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## REPORT OF ANALYSIS

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Environmental Protection Agency Blind Audit 2010

Submitted to:

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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, and to determine whether the vendor-supplied concentrations met the  $\pm 2.0\%$  uncertainty specification in 40 CFR Part 75, Appendix A, Section 5.1.4(b). The mixtures are tri-blends of Carbon Dioxide (CO<sub>2</sub>; range: 5 % mol/mol to 20 % mol/mol); Nitric Oxide (NO; range: 25  $\mu$ mol/mol to 1000  $\mu$ mol/mol (ppm) and Total Oxides of Nitrogen, NO<sub>x</sub>, within 1 % relative of NO) and Sulfur Dioxide (SO<sub>2</sub>; range: 50  $\mu$ mol/mol to 1000  $\mu$ mol/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. A private company (PC) was chosen to purchase the cylinders from the gas manufacturers, and a consulting company (CC) was chosen to coordinate transportation of said cylinders between PC and NIST.

### **Candidate Samples Ordered**

The basic criterion of the audit is that the gas manufactures 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 achieve other criteria:

- 1) All U.S. gas vendors and their sites to be represented.
- 2) Samples to be new and unused.
- 3) Samples 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]. For the 2008 audit, 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, 2010 audit where PC was chosen to purchase the samples directly from the gas vendors, and CC coordinated their shipment to and from NIST. Again, this approach was successful, satisfying all of the defined criteria.

PC purchased 57 gas mixture samples over three ranges. The nominal concentration (by mole) per component for each range was:

# of Samples	Range Type	CO <sub>2</sub> (% <sup>1</sup> )	NO (ppm <sup>2</sup> )	SO <sub>2</sub> (ppm <sup>2</sup> )
19	High	18.0	900	1000
19	Mid	12.0	400	500
19	Low	5.00	50.0	50.0

<sup>1</sup> 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.

<sup>2</sup> 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 per range (three 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, it was not possible to purchase directly from Specialty Air Technologies so PC was forced to go through a third party (Gilmore Liquid Air). Secondly, all vendors claimed to be first party. However, after taking delivery it was discovered that three vendors: DeLille Specialty Gases; GTS-Welco; and SpecAir Specialty Gas (underlined in table 1) had purchased their gas mixtures from third parties: Specialty Gases of America; Praxair (PA) and Matheson Trigas respectively (bolded in table 1). Thirdly, due to a production back log, Airgas (TX) transferred the manufacturing order to Airgas (IL). Lastly, Air Liquide was contacted to have product gas blends provided by four facilities, three facilities chose to respond. Consequently, there were the following deviations from the original objective:

- 1) Airgas (IL), Matheson Trigas, Praxair (PA), and Specialty Gases of America each provided six samples to the audit (instead of three).
- 2) Two known manufacturing sites were not represented: Air Liquide (PA) and Airgas (TX).
- 3) There are 10 first party vendors, not the apparent 14. (See table 2.)

It is NIST’s understanding, that these 10 vendors and their 17 manufacturing sites, including Air Liquide (PA) and Airgas (TX), fully represent the first party manufacturing of EPA protocol calibration gas mixtures in the U.S. Nothing can be said regarding the performance of any 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.

**NOTE:** NIST received, inspected, and analyzed 57 samples. However, in order to comply with the original objective of one sample per range per manufacturing site, the NIST certified concentrations for the extra samples from Airgas (IL) [order placed with Airgas (TX)], Matheson Trigas (via SpecAir Specialty Gas), Praxair (PA) (via GTS-Welco, PA), and Specialty Gases of America (via DeLille Specialty Gases) are not reported (see tables 13 – 15). Consequently, the total number of samples reported is 45.

### **Candidate Samples Received and Inspected**

Candidate samples were delivered to NIST in three batches of 19 (High, Mid and Low) from April to June 2010. Every sample was received with the cylinder valve shrink wrapped by the vendor and / or with a dust cap. (See tables 3.) This showed that the cylinders had not been used since leaving the gas manufacturing facility. The three deliveries of cylinders were controlled by a “Bill of Lading”.

All samples were inside 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 3a, 3b, and 3c in the attachments detail the samples received, together with the start and end gas pressures at NIST. Gas pressure was measured using a 0 to 3000 psi gauge with increments of 50 psi. A discrepancy of more than 200 psi, between the vendor reported certified pressure and NIST start pressure, was considered significant. No samples fell into this category.

All of the samples were in acceptable condition and were considered new since they had been vendor certified within three months of the delivery date to NIST.

**Note:** All pressures labeled “psi” in this report are equivalent to 6895 Pascals (Pa) in SI units. The designation “psi” is used as an equivalent unit and is standard industry usage.

### **Check of Vendor’s Certificate of Analysis (CoA)**

Each vendor’s CoA was checked for compliance to EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards (EPA-600/R-97/121), September 1997 (Protocol document). Each CoA was checked for the following:

- 1) Cylinder identification number
- 2) Certified concentrations to be in parts per million (ppm) or percent (%) and be reported to three or more significant digits.
- 3) Balance gas of the gas mixture.
- 4) Cylinder pressure at certification.
- 5) Statement that standard should not be used when gas pressure falls below 150 psig.
- 6) Date of the certification.
- 7) Certificate expiration date.
- 8) Identification of the reference standard used in each component assay.
- 9) 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).
- 10) Statement that the certification was performed according to the EPA protocol.
- 11) Statement of assay procedure – G1 or G2.
- 12) Identification of laboratory that performed the assay.

- 13) If applicable, statement that a correction factor had been used to account for analytical interference.

This checklist is the minimum requirement to comply with section 2.1.4 of the protocol document. Some non-conformities were observed, as detailed in tables 4a, 4b, and 4c of the attachments. These tables also contain comments about the CoA which may or may not be a non-conformity. Other than the exceptions stated in table 4, the following held for all of the CoAs:

- 1) Total oxides of nitrogen (NO<sub>x</sub>) or Nitrogen Dioxide (NO<sub>2</sub>) was < 1 % of the certified NO concentration.
- 2) NO<sub>x</sub> (or NO<sub>2</sub>) was reported as "Reference Only" or without an analytical uncertainty.
- 3) Shelf life was correctly determined as 24 months.
- 4) Analytical accuracy was ± 1 % or better.
- 5) The balance gas was nitrogen.
- 6) No correction factor to account for analytical interference was noted, even for the chemiluminescence (chemi) analysis of NO in the presence of CO<sub>2</sub>.

### **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, SO<sub>2</sub>, and CO<sub>2</sub>.

It was not possible to achieve these three aims for every component for the three EPA ranges. (See table 5.) The best compromise, which satisfied the ≤ 0.5 % uncertainty aim, was:

- a) NO, SO<sub>2</sub> and CO<sub>2</sub> certified by Non Dispersive Infrared (NDIR) for High and Mid range.
- b) SO<sub>2</sub> and CO<sub>2</sub> certified by NDIR for Low range. NDIR was too imprecise for Low range NO.
- c) NO and SO<sub>2</sub> certified 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 SO<sub>2</sub>.
- d) NO certified by chemiluminescence for Low Range.

In addition, for at least three samples per High and Mid range, the NO certification was checked by chemiluminescence and the SO<sub>2</sub> certification by NDUV.

Details of the instrumentation used are in table 6.

### **Standards Used**

The standards used to determine the CO<sub>2</sub>, SO<sub>2</sub>, and NO concentrations in the sample cylinders are detailed in tables: 7a, 7b, and 7c. The standards were SRM Lot Standards (LS) or Working Standards (WS), both of these types 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 N<sub>2</sub>.

The LSs used to determine possible analytical interference between the three components of interest are detailed in table 7d. The pure CO<sub>2</sub> 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 audit.

### **Overall Experimental Design**

1. Calibration curves consisting of binary mixtures of CO<sub>2</sub> or SO<sub>2</sub> or NO in balance N<sub>2</sub> 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 CO<sub>2</sub>; and mixtures of SO<sub>2</sub> with varying amounts of CO<sub>2</sub>.
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 WS-3 (see table 7e) 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 WS-3) at each range were analyzed using the "Reference".
6. The values determined for the Test cylinders (and WS-3) 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 Interference**

The same analytical techniques and instruments were used as in the 2006 and 2008 audits. Only certain combinations of components / analytical technique had previously exhibited an interference that required a correction factor [1,2]. Consequently, only these combinations were investigated to determine a current correction factor. (See Table 8.)

### **NDIR Analysis of NO or SO<sub>2</sub> in the presence of CO<sub>2</sub>**

It has previously been established that [2]:

- 1) There is interference by CO<sub>2</sub> on NO and, to a lesser extent, on SO<sub>2</sub>.
- 2) This interference is a combination of CO<sub>2</sub> absorption which increases response, and pressure broadening [3,4] which decreases response.
- 3) This interference cannot be mathematically modeled. However, since the effect is not overly dependent on the CO<sub>2</sub> and NO (or SO<sub>2</sub>) concentration, the same multiplication 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 7e with CO<sub>2</sub> and house N<sub>2</sub>. The CF for NO (or SO<sub>2</sub>) was calculated by:

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

The CF was determined for NO (and SO<sub>2</sub>) for each range and compared very favorably to the 2008 audit values:

EPA Mix Type	2010 Audit		2008 Audit	
	NO CF	SO <sub>2</sub> CF	NO CF	SO <sub>2</sub> CF
High	1.0162 ± 0.0019	1.0025 ± 0.0016	1.0157 ± 0.0019	1.0016 ± 0.0016
Mid	1.0022 ± 0.0019	1.0002 ± 0.0016	1.0017 ± 0.0019	1.0005 ± 0.0016
Low	N/A	0.9884 ± 0.0016	N/A	N/A

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

### NDUV Analysis of NO in the presence of SO<sub>2</sub>

SO<sub>2</sub> 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 SO<sub>2</sub> (> 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 SO<sub>2</sub> (48 ppm to 57 ppm) and NO (48 ppm to 52 ppm) is narrow, this adjustment will have little effect on the analytical ratio, effectively rendering the result interference free. (See table 18d for comparison between NO certified values by Chemi and NDUV.)

