However, since the effect is not overly dependent on the CO₂ and NO (or SO₂) concentration, the same multiplicative correction factor (CF) can be used for each range.

The High, Mid, and Low-range gas mixtures were created by blending an appropriate LS from table 6e with CO₂ and house N₂. The CF for NO (or SO₂) was calculated by:

$$\text{Correction Factor, CF} = \frac{\text{NDIR Response without CO}_2}{\text{NDIR Response with CO}_2} \quad (\text{Eq 1})$$

In order to monitor instrument performance, the CFs were determined for NO (and SO₂) ranges as defined in previous audits [2, 3]. These CFs compared very favorably to the 2010 audit values:

EPA Mix Type	2013 Audit		2010 Audit	
	NO CF	SO ₂ CF	NO CF	SO ₂ CF
High (Prev.)	1.0151 ± 0.0019	1.0019 ± 0.0016	1.0162 ± 0.0019	1.0025 ± 0.0016
Mid (Prev.)	0.9997 ± 0.0019	1.0004 ± 0.0016	1.0022 ± 0.0019	1.0002 ± 0.0016
Low (Prev.)	N/A	0.9865 ± 0.0016	N/A	0.9884 ± 0.0016

Where the CF is unitless and the uncertainty is expressed at $k = 1$.

The CFs were also determined for NO (and SO₂) ranges as defined by the current, 2013 audit:

EPA Mix Type	2013 Audit	
	NO CF	SO ₂ CF
High (2013)	1.0108 ± 0.0019	1.0004 ± 0.0016
Mid (2013)	0.9996 ± 0.0019	0.9995 ± 0.0016
Low (2013)	N/A	0.9765 ± 0.0016

And will be the values used for this audit.

NDUV Analysis of NO in the presence of SO₂

SO₂ exhibits a severe interference on the NDUV analysis of NO. The NDUV analyzer automatically adjusts for this interference, but tends to over-adjust at high levels of SO₂ (> 250 ppm). Consequently, NDUV was not considered to analyze NO at the High and Mid range. However, it was considered an appropriate technique at Low range where samples were analyzed against the Reference (see Determination of Audit Concentrations section below), because this adjustment would be small. Further, since the range of SO₂ (33 ppm to 37 ppm) and NO (39 ppm to 42 ppm) is narrow, this adjustment will have little effect on the analytical ratio, effectively rendering the result interference free. (See table 17d for comparison between NO NIST values by Chemi and NDUV.)

Chemi Analysis of NO in presence of CO₂:

The 2008 and 2010 audits showed that the CO₂ effect on the chemi analysis of NO is [2, 3]:

- 1) Independent of NO concentration in the range: 10 ppm – 1000 ppm.
- 2) Linear in CO₂ concentration up to 20%.

Consequently, the correction factor for CO₂ interference is expressed as:

$$\text{Correction Factor, } CF_{CO_2} = \text{Grad}_{CO_2} * [\text{CO}_2 \text{ conc. in \%}] + \text{Int}_{CO_2} \quad (\text{Eq. 2})$$

where the y-intercept, Int_{CO_2} , is expected to be 1. CF_{CO_2} values for 10 ppm and 1000 ppm NO were determined at 5 %, 15 %, 15 %, and 20 % CO₂ by using the gas blender, an appropriate LS from table 6d, pure CO₂ and house N₂. As expected, CF_{CO_2} was linear in CO₂ concentration, and independent of NO, with the gradient and y-intercept comparing very favorably to the 2008 and 2010 audits:

	2013 Audit	2010 Audit	2008 Audit
Grad _{CO2}	0.0055649	0.0056071	0.0055681
Int _{CO2}	0.99950	1.00012	1.00004

Calculating CF_{CO2} for each EPA range (as defined by the current audit) reveals that the correction has hardly changed from 2008. See table below:

EPA Range	CO ₂ (%)	2013 Audit	2010 Audit		2008 Audit	
		CF _{CO2}	CF _{CO2}	%Diff. to 2013	CF _{CO2}	%Diff. to 2013
High	15.00	1.084297	1.08423	0.12	1.08356	0.05
Mid	9.00	1.04958	1.05058	0.10	1.05015	0.05
Low	5.00	1.02732	1.02816	0.08	1.02788	0.05

The 2013 values will be used for the current audit:

$$\text{Correction Factor, CF}_{\text{CO}_2} = 0.0055649 * [\text{CO}_2 \text{ conc. in \%}] + 0.99950 \quad (\text{Eq. 3})$$

Calibration Curves

A LS was used as a control and periodically analyzed to account for instrument drift. Two samples (a standard or a dilution of a standard using the Gas Diluter, GD) were analyzed between the control. The instrument response of the control was divided into the instrument response of the sample giving a ratio, r . At least three ratios were obtained per sample. The calibration curve was generated by plotting the concentration of the samples against the ratios. All curves were linear (other than low CO₂ by NDIR and high SO₂ by NDUV), contained at least four data points and were fitted by orthogonal least squares analysis that complies with ISO-6143 [6]. See tables 6a-c for the standards used and table 8 for the twelve calibration curves created and their fits. The fits are expressed as a function of r :

$$f(r) = A * r^2 + B * r + C \quad (\text{Eq. 4})$$

where $f(r)$ is equivalent to the concentration, and A, B and C are fitted constants.

Determination of Reference and Test Cylinder Concentrations

For each audit range, one protocol gas mixture was chosen as a Reference and at least another two were chosen as Test cylinders. The same LS used as the control for the appropriate calibration curve above was used as a control during the analytical cycle of these audit samples (plus the 2008 audit WSs – see table 6d). At least five ratios were obtained by dividing the instrument response of the audit sample (adjusted for interference using the relevant correction factor, see Determination of Interference section above) by the response of the control. This ratio was used to determine each component concentration using equation 4 and the appropriate fitting parameters from table 8. See Tables 18a-c (High range), tables 9a-c (Mid range), and tables 10a-c (Low Range) for the audit Reference (and Test and WSs)

concentrations of CO₂, SO₂ and NO. For the Reference, WSs and some Test mixtures the concentrations were determined by two methods as:

Component	EPA Range	Method #1		Method #2		%Diff. for Reference
		Technique	Curve	Technique	Curve	
SO ₂	High	NDUV	SO2-NDUV-HI	NDIR	SO2-NDIR-HI	-0.30
NO	High	Chemi	NO-Chemi-HI	NDIR	NO-NDIR-HI	0.16
SO ₂	Mid	NDUV	SO2-NDUV-HI	NDIR	SO2-NDIR-HI	-0.30
NO	Mid	Chemi	NO-Chemi-HI	NDIR	NO-NDIR-MID	0.10
SO ₂	Low	NDUV	SO2-NDUV-LO	NDIR	SO2-NDIR-LO	-0.37

The difference between the methods was within the expanded uncertainty ($k = 2$) of the individual methods. (See table 19a.) The methods were hence statistically equivalent and the resultant concentrations were averaged. The Reference cylinder concentrations are highlighted in tables 9a-11c.

Determination of Audit Concentrations

For each range, the appropriate Reference cylinder was analyzed periodically, throughout the analytical cycle, to account for instrument drift. One sample (unknown and of the same range as the Reference) were analyzed between the Reference. At least five ratios (per sample) were obtained by dividing the instrument response of the unknown by the instrument response of the Reference. The unknown component concentration (CO₂, SO₂ and NO) was obtained by multiplying this ratio by the equivalent component concentration of the Reference. The audit cylinders were analyzed as:

EPA Range	Analytical Technique	Components Analyzed, at the same time		
		# 1	# 2	# 3
High	NDIR	CO ₂	SO ₂	NO
Mid	NDIR	CO ₂	SO ₂	NO
Low	NDIR	CO ₂	SO ₂	N/A
Low	NDUV	N/A	SO ₂	NO ^a

The determined NIST concentrations of CO₂, SO₂ and NO, including a comparison to the vendor concentrations (including standard type and analytical technique used by vendor) are contained in tables 12a-c (High range), tables 13a-c (Mid range), and tables 14a-c (Low range). For Low range SO₂ the NIST concentration was the average of the NDIR and NDUV analyses. (See table 17c)

Determination of Pass or Fail 2 % Tag Rule

The NIST concentration and Vendor certified values were compared using the "Paired t Test" [5]. The statistical parameters were:

NULL Hypothesis: NIST and Vendor Values are equivalent
 Level of Confidence: 95 % (i.e. $k = 2$)
 NIST Relative Uncertainty: 0.86 % (at $k = 2$), the largest uncertainty (see table 20b)

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 2.15% (in practice rounded to 2.2%) between NIST concentration and Vendor certified values meant that the sample component has failed the 2 % Tag Rule. Samples that failed are Blue in tables 13, 14, and 15. A summary of the number of failures expressed as a percentage of the number of cylinders and per component is given below:

Range	Number of Failures				
	Cylinders	NO	SO ₂	CO ₂	All Components
High	1	1	0	0	1
Mid	1	1	0	0	1
Low	3	1	2	0	3
Totals	5	3	2	0	5
% Total	6.3 %	3.1 %	2.5 %	0.0 %	2.1 %

Comparison of Reference and Test Cylinder Concentrations

Assigning the audit concentrations (per range) from the Reference (of the same range) was very efficient because it allowed the simultaneous NDIR analysis of CO₂, SO₂, and NO for the High and Mid ranges, and the simultaneous NDUV analysis of SO₂ and NO for the Low range. The only drawback was a small increase in the uncertainty. (See Tables 19a-b.) However, the question remained whether or not this approach was consistent with naming the concentration from the appropriate calibration curve. This concern was tested by comparing the results of the analysis from the appropriate calibration and directly from the appropriate reference.

The results of these comparisons are in tables 15a-c (High range), tables 16a-c (Mid range), and tables 17a,b,d (Low range). Without exception, the differences between the two approaches were within the expanded uncertainty ($k = 2$) of the individual approach. Therefore, it was concluded that the two approaches were statistically equivalent. In the case of NO Low range, the NIST concentration was the average of the chemi and NDUV analyses. (See table 15c.)

Comparison to 2008 and 2010 EPA Audits

During the 2008 audit, two ternary mixtures, similar to the protocol gas mixtures, were purchased by NIST and analyzed along with the cylinders being audited [2]. These were designated NIST Working Standards. In order to provide an analytical link to the 2008 audit (and validate the analytical methodology), these two working standards were analyzed during the current audit where the CO₂, SO₂, and NO concentrations were determined against the appropriate calibration curve and against the appropriate Reference. Both approaches were statistically equivalent. (See tables 15-17.) Further, the agreements between the current (against Reference) and previous analyses were within the uncertainty ($k = 2$) of the individual analysis, hence showing a consistency between the two audits. (See tables 18a-c.)

Uncertainty Analysis

The uncertainty, u_{ISO} , for each component of the Reference cylinders was calculated by an orthogonal least squares fit that complies with ISO-6143 [7]. u_{ISO} is the uncertainty due to: the calibration curve, the standards used and the analytical ratios obtained. The overall uncertainty in the Reference concentration, $u_{reference}$, is given by:

$$U_{reference} = \sqrt{u_{ISO}^2 + u_{reg}^2 + u_{cf}^2}$$

where u_{reg} is the uncertainty due to analyte interaction with the gas regulator used for the analysis and u_{cf} is the uncertainty in the correction factor employed. Table 19a lists the $u_{reference}$ for the three Reference cylinders as a function of component and analytical technique.

The uncertainty, u_c , for the audit samples was calculated as:

$$u_c = \sqrt{u_{reference}^2 + u_{ratio}^2 + u_{reg}^2}$$

where, u_{ratio} and u_{reg} are the uncertainties of the analytical ratios obtained and analyte interaction with the regulator employed respectively. Table 19b details the uncertainty, u_c , as a function of component analyzed and EPA range. The assumed distribution is Gaussian. The final uncertainty, U , is expressed as:

$$U = k u_c$$

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 $\pm U$ with a level of confidence of approximately 95 % [8].

Disposition of Cylinders

All 80 audit cylinders were returned to their respective vendors.

Corrective Actions Taken by Gas Vendors

Vendors were given the opportunity to reanalyze their cylinders. Two of the four vendors that had one or more analyses fail the "2% Tag Rule" reported the reanalyzed values, and provided statements about the reanalysis and the corrective action(s) taken. The pertinent portions of these vendor statements are presented below. See Table 20 for the results of the reanalysis, the percent change from the original certification, and the comparison to the NIST concentrations. In all cases, following the corrective actions, the samples passed the "2% Tag Rule".

Linde: Cylinder Number CC-63232 - Re-analysis by the producing lab in Alpha, NJ agreed within 1% of NIST's 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", nor deviation from internal Linde procedures. Based on the long-term behavior of this cylinder, we have concluded that the discrepancy seen between the Linde certified value and NIST's analyzed value for Nitric Oxide is attributable to operator error. Most likely the cylinder was not run long enough to allow for a stable reading.

While strict adherence to the Protocol was in place during the analysis, simply following the Protocol did not cause the cylinder to be rejected under these circumstances. An agreement of 0.75% between first and second analysis for the NO component should have indicated a potential problem, but is not currently a trigger for failing analysis. As a result of this investigation, Linde will be reviewing its internal pass/fail criteria for reactive EPA Protocol blends where analytical trending may be used to indicate long term stability of blended mixtures.

Specialty Gases of America (SGA): Cylinder Number EB0002964 - After re-evaluation, the lower than certified value of Nitric Oxide for this cylinder (as compared to the actual) was due in part to SGA's installation of a new FTIR instrument. Upon investigation, it was determined the difference in the certified values was attributable to an unstable instrument base line at the time of the original analysis.