### Chemi Analysis of NO in presence of CO<sub>2</sub>:

The 2006 and 2008 audits showed that the CO<sub>2</sub> effect on the chemi analysis of NO is [1,2]:

- 1) Independent of NO concentration in the range: 10 ppm to 1000 ppm.
- 2) Linear in CO<sub>2</sub> concentration up to 20%.

Consequently, the correction factor for CO<sub>2</sub> 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 Grad<sub>CO<sub>2</sub></sub> is the gradient (slope) and Int<sub>CO<sub>2</sub></sub> is the y-intercept (expected to be 1). CF<sub>CO<sub>2</sub></sub> values for 500 ppm NO were determined at 5 %, 15 %, 15 %, and 20 % CO<sub>2</sub> by using the gas blender, an appropriate LS from table 7e, pure CO<sub>2</sub> and house N<sub>2</sub>. As expected, CF<sub>CO<sub>2</sub></sub> was linear in CO<sub>2</sub> concentration with the gradient and y-intercept comparing very favorably to the 2006 and 2008 audits:

	2010 Audit	2008 Audit	2006 Audit
Grad <sub>CO<sub>2</sub></sub>	0.0056071	0.0055681	0.0051208
Int <sub>CO<sub>2</sub></sub>	1.00012	1.00004	1.00010

Calculating  $CF_{CO_2}$  for each EPA range (for each audit) revealed that the correction had become a little more severe since 2006, but hardly any difference from 2008. See table below:

EPA Range	CO <sub>2</sub> (%)	2010 Audit	2008 Audit		2006 Audit	
		CF <sub>CO2</sub>	CF <sub>CO2</sub>	%Diff. to 2010	CF <sub>CO2</sub>	%Diff. to 2010
High	18.00	1.10105	1.10027	-0.07	1.09227	-0.80
Mid	12.00	1.06741	1.06686	-0.05	1.06155	-0.55
Low	5.00	1.02816	1.02788	-0.03	1.02570	-0.24

The 2010 values will be used for the current audit:

$$\text{Correction Factor, } CF_{CO_2} = 0.0056071 * [\text{CO}_2 \text{ conc. in \%}] + 1.00012 \quad (\text{Eq. 3})$$

### 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 CO<sub>2</sub> by NDIR and high SO<sub>2</sub> by NDUV), contained at least four data points and were fitted by orthogonal least squares analysis that complies with ISO-6143 [5]. See tables 7a-c for the standards used and table 9 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.

### 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 7d). 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 9. See Tables 10a-c (High range), tables 11a-c (Mid-range), and tables 12a-c (Low Range) for the audit Reference (and Test and WS-3) concentrations of CO<sub>2</sub>, SO<sub>2</sub> and NO. For the Reference, WS-3 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 <sub>2</sub>	High	NDUV	SO2-NDUV-HI	NDIR	SO2-NDIR-HI	0.08
NO	High	Chemi	NO-Chemi-HI	NDIR	NO-NDIR-HI	0.11
SO <sub>2</sub>	Mid	NDUV	SO2-NDUV-HI	NDIR	SO2-NDIR-HI	0.03
NO	Mid	Chemi	NO-Chemi-HI	NDIR	NO-NDIR-MID	0.22
SO <sub>2</sub>	Low	NDUV	SO2-NDUV-LO	NDUV	SO2-NDIR-LO	0.00

The difference between the methods was within the expanded uncertainty ( $k = 2$ ) of the individual methods. (See table 20a.) The methods were hence statistically equivalent and the resultant concentrations were averaged. The Reference cylinder concentrations are highlighted in tables 10a-12c.

### **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 (CO<sub>2</sub>, SO<sub>2</sub> 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 same time		
		# 1	# 2	# 3
High	NDIR	CO <sub>2</sub>	SO <sub>2</sub>	NO
Mid	NDIR	CO <sub>2</sub>	SO <sub>2</sub>	NO
Low	NDIR	CO <sub>2</sub>	SO <sub>2</sub>	N/A
Low	NDUV	N/A	SO <sub>2</sub>	NO <sup>a</sup>

The determined NIST concentrations of CO<sub>2</sub>, SO<sub>2</sub> and NO, including a comparison to the vendor concentrations (including standard type and analytical technique used by vendor) are contained in tables 13a-c (High range), tables 14a-c (Mid-range), and tables 15a-c (Low range). For Low range SO<sub>2</sub> the NIST certified concentration was the average of the NDIR and NDUV analyses.

### **Determination of Pass or Fail 2 % Tag Rule**

The NIST 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 “2 % Tag Rule”



With these parameters NIST was able to determine that a  $> 2.15\%$  modulus (absolute value), relative difference between NIST and Vendor certified values meant that the sample component has failed the 2 % Tag Rule. This was rounded up to  $> 2.20\%$  fails 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 % of number of cylinders and per component is given below:

Range	Number of Failures				
	Cylinders	NO	SO <sub>2</sub>	CO <sub>2</sub>	All Components
High	3	3	2	0	5
Mid	2	1	1	1	3
Low	4	3	1	1	5
Totals	9	7	4	2	13
% Total	20.0 %	15.6%	8.9 %	4.4 %	9.6 %

### **Comparison of Reference and Test Cylinder Concentrations**

Naming the audit concentrations (per range) from the Reference (of the same range) was very efficient because it allowed the simultaneous NDIR analysis of CO<sub>2</sub>, SO<sub>2</sub>, and NO for the High and Mid ranges, and the simultaneous NDUV analysis of SO<sub>2</sub> and NO for the Low range. The only drawback was a small increase in the uncertainty. (See Tables 20a-b.) However, is this approach consistent with naming the concentration from the appropriate calibration curve? Of particular concern was the NDUV determination of NO concentration because of the analyzer auto adjustment of NO response due to SO<sub>2</sub> interference. (See section: Determination of Interference.) Consequently, all of the Low audit samples were analyzed for NO by chemi.

The results of the comparisons are in tables 16a-c (High range), tables 17a-c (Mid-range), and tables 18a,b,d (Low range). Without exception, the differences between the two approaches were well 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 certified concentration was the average of the chemi and NDUV analyses. (See table 15c.)

### **Comparison to 2008 EPA Audit**

During the 2008 audit, two trinary 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 CO<sub>2</sub>, SO<sub>2</sub>, and NO concentrations were determined against the appropriate calibration curve and against the appropriate Reference. Both approaches were statistically equivalent. (See tables 16-18.) Further, the agreements between the current (against Reference) and previous analyses were within the expanded uncertainty ( $k = 2$ ) of the individual analysis, hence showing a consistency between the two audits. (See tables 19a-c.)

### **Relative 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 [6].  $u_{ISO}$  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 20a 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:

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

where,  $u_{ratio}$  and  $u_{cf}$  are the uncertainties of the analytical ratios obtained and the correction factor employed respectively. Table 20b 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 covering factor,  $k$ , is equal to 2. The true concentration is asserted to lie within the interval expressed by the certified value  $\pm U$  with a level of confidence of approximately 95 % [7].

### **Disposition of Cylinders**

All 57 audit cylinders were returned to PC and controlled by a “Bill of Lading”.

### **Corrective Actions Taken by Gas Vendors**

Vendors were given the opportunity to reanalyze their cylinders. Those vendors that had one or more components fail the “2% Tag Rule” elected to reanalyze and provided statements about the reanalysis and the corrective action(s) taken. The pertinent portions of the vendor statements are presented below. See Table 21 for the results of the reanalysis, the %change from the original certification, and the comparison to NIST certified concentrations. In all cases, following the corrective actions, the samples passed the “2% Tag Rule”.

**Air Liquide:** Cylinder Number AAL12922 (MI) - Re-analysis by both the producing lab in Troy, MI and a secondary lab in PA agreed within 0.8% of NIST’s value, but indicated additional degradation of both the Nitric Oxide and Sulfur Dioxide components.

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,” September 1997, EPA–600/R–97/121, nor deviation from internal Air Liquide procedures. Based on the long-term behavior of this cylinder, and chemistry of NO, SO<sub>2</sub> and Oxygen reactions, we have concluded that the discrepancy seen between the certified value and NIST’s analyzed value for Nitric Oxide is attributable to trace level oxygen contamination in the cylinder. Most likely the contamination occurred at the point of blending.

While strict adherence to the Protocol was in place during the analysis, simply following the Protocol did not cause the cylinder to reject under these circumstances. An agreement of 0.98% between first and second analysis for the SO<sub>2</sub> component should have indicated a potential problem, but is not currently a trigger for failing analysis.

As a result of this investigation, Air Liquide America Specialty Gases 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

**Airgas:** After receiving the redacted reports relevant to the Airgas cylinders – from Durham, NC; Chicago, IL; and Riverton, NJ - we reviewed not only the two results that exceeded the required uncertainty. We evaluated the NIST data vs. our original results where the difference exceeded 1.2%. We also looked for a consistent one-direction bias between the NIST results and those from our laboratories. Since all of the analyses were originally analyzed on the Thermo Nicolet FTIR platform, fully automated with extensive controls on pressure, temperature, flow, purging, spectral region selection, curve fitting process, coupled with common SOPs and training – any such bias would suggest the need to potentially revise our parameters.

Durham (Cylinder Number CC201169) showed a positive bias at the 900ppm NO level of 2.22% and Riverton (Cylinder Number SG9112847) showed a similar (although passing) bias below 2.0%. Both labs used NTRMs from the same batch, but we have verified the integrity and stability of that NTRM batch. We reviewed the original FTIR spectral files from Riverton and Durham for all the runs of the NTRMs, Protocol mixtures, plus NTRMs and data points during the monthly multipoint curve fitting. We also overlaid 20% CO<sub>2</sub> runs and identified a previous unnoticed, extremely small peak from CO<sub>2</sub> – under “magnification” – that is believed to have contributed the positive interference. For NO levels between 500ppm to 3000ppm we utilize a separate spectral region than for lower concentrations.

After extensive studies, we have identified a different FTIR spectral region which shows a complete lack of interference from up to 20% CO<sub>2</sub>, from high levels of SO<sub>2</sub> and from any level of moisture, plus shows excellent regression fitting. Using this new spectral region, we re-evaluated the original spectral data for the high NO levels from Durham and Riverton and both now show agreement within 0.8% to the NIST values. Airgas Riverton reran all 12 returned audited Protocol cylinders (4 each high, mid and low) and

the results are within +/- 1% for all components and generally within 0.5%. We had initiated increased back purging of sample lines and additional FTIR cell purging in the late spring so that also led to improvements in the results for the low level mixes.

The discrepancy at Chicago (Cylinder Number CC87345) on the mid-range 12% CO<sub>2</sub> was, quite simply, operator error in improperly fitting the FTIR data – coupled with using a 20% NTRM standard instead of a closer nominal 10% or 12% CO<sub>2</sub> NTRM. When changed from first order to second order the results “electronically” match well within +/-1%. The chemists have been retrained and reminders sent out to all laboratory managers to manage this aspect of their quality program.

**Liquid Technology Inc.:** Our facility continues to regularly upgrade instrumentation utilized in our Protocol program including the addition of multiple IR and Chemiluminescence analyzers. The Blind Audit samples were re-analyzed utilizing FTIR.

**Matheson Tri-Gas, Inc.:** Interaction with Matheson customers during the same timeframe identified that biases were occurring on some other Matheson cylinders. Matheson initiated an internal review and discovered that there were issues affecting the sampling manifold. The sampling manifold was rebuilt and the FTIR was recalibrated before the system was brought back on-line in June 2010. The sampling manifold issues were responsible for biased SO<sub>2</sub> concentrations. Matheson also addressed the CO<sub>2</sub> interference algorithm on the NO concentration in the high concentration audit sample.

**Praxair Distribution, Inc (PDI):** Cylinder Number SA13440 (CA) – After re-evaluation, the lower than certified value of Nitric Oxide for this cylinder (as compared to the actual) was due in part to PDI’s installation of a new Chemi instrument. Upon receipt of these results, PDI performed the proper Carbon Dioxide interference tests throughout the used range of the instrument, calculated the correction factors and realized that at the lower levels of Carbon Dioxide, PDI’s calculated interference had deviated from our calculated value as the instrument aged. The same instrument was used for the mid and high range Nitric Oxide tests and the calculated interference factor did not vary from the initially calculated value. PDI intends to validate the Carbon Dioxide’s interference factor more frequently than previously administered moving forward.

In addition to the cylinder observations noted above, Praxair has determined the issues related to paper work, specifically relating to Certificates of Analysis, were attributable to changes in Praxair electronic certificate of analysis program. Under the previous certificate of analysis program, the SRM sample and serial number data automatically populated to the printed certificate. When Praxair switched to the new program the Chemists were initially inconsistent when entering the required data into the program. The result was inconsistent data printing on the Certificates of Analysis supplied with our products. This discrepancy was not observed by the Praxair Quality Assurance Reviewers. Every standard was updated in the new certificate of analysis program and all of the Chemists and Quality Assurance Reviewers understand the importance of the validity of these data fields.

**References:**

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2. Environmental Protection Agency Protocol Gas Analysis 2008; ROA#: 839.03-09-10 [12/04/2008]
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5. Quality Assurance for the Analytical Chemistry Laboratory; D. Brynn Hibbert; pp. 48-49, (2007)
6. Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures, ISO 6143, 2<sup>nd</sup> Edition 2001-05-01, 2001.
7. Guide to the Expression of Uncertainty, ISBN 92-67-10188-9, 1<sup>st</sup> Edition, ISO, Geneva, Switzerland, 1993

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**Table 1:** Apparent First Party Participating Vendors

Producer/Vendor	Contact Address	Production Address
Air Liquide (CO)	500 Weaver Park Road Longmont, CO 80501	500 Weaver Park Road Longmont, CO 80501
Air Liquide (MI)	1290 Combermere Street Troy, MI 48083	1290 Combermere Street Troy, MI 48083
Air Liquide (TX)	11426 Fairmont Parkway La Porte, TX 77571	11426 Fairmont Pkwy. La Porte, TX 77571
Airgas (IL)	1250 W. Washington St. West Chicago, IL 60185	12722 S. Wentworth Ave. Chicago, IL 60628
Airgas (NC)	4301 Capital Blvd. Raleigh, NC 27604	630 United Drive Durham, NC 27713
Airgas (NJ)	120 Telmore Road East Greenwich, RI 02818	600 Union Landing Road Riverton, NJ 08077
Airgas (TX)	616 Miller Cut Off Road La Porte, TX 77571	<b>Airgas (IL)</b> 12722 S. Wentworth Ave. Chicago, IL 60628
<u>DeLille Specialty Gases</u>	772 Marion Road Columbus, OH 43207	<b>Specialty Gases of America</b> 6055 Brent Drive Toledo, OH 43611
<u>Gilmore Liquid Air</u>	9503 E. Rush St. South El Monte, CA 91733	<b>Specialty Air Technologies</b> 6544 Cherry Avenue Long Beach, CA 90805
<u>GTS - Welco</u>	5275 Tilghman Street Allentown, PA 18104	<b>Praxair (PA)</b> 145 Shimersville Road Bethlehem, PA 18015
Linde	1 Greenwich Street Suite 100 Stewartsville, NJ 08886	80 Industrial Drive Alpha, NJ 08865
Liquid Technology	2564 Pemerton Drive Apoka, FL 32703	2564 Pemberton Dr. Apopka, FL 32703
<b>Matheson Trigas</b>	6002 Triangle Drive Raleigh, NC 27617	1650 Enterprise Parkway Twinsburg, OH 44087

**Table 1 (cont.):** Apparent First Party Participating Vendors and Contact Details

Producer/Vendor	Contact Address	Production Address
Praxair (CA)	3505 Buck Owens Blvd. Bakersfield, CA 93308	5700 South Alameda Street Los Angeles, CA 90058
<b>Praxair (PA)</b>	1510 Hawkins Ave. Sanford, NC 27330	145 Shimersville Road Bethlehem, PA 18015
Red Ball Technical Gas Services	PO Box 7316 Shreveport, LA 71137-7316	555 Fontenac St. Shreveport, LA 71107
Scott-Marrin, Inc.	6531 Box Springs Blvd. Riverside, CA 92507-0725	6531 Box Springs Blvd. Riverside, CA 92507
<u>SpecAir Specialty Gas</u>	22 Albiston Way Auburn, ME 04210	<b>Matheson Trigas</b> 650 Enterprise Parkway Twinsburg, OH 44087
<b>Specialty Air Technologies</b>	N/A	6544 Cherry Avenue Long Beach, CA 90805
<b>Specialty Gases of America</b>	6055 Brent Dr. Toledo, OH 43611	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 2:** Actual First Party Participating Vendors, number of sites and number of samples received (and reported)

Vendor Name	# of Sites	# of Samples Received (and Reported)		
		High	Mid	Low
Air Liquide	3	3 (3)	3 (3)	3 (3)
Airgas	3	4 (3)	4 (3)	4 (3)
Linde	1	1 (1)	1 (1)	1 (1)
Liquid Technology	1	1 (1)	1 (1)	1 (1)
Matheson Trigas	1	2 (1)	2 (1)	2 (1)
Praxair	2	3 (2)	3 (2)	3 (2)
Red Ball Technical Gas Services	1	1 (1)	1 (1)	1 (1)
Scott-Marrin, Inc.	1	1 (1)	1 (1)	1 (1)
Specialty Air Technologies	1	1 (1)	1 (1)	1 (1)
Specialty Gases of America	1	2 (1)	2 (1)	2 (1)

**Table 3a:** Cylinders Received and Package Inspection – High Range

Manufacturer	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 (CO)	ALM050334	3/23/2010	2/2/2010	Yes	No	2000	2000	1725	Analytical cylinder valve tag. Used as Reference.
Air Liquide (MI)	ALM036816	3/23/2010	2/16/2010	Yes	No	1929	1975	1825	Analytical cylinder valve tag.
Air Liquide (TX)	CC233409	3/23/2010	2/1/2010	Yes	No	1854	1850	1825	Analytical cylinder valve tag.