References:

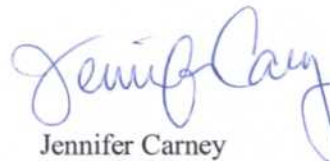
1. Environmental Protection Agency Protocol Gas Verification Program 2006; ROA#: 839.03-07-070a [10/16/2007]
2. Environmental Protection Agency Protocol Gas Analysis 2008; ROA#: 839.03-09-10 [12/04/2008]
3. Environmental Protection Agency Protocol Gas Analysis 2010; ROA#: 639.03-11-26a [01/13/2011]
4. Short range force effects in semiclassical molecular line broadening calculations; D. Robert and J. Bonamy; Journal of Physics (France) **40**; pp. 923-943 (1979)
5. Rare Gas Pressure Broadening of the NO Fundamental Vibration Band; Robert S. Pope and Paul J. Wolf; Journal of Molecular Spectroscopy **208**; pp. 153-160 (2001)
6. Quality Assurance for the Analytical Chemistry Laboratory; D. Brynn Hibbert; pp. 48-49, (2007)
7. Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures, ISO 6143, 2nd Edition 2001-05-01, 2001.
8. Guide to the Expression of Uncertainty, ISBN 92-67-10188-9, 1st Edition, ISO, Geneva, Switzerland, 1993

Notebooks: Protgasver #01 [ACD#: 3545], pp. 81-100
Protgasver #02 [ACD#: 3694], pp. 1-22

Prepared by:

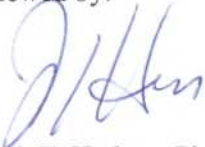


Lyn Gameson
Research Chemist



Jennifer Carney
Research Chemist

Reviewed by:



Joseph T. Hodges, Ph.D.
Group Leader
Gas Sensing Metrology Group



Franklin R. Guenther, Ph.D.
Research Chemist

Table 1: Initial Participating Vendors and their 2012 Protocol Gas Verification Program ID values (PGVP ID#).

Producer/Vendor	PGVP ID#	First-party Vendor	Number of Samples Provided	Audit Participation	Production Address
Air Liquide (CA)	A52012	Yes	4	Yes	8832 Dice Road, Santa Fe Springs, CA 90670
Air Liquide (CO)	A42012	Yes	0	No	Air Liquide (TX) , 11426 Fairmont Pkwy, La Porte, TX 77571
Air Liquide (MI)	A22012	Yes	4	Yes	1290 Combermere Street, Troy, MI 48083
Air Liquide (PA)	A12012	Yes	4	Yes	6141 Easton Road, Bldg 1, Plumsteadville, PA 18949
Air Liquide (TX)	A32012	Yes	8	Yes	11426 Fairmont Pkwy, La Porte, TX 77571
Airgas (CA)	B32012	Yes	4	Yes	11711 S. Alameda Str., Los Angeles, CA 90059
Airgas (IL)	B12012	Yes	4	Yes	12722 S. Wentworth Avenue, Chicago, IL 60628
Airgas (LA)	B42012	Yes	4	Yes	1075 Cinclare Drive, Port Allen, LA 70767
Airgas (MI)	B62012	Yes	4	Yes	2009 Bellaire Ave., Royal Oak, MI 48067
Airgas (NC)	B22012	Yes	4	Yes	630 United Drive, Durham, NC 27713
Airgas (NJ)	B52012	Yes	4	Yes	600 Union Landing Road, Riverton, NJ 08077
Applied Gas	M12012	Not Known	0	No	13903 Highway 34, Danbury, TX 77534
<u>Coastal Specialty Gas</u>	O12012	No	0	No	Specialty Gases of America , 6055 Brent Drive, Toledo, OH 43611
Global Calibration Gases	N12012	Yes	4	Yes	1090 Commerce Blvd, North Sarasota, FL 34243
Industrial Welding Supply	K12012	Yes	4	Yes	111 Buras Drive, Belle Chasse, LA 70037
Linde (Canada)	L12012	Yes	2	No	530 Watson St. East, Whitby, Ontario, Canada, L1N 5R9
Linde (NJ)	I12012	Yes	6	Yes	80 Industrial Drive, Alpha, NJ 08865
Liquid Technology	E12012	Yes	4	Yes	2048 Apex Court, Apopka, FL 32703

Table 1 (cont.): Initial Participating Vendors and their 2012 Protocol Gas Verification Program ID values (PGVP ID#).

Producer/Vendor	PGVP ID#	First-party Vendor	Number of Samples Provided	Audit Participation	Production Address
Matheson Trigas (OH)	D42012	Yes	8	Yes	1650 Enterprise Parkway, Twinsburg, OH 44087
Matheson Trigas (TN)	D52012	Yes	4	Yes	1799 Scepter Rd., Waverly, TN 37185
Matheson Trigas (TX)	N/A	N/A	0	No	Matheson Trigas (OH) , 1650 Enterprise Parkway, Twinsburg, OH 44087
<u>Norco/Norlab</u>	P12012	No	0	No	Specialty Gases of America , 6055 Brent Drive, Toledo, OH 43611
Praxair (CA)	F22012	Yes	12	Yes	5700 South Alameda Street, Los Angeles, CA 90058
Praxair (PA)	N/A	N/A	0	No	Praxair (CA) , 5700 South Alameda Street, Los Angeles, CA 90058
Red Ball Technical Gas Services	G12012	Yes	4	Yes	555 Craig Kennedy Way, Shreveport, LA 71107
Scott-Marrin, Inc.	H12012	Yes	4	Yes	6531 Box Springs Blvd., Riverside, CA 92507
<u>Specialty Air Technology</u>	J12012	No	0	No	Praxair (CA) , 5700 South Alameda Street, Los Angeles, CA 90058
Specialty Gases of America	C12012	Yes	12	Yes	6055 Brent Drive, Toledo, OH 43611

Vendors that claimed to be first-party, but purchased the gas mixture from another vendor (bolded) are underlined.

Table 2a: Cylinders Received and Package Inspection – High Range

Manufacturer (and State Location)	Cylinder Number	Received at NIST	Vendor Certification Date	Valve Shrink Wrapped by Vendor?	Dust Plug?	Vendor Reported Pressure (psig)	NIST Start Pressure (psig)	NIST End Pressure (psig)	Package Comments
Air Liquide (CA)	CC204826	4/3/2013	9/14/2011	Yes	No	2015	2000	1975	Analytical cylinder valve tag.
Air Liquide (MI)	ALM040137	4/3/2013	8/31/2011	Yes	No	2015	2000	1950	Analytical cylinder valve tag.
Air Liquide (PA)	ALM011324	4/3/2013	8/20/2011	Yes	No	1936	1900	1875	Analytical cylinder valve tag.
Air Liquide (TX)	ALM058073	4/3/2013	1/3/2012	Yes	Yes	2000	2000	1950	Analytical cylinder valve tag.
Airgas (CA)	SG9165679BAL	4/3/2013	10/11/2011	Yes	No	2015	1850	1825	
Airgas (IL)	CC197859	4/3/2013	10/5/2011	Yes	No	2015	1950	1925	
Airgas (LA)	CC142865	4/3/2013	9/20/2011	Yes	No	2015	1975	1950	
Airgas (MI)	XC026640B	4/3/2013	8/27/2011	Yes	No	2015	1975	1950	
Airgas (NJ)	CC58790	4/3/2013	8/30/2011	Yes	Yes	2015	2000	1475	Inside of cylinder valve was dirty. Cleaned with Kimwipe before use. Used as Reference .
Airgas (NC)	CC359021	4/3/2013	8/16/2011	Yes	No	2015	1950	1925	
Global Calibration Gases	EB0028690	4/3/2013	10/31/2011	Yes	No	2000	1900	1875	
Industrial Welding Supply	EB0020696	4/3/2013	9/1/2011	Yes	No	2015	2025	2000	
Linde (NJ)	CC110192	4/3/2013	9/9/2011	Yes	Yes	2000	1850	1825	Analytical cylinder valve tag. CGA 660 washer provided.
Liquid Technology	EB0026503	4/3/2013	9/2/2011	Yes	No	1900	1775	1725	
Matheson (OH)	SX43906	4/3/2013	8/23/2011	Yes	Yes	2000	1850	1825	

Table 2a (cont.): Cylinders Received and Package Inspection – High Range

Manufacturer (and State Location)	Cylinder Number	Received at NIST	Vendor Certification Date	Valve Shrink Wrapped by Vendor?	Dust Plug?	Vendor Reported Pressure (psig)	NIST Start Pressure (psig)	NIST End Pressure (psig)	Package Comments
Matheson (TN)	SX52734	4/3/2013	1/3/2012	Yes	Yes	1900	1800	1750	Two cylinder numbers were engraved in the container - CC339174 and SX52734. Presumably the latter is the current one, but the former number should be stamped out in order to avoid confusion.
Praxair (CA)	CC179522	4/3/2013	10/5/2011	Yes	Yes	2000	1850	1825	Analytical cylinder valve tag.
Red Ball Oxygen	EB0026353	4/3/2013	9/16/2011	Yes	No	1900	1750	1700	
Scott-Marrin	CC1806	4/3/2013	10/7/2011	No	Yes	2000	1800	1775	Analytical cylinder valve tag.
Specialty Gases of America	EB0003845	4/3/2013	9/20/2011	Yes	Yes	2215 at 85°F	2000	1975	

Table 2b: Cylinders Received and Package Inspection – Mid Range

Manufacturer and State Location	Cylinder Number	Received at NIST	Vendor Certification Date	Valve Shrink Wrapped by Vendor?	Dust Plug?	Vendor Reported Pressure (psig)	NIST Start Pressure (psig)	NIST End Pressure (psig)	Package Comments
Air Liquide (CA)	CC204826	5/31/2013	9/13/2011	Yes	No	1900	2050	2025	Analytical cylinder valve tag.
Air Liquide (MI)	CC171879	5/31/2013	9/9/2011	Yes	No	2015	1950	1925	Analytical cylinder valve tag.
Air Liquide (PA)	ALM039193	5/31/2013	9/20/2011	Yes	No	1962	1925	1900	Analytical cylinder valve tag.
Air Liquide (TX)	CC62138	5/31/2013	1/16/2012	Yes	Yes	2000	2000	1975	Analytical cylinder valve tag.
Airgas (CA)	CC304164	5/31/2013	10/10/2011	Yes	No	2015	1900	1500	Used as Reference .
Airgas (IL)	CC74428	5/31/2013	10/5/2011	Yes	No	2015	1950	1875	

Table 2b (cont.): Cylinders Received and Package Inspection – Mid Range

Manufacturer and State Location	Cylinder Number	Received at NIST	Vendor Certification Date	Valve Shrink Wrapped by Vendor?	Dust Plug?	Vendor Reported Pressure (psig)	NIST Start Pressure (psig)	NIST End Pressure (psig)	Package Comments
Airgas (LA)	XC022025B	5/31/2013	9/20/2011	Yes	No	2015	2000	1925	
Airgas (MI)	EB0013529	5/31/2013	8/26/2011	Yes	No	2015	2000	1975	
Airgas (NJ)	CC286961	5/31/2013	8/31/2011	Yes	Yes	2015	1925	1900	
Airgas (NC)	CC357442	5/31/2013	8/15/2011	Yes	No	2015	1950	1925	
Global Calibration Gases	EB0030321	5/31/2013	11/3/2011	Yes	No	2000	1875	1850	
Industrial Welding Supply	EB0010395	5/31/2013	9/1/2011	Yes	No	2015	2000	1950	
Linde (NJ)	CC20160	5/31/2013	9/9/2011	Yes	Yes	2000	1900	1850	Analytical cylinder valve tag. CGA 660 washer provided.
Liquid Technology	EB0023222	5/31/2013	8/25/2011	Yes	No	1900	1875	1800	
Matheson (OH)	SX40676	5/31/2013	8/26/2011	Yes	Yes	2000	1875	1850	
Matheson (TN)	EB0001803	5/31/2013	5/24/2012	Yes	Yes	1850	1800	1750	
Praxair (CA)	CC145327	5/31/2013	10/5/2011	Yes	Yes	2000	1800	1750	Analytical cylinder valve tag.
Red Ball Oxygen	EB0020045	5/31/2013	11/7/2011	Yes	No	1900	1825	1800	
Scott-Marrin	CC68813	5/31/2013	10/7/2011	No	Yes	2000	1900	1875	Analytical cylinder valve tag.
Specialty Gases of America	EB0002964	5/31/2013	9/10/2011	Yes	Yes	2215 at 85°F	2075	2050	