**Table 3a (cont.):** Cylinders Received and Package Inspection – High Range

Manufacturer	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 (IL)	CC276179	3/23/2010	1/27/2010	Yes	No	2015	2000	1925	
Airgas (NC)	CC201169	3/23/2010	2/2/2010	Yes	No	2015	1900	1800	
Airgas (NJ)	SG9112847	3/23/2010	1/21/2010	Yes	Yes	2015	1950	1900	
Linde (NJ)	CC-114071	3/23/2010	2/4/2010	No	Yes	2000	1875	1800	Analytical cylinder valve tag. CGA 660 washer provided.
Liquid Technology	CC-231468	3/23/2010	1/27/2010	Yes	No	2000	1800	1750	
Matheson (OH)	SX-45104	3/23/2010	2/26/2010	Yes	Yes	2000	1800	1675	Analytical cylinder valve tag.
Praxair (CA)	CC157996	3/24/2010	3/5/2010	Yes	No	2000	1900	1775	Analytical cylinder valve tag.
Praxair (PA)	CC239282	3/23/2010	2/5/2010	Yes	Yes	2000	2000	2000 <sup>a</sup>	Analytical cylinder valve tag.
Red Ball	EB0018491	3/23/2010	2/15/2010	Yes	No	1700	1600	1600 <sup>a</sup>	
Scott-Marrin	CC103699	3/23/2010	2/3/2010	No	Yes	2000	1850	1800	
Specialty Air Technologies	ALM-036855	3/24/2010	2/17/2010	Yes	No	2000	1975	1925	
Specialty Gases of America	EB0018749	3/23/2010	2/12/2010	No	Yes	2015	2000	1975	

<sup>a</sup> Equal NIST start and end pressures means that < 25 psi gas was used for the NIST analysis

**Table 3b:** Cylinders Received and Package Inspection – Mid-Range

Manufacturer	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)	Comments
Air Liquide (CO)	ALM053737	4/13/2010	2/2/2010	Yes	No	2000	2050	2000	Analytical cylinder valve tag.
Air Liquide (MI)	ALM057383	4/13/2010	2/16/2010	Yes	No	1966	1950	1950 <sup>a</sup>	Analytical cylinder valve tag.
Air Liquide (TX)	CC109172	4/13/2010	2/1/2010	Yes	No	1808	1850	1800	Analytical cylinder valve tag.
Airgas (IL)	CC87345	4/13/2010	1/27/2010	Yes	No	2015	2000	1950	
Airgas (NC)	CC47476	4/13/2010	1/27/2010	Yes	No	2015	1900	1875	
Airgas (NJ)	SG9149394	4/13/2010	2/10/2010	Yes	Yes	2015	1950	1925	Difficult to read cylinder number due to excessive level of paint on cylinder surface.
Linde (NJ)	CC-143271	4/13/2010	2/4/2010	Yes	Yes	2000	1900	1575	Analytical cylinder valve tag. CGA 660 washer provided. Used as Reference.
Liquid Technology	EB-0019812	4/13/2010	1/27/2010	Yes	No	2000	1800	1750	
Matheson (OH)	SX-48952	4/13/2010	3/2/2010	Yes	Yes	2000	1850	1850 <sup>a</sup>	Analytical cylinder valve tag. Two cylinder numbers were engraved in the container - CC312885 and SX48952. Presumably the latter is the current one, but the former number should be stamped out in order to avoid confusion.
Praxair (CA)	SA20483	4/13/2010	2/16/2010	Yes	Yes	2000	1950	1925	Analytical cylinder valve tag.
Praxair (PA)	SA21915	4/13/2010	2/5/2010	Yes	Yes	2000	1950	1950 <sup>a</sup>	Analytical cylinder valve tag.

**Table 3b (cont.):** Cylinders Received and Package Inspection – Mid-Range

Manufacturer	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)	Comments
Red Ball	EB0006725	4/13/2010	2/15/2010	Yes	No	1700	1800	1800 <sup>a</sup>	
Scott-Marrin	CC94437	4/13/2010	1/29/2010	No	Yes	2000	1950	1950 <sup>a</sup>	Analytical cylinder valve tag.
Specialty Air Technologies	SA12310	4/13/2010	2/16/2010	Yes	No	2000	2000	2000 <sup>a</sup>	
Specialty Gases of America	EB0018605	4/13/2010	2/15/2010	Yes	Yes	2015	2000	1875	

<sup>a</sup> Equal NIST start and end pressures means that < 25 psi gas was used for the NIST analysis

**Table 3c:** Cylinders Received and Package Inspection – Low Range

Manufacturer	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)	Comments
Air Liquide (CO)	ALM050278	5/20/2010	2/4/2010	Yes	No	1910	1900	1850	Analytical cylinder valve tag.
Air Liquide (MI)	AAL12922	5/20/2010	2/15/2010	Yes	No	2015	2050	2000	Analytical cylinder valve tag.
Air Liquide (TX)	CC81064	5/20/2010	2/13/2010	Yes	No	1861	1900	1750	Analytical cylinder valve tag.
Airgas (IL)	CC33482	5/20/2010	2/3/2010	Yes	No	2015	1950	1825	

**Table 3c (cont.):** Cylinders Received and Package Inspection – Low Range

Manufacturer	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)	Comments
Airgas (NC)	CC323784	5/20/2010	1/26/2010	Yes	No	2015	1950	1800	
Airgas (NJ)	CC5459	5/20/2010	1/21/2010	Yes	Yes	2015	1950	1875	
Linde	CC-241882	5/20/2010	2/4/2010	Yes	Yes	2000	1950	1900	Analytical cylinder valve tag. CGA 660 washer provided.
Liquid Technology Corp.	CC-251845	5/20/2010	1/26/2010	Yes	No	2000	1825	1675	
Matheson	SX-16262	5/20/2010	2/25/2010	Yes	Yes	2000	1900	1850	Analytical cylinder valve tag.
Praxair (CA)	SA13440	5/20/2010	2/10/2010	Yes	Yes	2000	1950	1925	Analytical cylinder valve tag.
Praxair (PA)	CC187418	5/20/2010	2/15/2010	Yes	Yes	2000	1975	1925	Analytical cylinder valve tag.
Red Ball	EB0004947	5/20/2010	2/15/2010	Yes	No	1700	1700	1650	
Scott-Marrin	CC37789	5/20/2010	3/11/2010	Yes	Yes	2000	1900	1750	Analytical cylinder valve tag.
Specialty Air Technologies	CC86708	5/20/2010	2/18/2010	Yes	No	2000	2000	1775	
Specialty Gases of America	EB0018729	5/20/2010	2/11/2010	Yes	Yes	2015	2050	2000	

**Table 4a:** Nonconformities and Comments of Vendor Certificate of Analysis (CoA) – High Range

Manufacturer	Cylinder Number	Nonconformities	Comments
Airgas (IL)	CC276179		The "Lot ID" column for NTRMs is a mixture of Batch ID and Sample IDs. The NO NTRM Sample ID for cylinder# CC209631 is incorrect (stated as 06120608, but should be 06120605). Also, the expiration date for this NTRM is incorrect (stated as Nov 01, 2010 but should be Jul 01, 2010). The CO <sub>2</sub> Batch ID is incorrect (stated as 40604, but should be 040604).
Matheson (OH)	SX-45104	Incorrect Sample and Cylinder numbers reported for SO <sub>2</sub> . Reported as 95-G-47 and FF-01795; correct is 93-G-47 and FF-17195.	
Praxair (CA)	CC157996	No correction factor to account for the CO <sub>2</sub> interference on chemi analysis of NO was stated. However, as part of Praxair's Corrective Action, they stated that a change in the CO <sub>2</sub> correction factor was employed. As per Item 12, section 2.1.4 of the EPA Document, if a correction factor is used, then this must be stated on the CoA.	
Praxair (PA)	CC239282	No correction factor to account for the CO <sub>2</sub> interference on chemi analysis of NO was stated. However, as part of Praxair's Corrective Action, they stated that a change in the CO <sub>2</sub> correction factor was employed. As per Item 12, section 2.1.4 of the EPA Document, if a correction factor is used, then this must be stated on the CoA.	Contradictory information reported for the SO <sub>2</sub> SRM. Sample # 91-E-21 is not cylinder# CAL010828, but CAL017011. Cylinder# CAL010828 is Sample# 91-D-49.
Red Ball	EB0018491		Confusing whether a GMIS or SRM was used for triad analysis of NO. Assumed the GMIS was used based on the analytical data reported. Missing Sample ID (46-E-26) for NO SRM cylinder# FF20506.
Scott-Marrin	CC103699		Scott-Marrin indicates that the chemi technique they use minimizes CO <sub>2</sub> interference with the analyzer. Therefore, a CO <sub>2</sub> interference instrument correction factor is not applied to their NO (and NO <sub>x</sub> ) chemi analyzer data.

**Table 4a (cont.):** Nonconformities and Comments of Vendor Certificate of Analysis (CoA) – High Range

Manufacturer	Cylinder Number	Nonconformities	Comments
Specialty Air Technologies	ALM-036855		No NOx reported.
Specialty Gases of America	EB0018749		Specialty Gases of America indicates that they do not use CO <sub>2</sub> interference instrument correction factors because of their NO <sub>x</sub> /CO <sub>2</sub> blend testing practices. They account for the quenching process by blending the mix with their gas flow divider (G2 Procedure). Since the G2 procedure is used, then NO (and NO <sub>x</sub> ) is reported at 2% relative uncertainty.

**Table 4b:** Nonconformities and Comments of Vendor Certificate of Analysis (CoA) – Mid-Range

Manufacturer	Cylinder Number	Nonconformities	Comments
Airgas (IL)	CC87345		The "Lot ID" column for NTRMs is a mixture of Batch ID and Sample IDs. The NO Batch ID (stated as 61207, but should be 061207) and the CO <sub>2</sub> Batch ID (stated as 40604, but should be 040604) are incorrect .
Praxair (CA)	SA20483	No correction factor to account for the CO <sub>2</sub> interference on chemi analysis of NO was stated. However, as part of Praxair's Corrective Action, they stated that a change in the CO <sub>2</sub> correction factor was employed. As per Item 12, section 2.1.4 of the EPA Document, if a correction factor is used, then this must be stated on the CoA.	
Praxair (PA)	SA21915	No correction factor to account for the CO <sub>2</sub> interference on chemi analysis of NO was stated. However, as part of Praxair's Corrective Action, they stated that a change in the CO <sub>2</sub> correction factor was employed. As per Item 12, section 2.1.4 of the EPA Document, if a correction factor is used, then this must be stated on the CoA.	
Red Ball	EB0006725		Confusing whether a GMIS or SRM was used for triad analysis of NO. Assumed the GMIS was used based on the analytical data reported. Missing Sample ID (46-E-26) for NO SRM cylinder# FF20506.

**Table 4b (cont.):** Nonconformities and Comments of Vendor Certificate of Analysis (CoA) – Mid-Range

Manufacturer	Cylinder Number	Nonconformities	Comments
Scott-Marrin	CC94437		Scott-Marrin stated that the chemiluminescence technique they use minimizes CO <sub>2</sub> interference with the analyzer. Therefore, a CO <sub>2</sub> interference instrument correction factor is not applied to their NO (and NO <sub>x</sub> ) chemi analyzer data.
Specialty Gases of America	EB0018605		Specialty Gases of America indicates that they do not use CO <sub>2</sub> interference instrument correction factors because of their NO <sub>x</sub> /CO <sub>2</sub> blend testing practices. They account for the quenching process by blending the mix with their gas flow divider (G2 Procedure). Since the G2 procedure is used, then NO (and NO <sub>x</sub> ) is reported at 2% relative uncertainty.

**Table 4c:** Nonconformities and Comments of Vendor Certificate of Analysis (CoA) – Low Range

Manufacturer	Cylinder Number	Nonconformities	COA Comments
Airgas (IL)	CC33482		The "Lot ID" for the NO NTRM (cylinder# CC237887) is incorrect. It is reported as 16208, but should be 080601.
Praxair (CA)	SA13440	No correction factor to account for the CO <sub>2</sub> interference on chemi analysis of NO was stated. However, as part of Praxair's Corrective Action, they stated that a change in the CO <sub>2</sub> correction factor was employed. As per Item 12, section 2.1.4 of the EPA Document, if a correction factor is used, then this must be stated on the CoA.	

**Table 4c (cont.):** Nonconformities and Comments of Vendor Certificate of Analysis (CoA) – Low Range

Manufacturer	Cylinder Number	Nonconformities	COA Comments
Praxair (PA)	CC187418	No correction factor to account for the CO <sub>2</sub> interference on chemi analysis of NO was stated. However, as part of Praxair's Corrective Action, they stated that a change in the CO <sub>2</sub> correction factor was employed. As per Item 12, section 2.1.4 of the EPA Document, if a correction factor is used, then this must be stated on the CoA.	Contradictory information reported for NO SRM. Vendor incorrectly reported Sample ID 45-U-25 as cylinder# CAL015652. As per NIST records Sample ID 45-U-25 is cylinder# CAL015623 and cylinder# CAL015652 is Sample ID 45-U-17. Missing Sample ID for SO <sub>2</sub> SRM.
Red Ball	EB0004947		Confusing whether a GMIS or SRM was used for the triad analysis of NO. Also, confusing whether a GMIS or NTRM was used for the triad analysis of SO <sub>2</sub> . Assumed the GMIS (for NO and SO <sub>2</sub> ) was used based on the raw analytical data reported. Missing Sample ID (44-S-55) for NO SRM cylinder# CAL015666.
Scott-Marrin	CC37789		Scott-Marrin stated that the chemiluminescence technique they use minimizes CO <sub>2</sub> interference with the analyzer. Therefore, a CO <sub>2</sub> interference instrument correction factor is not applied to their NO (and NO <sub>x</sub> ) chemi analyzer data.
Specialty Air Technologies	CC86708		No NO <sub>x</sub> reported.
Specialty Gases of America	EB0018729		Specialty Gases of America indicates that they do not use CO <sub>2</sub> interference instrument correction factors because of their NO <sub>x</sub> /CO <sub>2</sub> blend testing practices. They account for the quenching process by blending the mix with their gas flow divider (G2 Procedure). Since the G2 procedure is used, then NO (and NO <sub>x</sub> ) is reported at 2% relative uncertainty.



**Table 5:** Analytical Techniques as a function of High, Mid and Low EPA Samples, uncertainty is stated at  $k = 1$ 

Analytical Technique	NO			SO <sub>2</sub>			CO <sub>2</sub>		
	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 6:** Instrumentation and Analytical Techniques used

Manufacturer	Description / Analytical Technique	NIST#	Purpose
Horiba	Model VA-3000 NDIR	631375	Analyze CO <sub>2</sub> in Range: 4 % – 23% Analyze SO <sub>2</sub> in Range: 50 ppm – 1250 ppm Analyze NO in Range: 200 ppm – 1200 ppm
Ametek	Series 9000 NDUV	613059	Analyze SO <sub>2</sub> 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 <sub>2</sub> and / or SO <sub>2</sub> and / or NO
Bios International	Drycal ML-800	626779	Used to determine correction factor to account for any interference between CO <sub>2</sub> and / or SO <sub>2</sub> and / or NO
NIST	Gas Dilutor	N/A	Used to create calibration curves for NO, SO <sub>2</sub> and CO <sub>2</sub>

**Note:** The commercial products in this table are for information only; it does not imply recommendation or endorsement by NIST or EPA.

**Table 7a:** Standards (in balance nitrogen) used to determine CO<sub>2</sub> 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	10/1/2010	652	839.03-05-002 [11/15/2004]
1675	6-FL-01	AAL053273	13.956	0.022	10/1/2010	500	839.03-05-002[11/15/2004]
2626a	37-01-EL	ALM045206	3.916	0.003	3/16/2015	800	839.03-07-078[3/16/2007]

**Table 7b:** Standards (in balance nitrogen) used to determine SO<sub>2</sub> 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-CL-02	AAL06779	3520.8	11.3	11/8/2012	1300	839.03-07-035 [11/8/2006]
1663a	LS	92-EL-01	AAL053243	1476.0	1.8	9/15/2010	250	839.03-04-068 [4/9/2004]
1662a	LS	93-GL-02	CA04089	973.8	0.3	6/1/2015	1175	839.03-07-116 [5/22/2007]
1662a	LS	93-HL-01	AAL072013	978.18	0.90	6/1/2015	750	839.03-07-116 [5/22/2007]
1661a	LS	94-HL-01	CC142052	491.25	0.45	5/23/2011	350	839.03-05-117b [9/28/2005]
N/A	WS	SO2-WS-2	KAL003797	255.57	0.14	1/21/2015	1900	839.03-08-17 [11/21/2007]
1694a	LS	95-JL-02	AAL071390	98.59	0.05	12/12/2015	200	839.03-08-032 [12/12/2007]
1693a	LS	96-KL-02	AAL070433	49.75	0.12	5/23/2011	400	839.03-05-116 [6/13/2005]

**Table 7c:** 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	2952.9	1.4	3/1/2012	900	839.03-06-076 [2/24/2006]
1687b	LS	41-JL-01	CC90603	985.9	2.5	3/5/2018	500	839.03-10-061 [3/5/2010]
2735	LS	141-CL-01	AAL070909	779.8	1.0	1/31/2013	850	839.03-09-039 [1/31/2009]
1686b	LS	42-KL-01	CC90574	491.3	1.3	7/1/2012	400	839.03-06-153 [6/12/2006]
1685b	LS	43-LL-01	AAL072023	244.79	0.21	11/2/2015	650	839.03-08-013 [11/2/2007]
1684b	LS	44-SL-02	AAL070456	97.62	0.04	9/1/2011	1075	839.03-05-159 [8/19/2005]
1683b	LS	45-UL-02	AAL070437	48.667	0.019	9/1/2011	1750	839.03-05-169 [9/16/2005]
2629a	LS	50-GL-02	CC166201	18.99	0.08	5/14/2011	1600	839.03-08-111a [5/14/2011]
2628a	LS	49-HL-04	AAL071142	10.00	0.04	9/1/2011	500	839.03-07-130 [8/25/2007]

**Table 7d:** 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 <sub>2</sub>	LS	90-DL-03	AAL071145	3395.3	0.90	11/8/2012	1850	839.03-07-035 [11/8/2006]
1687b	SO <sub>2</sub>	WS	SO2-WS-2	KAL003797	255.57	0.14	1/21/2015	1900	839.03-08-17 [11/21/2007]
2631a	NO	LS	47-FL-01	AAL071135	2952.9	1.4	3/1/2012	900	839.03-06-076 [2/24/2006]

**Table 7e:** Working Standards (in balance nitrogen) certified from 2008, with uncertainty (k=1) [2]

Sample ID	Cylinder Number	CO <sub>2</sub> (%)	SO <sub>2</sub> (ppm)	NO (ppm)	Expiration Date	Pressure (psig)
WS-EPA8-L1	CA08181	5.111 ± 0.011	51.35 ± 0.14	50.85 ± 0.17	11/1/2011	1800
WS-EPA8-L2	ALM054809	5.0110 ± 0.0075	51.61 ± 0.10	51.45 ± 0.13	11/1/2011	800
WS-EPA8-M1	CC5188	12.186 ± 0.018	515.1 ± 1.2	408.4 ± 1.1	11/1/2011	1800
WS-EPA8-M2	CA08177	12.073 ± 0.025	497.2 ± 1.5	399.5 ± 1.4	11/1/2011	1825
WS-EPA8-H1	CA08268	18.038 ± 0.038	998.0 ± 3.0	895.8 ± 3.0	11/1/2011	1800
WS-EPA8-H2	SA10582	18.208 ± 0.027	1003.5 ± 2.3	929.8 ± 2.5	11/1/2011	1800