Table 2c: Cylinders Received and Package Inspection – Low Range

Manufacturer and State Location	Cylinder Number	Received at NIST	Vendor Certification Date	Valve Shrink Wrapped by Vendor?	Dust Plug?	Vendor Reported Pressure (psig)	NIST Start Pressure (psig)	NIST End Pressure (psig)	Package Comments
Air Liquide (CA)	CC153077	8/23/2013	10/19/2012	Yes	No	2000	1900	1850	Analytical cylinder valve tag.
Air Liquide (CA)	ALM000366	8/23/2013	10/12/2012	Yes	No	2000	1950	1900	Analytical cylinder valve tag.
Air Liquide (MI)	CC70168	8/23/2013	8/3/2012	Yes	No	1987	1875	1775	Analytical cylinder valve tag.
Air Liquide (MI)	CC62787	8/23/2013	8/3/2012	Yes	No	2001	1850	750	Analytical cylinder valve tag.
Air Liquide (PA)	ALM019988	8/23/2013	8/2/2012	Yes	No	2015	1975	1875	Analytical cylinder valve tag.
Air Liquide (PA)	ALM057617	8/23/2013	10/25/2012	Yes	No	1975	1925	1900	Analytical cylinder valve tag.
Air Liquide (TX)	CC149707	8/23/2013	8/27/2012	No	Yes	1876	1800	1775	Analytical cylinder valve tag.
Air Liquide (TX)	CC151832	8/23/2013	4/9/2012	No	Yes	1969	1875	1850	Analytical cylinder valve tag.
Airgas (CA)	CC1742	8/23/2013	8/7/2012	Yes	No	2000	1925	1900	
Airgas (CA)	SG9153513BAL	8/23/2013	8/7/2012	Yes	No	2000	1900	1850	Inside of cylinder valve was dirty. Cleaned with Kimwipe before use.
Airgas (IL)	CC126041	8/23/2013	8/6/2012	Yes	No	2015	1900	1875	
Airgas (IL)	CC351018	8/23/2013	8/6/2012	Yes	No	1900	1800	1725	
Airgas (LA)	CC343375	8/23/2013	9/25/2012	Yes	No	1900	1875	1825	
Airgas (LA)	CC274644	8/23/2013	9/7/2012	Yes	No	1950	1875	1850	
Airgas (MI)	CC29753	8/23/2013	8/21/2012	Yes	No	2000	1950	1900	
Airgas (MI)	CC231152	8/23/2013	8/21/2012	Yes	No	2000	1925	1850	
Airgas (NC)	CC357651	8/23/2013	7/26/2012	Yes	No	2000	1900	1875	
Airgas (NC)	CC357483	8/23/2013	7/26/2012	Yes	No	2000	1950	1925	
Airgas (NJ)	CC310530	8/23/2013	8/8/2012	Yes	Yes	1900	1925	1875	
Airgas (NJ)	CC346498	8/23/2013	8/8/2012	Yes	Yes	1900	1875	1825	

Table 2c (cont.): Cylinders Received and Package Inspection – Low Range

Manufacturer and State Location	Cylinder Number	Received at NIST	Vendor Certification Date	Valve Shrink Wrapped by Vendor?	Dust Plug?	Vendor Reported Pressure (psig)	NIST Start Pressure (psig)	NIST End Pressure (psig)	Package Comments
Global Calibration Gases	EB0030274	10/21/2013	8/17/2012	Yes	No	1500	1850	1800	
Global Calibration Gases	EB0028074	10/21/2013	8/17/2012	Yes	No	1500	1850	1775	
Industrial Welding Supply	EB0016137	10/21/2013	7/24/2012	Yes	No	2015	2000	1975	
Industrial Welding Supply	EB0019069	10/21/2013	7/24/2012	Yes	No	2015	2000	1875	
Linde (NJ)	CC128334	10/21/2013	8/14/2012	Yes	Yes	2000	1000	950	Analytical cylinder valve tag. CGA 660 washer provided. Slow leak at valve / cylinder connection.
Linde (NJ)	CC63232	10/21/2013	8/14/2012	Yes	Yes	2000	1900	1850	Analytical cylinder valve tag. CGA 660 washer provided.
Liquid Technology	CC233824	8/23/2013	7/25/2012	Yes	No	1900	1750	1725	
Liquid Technology	CC310794	8/23/2013	7/25/2012	Yes	No	1900	1800	1775	
Matheson (OH)	SX45138	10/21/2013	10/18/2012	Yes	Yes	1975	1825	1800	
Matheson (OH)	SX48647	10/21/2013	10/18/2012	Yes	Yes	1975	1850	1800	Two cylinder numbers were engraved in the container - CC312921 and SX48647. Presumably the latter is the current one, but the former number should be stamped out in order to avoid confusion.

Table 2c (cont.): Cylinders Received and Package Inspection – Low Range

Manufacturer and State Location	Cylinder Number	Received at NIST	Vendor Certification Date	Valve Shrink Wrapped by Vendor?	Dust Plug?	Vendor Reported Pressure (psig)	NIST Start Pressure (psig)	NIST End Pressure (psig)	Package Comments
Matheson (TN)	SX49346	10/21/2013	10/24/2012	Yes	Yes	1500	1700	1675	Two cylinder numbers were engraved in the container - CC321995 and SX49346. Presumably the latter is the current one, but the former number should be stamped out in order to avoid confusion.
Matheson (TN)	SX51685	10/21/2013	10/24/2012	Yes	Yes	1500	1700	1675	
Praxair (CA)	CC326016	10/21/2013	9/17/2012	Yes	Yes	2000	1900	1850	Analytical cylinder valve tag.
Praxair (CA)	CC179626	10/21/2013	9/17/2012	Yes	Yes	2000	1875	1825	Analytical cylinder valve tag.
Red Ball Oxygen	EB0005534	10/21/2013	10/9/2012	Yes	No	1900	1775	1750	
Red Ball Oxygen	EB0007021	10/21/2013	10/9/2012	Yes	No	1900	1775	1700	
Scott-Marrin	CC78131	10/21/2013	9/7/2012	No	Yes	2000	1925	1850	
Scott-Marrin	CC12706	10/21/2013	9/7/2012	No	Yes	2000	1900	1825	Analytical cylinder valve tag.
Specialty Gases of America	EB0002973	10/21/2013	8/18/2012	Yes	Yes	2000	1950	1900	Inside of cylinder valve was dirty. Cleaned with Kimwipe before use.
Specialty Gases of America	EB0002792	10/21/2013	8/18/2012	Yes	Yes	1950	1825	1800	

Table 3a: Nonconformities and Comments of Vendor Certificate of Analysis (CoA) – High Range

Manufacturer (and State Location)	Cylinder Number	Protocol Non-Conformities	COA Comments
Air Liquide (CA)	CC204826		Missing component name for NTRM 1687 - presumably nitric oxide.
Airgas (NC)	CC359021		By mistake, the Lot ID was entered as the standard type for carbon dioxide. Presumably a NTRM was used.
Global Calibration Gases	EB0028690	Missing NIST Sample Number for the SRM used for the NO analysis.	Confusing what > 1% means for the certified concentration of NOx. Presumably this means that NOx is within 1% of the NO certified value? Also confusing what Analytical Method was used for each Component. Suggest adding a Component column in the Instrument section.
Industrial Welding Supply	EB0020696	Missing NIST Sample Numbers for the SRMs used for the sulfur dioxide and nitric oxide analysis. IWS stated that they have added the NIST sample number to their certificates of analysis.	Typing mistake for the sulfur dioxide standard type used - SMR instead of SRM. Why no correction for the CO ₂ interference of the Chemi analysis of NO? IWS stated they have added this correction on their certificates of analysis.
Matheson (TN)	SX52734		The Measurement Principle for Nitric Oxide is stated as NDIR. However, the Make / Model used (Horiba CLA-510SS) is chemiluminescence. Which is correct: the principle or the model? Matheson stated that the incorrect analytical principle was stated on the certificate – NDIR instead of chemiluminescence.
Red Ball Oxygen	EB0026353	Missing NIST Sample Number for the SRM used for the CO ₂ analysis.	

Table 3b: Nonconformities and Comments of Vendor Certificate of Analysis (CoA) – Mid Range

Manufacturer (and State Location)	Cylinder Number	Protocol Non-Conformities	COA Comments
Air Liquide (CA)	CC204826		Missing component name for NTRM 1685 - presumably nitric oxide.
Airgas (NC)	CC357442		By mistake, the Lot ID was entered as this standard type for carbon dioxide and nitric oxide. Presumably a NTRM was used in each case.
Global Calibration Gases	EB0030321	Missing NIST Sample Number for the SRM used for the NO analysis.	Confusing what > 1% means for the certified concentration of NO _x . Presumably this means that NO _x is within 1% of the NO certified value? Also confusing what Analytical Method was used for each Component. Suggest adding a Component column in the Instrument section.
Industrial Welding Supply	EB0010395	Missing NIST Sample Numbers for the SRMs used for the sulfur dioxide and nitric oxide analysis. IWS stated that they have added the NIST sample number to their certificates of analysis.	Why no correction for the CO ₂ interference of the Chemi analysis of NO? IWS stated they have added this correction on their certificates of analysis.
Matheson (TN)	EB0001803		Why no correction for the CO ₂ interference of the Chemi analysis of NO? Matheson stated that their Analytical Team did not observe a statistically significant CO ₂ interference with the instrument used for the chemi analysis of NO. Therefore, no correction factor was employed.

Table 3c: Nonconformities and Comments of Vendor Certificate of Analysis (CoA) – Low Range

Manufacturer (and State Location)	Cylinder Number	Protocol Non-Conformities	COA Comments
Airgas (MI)	CC231152	No Expiration Date reported.	
Global Calibration Gases	EB0030274	Missing NIST Sample Number for the SRM used for the SO ₂ analysis.	Confusing what > 1% means for the certified concentration of NO _x . Presumably this means that NO _x is within 1% of the NO certified value? Also confusing what Analytical Method was used for each Component. Suggest adding a Component column in the Instrument section. Mistake on the Last Date Calibrated entry for CO ₂ - reported as 9/17/2012 one month AFTER the reported Certification Date of 8/17/2012.
Global Calibration Gases	EB0028074	Missing NIST Sample Number for the SRM used for the SO ₂ analysis.	Confusing what > 1% means for the certified concentration of NO _x . Presumably this means that NO _x is within 1% of the NO certified value? Also confusing what Analytical Method was used for each Component. Suggest adding a Component column in the Instrument section. Mistake on the Last Date Calibrated entry for CO ₂ - reported as 9/17/2012 one month AFTER the reported Certification Date of 8/17/2012.
Industrial Welding Supply	EB0016137		Why no correction for the CO ₂ interference of the Chemi analysis of NO? IWS stated they have added this correction on their certificates of analysis.
Industrial Welding Supply	EB0019069		Why no correction for the CO ₂ interference of the Chemi analysis of NO? IWS stated they have added this correction on their certificates of analysis.
Matheson (OH)	SX45138		Why no correction for the CO ₂ interference of the Chemi analysis of NO? Matheson stated that their Analytical Team did not observe a statistically significant CO ₂ interference with the instrument used for the chemi analysis of NO. Therefore, no correction factor was employed.

Table 3c (cont.): Nonconformities and Comments of Vendor Certificate of Analysis (CoA) – Low Range

Manufacturer (and State Location)	Cylinder Number	Protocol Non-Conformities	COA Comments
Matheson (OH)	SX48647		Why no correction for the CO ₂ interference of the Chemi analysis of NO? Matheson stated that their Analytical Team did not observe a statistically significant CO ₂ interference with the instrument used for chemi analysis of NO. Therefore, no correction factor was employed.
Matheson (TN)	SX49346		Why no correction for the CO ₂ interference of the Chemi analysis of NO? Matheson stated that their Analytical Team did not observe a statistically significant CO ₂ interference with the instrument used for the chemi analysis of NO. Therefore, no correction factor was employed..
Matheson (TN)	SX51685		Why no correction for the CO ₂ interference of the Chemi analysis of NO? Matheson stated that their Analytical Team did not observe a statistically significant CO ₂ interference with the instrument used for the chemi analysis of NO. Therefore, no correction factor was employed.
Praxair (CA)	CC326016		Why no correction for the CO ₂ interference of the Chemi analysis of NO? Praxair stated that there was a program error that caused the CO ₂ correction statement to be over written for re-certified gas mixtures. This program error has been rectified.
Praxair (CA)	CC179626		Why no correction for the CO ₂ interference of the Chemi analysis of NO? ? Praxair stated that there was a program error that caused the CO ₂ correction statement to be over written for re-certified gas mixtures. This program error has been rectified.

Table 4: Analytical Techniques as a function of High, Mid and Low EPA Samples, uncertainty is stated at $k = 2$

Analytical Technique	NO			SO ₂			CO ₂		
	Range	Interference Free?	% Uncertainty	Range	Interference Free?	% Uncertainty	Range	Interference Free?	% Uncertainty
Non Dispersive Infrared (NDIR)	High	No	≤ 0.5	High	No	≤ 0.5	High	Yes	≤ 0.5
	Mid	No	≤ 0.5	Mid	No	≤ 0.5	Mid	Yes	≤ 0.5
	Low	No	> 0.5	Low	No	≤ 0.5	Low	Yes	≤ 0.5
Non Dispersive Ultra Violet (NDUV)	High	No	> 0.5	High	Yes	≤ 0.5	High	N/A	N/A
	Mid	No	> 0.5	Mid	Yes	≤ 0.5	Mid	N/A	N/A
	Low	No	≤ 0.5	Low	Yes	≤ 0.5	Low	N/A	N/A
Chemiluminescence (Chemi)	High	No	≤ 0.5	High	N/A	N/A	High	N/A	N/A
	Mid	No	≤ 0.5	Mid	N/A	N/A	Mid	N/A	N/A
	Low	No	≤ 0.5	Low	N/A	N/A	Low	N/A	N/A
Fourier Transform Infrared (FTIR)	High	Maybe	> 0.5	High	Maybe	> 0.5	High	Yes	> 0.5
	Mid	Maybe	> 0.5	Mid	Maybe	> 0.5	Mid	Yes	> 0.5
	Low	Maybe	> 0.5	Low	Maybe	> 0.5	Low	Yes	> 0.5

Table 5: Instrumentation and Analytical Techniques used

Manufacturer	Description / Analytical Technique	NIST#	Purpose
Horiba	Model VA-3000 NDIR	631375	Analyze CO ₂ in Range: 4 % – 23% Analyze SO ₂ in Range: 50 ppm – 1250 ppm Analyze NO in Range: 200 ppm – 1200 ppm
Ametek	Series 9000 NDUV	613059	Analyze SO ₂ in Range: 25 ppm – 1000 ppm Analyze NO in Range: 47 ppm – 53 ppm
Thermo	Model 42C Chemiluminescence	586629	Analyze NO in Range: 10 ppm - 1000 ppm
EnviroNics	Series 2040 Gas Blending System	594333	Used to determine correction factor to account for any interference between CO ₂ and / or SO ₂ and / or NO
Bios International	Drycal ML-800	626779	Used to determine correction factor to account for any interference between CO ₂ and / or SO ₂ and / or NO
NIST	Gas Dilutor	N/A	Used to create calibration curves for NO, SO ₂ and CO ₂

Table 6a: Standards (in balance nitrogen) used to determine CO₂ Concentration, with uncertainty (k=1)

SRM Number	Lot Standard	Cylinder Number	Conc. (%)	Uncertainty (%)	Expiration Date	Pressure (psig)	ROA# [Report Date]
2745	9-BL-01	AAL067828	15.700	0.010	11/05/2020	250	646.03-13-005 [11/05/2012]
1675b	6-FL-01	AAL053273	13.9646	0.0033	11/9/2019	100	639.03-12-034[11/10/2011]
2626a	37-01-EL	ALM045206	3.916	0.003	3/16/2015	250	839.03-07-078[3/16/2007]

Table 6b: Standards (in balance nitrogen) used to determine SO₂ Concentration, with uncertainty (k=1)

SRM Number	Standard Type	Standard ID	Cylinder Number	Conc. (ppm)	Uncertainty (ppm)	Expiration Date	Pressure (psig)	ROA# [Report Date]
1696a	LS	90-DL-01	AAL071137	3395.7	0.8	5/21/2021	100	646.03-13-102 [5/21/2013]
1663a	LS	92-EL-01	AAL053243	1476	1.8	7/6/2017	100	839.03-08-150b [7/6/2009]
1662a	LS	93-GL-02	CA04089	973.8	2.0	6/1/2015	950	839.03-07-116 [5/22/2007]
1662a	LS	93-HL-01	AAL072013	978.18	0.90	6/1/2015	550	839.03-07-116 [5/22/2007]
1661a	LS	94-HL-02	CC142045	491.10	0.45	8/30/2021	1000	646.03-13-138. [8/30/2013]
N/A	WS	SO2-WS-2	KAL003797	255.57	0.14	11/21/2015	1250	839.03-08-017 [11/21/2007]
1694a	LS	95-JL-02	AAL071390	98.59	0.05	12/12/2015	100	839.03-08-032 [12/12/2007]
1693a	LS	96-IL-02	AAL053248	50.15	0.12	3/22/2019	300	639.03-11-065 [3/22/2011]

Table 6c: Standards (in balance nitrogen) used to determine NO Concentration, with uncertainty (k=1)

SRM Number	Standard Type	Lot Standard	Cylinder Number	Conc. (ppm)	Uncertainty (ppm)	Expiration Date	Pressure (psig)	ROA# [Report Date]
2631a	LS	47-FL-01	AAL071135	2958.9	1.4	7/3/2019	700	646.03-13-130 [7/3/2011]
1687b	LS	41-JL-01	CC90603	985.9	2.5	3/5/2018	300	839.03-10-061 [3/5/2010]
2735	LS	141-CL-01	AAL070909	779.8	1.0	11/15/2015	500	639.03-12-037 [11/15/2011]
1686b	LS	42-KL-01	CC90574	491.3	1.3	10/8/2017	300	839.03-10-004 [10/8/2009]
1685b	LS	43-LL-01	AAL072023	244.08	0.21	1/15/2018	400	646.03-13-024 [1/15/2012]
1684b	LS	44-SL-02	AAL070456	97.62	0.04	1/25/2020	1000	639.03-12-117 [1/25/2012]
1683b	LS	45-UL-02	AAL070437	48.667	0.019	3/25/2019	800	639.03-12-032 [3/25/2011]
2629a	LS	50-FL-01	XC019684B	19.60	0.08	4/1/2016	500	646.03-13-066 [4/1/2013]
2628a	WS	NO-WS-1	ALM038428	9.979	0.010	4/4/2016	1000	646.03-13-071 [4/4/2013]

Table 6d: Standards (in balance nitrogen) used to determine Analytical Interference, with uncertainty (k=1)

SRM Number	Component	Standard Type	Lot Standard	Cylinder Number	Conc. (ppm)	Uncertainty (ppm)	Expiration Date	Pressure (psig)	ROA# [Report Date]
2631a	SO ₂	LS	90-DL-03	AAL071145	3395.3	0.9	5/21/2021	1850	646.03-13-102 [5/21/2013]
1687b	SO ₂	WS	SO2-WS-2	KAL003797	255.57	0.14	1/21/2015	1250	839.03-08-17 [11/21/2007]
2631a	NO	LS	47-FL-01	AAL071135	2958.7	1.4	11/15/2015	900	639.03-12-007 [11/15/2011]

Table 6e: Working Standards (in balance nitrogen) certified from 2008, with uncertainty (k=1) [2]

Sample ID	Cylinder Number	CO ₂ (%)	SO ₂ (ppm)	NO (ppm)	Expiration Date	Pressure (psig)
WS-EPA8-L1	CA08181	5.111 ± 0.011	51.35 ± 0.14	50.85 ± 0.17	1/11/2015	1600
WS-EPA8-L2	ALM054809	5.0110 ± 0.0075	51.61 ± 0.10	51.45 ± 0.13	1/11/2015	700
WS-EPA8-M1	CC5188	12.186 ± 0.018	515.1 ± 1.2	408.4 ± 1.1	1/11/2015	1700
WS-EPA8-M2	CA08177	12.073 ± 0.025	497.2 ± 1.5	399.5 ± 1.4	1/11/2015	1700
WS-EPA8-H1	CA08268	18.038 ± 0.038	998.0 ± 3.0	895.8 ± 3.0	1/11/2015	1700
WS-EPA8-H2	SA10582	18.208 ± 0.027	1003.5 ± 2.3	929.8 ± 2.5	1/11/2015	1700

Table 7: Summary of Component Interference per Analytical Technique

Analyzed Component	Analytical Technique	Interference Component	Interference
CO ₂	NDIR	NO	None observed up to 2900 ppm NO
CO ₂	NDIR	SO ₂	None observed up to 2500 ppm SO ₂
SO ₂	NDIR	NO	None observed up to 2900 ppm NO
SO ₂	NDIR	CO ₂	Complex interference caused by a combination of CO ₂ absorption (increases signal) and pressure broadening (decreases signal). Not possible to model, but the effect is not overly dependent on SO ₂ and CO ₂ . Use CF of 1.0014 for EPA High range, 0.9995 for EPA Mid range, and 0.9765 for Low range. CFs are instrument dependent. Use for NIST#: 631375 only
NO	NDIR	SO ₂	None observed up to 2500 ppm SO ₂
NO	NDIR	CO ₂	Complex interference caused by a combination of CO ₂ absorption (increases signal) and pressure broadening (decreases signal). Not possible to model, but the effect is not overly dependent on NO and CO ₂ . Use CF of 1.0108 for EPA High range and 0.9996 for EPA Mid range CFs are instrument dependent. Use for NIST#: 631375 only
SO ₂	NDUV	CO ₂	None observed up to 20 % CO ₂
SO ₂	NDUV	NO	None observed up to 1500 ppm NO
SO ₂	NDUV	CO	None observed up to 50 ppm NO
NO	NDUV	SO ₂	Severe interference. However, the NO analytical ratio is not effected over the narrow range of SO ₂ (33 ppm to 37 ppm) and NO (39 ppm to 42 ppm).
NO	Chemi	CO ₂	Large reduction in instrument response that can accurately be determined. Correction equation is linear in CO ₂ concentration and independent on NO. The equation developed is valid for 10 - 1000 ppm NO in the presence of up to 20 % CO ₂ ($CF_{co2} = 0.00556489 * [CO_2 \text{ in } \%] + 0.999469$) CF is instrument dependent. Use for NIST#: 586629 only.
NO	Chemi	SO ₂	None observed up to 1050 ppm SO ₂

Table 8: Calibration Curves created as a function of Component and Analytical Technique. All standards used were single component in balance N₂.

Component	Analytical Technique	Control	Binary Dilution of	# of Points	Fitting Type	Fitting Parameters			Fitting Range	Curve Name
						A	B	C		
NO	NDIR	141-CL-01	47-FL-01	11	Linear	N/A	780.490	-0.742	550 ppm - 1050 ppm	NO-NDIR-HI
NO	NDIR	43-LL-01	47-FL-01	10	Linear	N/A	243.140	0.948	90 ppm - 450 ppm	NO-NDIR-MID
NO	Chemi	141-CL-01	N/A	4	Linear	N/A	781.079	0.401	200 ppm - 1000 ppm	NO-CHEMI-HI
NO	Chemi	45-UL-02	N/A	4	Linear	N/A	48.636	-0.034	20 ppm - 100 ppm	NO-CHEMI-LO
SO ₂	NDIR	93-GL-02	90-DL-01	11	Linear	N/A	977.626	-3.978	550 ppm - 1050 ppm	SO2-NDIR-HI
SO ₂	NDIR	WS-SO2-2	90-DL-01	8	Linear	N/A	255.617	-0.061	160 ppm - 550 ppm	SO2-NDIR-MID
SO ₂	NDIR	96-IL-02	WS-SO2-2	9	Linear	N/A	49.048	1.104	25 ppm - 55 ppm	SO2-NDIR-LO
SO ₂	NDUV	93-GL-02	N/A	5	Quadratic	-22.701	998.544	-2.154	100 ppm - 1000 ppm	SO2-NDUV-HI
SO ₂	NDUV	96-IL-02	WS-SO2-2	9	Linear	N/A	50.250	-0.0998	25 ppm - 55 ppm	SO2-NDUV-LO
CO ₂	NDIR	6-FL-01	Pure CO ₂	8	Linear	N/A	13.926	0.037	10 % - 19.5 %	CO2-NDIR-HI
CO ₂	NDIR	6-FL-01	Pure CO ₂	6	Linear	N/A	13.908	0.055	7.5 % - 14 %	CO2-NDIR-MID
CO ₂	NDIR	37-01-EL	9-BL-01	10	Quadratic	-0.05741	4.289	-0.315	3.8 % - 5.8 %	CO2-NDIR-LO

Table 9a: NIST CO₂ Concentrations of Reference (highlighted), 2008 audit WSs and Test cylinders - EPA High Range with Expanded Uncertainty (k = 2)

Vendor / Sample ID	Cyl#	Audit Type	CO ₂		
			Using Curve	Conc. (%)	± (%)
Airgas (NJ)	CC58790	Reference	CO2-NDIR-HI	15.036	0.045
WS-EPA8-H1	CA08268	2008	CO2-NDIR-HI	18.047	0.054
WS-EPA8-H2	SA10582	2008	CO2-NDIR-HI	18.211	0.055
Air Liquide (MI)	ALM040137	Test	CO2-NDIR-HI	15.067	0.045
Air Liquide (TX)	ALM058073	Test	CO2-NDIR-HI	14.918	0.045
Liq. Technology	EB0026503	Test	CO2-NDIR-HI	14.988	0.045
Matheson (TN)	SX52734	Test	CO2-NDIR-HI	14.952	0.045

Table 9b: NIST SO₂ Concentrations of Reference (highlighted), 2008 audit WSs and Test cylinders - EPA High Range with Expanded Uncertainty (k = 2)

Vendor / Sample ID	Cyl#	Audit Type	SO ₂ ^a			SO ₂			SO ₂ (ppm)		
			Using Curve	Conc. (ppm)	± (ppm)	Using Curve	Conc. (ppm)	± (ppm)	%Diff	Mean	± (ppm)
Airgas (NJ)	CC58790	Reference	SO2-NDIR-HI	797.0	4.3	SO2-NDUV-HI	799.4	3.5	-0.30	798.2	3.9
WS-EPA8-H1	CA08268	2008	SO2-NDIR-HI	998.2	5.4	SO2-NDUV-HI	998.4	4.0	-0.01	998.3	4.7
WS-EPA8-H2	SA10582	2008	SO2-NDIR-HI	1001.3	5.4	SO2-NDUV-HI	1001.1	4.0	0.01	1001.2	4.7
Air Liquide (MI)	ALM040137	Test	SO2-NDIR-HI	795.5	4.3						
Air Liquide (TX)	ALM058073	Test	SO2-NDIR-HI	789.5	4.3						
Liq. Technology	EB0026503	Test	SO2-NDIR-HI	800.0	4.3						
Matheson (TN)	SX52734	Test	SO2-NDIR-HI	837.3	4.5						

^a Using EPA High SO₂ NDIR correction factors of 1.0014 for 2013 samples, and 1.0019 for 2008 WSs

Table 9c: NIST NO Concentrations of Reference (highlighted), 2008 audit WSs and Test cylinders - EPA High Range with Expanded Uncertainty ($k = 2$)

Vendor / Sample ID	Cyl#	Audit Type	NO ^a			NO ^b			NO (ppm)		
			Using Curve	Conc. (ppm)	± (ppm)	Using Curve	Conc. (ppm)	± (ppm)	%Diff.	Mean	± (ppm)
Airgas (NJ)	CC58790	Reference	NO-NDIR-HI	745.5	3.9	NO-CHEMI-HI	744.3	4.2	0.16	744.9	4.0
WS-EPA8-H1	CA08268	2008	NO-NDIR-HI	897.1	4.7	NO-CHEMI-HI	892.0	5.0	0.57	894.5	4.9
WS-EPA8-H2	SA10582	2008	NO-NDIR-HI	932.1	4.9	NO-CHEMI-HI	926.5	5.2	0.60	929.3	5.0
Air Liquide (MI)	ALM040137	Test	NO-NDIR-HI	745.6	3.9						
Air Liquide (TX)	ALM058073	Test	NO-NDIR-HI	745.6	3.9						
Liq. Technology	EB0026503	Test	NO-NDIR-HI	759.6	4.0						
Matheson (TN)	SX52734	Test	NO-NDIR-HI	754.4	4.0						