**Table 8:** Summary of Component Interference per Analytical Technique

Analyzed Component	Analytical Technique	Interference Component	Interference
CO <sub>2</sub>	NDIR	NO	None observed up to 2900 ppm NO
CO <sub>2</sub>	NDIR	SO <sub>2</sub>	None observed up to 2500 ppm SO <sub>2</sub>
SO <sub>2</sub>	NDIR	NO	None observed up to 2900 ppm NO
SO <sub>2</sub>	NDIR	CO <sub>2</sub>	Complex interference caused by a combination of CO <sub>2</sub> absorption (increases signal) and pressure broadening (decreases signal). Not possible to model, but the effect is not overly dependent on SO <sub>2</sub> and CO <sub>2</sub> . Use CF of 1.0025 for EPA High range, 1.0002 for EPA Mid-range, and 0.9884 for Low range. CFs are instrument dependent. Use for NIST#: 631375 only
NO	NDIR	SO <sub>2</sub>	None observed up to 2500 ppm SO <sub>2</sub>
NO	NDIR	CO <sub>2</sub>	Complex interference caused by a combination of CO <sub>2</sub> absorption (increases signal) and pressure broadening (decreases signal). Not possible to model, but the effect is not overly dependent on NO and CO <sub>2</sub> . Use CF of 1.0162 for EPA High range and 1.0022 for EPA Mid-range. CFs are instrument dependent. Use for NIST#: 631375 only
SO <sub>2</sub>	NDUV	CO <sub>2</sub>	None observed up to 20 % CO <sub>2</sub>
SO <sub>2</sub>	NDUV	NO	None observed up to 1500 ppm NO
SO <sub>2</sub>	NDUV	CO	None observed up to 50 ppm NO
NO	NDUV	SO <sub>2</sub>	Severe interference. However, the NO analytical ratio is not effected over the narrow range of SO <sub>2</sub> (48 ppm to 57 ppm) and NO (48 ppm to 52 ppm).
NO	Chemi	CO <sub>2</sub>	Large reduction in instrument response that can accurately be determined. Correction equation is linear in CO <sub>2</sub> concentration and independent on NO. The equation developed is valid for 40 - 950 ppm NO in the presence of up to 20 % CO <sub>2</sub> ( $CF_{CO_2} = 0.0056071 * [CO_2 \text{ in } \%] + 1.000012$ ) CF is instrument dependent. Use for NIST#: 586629 only.
NO	Chemi	SO <sub>2</sub>	None observed up to 1050 ppm SO <sub>2</sub>

**Table 9:** Calibration Curves created as a function of Component and Analytical Technique. All standards used were single component in balance N<sub>2</sub>.

Component	Analytical Technique	Control	Binary Dilution of	# of Points	Fitting Type	Fitting Parameters			Fitting Range	Curve Name
						A	B	C		
NO	NDIR	41-JL-01	47-FL-01	16	Linear	N/A	974.258	11.903	600 ppm to 1200 ppm	NO-NDIR-HI
NO	NDIR	42-KL-01	47-FL-01	11	Linear	N/A	489.999	1.340	200 ppm to 600 ppm	NO-NDIR-MID
NO	Chemi	41-JL-01	N/A	4	Linear	N/A	986.071	0.858	250 ppm to 1000 ppm	NO-CHEMI-HI
NO	Chemi	45-UL-02	N/A	4	Linear	N/A	48.7523	-0.1229	20 ppm to 100 ppm	NO-CHEMI-LO
SO <sub>2</sub>	NDIR	93-GL-02	90-CL-02	14	Linear	N/A	981.922	-8.148	650 ppm to 1250 ppm	SO2-NDIR-HI
SO <sub>2</sub>	NDIR	94-HL-01	90-CL-02	11	Linear	N/A	491.936	-0.793	300 ppm to 750 ppm	SO2-NDIR-MID
SO <sub>2</sub>	NDIR	96-KL-02	94-HL-01	9	Linear	N/A	49.422	0.325	25 ppm to 75 ppm	SO2-NDIR-LO
SO <sub>2</sub>	NDUV	94-HL-01	N/A	5	Quadratic	-15.913	994.017	0.089	100 ppm to 1000 ppm	SO2-NDUV-HI
SO <sub>2</sub>	NDUV	96-KL-02	94-HL-01	9	Linear	N/A	49.813	-0.057	25 ppm to 75 ppm	SO2-NDUV-LO
CO <sub>2</sub>	NDIR	9-BL-01	Pure CO <sub>2</sub>	10	Linear	N/A	15.695	0.004	13 % to 23 %	CO2-NDIR-HI
CO <sub>2</sub>	NDIR	6-FL-01	Pure CO <sub>2</sub>	7	Linear	N/A	13.911	0.053	9 % to 15 %	CO2-NDIR-MID
CO <sub>2</sub>	NDIR	37-01-EL	9-BL-01	12	Quadratic	-0.2371	4.7345	-0.5838	4 % to 6 %	CO2-NDIR-LO

**Table 10a:** NIST Certified CO<sub>2</sub> 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 <sub>2</sub>		
			Using Curve	Conc. (%)	± (%)
<b>Air Liquide (CO)</b>	<b>ALM050334</b>	<b>Reference</b>	<b>CO2-NDIR-HI</b>	<b>18.117</b>	0.054
WS-EPA8-H1	CA08268	2008	CO2-NDIR-HI	18.033	0.054
WS-EPA8-H1	SA10582	2008	CO2-NDIR-HI	18.196	0.055
Airgas (IL)	CC40347	Test	CO2-NDIR-HI	18.062	0.054
Matheson	SX45104	Test	CO2-NDIR-HI	18.066	0.054
Praxair	CC157996	Test	CO2-NDIR-HI	17.723	0.053
Spec. Gas of Amer.	EB0020538	Test	CO2-NDIR-HI	18.084	0.054

**Table 10b:** NIST Certified SO<sub>2</sub> 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 <sub>2</sub> <sup>a</sup>			SO <sub>2</sub>			SO <sub>2</sub> (ppm)		
			Using Curve	Conc. (ppm)	± (ppm)	Using Curve	Conc. (ppm)	± (ppm)	%Diff.	Mean	± (ppm)
<b>Air Liquide (CO)</b>	<b>ALM050334</b>	<b>Reference</b>	SO2-NDIR-HI	1004.0	5.4	SO2-NDUV-HI	1003.2	4.4	0.08	<b>1003.6</b>	4.9
WS-EPA8-H1	CA08268	2008	SO2-NDIR-HI	997.6	5.4	SO2-NDUV-HI	999.2	4.0	-0.16	998.4	4.7
WS-EPA8-H2	SA10582	2008	SO2-NDIR-HI	999.1	5.4	SO2-NDUV-HI	1001.1	4.0	-0.20	1000.1	4.7
Airgas (IL)	CC40347	Test	SO2-NDIR-HI	988.8	5.3						
Matheson	SX45104	Test	SO2-NDIR-HI	981.5	5.3						
Praxair	CC157996	Test	SO2-NDIR-HI	1028.9	5.6						
Spec. Gas of Amer.	EB0020538	Test	SO2-NDIR-HI	949.4	5.1						

<sup>a</sup> Using EPA High SO<sub>2</sub> NDIR correction factor of 1.0025

**Table 10c:** NIST Certified 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 <sup>a</sup>			NO <sup>b</sup>			NO (ppm)		
			Using Curve	Conc. (ppm)	± (ppm)	Using Curve	Conc. (ppm)	± (ppm)	%Diff.	Mean	± (ppm)
Air Liquide (CO)	ALM050334	Reference	NO-NDIR-HI	907.3	4.8	NO-CHEMI-HI	906.3	5.1	0.11	906.8	4.9
WS-EPA8-H1	CA08268	2008	NO-NDIR-HI	892.9	4.7	NO-CHEMI-HI	893.4	5.0	-0.05	893.2	4.8
WS-EPA8-H2	SA10582	2008	NO-NDIR-HI	926.5	4.9	NO-CHEMI-HI	928.9	5.2	-0.26	927.7	5.0
Airgas (IL)	CC40347	Test	NO-NDIR-HI	876.3	4.6						
Matheson	SX45104	Test	NO-NDIR-HI	877.7	4.6						
Praxair	CC157996	Test	NO-NDIR-HI	890.4	4.7						
Spec. Gas of Amer.	EB0020538	Test	NO-Chemi-HI	946.1	5.0						

<sup>a</sup> Using CO<sub>2</sub> correction factor (Equation 3)

<sup>b</sup> Using EPA High NO NDIR correction factor of 1.0162



**Table 11a:** NIST Certified CO<sub>2</sub> 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 <sub>2</sub>		
			Using Curve	Conc. (%)	± (%)
<b>Linde</b>	<b>CC143271</b>	<b>Reference</b>	CO2-NDIR-MID	<b>12.045</b>	0.036
WS-EPA8-M1	CC51188	2008	CO2-NDIR-MID	12.181	0.037
WS-EPA8-M2	CA08177	2008	CO2-NDIR-MID	12.072	0.036
Airgas (IL)	CC87345	Test	CO2-NDIR-MID	12.020	0.036
Airgas (IL)	SG9164934BAL	Test	CO2-NDIR-MID	12.031	0.036
Airgas (NC)	CC47476	Test	CO2-NDIR-MID	11.833	0.035
Spec. Gas of Amer.	EB0020755	Test	CO2-NDIR-MID	12.003	0.036

**Table 11b:** NIST Certified SO<sub>2</sub> 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 <sub>2</sub> <sup>a</sup>			SO <sub>2</sub>			SO <sub>2</sub> (ppm)		
			Using Curve	Conc. (ppm)	± (ppm)	Using Curve	Conc. (ppm)	± (ppm)	%Diff.	Mean	± (ppm)
<b>Linde</b>	<b>CC143271</b>	<b>Reference</b>	SO2-NDIR-MID	501.5	2.7	SO2-NDUV-HI	501.3	2.2	0.03	<b>501.4</b>	2.5
WS-EPA8-M1	CC51188	2008	SO2-NDIR-MID	515.7	2.8	SO2-NDUV-HI	515.3	2.3	0.08	515.5	2.5
WS-EPA8-M2	CA08177	2008	SO2-NDIR-MID	498.6	2.7	SO2-NDUV-HI	498.5	2.2	0.01	498.5	2.4
Airgas (IL)	CC87345	Test	SO2-NDIR-MID	524.8	2.8						
Airgas (IL)	SG9164934BAL	Test	SO2-NDIR-MID	501.0	2.7						
Airgas (NC)	CC47476	Test	SO2-NDIR-MID	503.6	2.7						
Spec. Gas of Amer.	EB0020755	Test	SO2-NDIR-MID	446.5	2.4						

<sup>a</sup> Using EPA Mid SO<sub>2</sub> NDIR correction factor of 1.0002

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

Vendor / Sample ID	Cyl#	Audit Type	NO <sup>a</sup>			NO <sup>b</sup>			NO (ppm)		
			Using Curve	Conc. (ppm)	± (ppm)	Using Curve	Conc. (ppm)	± (ppm)	%Diff.	Mean	± (ppm)
Linde	CC143271	Reference	NO-NDIR-MID	398.1	2.2	NO-CHEMI-HI	397.2	2.1	0.22	397.7	2.2
WS-EPA8-M1	CC51188	2008	NO-NDIR-MID	409.1	2.3	NO-CHEMI-HI	408.5	2.2	0.15	408.8	2.2
WS-EPA8-M2	CA08177	2008	NO-NDIR-MID	399.3	2.2	NO-CHEMI-HI	399.3	2.2	0.00	399.3	2.2
Airgas (IL)	CC87345	Test	NO-NDIR-MID	398.9	2.2						
Airgas (IL)	SG9164934BAL	Test	NO-NDIR-MID	392.2	2.1						
Airgas (NC)	CC47476	Test	NO-NDIR-MID	408.0	2.2						
Spec. Gas of Amer.	EB0020755	Test	NO-NDIR-MID	438.0	2.4						

<sup>a</sup> Using CO<sub>2</sub> correction factor (Equation 4)

<sup>b</sup> Using EPA Mid NO NDIR correction factor of 1.0022

**Table 12a:** NIST Certified CO<sub>2</sub> 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 <sub>2</sub>		
			Using Curve	Conc. (%)	± (%)
<b>Praxair (PA)</b>	<b>CC171777</b>	<b>Reference</b>	CO2-NDIR-LO	<b>4.958</b>	0.015
WS-EPA8-L1	CA08181	2008	CO2-NDIR-LO	5.119	0.015
WS-EPA8-L2	ALM054809	2008	CO2-NDIR-LO	5.014	0.015
Air Liquide (TX)	CC81064	Test	CO2-NDIR-LO	4.961	0.015
Airgas (NC)	CC323784	Test	CO2-NDIR-LO	5.025	0.015
Liq. Tech.	CC251845	Test	CO2-NDIR-LO	4.990	0.015
Scott-Marrin	CC37789	Test	CO2-NDIR-LO	5.021	0.015
Spec. Air	CC86708	Test	CO2-NDIR-LO	5.006	0.015

**Table 12b:** NIST Certified SO<sub>2</sub> 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 <sub>2</sub> <sup>a</sup>			SO <sub>2</sub>			SO <sub>2</sub> (ppm)		
			Using Curve	Conc. (ppm)	± (ppm)	Using Curve	Conc. (ppm)	± (ppm)	%Diff.	Mean	± (ppm)
<b>Praxair (PA)</b>	<b>CC171777</b>	<b>Reference</b>	SO2-NDIR-LO	50.90	0.34	SO2-NDUV-LO	50.90	0.29	0.00	<b>50.90</b>	0.31
WS-EPA8-L1	CA08181	2008	SO2-NDIR-LO	51.13	0.34	SO2-NDUV-LO	51.15	0.29	-0.04	51.14	0.31
WS-EPA8-L2	ALM054809	2008	SO2-NDIR-LO	51.49	0.34	SO2-NDUV-LO	51.52	0.29	-0.06	51.51	0.31
Air Liquide (TX)	CC81064	Test	SO2-NDIR-LO	48.71	0.32	SO2-NDUV-LO	48.69	0.27	0.03	48.70	0.30
Airgas (NC)	CC323784	Test	SO2-NDIR-LO	50.81	0.34	SO2-NDUV-LO	50.72	0.28	0.19	50.76	0.31
Liq. Tech.	CC251845	Test	SO2-NDIR-LO	49.08	0.32	SO2-NDUV-LO	48.89	0.27	0.39	48.99	0.30
Scott-Marrin	CC37789	Test	SO2-NDIR-LO	50.51	0.33	SO2-NDUV-LO	50.54	0.28	-0.06	50.52	0.31
Spec. Air	CC86708	Test	SO2-NDIR-LO	57.03	0.38	SO2-NDUV-LO	56.95	0.32	0.15	56.99	0.35

<sup>a</sup> Using EPA Low SO<sub>2</sub> NDIR correction factor of 0.9884

**Table 12c:** NIST Certified NO Concentrations of Reference (highlighted), 2008 audit WSs and Test cylinders - EPA Low Range with Expanded Uncertainty (k = 2)

Vendor / Sample ID	Cyl#	Audit Type	NO <sup>a</sup>		
			Using Curve	Conc. (ppm)	± (ppm)
Praxair (PA)	CC171777	Reference	NO-Chemi-LO	51.10	0.34
WS-EPA8-L1	CA08181	2008	NO-Chemi-LO	50.79	0.34
WS-EPA8-L2	ALM054809	2008	NO-Chemi-LO	51.35	0.34
Air Liquide (TX)	CC81064	Test	NO-Chemi-LO	49.82	0.33
Airgas (NC)	CC323784	Test	NO-Chemi-LO	51.80	0.34
Liq. Tech.	CC251845	Test	NO-Chemi-LO	52.33	0.35
Scott-Marrin	CC37789	Test	NO-Chemi-LO	48.95	0.32
Spec. Air	CC86708	Test	NO-Chemi-LO	49.87	0.33
Air Liquide (CO)	ALM050278	Sample	NO-Chemi-LO	50.37	0.33
Air Liquide (MI)	AAL12922	Sample	NO-Chemi-LO	48.95	0.32
Airgas (IL)	CC33482	Sample	NO-Chemi-LO	52.17	0.34
Airgas (IL)	XC024418B	Sample	NO-Chemi-LO	51.11	0.34
Airgas (NJ)	CC5459	Sample	NO-Chemi-LO	51.10	0.34
Linde	CC-241882	Sample	NO-Chemi-LO	50.58	0.33
Matheson	SX-16262	Sample	NO-Chemi-LO	50.64	0.33
Praxair (CA)	SA13440	Sample	NO-Chemi-LO	51.39	0.34
Praxair (PA)	CC187418	Sample	NO-Chemi-LO	50.23	0.33
Red Ball	EB0004947	Sample	NO-Chemi-LO	50.99	0.34
Spec. Gases of America	EB0018729	Sample	NO-Chemi-LO	50.59	0.33

<sup>a</sup> Using CO<sub>2</sub> correction factor (Equation 3)

**Table 13a:** Vendor and NIST Certified Concentrations – EPA High Range – CO<sub>2</sub>

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST NDIR (%)	Vendor (%)	%Diff. <sup>a</sup>
Air Liquide (CO)	ALM050334	NTRM	FTIR	<b>18.117</b>	18.1	-0.10
Air Liquide (MI)	ALM036816	NTRM	FTIR	18.041	18.1	0.33
Air Liquide (TX)	CC233409	NTRM	FTIR	17.846	17.8	-0.26
Airgas (IL)	CC276179	NTRM	FTIR	18.053	18.15	0.54
Airgas (NC)	CC201169	NTRM	FTIR	17.898	17.91	0.06
Airgas (NJ)	SG9112847	NTRM	FTIR	18.034	17.73	-1.69
Linde	CC-114071	GMIS	NDIR	18.027	18.02	-0.04
Liquid Technology	CC-231468	GMIS	GC-TCD	17.989	17.9	-0.49
Matheson	SX-45104	SRM	FTIR	18.070	17.9	-0.94
Praxair (CA)	CC157996	GMIS	NDIR	17.725	17.54	-1.05
Praxair (PA)	CC239282	GMIS	NDIR	18.187	17.97	-1.19
Red Ball	EB0018491	SRM	NDIR	18.055	18.0	-0.31
Scott-Marrin	CC103699	GMIS	GC-TCD	18.041	17.94	-0.56
Specialty Air Technologies	ALM-036855	GMIS	NDIR	18.016	18.05	0.19
Specialty Gases of America	EB0018749	GMIS	GC-TCD	18.065	17.9	-0.92

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

Value of Reference is highlighted.

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

**Table 13b:** Vendor and NIST Certified Concentrations – EPA High Range – SO<sub>2</sub>

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST NDIR (ppm)	Vendor (ppm)	%Diff. <sup>a</sup>
Air Liquide (CO)	ALM050334	NTRM	FTIR	<b>1003.6</b>	1000	-0.36
Air Liquide (MI)	ALM036816	NTRM	FTIR	998.0	998	0.00
Air Liquide (TX)	CC233409	NTRM	FTIR	998.7	998	-0.08
Airgas (IL)	CC276179	NTRM	FTIR	989.2	987.7	-0.16
Airgas (NC)	CC201169	NTRM	FTIR	952.5	950.6	-0.20
Airgas (NJ)	SG9112847	NTRM	FTIR	1002.8	1005	0.22
Linde	CC-114071	NTRM	FTIR	996.4	996	-0.04
Liquid Technology	CC-231468	GMIS	FTIR	1004.1	975	<b>-2.90</b>
Matheson	SX-45104	SRM	FTIR	981.9	947	<b>-3.56</b>
Praxair (CA)	CC157996	GMIS	NDIR	1026.8	1026	-0.08
Praxair (PA)	CC239282	GMIS	NDIR	993.8	990.1	-0.38
Red Ball	EB0018491	SRM	NDIR	1005.0	1008	0.30
Scott-Marrin	CC103699	GMIS	UV Photometry	999.5	999	-0.05
Specialty Air Technologies	ALM-036855	GMIS	Pulsed Fluor.	1026.0	1018	-0.78
Specialty Gases of America	EB0018749	GMIS	NDUV	994.3	996	0.17

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

Value of Reference is highlighted.