^a Using EPA High NO NDIR correction factors of 1.0108 for 2013 samples, and 1.0151 for 2008 WSs

^b Using CO₂ correction factor (Equation 3)

Table 10a: NIST CO₂ Concentrations of Reference (highlighted), 2008 audit WSs and Test cylinders - EPA Mid Range with Expanded Uncertainty ($k = 2$)

Vendor / Sample ID	Cyl#	Audit Type	CO ₂		
			Using Curve	Conc. (%)	± (%)
Airgas (CA)	CC304164	Reference	CO2-NDIR-MID	9.005	0.027
WS-EPA8-M1	CC51188	2008	CO2-NDIR-MID	12.171	0.037
WS-EPA8-M2	CA08177	2008	CO2-NDIR-MID	12.079	0.036
Air Liquide (TX)	CC62138	Test	CO2-NDIR-MID	8.997	0.027
Airgas (IL)	CC74428	Test	CO2-NDIR-MID	9.025	0.027
Airgas (LA)	XC022025B	Test	CO2-NDIR-MID	9.032	0.027
Ind. Welding Supply	EB0010395	Test	CO2-NDIR-MID	9.008	0.027
Liquid Technology	EB0023222	Test	CO2-NDIR-MID	8.946	0.027
Praxair (CA)	CC145327	Test	CO2-NDIR-MID	9.100	0.027

Table 10b: NIST SO₂ Concentrations of Reference (highlighted), 2008 audit WSs and Test cylinders - EPA Mid Range with Expanded Uncertainty (k = 2)

Vendor / Sample ID	Cyl#	Audit Type	SO ₂ ^a			SO ₂			SO ₂ (ppm)		
			Using Curve	Conc. (ppm)	± (ppm)	Using Curve	Conc. (ppm)	± (ppm)	%Diff.	Mean	± (ppm)
Airgas (CA)	CC304164	Reference	SO2-NDIR-MID	320.2	1.7	SO2-NDUV-HI	321.2	1.4	-0.30	320.7	1.6
WS-EPA8-M1	CC51188	2008	SO2-NDIR-MID	511.6	2.8	SO2-NDUV-HI	515.1	2.3	-0.69	513.4	2.5
WS-EPA8-M2	CA08177	2008	SO2-NDIR-MID	495.3	2.7	SO2-NDUV-HI	499.2	2.2	-0.76	497.2	2.4
Air Liquide (TX)	CC62138	Test	SO2-NDIR-MID	327.8	1.8						
Airgas (IL)	CC74428	Test	SO2-NDIR-MID	315.2	1.7						
Airgas (LA)	XC022025B	Test	SO2-NDIR-MID	323.8	1.7						
Ind. Welding Supply	EB0010395	Test	SO2-NDIR-MID	320.4	1.7						
Liquid Technology	EB0023222	Test	SO2-NDIR-MID	324.3	1.8						
Praxair (CA)	CC145327	Test	SO2-NDIR-MID	321.2	1.7						

^a Using EPA Mid SO₂ NDIR correction factors of 0.9995 for 2013 samples, and 1.0004 for 2008 WSs

Table 10c: NIST NO Concentrations of Reference (highlighted), 2008 audit WSs and Test cylinders - EPA Mid Range with Expanded Uncertainty ($k = 2$)

Vendor / Vendor ID	Cyl#	Audit Type	NO ^a			NO ^b			NO (ppm)		
			Using Curve	Conc. (ppm)	± (ppm)	Using Curve	Conc. (ppm)	± (ppm)	%Diff.	Mean	± (ppm)
Airgas (CA)	CC304164	Reference	NO-NDIR-MID	212.2	1.2	NO-CHEMI-HI	212.4	1.1	-0.10	212.3	1.2
WS-EPA8-M1	CC51188	2008	NO-NDIR-MID	405.9	2.3	NO-CHEMI-HI	407.0	2.2	-0.27	406.4	2.2
WS-EPA8-M2	CA08177	2008	NO-NDIR-MID	397.8	2.2	NO-CHEMI-HI	399.3	2.2	-0.39	398.6	2.2
Air Liquide (TX)	CC62138	Test	NO-NDIR-MID	203.0	1.1						
Airgas (IL)	CC74428	Test	NO-NDIR-MID	206.8	1.1						
Airgas (LA)	XC022025B	Test	NO-NDIR-MID	209.6	1.1						
Ind. Welding Supply	EB0010395	Test	NO-NDIR-MID	219.4	1.2						
Liquid Technology	EB0023222	Test	NO-NDIR-MID	218.0	1.2						
Praxair (CA)	CC145327	Test	NO-NDIR-MID	213.4	1.2						

^a Using EPA Mid NO NDIR correction factors of 0.9863 for 2013 samples, and 0.9997 for the 2008 WSs

^b Using CO₂ correction factor (Equation 3)

Table 11a: NIST CO₂ Concentrations of Reference (highlighted), 2008 audit WSs and Test cylinders - EPA Low Range with Expanded Uncertainty (k = 2)

Vendor / Sample ID	Cyl#	Audit Type	CO ₂		
			Using Curve	Conc. (%)	± (%)
Air Liquide (MI)	CC171777	Reference	CO2-NDIR-LO	4.992	0.015
WS-EPA8-L1	CA08181	2008	CO2-NDIR-LO	5.113	0.015
WS-EPA8-L2	ALM054809	2008	CO2-NDIR-LO	5.007	0.015
Liquid Technology	CC233824	Test	CO2-NDIR-LO	4.924	0.015

Table 11b: NIST SO₂ Concentrations of Reference (highlighted), 2008 audit WSs and Test cylinders - EPA Low Range with Expanded Uncertainty (k = 2)

Vendor / Sample ID	Cyl#	Audit Type	SO ₂ ^a			SO ₂			SO ₂ (ppm)		
			Using Curve	Conc. (ppm)	± (ppm)	Using Curve	Conc. (ppm)	± (ppm)	%Diff	Mean	± (ppm)
Air Liquide (MI)	CC171777	Reference	SO2-NDIR-LO	34.76	0.23	SO2-NDUV-LO	34.63	0.19	0.37	34.70	0.21
WS-EPA8-L1	CA08181	2008	SO2-NDIR-LO	51.49	0.34	SO2-NDUV-LO	51.32	0.29	0.33	51.40	0.31
WS-EPA8-L2	ALM054809	2008	SO2-NDIR-LO	51.42	0.34	SO2-NDUV-LO	51.32	0.29	0.18	51.37	0.31
Liquid Technology	CC233824	Test	SO2-NDIR-LO	34.91	0.23	SO2-NDUV-LO	34.81	0.19	0.27	34.86	0.21

^a Using EPA Low SO₂ NDIR correction factors of 0.9765 for 2013 samples, and 0.9865 for 2008 WSs

Table 11c: NIST NO Concentrations of Reference (highlighted), 2008 audit WSs and Test cylinders - EPA Low Range with Expanded Uncertainty ($k = 2$)

			NO ^a		
Vendor / Sample ID	Cyl#	Audit Type	Using Curve	Conc. (ppm)	\pm (ppm)
Air Liquide (MI)	CC171777	Reference	NO-Chemi-LO	40.05	0.26
WS-EPA8-L1	CA08181	2008	NO-Chemi-LO	50.55	0.33
WS-EPA8-L2	ALM054809	2008	NO-Chemi-LO	51.08	0.34
Global Calibration. Gases	EB0028074	Test	NO-Chemi-LO	39.30	0.26
Liquid Technology	CC233824	Test	NO-Chemi-LO	41.37	0.27
Matheson (TN)	SX49346	Test	NO-Chemi-LO	41.16	0.27
Praxair (CA)	CC179626	Test	NO-Chemi-LO	40.72	0.27
Praxair (CA)	CC326016	Test	NO-Chemi-LO	40.38	0.27
Red Ball	EB0005534	Test	NO-Chemi-LO	41.31	0.27

Table 12a: Vendor Certified and NIST Concentrations – EPA High Range – CO₂
 (Data from Workbook: 2013_June_High_NDIR_Ratios.xls Worksheet: Table_12a_CO2_Hi on 5/17/2014)

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST NDIR (%)	Vendor (%)	%Diff ^a
Air Liquide (CA)	CC204826	NTRM	FTIR	15.04	15.0	-0.26
Air Liquide (MI)	ALM040137	NTRM	FTIR	15.07	15.1	0.21
Air Liquide (PA)	ALM011324	NTRM	FTIR	15.09	15.08	-0.07
Air Liquide (TX)	ALM058073	NTRM	FTIR	14.92	14.9	-0.11
Airgas (CA)	SG9165679BAL	NTRM	FTIR	15.02	15.02	-0.03
Airgas (IL)	CC197859	NTRM	NDIR	15.08	15.04	-0.25
Airgas (LA)	CC142865	NTRM	FTIR	15.05	14.99	-0.39
Airgas (MI)	XC026640B	NTRM	FTIR	15.04	15.14	0.68
Airgas (NC)	CC359021	NTRM	FTIR	15.02	14.82	-1.36
Airgas (NJ)	CC58790	NTRM	FTIR	15.04	15.06	0.16
Global Calibration	EB0028690	GMIS	GC-TCD	15.05	15.13	0.55
Industrial Welding Supply	EB0020696	GMIS	NDIR	15.05	15.04	-0.06
Linde	CC110192	NTRM	NDIR	15.10	15.05	-0.34
Liquid Technology	EB0026503	GMIS	FTIR	15.00	15.05	0.31
Matheson (OH)	SX43906	SRM	FTIR	15.03	15.1	0.45
Matheson (TN)	SX52734	GMIS	NDIR	14.96	14.96	-0.03
Praxair	CC179522	GMIS	NDIR	15.06	15.07	0.05
Red Ball	EB0026353	SRM	NDIR	15.05	15.0	-0.35
Scott-Marrin	CC1806	GMIS	GC-TCD	15.05	14.99	-0.38
Specialty Gases of America	EB0003845	GMIS	FTIR	15.00	15.1	0.69

^a %Diff. computed as $100 * (\text{Vendor Conc.} - \text{NIST Conc.}) / \text{NIST Conc.}$

Value of Reference is highlighted.

Color code: Black is ≤ 2.20 % difference, and blue is > 2.2 % difference and fails the audit.

Table 12b: Vendor Certified and NIST Concentrations – EPA High Range – SO₂
 (Data from Workbook: 2013_June_High_NDIR_Ratios.xls Worksheet: Table_12b_SO2_Hi on 5/17/2014)

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST NDIR (%)	Vendor (ppm)	%Diff ^a
Air Liquide (CA)	CC204826	NTRM	FTIR	803.1	800	-0.39
Air Liquide (MI)	ALM040137	NTRM	FTIR	796.9	795	-0.24
Air Liquide (PA)	ALM011324	NTRM	FTIR	797.1	796	-0.14
Air Liquide (TX)	ALM058073	NTRM	FTIR	790.8	790	-0.10
Airgas (CA)	SG9165679BAL	NTRM	FTIR	804.8	805.9	0.14
Airgas (IL)	CC197859	NTRM	FTIR	800.7	799.9	-0.10
Airgas (LA)	CC142865	NTRM	FTIR	804.0	807.4	0.42
Airgas (MI)	XC026640B	NTRM	FTIR	808.0	807.7	-0.04
Airgas (NC)	CC359021	NTRM	FTIR	807.6	812.3	0.58
Airgas (NJ)	CC58790	NTRM	FTIR	798.2	800.3	0.27
Global Calibration	EB0028690	GMIS	NDIR	807.1	798.3	-1.09
Industrial Welding Supply	EB0020696	SRM	NDIR	796.5	807.7	1.41
Linde	CC110192	NTRM	NDIR	804.9	809	0.51
Liquid Technology	EB0026503	GMIS	FTIR	801.4	801	-0.05
Matheson (OH)	SX43906	SRM	FTIR	804.2	801	-0.39
Matheson (TN)	SX52734	SRM	NDIR	839.0	839	0.00
Praxair	CC179522	GMIS	NDIR	793.9	799	0.64
Red Ball	EB0026353	GMIS	NDIR	796.7	796	-0.08
Scott-Marrin	CC1806	GMIS	UV Photometry	797.5	802	0.57
Specialty Gases of America	EB0003845	GMIS	FTIR	796.1	795	-0.14

^a %Diff. computed as 100 * (Vendor Conc. – NIST Conc.) / NIST Conc.

Value of Reference is highlighted.

Color code: Black is ≤ 2.20 % difference, and blue is > 2.2 % difference and fails the audit..

Table 12c: Vendor Certified and NIST Concentrations – EPA High Range – NO
(Data from Workbook: 2013_June_High_NDIR_Ratios.xls Worksheet: Table_12c_NO_Hi on 5/17/2014)

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST NDIR (%)	Vendor (ppm)	%Diff ^a
Air Liquide (CA)	CC204826	NTRM	FTIR	757.3	755	-0.31
Air Liquide (MI)	ALM040137	NTRM	FTIR	746.3	739	-0.98
Air Liquide (PA)	ALM011324	NTRM	FTIR	751.6	746	-0.74
Air Liquide (TX)	ALM058073	NTRM	FTIR	745.8	739	-0.91
Airgas (CA)	SG9165679BAL	NTRM	FTIR	757.2	759.0	0.23
Airgas (IL)	CC197859	NTRM	FTIR	751.9	757.7	0.77
Airgas (LA)	CC142865	NTRM	FTIR	757.5	757.2	-0.04
Airgas (MI)	XC026640B	NTRM	FTIR	754.8	758.6	0.50
Airgas (NC)	CC359021	NTRM	FTIR	769.6	775.6	0.78
Airgas (NJ)	CC58790	NTRM	FTIR	744.9	752.4	1.01
Global Calibration	EB0028690	SRM	Chemi	774.0	764.5	-1.23
Industrial Welding Supply	EB0020696	SRM	Chemi	771.9	769.9	-0.26
Linde	CC110192	GMIS	FTIR	750.6	751	0.05
Liquid Technology	EB0026503	GMIS	FTIR	758.6	781	2.95
Matheson (OH)	SX43906	SRM	FTIR	756.6	752	-0.60
Matheson (TN)	SX52734	SRM	Chemi	754.2	756	0.24
Praxair	CC179522	GMIS	Chemi	759.5	754	-0.72
Red Ball	EB0026353	GMIS	NDIR	755.5	753	-0.34
Scott-Marrin	CC1806	GMIS	Chemi	749.8	745	-0.64
Specialty Gases of America	EB0003845	GMIS	FTIR	745.2	758	1.72

^a %Diff. computed as $100 * (\text{Vendor Conc.} - \text{NIST Conc.}) / \text{NIST Conc.}$

Value of Reference is highlighted.

Color code: Black is ≤ 2.20 % difference, and blue is > 2.2 % difference and fails the audit..

Table 13a: Vendor Certified and NIST Concentrations – EPA Mid Range – CO₂
 (Data from Workbook: 2013_July_Mid_NDIR_Ratios.xls Worksheet: Table_13a_CO2_Mid on 5/17/2014)

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST NDIR (%)	Vendor (%)	%Diff ^a
Air Liquide (CA)	EB0007513	NTRM	FTIR	8.989	8.99	0.01
Air Liquide (MI)	CC171879	NTRM	FTIR	8.996	9.06	0.72
Air Liquide (PA)	ALM039193	NTRM	FTIR	8.997	9.01	0.14
Air Liquide (TX)	CC62138	NTRM	FTIR	8.992	8.97	-0.24
Airgas (CA)	CC304164	NTRM	FTIR	9.005	9.008	0.03
Airgas (IL)	CC74428	NTRM	NDIR	9.023	8.992	-0.35
Airgas (LA)	XC022025B	NTRM	FTIR	9.037	9.075	0.42
Airgas (MI)	EB0013529	NTRM	FTIR	9.007	9.057	0.55
Airgas (NC)	CC357442	NTRM	FTIR	9.003	9.010	0.08
Airgas (NJ)	CC286961	NTRM	FTIR	8.986	8.926	-0.66
Global Calibration	EB0030321	GMIS	GC-TCD	9.013	9.05	0.41
Industrial Welding Supply	EB0010395	GMIS	NDIR	9.010	8.879	-1.45
Linde	CC20160	GMIS	NDIR	9.051	9.02	-0.35
Liquid Technology	EB0023222	GMIS	FTIR	8.936	9.03	1.05
Matheson (OH)	SX40676	SRM	FTIR	9.016	9.15	1.48
Matheson (TN)	EB0001803	SRM	NDIR	9.109	8.97	-1.53
Praxair	CC145327	GMIS	NDIR	9.104	9.21	1.17
Red Ball	EB0020045	GMIS	NDIR	9.022	9.07	0.54
Scott-Marrin	CC68813	GMIS	GC-TCD	8.999	8.96	-0.44
Specialty Gases of America	EB0002964	GMIS	FTIR	8.944	9.09	1.63

^a %Diff. computed as $100 * (\text{Vendor Conc.} - \text{NIST Conc.}) / \text{NIST Conc.}$

Value of Reference is highlighted.

Color code: Black is ≤ 2.20 % difference, and blue is > 2.2 % difference and fails the audit.

Table 13b: Vendor Certified and NIST Concentrations – EPA Mid Range – SO₂
 (Data from Workbook: 2013_July_Mid_NDIR_Ratios.xls Worksheet: Table_13b_SO2_Mid on 5/17/2014)

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST (ppm)	Vendor (ppm)	%Diff ^a
Air Liquide (CA)	EB0007513	NTRM	FTIR	322.6	325	0.75
Air Liquide (MI)	CC171879	NTRM	FTIR	320.1	321	0.27
Air Liquide (PA)	ALM039193	NTRM	FTIR	318.1	317	-0.33
Air Liquide (TX)	CC62138	NTRM	FTIR	328.1	327	-0.32
Airgas (CA)	CC304164	NTRM	FTIR	320.7	322.2	0.47
Airgas (IL)	CC74428	NTRM	FTIR	315.8	316.5	0.22
Airgas (LA)	XC022025B	NTRM	FTIR	324.4	328.0	1.11
Airgas (MI)	EB0013529	NTRM	FTIR	320.7	321.2	0.14
Airgas (NC)	CC357442	NTRM	FTIR	316.0	317.5	0.48
Airgas (NJ)	CC286961	NTRM	FTIR	323.0	324.1	0.33
Global Calibration	EB0030321	GMIS	NDIR	327.8	326.8	-0.31
Industrial Welding Supply	EB0010395	SRM	NDIR	322.3	319.0	-1.02
Linde	CC20160	GMIS	NDIR	320.4	317	-1.05
Liquid Technology	EB0023222	GMIS	FTIR	324.8	320	-1.46
Matheson (OH)	SX40676	SRM	FTIR	326.1	327.5	0.43
Matheson (TN)	EB0001803	SRM	NDIR	322.0	321.6	-0.13
Praxair	CC145327	GMIS	NDIR	321.9	324	0.66
Red Ball	EB0020045	GMIS	NDIR	316.2	317	0.26
Scott-Marrin	CC68813	GMIS	UV Photometry	319.9	319	-0.29
Specialty Gases of America	EB0002964	GMIS	FTIR	319.1	320	0.27

^a %Diff. computed as $100 * (\text{Vendor Conc.} - \text{NIST Conc.}) / \text{NIST Conc.}$

Value of Reference is highlighted.

Color code: Black is ≤ 2.20 % difference, and blue is > 2.2 % difference and fails the audit..

Table 13c: Vendor Certified and NIST Concentrations – EPA Mid Range – NO
(Data from Workbook: 2013_July_Mid_NDIR_Ratios.xls Worksheet: Table_13c_NO_Mid on 5/17/2014)

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST (ppm)	Vendor (ppm)	%Diff ^a
Air Liquide (CA)	EB0007513	NTRM	FTIR	213.0	213	-0.01
Air Liquide (MI)	CC171879	NTRM	FTIR	212.4	213	0.27
Air Liquide (PA)	ALM039193	NTRM	FTIR	211.8	212	0.11
Air Liquide (TX)	CC62138	NTRM	FTIR	203.4	204	0.31
Airgas (CA)	CC304164	NTRM	FTIR	212.3	211.3	-0.47
Airgas (IL)	CC74428	NTRM	FTIR	207.1	206.6	-0.24
Airgas (LA)	XC022025B	NTRM	FTIR	210.1	209.0	-0.53
Airgas (MI)	EB0013529	NTRM	FTIR	211.9	211.2	-0.32
Airgas (NC)	CC357442	NTRM	FTIR	212.4	211.7	-0.33
Airgas (NJ)	CC286961	NTRM	FTIR	210.1	208.4	-0.81
Global Calibration	EB0030321	SRM	Chemi	215.9	215.8	-0.06
Industrial Welding Supply	EB0010395	SRM	Chemi	219.3	218.0	-0.59
Linde	CC20160	GMIS	FTIR	212.1	212	-0.03
Liquid Technology	EB0023222	GMIS	FTIR	217.3	220	1.25
Matheson (OH)	SX40676	SRM	FTIR	211.5	209.8	-0.83
Matheson (TN)	EB0001803	SRM	Chemi	214.8	211.1	-1.73
Praxair	CC145327	GMIS	Chemi	214.0	211	-1.41
Red Ball	EB0020045	GMIS	NDIR	215.7	216	0.14
Scott-Marrin	CC68813	GMIS	Chemi	207.8	206.5	-0.61
Specialty Gases of America	EB0002964	GMIS	FTIR	209.4	215	2.68

^a %Diff. computed as $100 * (\text{Vendor Conc.} - \text{NIST Conc.}) / \text{NIST Conc.}$

Value of Reference is highlighted.

Color code: Black is ≤ 2.20 % difference, and blue is > 2.2 % difference and fails the audit.

Table 14a: Vendor Certified and NIST Concentrations – EPA Low Range – CO₂
 (Data from Workbook: 2013_August_Low_NDIR_Ratios.xls Worksheet: Table_14a_CO2_Low on 5/17/2014)

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST (%)	Vendor (%)	%Diff ^a
Air Liquide (CA)	ALM000366	NTRM	FTIR	5.012	5.02	0.16
Air Liquide (CA)	CC153077	NTRM	FTIR	5.024	5.03	0.12
Air Liquide (MI)	CC70168	NTRM	FTIR	4.993	5.00	0.15
Air Liquide (MI)	CC62787	NTRM	FTIR	4.992	5.01	0.36
Air Liquide (PA)	ALM019988	NTRM	FTIR	5.022	5.03	0.16
Air Liquide (PA)	ALM057617	NTRM	FTIR	4.974	4.98	0.12
Air Liquide (TX)	CC149707	NTRM	FTIR	5.030	5.04	0.21
Air Liquide (TX)	CC151832	NTRM	FTIR	5.029	5.04	0.22
Airgas (CA)	CC1742	NTRM	FTIR	5.002	4.969	-0.65
Airgas (CA)	SG9153513BAL	NTRM	FTIR	5.004	4.979	-0.50
Airgas (IL)	CC126041	NTRM	NDIR	5.017	5.005	-0.23
Airgas (IL)	CC351018	NTRM	NDIR	5.020	5.013	-0.13
Airgas (LA)	CC274644	NTRM	FTIR	5.012	5.016	0.09
Airgas (LA)	CC343375	NTRM	FTIR	5.030	5.008	-0.43
Airgas (MI)	CC231152	NTRM	FTIR	4.999	4.998	-0.02
Airgas (MI)	CC29753	NTRM	FTIR	5.006	4.990	-0.31
Airgas (NC)	CC357483	NTRM	FTIR	4.991	4.988	-0.05
Airgas (NC)	CC357651	NTRM	FTIR	5.005	5.002	-0.05
Airgas (NJ)	CC310530	NTRM	FTIR	5.000	4.990	-0.19
Airgas (NJ)	CC346498	NTRM	FTIR	5.002	4.978	-0.47
Global Calibration	EB0028074	GMIS	GC-TCD	5.032	5.07	0.76
Global Calibration	EB0030274	GMIS	GC-TCD	5.045	5.070	0.50
Industrial Welding Supply	EB0016137	GMIS	NDIR	5.013	5.001	-0.23
Industrial Welding Supply	EB0019069	GMIS	NDIR	5.016	5.00	-0.29
Linde	CC128334	GMIS	NDIR	5.024	5.05	0.52
Linde	CC63232	GMIS	NDIR	5.011	5.04	0.58
Liquid Technology	CC233824	GMIS	FTIR	4.930	4.85	-1.63
Liquid Technology	CC310794	GMIS	FTIR	4.931	4.86	-1.45
Matheson (OH)	SX45138	SRM	NDIR	4.900	4.93	0.61

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST (%)	Vendor (%)	%Diff ^a
Matheson (OH)	SX48647	SRM	NDIR	4.903	4.93	0.54
Matheson (TN)	SX49346	PRM	NDIR	4.995	5.03	0.71
Matheson (TN)	SX51685	PRM	NDIR	4.990	5.01	0.40
Praxair	CC179626	GMIS	NDIR	5.013	5.02	0.14
Praxair	CC326016	GMIS	NDIR	5.009	5.02	0.23
Red Ball	EB0005534	GMIS	NDIR	5.012	4.99	-0.44
Red Ball	EB0007021	GMIS	NDIR	5.005	5.00	-0.10
Scott-Marrin	CC12706	GMIS	GC-TCD	5.089	5.07	-0.36
Scott-Marrin	CC78131	GMIS	GC-TCD	5.022	5.00	-0.43
Specialty Gases of America	EB0002792	GMIS	FTIR	4.968	4.94	-0.57
Specialty Gases of America	EB0002973	GMIS	FTIR	4.964	4.94	-0.48

^a %Diff. computed as $100 * (\text{Vendor Conc.} - \text{NIST Conc.}) / \text{NIST Conc.}$

Value of Reference is highlighted.

Color code: Black is ≤ 2.20 % difference, and blue is > 2.2 % difference and fails the audit.

Table 14b: Vendor Certified and NIST Concentrations – EPA Low Range – SO₂
 (Data from Workbook: 2013_NDIR_&_NDUV_Low.xls Worksheet: Table_14b_SO2_Low on 5/17/2014)

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST NDIR and NDUV (ppm)	Vendor (ppm)	% Diff ^a
Air Liquide (CA)	ALM000366	NTRM	FTIR	34.42	34.9	1.39
Air Liquide (CA)	CC153077	NTRM	FTIR	34.58	34.6	0.07
Air Liquide (MI)	CC62787	NTRM	FTIR	34.70	35.0	0.86
Air Liquide (MI)	CC70168	NTRM	FTIR	34.64	35.0	1.04
Air Liquide (PA)	ALM019988	NTRM	FTIR	35.39	35.6	0.59
Air Liquide (PA)	ALM057617	NTRM	FTIR	34.84	35.1	0.74
Air Liquide (TX)	CC149707	NTRM	FTIR	34.67	35.0	0.86
Air Liquide (TX)	CC151832	NTRM	FTIR	34.59	34.9	0.80
Airgas (CA)	CC1742	NTRM	FTIR	35.53	35.48	-0.15
Airgas (CA)	SG9153513BAL	NTRM	FTIR	35.53	35.47	-0.17
Airgas (IL)	CC126041	NTRM	FTIR	35.32	34.97	-0.98
Airgas (IL)	CC351018	NTRM	FTIR	35.30	35.19	-0.31
Airgas (LA)	CC274644	NTRM	FTIR	35.10	34.78	-0.92
Airgas (LA)	CC343375	NTRM	FTIR	35.29	35.09	-0.56
Airgas (MI)	CC231152	NTRM	FTIR	35.31	34.84	-1.34
Airgas (MI)	CC29753	NTRM	FTIR	35.19	34.77	-1.19
Airgas (NC)	CC357483	NTRM	FTIR	35.08	34.89	-0.55
Airgas (NC)	CC357651	NTRM	FTIR	35.29	35.180	-0.32
Airgas (NJ)	CC310530	NTRM	FTIR	35.54	35.22	-0.90
Airgas (NJ)	CC346498	NTRM	FTIR	35.50	35.16	-0.95
Global Calibration	EB0028074	SRM	NDIR	33.20	35.4	6.63
Global Calibration	EB0030274	SRM	NDIR	34.13	35.7	4.61
Industrial Welding Supply	EB0016137	GMIS	NDIR	35.09	34.74	-1.01
Industrial Welding Supply	EB0019069	GMIS	NDIR	34.66	34.18	-1.38
Linde	CC128334	NTRM	NDIR	35.26	35.2	-0.17
Linde	CC63232	NTRM	NDIR	34.83	35.2	1.07
Liquid Technology	CC233824	GMIS	FTIR	34.89	34.9	0.04
Liquid Technology	CC310794	GMIS	FTIR	34.88	34.7	-0.53

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST NDIR and NDUV (ppm)	Vendor (ppm)	% Diff ^a
Matheson (OH)	SX45138	SRM	NDIR	34.42	34.7	0.81
Matheson (OH)	SX48647	SRM	NDIR	34.38	34.7	0.92
Matheson (TN)	SX49346	SRM	NDIR	36.76	36.43	-0.91
Matheson (TN)	SX51685	SRM	NDIR	36.26	36.29	0.08
Praxair	CC179626	GMIS	NDUV	36.28	36.3	0.05
Praxair	CC326016	GMIS	NDUV	36.32	36.2	-0.33
Red Ball	EB0005534	GMIS	NDIR	33.60	33.9	0.90
Red Ball	EB0007021	GMIS	NDIR	34.12	34.2	0.25
Scott-Marrin	CC12706	GMIS	UV Photometry	36.10	35.8	-0.82
Scott-Marrin	CC78131	GMIS	UV Photometry	35.79	35.6	-0.53
Specialty Gases of America	EB0002792	GMIS	FTIR	35.27	34.7	-1.61
Specialty Gases of America	EB0002973	GMIS	FTIR	34.75	34.6	-0.44

^a %Diff. computed as $100 * (\text{Vendor Conc.} - \text{NIST Conc.}) / \text{NIST Conc.}$

^b NIST SO₂ concentration calculated as an average of NDUV (against Low Reference) and NDIR (against Low Reference) analyses. See Table 17c for comparison of these two analyses.

Value of Reference is highlighted.

Color code: Black is ≤ 2.20 % difference, and blue is > 2.2 % difference and fails the audit.

Table 14c: Vendor Certified and NIST Concentrations – EPA Low Range – NO
(Data from Workbook: 2013_Septemebr_Low_NDUV_Ratios.xls Worksheet: Table_14c_NO on 5/17/2014)

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST (ppm)	Vendor (ppm)	% Diff ^a
Air Liquide (CA)	ALM000366	NTRM	FTIR	40.59	40.5	-0.23
Air Liquide (CA)	CC153077	NTRM	FTIR	40.53	40.5	-0.08
Air Liquide (MI)	CC62787	NTRM	FTIR	40.05	40.3	0.62
Air Liquide (MI)	CC70168	NTRM	FTIR	40.40	40.4	-0.01
Air Liquide (PA)	ALM019988	NTRM	FTIR	39.91	39.9	-0.01
Air Liquide (PA)	ALM057617	NTRM	FTIR	40.61	40.4	-0.52
Air Liquide (TX)	CC149707	NTRM	FTIR	41.70	41.9	0.49
Air Liquide (TX)	CC151832	NTRM	FTIR	41.79	41.6	-0.45
Airgas (CA)	CC1742	NTRM	FTIR	40.99	41.16	0.41
Airgas (CA)	SG9153513BAL	NTRM	FTIR	41.20	41.23	0.07
Airgas (IL)	CC126041	NTRM	FTIR	40.88	40.97	0.23
Airgas (IL)	CC351018	NTRM	FTIR	40.37	40.63	0.63
Airgas (LA)	CC274644	NTRM	FTIR	40.45	40.57	0.30
Airgas (LA)	CC343375	NTRM	FTIR	40.42	40.66	0.59
Airgas (MI)	CC231152	NTRM	FTIR	39.74	40.12	0.95
Airgas (MI)	CC29753	NTRM	FTIR	40.73	40.74	0.03
Airgas (NC)	CC357483	NTRM	FTIR	39.94	40.10	0.40
Airgas (NC)	CC357651	NTRM	FTIR	39.95	40.14	0.48
Airgas (NJ)	CC310530	NTRM	FTIR	39.84	39.90	0.15
Airgas (NJ)	CC346498	NTRM	FTIR	39.95	40.08	0.32
Global Calibration	EB0028074	GMIS	Chemi	39.47	39.9	1.09
Global Calibration	EB0030274	GMIS	Chemi	39.58	39.9	0.82
Industrial Welding Supply	EB0016137	GMIS	Chemi	41.54	41.44	-0.24
Industrial Welding Supply	EB0019069	GMIS	Chemi	41.43	41.19	-0.58
Linde	CC128334	GMIS	FTIR	40.50	40.4	-0.25
Linde	CC63232	GMIS	FTIR	41.03	40.0	-2.50
Liquid Technology	CC233824	GMIS	FTIR	41.47	40.9	-1.37
Liquid Technology	CC310794	GMIS	FTIR	40.98	40.4	-1.43
Matheson (OH)	SX45138	PRM	Chemi	41.20	41.3	0.23
Matheson (OH)	SX48647	PRM	Chemi	40.93	41.2	0.66

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST (ppm)	Vendor (ppm)	%Diff ^a
Matheson (TN)	SX49346	PRM	Chemi	41.18	41.30	0.30
Matheson (TN)	SX51685	PRM	Chemi	40.71	40.96	0.60
Praxair	CC179626	GMIS	Chemi	40.71	40.4	-0.77
Praxair	CC326016	GMIS	Chemi	40.49	40.3	-0.47
Red Ball	EB0005534	GMIS	NDIR	41.59	41.8	0.51
Red Ball	EB0007021	GMIS	NDIR	41.44	41.7	0.63
Scott-Marrin	CC12706	GMIS	Chemi	40.42	40.0	-1.04
Scott-Marrin	CC78131	GMIS	Chemi	39.98	39.4	-1.46
Specialty Gases of America	EB0002792	GMIS	FTIR	40.65	41.1	1.11
Specialty Gases of America	EB0002973	GMIS	FTIR	40.69	41.10	1.02

^a %Diff. computed as $100 * (\text{Vendor Conc.} - \text{NIST Conc.}) / \text{NIST Conc.}$

Value of Reference is highlighted.

Color code: Black is ≤ 2.20 % difference, and blue is > 2.2 % difference and fails the audit.

Table 15a: Comparison of NIST CO₂ Concentrations of 2008 audit WSs and Test cylinders of EPA High Range, with Uncertainty (k = 2)

Vendor	Cyl#	CO ₂ against Curve, NDIR		CO ₂ against Reference, NDIR		%Diff.
		Conc. (%)	± (%)	Conc. (%)	± (%)	
WS-EPA8-H1	CA08268	18.047	0.054	18.127	0.077	-0.45
WS-EPA8-H2	SA10582	18.211	0.05	18.281	0.08	-0.38
Air Liquide (MI)	ALM040137	15.067	0.045	15.068	0.064	-0.01
Air Liquide (TX)	ALM058073	14.918	0.045	14.916	0.063	0.01
Liquid Technology	EB0026503	14.988	0.045	15.003	0.064	-0.10
Matheson (TN)	SX52734	14.952	0.045	14.964	0.063	-0.08

Table 15b: Comparison of NIST SO₂ Concentrations of 2008 audit WSs and Test cylinders of EPA High Range, with Uncertainty (k = 2)

Vendor	Cyl#	SO ₂ against Curves, NDUV and NDIR ^a		SO ₂ against Reference, NDIR		%Diff.
		Conc. (ppm) ^a	± (ppm)	Conc. (ppm)	± (ppm)	
WS-EPA8-H1	CA08268	998.3	4.2	1000.2	6.6	-0.19
WS-EPA8-H2	SA10582	1001.2	4.2	1002.1	6.6	-0.09
Air Liquide (MI)	ALM040137	795.5	3.3	796.9	5.3	-0.18
Air Liquide (TX)	ALM058073	789.5	3.3	790.8	5.2	-0.16
Liquid Technology	EB0026503	800.0	3.4	801.4	5.3	-0.18
Matheson (TN)	SX52734	837.3	3.5	839.0	5.5	-0.20

^a Using EPA High SO₂ NDIR correction factor of 1.0019 for WSs, and 1.0014 for the 2013 samples

Table 15c: Comparison of NIST NO Concentrations of 2008 audit WSs and Test cylinders of EPA High Range, with Uncertainty (k = 2)

Vendor	Cyl#	NO against Curves, Chemi ^a and NDIR ^b		NO against Reference, NDIR		
		Conc. (ppm) ^a	± (ppm)	Conc. (ppm)	± (ppm)	%Diff.
WS-EPA8-H1	CA08268	894.5	4.7	896.4	6.1	-0.21
WS-EPA8-H2	SA10582	929.3	4.9	931.9	6.3	-0.28
Air Liquide (MI)	ALM040137	745.6	3.9	746.3	5.1	-0.09
Air Liquide (TX)	ALM058073	745.6	3.9	745.8	5.1	-0.02
Liquid Technology	EB0026503	759.6	4.0	758.6	5.2	0.13
Matheson (TN)	SX52734	754.4	4.0	754.2	5.1	0.03

^a Using CO₂ correction factor (Equation 3)^b Using EPA High NO NDIR correction factor of 1.0151 for the WSs, and 1.0108 for the 2013 samples**Table 16a:** Comparison of NIST CO₂ Concentrations of 2008 audit WSs and Test cylinders of EPA Mid Range, with Uncertainty (k = 2)

Vendor	Cyl#	CO ₂ against Curve, NDIR		CO ₂ against Reference, NDIR		%Diff.
		Conc. (%)	± (%)	Conc. (%)	± (%)	
WS-EPA8-M1	CC51188	12.171	0.037	12.180	0.061	-0.08
WS-EPA8-M2	CA08177	12.079	0.04	12.091	0.060	-0.10
Air Liquide (TX)	CC62138	8.997	0.027	8.991	0.045	0.06
Airgas (IL)	CC74428	9.025	0.027	9.023	0.045	0.02
Airgas (LA)	XC022025B	9.032	0.027	9.037	0.045	-0.05
Ind. Welding Supply	EB0010395	9.008	0.027	9.010	0.045	-0.01
Liquid Technology	EB0023222	8.946	0.027	8.936	0.045	0.11
Praxair (CA)	CC145327	9.100	0.027	9.103	0.046	-0.03

Table 16b: Comparison of NIST SO₂ Concentrations of 2008 audit WSs and Test cylinders of EPA Mid Range, with Uncertainty (k = 2)

Vendor	Cyl#	SO ₂ against Curves, NDUV and NDIR ^a		SO ₂ against Reference, NDIR		%Diff.
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	
WS-EPA8-M1	CC51188	513.4	2.8	512.5	3.5	0.18
WS-EPA8-M2	CA08177	497.2	2.7	496.1	3.4	0.23
Air Liquide (TX)	CC62138	327.8	1.8	328.1	2.2	-0.08
Airgas (IL)	CC74428	315.2	1.7	315.8	2.1	-0.18
Airgas (LA)	XC022025B	323.8	1.7	324.4	2.2	-0.19
Ind. Welding Supply	EB0010395	320.4	1.7	320.8	2.2	-0.14
Liquid Technology	EB0023222	324.3	1.8	324.8	2.2	-0.14
Praxair (CA)	CC145327	321.2	1.7	321.9	2.2	-0.19

^a Using EPA Mid SO₂ NDIR correction factor of 1.0004 for the WSs. and 0.9995 for the 2013 samples

Table 16c: Comparison of NIST NO Concentrations of 2008 audit WSs and Test cylinders of EPA Mid Range, with Uncertainty (k = 2)

Vendor	Cyl#	NO against Curves, Chemi ^a and NDIR ^b		NO against Reference, NDIR		%Diff.
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	
WS-EPA8-M1	CC51188	407.0	2.1	407.8	2.7	-0.20
WS-EPA8-M2	CA08177	399.3	2.1	399.5	2.6	-0.05
Air Liquide (TX)	CC62138	203.0	1.1	203.4	1.3	-0.20
Airgas (IL)	CC74428	206.8	1.1	207.1	1.4	-0.13
Airgas (LA)	XC022025B	209.6	1.1	210.1	1.4	-0.23
Ind. Welding Supply	EB0010395	219.4	1.2	219.3	1.4	0.05
Liquid Technology	EB0023222	218.0	1.2	217.3	1.4	0.34
Praxair (CA)	CC145327	213.4	1.2	214.0	1.4	-0.30

^a Using CO₂ correction factor (Equation 3)

^b Using EPA Mid NO NDIR correction factor of 0.9997 for WSs, and 0.9996 for 2013 samples

Table 17a: Comparison of NIST CO₂ Concentrations of 2008 audit WSs and Test cylinders of EPA Low Range, with Uncertainty (k = 2)

Vendor	Cyl#	CO ₂ against Curve, NDIR		CO ₂ against Reference, NDIR		%Diff.
		Conc. (%)	± (%)	Conc. (%)	± (%)	
WS-EPA8-L1	CA08181	5.113	0.015	5.111	0.021	0.06
WS-EPA8-L2	ALM054809	5.007	0.015	5.009	0.021	-0.04
Liquid Technology	CC233824	4.924	0.015	4.930	0.021	-0.13

Table 17b: Comparison of NIST SO₂ Concentrations of 2008 audit WSs and Test cylinders of EPA Low Range, with Uncertainty (k = 2)

Vendor	Cyl#	SO ₂ against Curve, NDUV and NDIR ^a		SO ₂ against Reference, NDUV and NDIR		%Diff.
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	
WS-EPA8-L1	CA08181	51.40	0.31	51.45	0.43	-0.08
WS-EPA8-L2	ALM054809	51.37	0.31	51.37	0.43	0.00
Liquid Technology	CC233824	34.86	0.21	34.88	0.29	-0.06

^a Using EPA Low SO₂ NDIR correction factor of 0.9865 for WSs, and 0.9765 for the 2013 samples

Table 17c: Comparison of NDIR and NDUV Analysis of SO₂ (against Reference) at Low Range, with uncertainty (k=2)

Vendor	Cyl#	SO ₂ against Reference, NDIR		SO ₂ against Reference, NDUV		Reported NIST SO ₂		
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	%Diff.	Mean (ppm)	± (ppm)
Air Liquide (CA)	ALM000366	34.42	0.30	34.42	0.28	0.00	34.42	0.29
Air Liquide (CA)	CC153077	34.53	0.30	34.62	0.28	-0.26	34.58	0.29
Air Liquide (MI)	CC70168	34.61	0.30	34.67	0.28	-0.16	34.64	0.29
Air Liquide (PA)	ALM019988	35.36	0.30	35.43	0.28	-0.19	35.39	0.29
Air Liquide (PA)	ALM057617	34.82	0.30	34.86	0.28	-0.10	34.84	0.29
Air Liquide (TX)	CC149707	34.67	0.30	34.67	0.28	0.00	34.67	0.29
Air Liquide (TX)	CC151832	34.56	0.30	34.61	0.28	-0.12	34.59	0.29
Airgas (CA)	CC1742	35.51	0.31	35.56	0.28	-0.14	35.53	0.29
Airgas (CA)	SG9153513BAL	35.49	0.31	35.57	0.28	-0.24	35.53	0.29
Airgas (IL)	CC126041	35.32	0.30	35.32	0.28	0.00	35.32	0.29
Airgas (IL)	CC351018	35.27	0.30	35.33	0.28	-0.18	35.30	0.29
Airgas (LA)	CC274644	35.06	0.30	35.14	0.28	-0.24	35.10	0.29
Airgas (LA)	CC343375	35.28	0.30	35.29	0.28	-0.02	35.29	0.29
Airgas (MI)	CC231152	35.26	0.30	35.36	0.28	-0.28	35.31	0.29
Airgas (MI)	CC29753	35.21	0.30	35.17	0.28	0.10	35.19	0.29
Airgas (NC)	CC357483	35.06	0.30	35.10	0.28	-0.12	35.08	0.29
Airgas (NC)	CC357651	35.25	0.30	35.33	0.28	-0.23	35.29	0.29
Airgas (NJ)	CC310530	35.49	0.31	35.59	0.28	-0.27	35.54	0.29
Airgas (NJ)	CC346498	35.45	0.30	35.55	0.28	-0.27	35.50	0.29
Global Calibration	EB0028074	33.21	0.29	33.19	0.27	0.06	33.20	0.28
Global Calibration	EB0030274	34.14	0.29	34.11	0.27	0.07	34.13	0.28
Industrial Welding Supply	EB0016137	35.09	0.30	35.10	0.28	-0.05	35.09	0.29
Industrial Welding Supply	EB0019069	34.69	0.30	34.63	0.28	0.16	34.66	0.29
Linde	CC128334	35.23	0.30	35.29	0.28	-0.15	35.26	0.29
Linde	CC63232	34.80	0.30	34.86	0.28	-0.17	34.83	0.29
Liquid Technology	CC233824	34.90	0.30	34.87	0.28	0.11	34.89	0.29
Liquid Technology	CC310794	34.84	0.30	34.93	0.28	-0.26	34.88	0.29
Matheson (OH)	SX45138	34.44	0.30	34.41	0.28	0.10	34.42	0.29

Vendor	Cyl#	SO ₂ against Reference, NDIR		SO ₂ against Reference, NDUV		Reported NIST SO ₂		
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	%Diff.	Mean (ppm)	± (ppm)
Matheson (OH)	SX48647	34.38	0.30	34.39	0.28	-0.02	34.38	0.29
Matheson (TN)	SX49346	36.76	0.32	36.76	0.29	0.00	36.76	0.31
Matheson (TN)	SX51685	36.19	0.31	36.34	0.29	-0.42	36.26	0.30
Praxair	CC179626	36.17	0.31	36.39	0.29	-0.59	36.28	0.30
Praxair	CC326016	36.33	0.31	36.31	0.29	0.08	36.32	0.30
Red Ball	EB0005534	33.64	0.29	33.55	0.27	0.25	33.60	0.28
Red Ball	EB0007021	34.11	0.29	34.12	0.27	-0.05	34.12	0.28
Scott-Marrin	CC12706	36.07	0.31	36.12	0.29	-0.12	36.10	0.30
Scott-Marrin	CC78131	35.74	0.31	35.84	0.29	-0.29	35.79	0.30
Specialty Gases of America	EB0002792	35.24	0.30	35.30	0.28	-0.17	35.27	0.29
Specialty Gases of America	EB0002973	34.82	0.30	34.69	0.28	0.39	34.75	0.29

Table 17d: Comparison of NIST NO Concentrations of 2008 audit WSs and Test cylinders of EPA Low Range, with Uncertainty (k = 2)

Vendor	Cyl#	NO against Curve, Chemi ^a		NO against Reference, NDUV		%Diff.
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	
WS-EPA8-L1	CA08181	50.55	0.33	50.31	0.43	0.48
WS-EPA8-L2	ALM054809	51.08	0.34	50.78	0.44	0.59
Global Calibration Gases	EB0028074	39.30	0.26	39.47	0.34	-0.43
Liquid Technology	CC233824	41.37	0.27	41.47	0.36	-0.25
Matheson (TN)	SX49346	41.16	0.27	41.18	0.35	-0.04
Praxair (CA)	CC179626	40.72	0.27	40.72	0.35	0.02
Praxair (CA)	CC326016	40.38	0.27	40.49	0.35	-0.28
Red Ball	EB0005534	41.31	0.27	41.59	0.36	-0.68

^a Using CO₂ correction factor (Equation 3)

Table 18a: Comparison to Working Standards from 2008 Audit for CO₂, with uncertainty (k=2)

Sample ID	Certification in 2008		Current Analysis Vrs Reference		%Diff.
	CO ₂ Conc. (%)	± (%)	CO ₂ Conc. (%)	± (%)	
WS-EPA8-L1	5.111	0.022	5.111	0.021	0.01
WS-EPA8-L2	5.011	0.015	5.009	0.021	0.04
WS-EPA8-M1	12.186	0.038	12.180	0.061	0.05
WS-EPA8-M2	12.073	0.050	12.091	0.060	-0.15
WS-EPA8-H1	18.038	0.076	18.127	0.077	-0.49
WS-EPA8-H2	18.208	0.054	18.281	0.078	-0.40

Table 18b: Comparison to Working Standards from 2008 Audit for SO₂, with uncertainty (k=2)

Sample ID	Certification in 2008		Current Analysis Vrs Reference		%Diff.
	SO ₂ Conc. (ppm)	± (ppm)	SO ₂ Conc. (ppm)	± (ppm)	
WS-EPA8-L1	51.35	0.28	51.53	0.44	-0.35
WS-EPA8-L2	51.61	0.20	51.43	0.44	0.35
WS-EPA8-M1	515.1	2.4	512.5	3.5	0.52
WS-EPA8-M2	497.2	3.0	496.09	3.4	0.22
WS-EPA8-H1	998.0	6.0	1000.2	6.6	-0.22
WS-EPA8-H2	1003.5	4.6	1002.1	6.6	0.14

Table 18c: Comparison to Working Standards from 2008 Audit for NO, with uncertainty (k=2)

Sample ID	Certification in 2008		Current Analysis Vrs Reference		%Diff.
	NO Conc. (ppm)	± (ppm)	NO Conc. (ppm)	± (ppm)	
WS-EPA8-L1	50.85	0.34	50.55	0.43	0.59
WS-EPA8-L2	51.45	0.26	51.08	0.44	0.73
WS-EPA8-M1	408.4	2.2	407.8	2.7	0.15
WS-EPA8-M2	399.5	2.8	399.5	2.6	-0.01
WS-EPA8-H1	895.8	6.0	896.4	6.1	-0.07
WS-EPA8-H2	929.8	5.0	931.9	6.3	-0.22

Table 19a: Uncertainty of References as a function of Component Analyzed, EPA Range, and Analytical Technique (at $k = 1$)

Component Analyzed	EPA Range	Analytical Technique	$u_{ISO}(\%)$	$u_{reg}(\%)$	$u_{cf}(\%)$	$u_{reference}(\%)$
CO ₂	High	NDIR	0.15	0.00	0.00	0.15
SO ₂	High	NDIR	0.20	0.05	0.16	0.26
SO ₂	High	NDUV	0.20	0.05	0.00	0.21
NO	High	NDIR	0.20	0.00	0.19	0.28
NO	High	Chemi	0.20	0.00	0.17	0.26
CO ₂	Mid	NDIR	0.15	0.00	0.00	0.15
SO ₂	Mid	NDIR	0.20	0.10	0.16	0.27
SO ₂	Mid	NDUV	0.20	0.10	0.00	0.22
NO	Mid	NDIR	0.20	0.05	0.19	0.28
NO	Mid	Chemi	0.20	0.05	0.17	0.27
CO ₂	Low	NDIR	0.15	0.00	0.00	0.15
SO ₂	Low	NDUV	0.20	0.20	0.00	0.28
SO ₂	Low	NDIR	0.20	0.20	0.17	0.33
NO	Low	Chemi	0.20	0.20	0.17	0.33

Table19b: Uncertainty of Audit Samples as a function of Component Analyzed and EPA Range (at $k = 1$)

Component Analyzed	EPA Range	Analytical Technique	$u_{reference}(\%)$	$u_{ratio}(\%)$	$u_{reg}(\%)$	$u_C(\%)$
CO ₂	High	NDIR	0.15	0.15	0.00	0.21
SO ₂	High	NDIR	0.26	0.20	0.05	0.33
NO	High	NDIR	0.28	0.20	0.00	0.34
CO ₂	Mid	NDIR	0.15	0.15	0.00	0.21
SO ₂	Mid	NDIR	0.27	0.20	0.10	0.35
NO	Mid	NDIR	0.27	0.20	0.05	0.34
CO ₂	Low	NDIR	0.15	0.15	0.00	0.21
SO ₂	Low	NDUV	0.28	0.20	0.20	0.40
SO ₂	Low	NDIR	0.33	0.20	0.20	0.43
NO	Low	NDUV	0.33	0.20	0.20	0.43

Table 20: Vendor Reanalysis of samples that failed the “2 % Tag Rule”

Vendor	Cylinder #	Component	Vendor Concentrations			NIST		
			Original (ppm)	Reanalysis (ppm)	% Diff. _a	Conc. (ppm)	% Diff. to Original _b	% Diff. to Reanalysis _c
Liquid Technology	EB0026503	NO	781	Not Re-Analyzed	N/A	758.6	2.95	N/A
Specialty Gases of America	EB0002964	NO	215	210.1	-2.28	209.4	2.68	0.33
Global Calibration	EB0028074	SO2	35.4	Not Re-Analyzed	N/A	33.20	6.63	N/A
Global Calibration	EB0030274	SO2	35.7	Not Re-Analyzed	N/A	34.13	4.61	N/A
Linde	CC63232	NO	40.0	41.38	3.45	41.03	-2.50	0.85

^a % Diff. computed as $100 * (\text{Reanalysis Conc.} - \text{Original Conc.}) / \text{Original Conc.}$

^b % Diff. computed as $100 * (\text{Original Conc.} - \text{NIST Conc.}) / \text{NIST Conc.}$

^c % Diff. computed as $100 * (\text{Reanalysis Conc.} - \text{NIST Conc.}) / \text{NIST Conc.}$

Color code: Black is less than or equal to 2.20 % difference, and blue is greater than 2.20 % difference and fails the audit.