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

**Table 13c:** Vendor and NIST Certified Concentrations – EPA High Range – NO

Vendor	Cyl#	Vendor Standard	Vendor Technique	NIST NDIR (ppm)	Vendor (ppm)	%Diff. <sup>a</sup>
Air Liquide (CO)	ALM050334	NTRM	FTIR	<b>906.8</b>	904	-0.31
Air Liquide (MI)	ALM036816	NTRM	FTIR	914.8	917	0.24
Air Liquide (TX)	CC233409	NTRM	FTIR	909.7	913	0.36
Airgas (IL)	CC276179	NTRM	FTIR	884.7	888.0	0.37
Airgas (NC)	CC201169	NTRM	FTIR	907.6	927.8	<b>2.22</b>
Airgas (NJ)	SG9112847	NTRM	FTIR	916.3	934.6	1.99
Linde	CC-114071	GMIS	FTIR	905.9	907	0.13
Liquid Technology	CC-231468	GMIS	FTIR	890.3	913	<b>2.55</b>
Matheson	SX-45104	SRM	FTIR	875.8	901	<b>2.88</b>
Praxair (CA)	CC157996	GMIS	Chemi	889.3	884	-0.60
Praxair (PA)	CC239282	GMIS	Chemi	915.9	896.4	-2.13
Red Ball	EB0018491	PRM	NDIR	890.9	881	-1.11
Scott-Marrin	CC103699	GMIS	Chemi	899.5	885	-1.61
Specialty Air Technologies	ALM-036855	GMIS	NDIR	894.8	885.7	-1.01
Specialty Gases of America	EB0018749	GMIS	Chemi	901.8	892	-1.09

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

Value of Reference is highlighted.

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

**Table 14a:** Vendor and NIST Certified Concentrations – EPA Mid-Range – CO<sub>2</sub>

Vendor	Cylinder#	Vendor Standard	Vendor Technique	NIST NDIR, CO <sub>2</sub> (%)	Vendor CO <sub>2</sub> (%)	%Diff. <sup>a</sup>
Air Liquide (CO)	ALM053737	NTRM	FTIR	11.969	12.0	0.26
Air Liquide (MI)	ALM057383	NTRM	FTIR	12.025	12.0	-0.21
Air Liquide (TX)	CC109172	NTRM	FTIR	11.910	11.9	-0.08
Airgas (IL)	CC87345	NTRM	FTIR	12.030	12.35	<b>2.66</b>
Airgas (NC)	CC47476	NTRM	FTIR	11.846	11.79	-0.47
Airgas (NJ)	SG9149394	NTRM	FTIR	12.042	11.95	-0.76
Linde	CC-143271	GMIS	NDIR	<b>12.045</b>	12.07	0.21
Liquid Technology	EB-0019812	GMIS	GC/TCD	11.983	12.1	0.97
Matheson	SX-48952	SRM	FTIR	12.063	12.0	-0.53
Praxair (CA)	SA20483	GMIS	NDIR	12.271	12.31	0.31
Praxair (PA)	SA21915	GMIS	NDIR	12.014	12.08	0.55
Red Ball	EB0006725	GMIS	NDIR	12.047	12.1	0.44
Scott-Marrin	CC94437	GMIS	GC/TCD	12.033	12.00	-0.27
Specialty Air Technologies	SA12310	GMIS	NDIR	12.003	11.93	-0.61
Specialty Gases of America	EB0018605	GMIS	GC/TCD	12.045	12.0	-0.38

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

Value of Reference is highlighted.

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



**Table 14b:** Vendor and NIST Certified Concentrations – EPA Mid-Range – SO<sub>2</sub>

Vendor	Cylinder#	Vendor Standard	Vendor Technique	NIST NDIR, SO <sub>2</sub> (ppm)	Vendor (ppm)	%Diff. <sup>a</sup>
Air Liquide (CO)	ALM053737	NTRM	FTIR	501.4	499	-0.47
Air Liquide (MI)	ALM057383	NTRM	FTIR	501.8	501	-0.15
Air Liquide (TX)	CC109172	NTRM	FTIR	485.6	486	0.09
Airgas (IL)	CC87345	NTRM	FTIR	525.7	525.3	-0.08
Airgas (NC)	CC47476	NTRM	FTIR	504.3	503.9	-0.08
Airgas (NJ)	SG9149394	NTRM	FTIR	507.1	507.6	0.09
Linde	CC-143271	NTRM	FTIR	<b>501.4</b>	501	-0.08
Liquid Technology	EB-0019812	GMIS	FTIR	497.4	485	<b>-2.50</b>
Matheson	SX-48952	SRM	FTIR	505.0	501	-0.78
Praxair (CA)	SA20483	GMIS	NDIR	503.4	501	-0.49
Praxair (PA)	SA21915	GMIS	NDIR	505.1	503.6	-0.30
Red Ball	EB0006725	GMIS	NDIR	493.4	495	0.33
Scott-Marrin	CC94437	GMIS	UV Photo	499.6	500	0.08
Specialty Air Technologies	SA12310	GMIS	Pulsed Fluor	524.3	519.7	-0.88
Specialty Gases of America	EB0018605	GMIS	NDUV	500.3	498	-0.45

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

Value of Reference is highlighted.

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

**Table 14c:** Vendor and NIST Certified Concentrations – EPA Mid-Range – NO

Vendor	Cylinder#	Vendor Standard	Vendor Technique	NIST NDIR, NO (ppm)	Vendor NO (ppm)	%Diff. <sup>a</sup>
Air Liquide (CO)	ALM053737	NTRM	FTIR	419.5	418	-0.35
Air Liquide (MI)	ALM057383	NTRM	FTIR	402.4	402	-0.09
Air Liquide (TX)	CC109172	NTRM	FTIR	399.8	403	0.81
Airgas (IL)	CC87345	NTRM	FTIR	399.4	398.1	-0.34
Airgas (NC)	CC47476	NTRM	FTIR	408.3	413.0	1.16
Airgas (NJ)	SG9149394	NTRM	FTIR	407.9	407.4	-0.12
Linde	CC-143271	GMIS	FTIR	<b>397.7</b>	399	0.34
Liquid Technology	EB-0019812	GMIS	FTIR	396.0	406	<b>2.53</b>
Matheson	SX-48952	SRM	FTIR	401.0	401	0.01
Praxair (CA)	SA20483	GMIS	Chemi	405.8	402	-0.93
Praxair (PA)	SA21915	GMIS	Chemi	405.0	399	-1.49
Red Ball	EB0006725	GMIS	NDIR	395.4	395	-0.09
Scott-Marrin	CC94437	GMIS	Chemi	400.7	397	-0.92
Specialty Air Technologies	SA12310	GMIS	NDIR	416.2	415.3	-0.22
Specialty Gases of America	EB0018605	GMIS	Chemi	398.0	395	-0.75

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

Value of Reference is highlighted.

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

**Table 15a:** Vendor and NIST Certified Concentrations – EPA Low Range – CO<sub>2</sub>

Vendor	Cylinder#	Vendor Standard	Vendor Technique	NIST NDIR, CO <sub>2</sub> (%)	Vendor CO <sub>2</sub> (%)	%Diff. <sup>a</sup>
Air Liquide (CO)	ALM050278	NTRM	FTIR	5.043	5.05	0.14
Air Liquide (MI)	AAL12922	NTRM	FTIR	5.008	5.04	0.63
Air Liquide (TX)	CC81064	NTRM	FTIR	4.959	4.96	0.01
Airgas (IL)	CC33482	NTRM	FTIR	5.007	4.966	-0.82
Airgas (NC)	CC323784	NTRM	FTIR	5.004	4.985	-0.37
Airgas (NJ)	CC5459	NTRM	FTIR	5.019	5.002	-0.33
Linde	CC-241882	GMIS	NDIR	5.013	5.04	0.54
Liquid Technology Corp.	CC-251845	GMIS	GC/TCD	4.989	5.15	<b>3.24</b>
Matheson	SX-16262	SRM	FTIR	5.023	5.00	-0.45
Praxair (CA)	SA13440	GMIS	NDIR	5.103	5.11	0.15
Praxair (PA)	CC187418	GMIS	NDIR	5.052	5.08	0.56
Red Ball	EB0004947	GMIS	NDIR	5.016	4.99	-0.52
Scott-Marrin	CC37789	GMIS	GC/TCD	5.017	5.01	-0.13
Specialty Air Technologies	CC86708	GMIS	NDIR	5.005	4.995	-0.19
Specialty Gases of America	EB0018729	GMIS	GC/TCD	5.028	5.04	0.24

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

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

**Table 15b:** Vendor and NIST Certified Concentrations – EPA Low Range – SO<sub>2</sub>

Vendor	Cylinder#	Vendor Standard	Vendor Technique	NIST NDUV and NDIR, SO <sub>2</sub> (ppm)	Vendor SO <sub>2</sub> (ppm)	%Diff. <sup>a</sup>
Air Liquide (CO)	ALM050278	NTRM	FTIR	50.60	50.9	0.60
Air Liquide (MI)	AAL12922	NTRM	FTIR	49.58	49.8	0.44
Air Liquide (TX)	CC81064	NTRM	FTIR	48.71	48.3	-0.84
Airgas (IL)	CC33482	NTRM	FTIR	48.97	49.90	1.90
Airgas (NC)	CC323784	NTRM	FTIR	50.82	50.71	-0.22
Airgas (NJ)	CC5459	NTRM	FTIR	50.09	50.91	1.64
Linde (NJ)	CC-241882	NTRM	NDIR	49.62	50.3	1.38
Liquid Technology Corp.	CC-251845	GMIS	FTIR	48.99	48.0	-2.03
Matheson (OH)	SX-16262	SRM	FTIR	51.82	49.2	<b>-5.05</b>
Praxair (CA)	SA13440	GMIS	UV	51.67	51.5	-0.34
Praxair (PA)	CC187418	GMIS	NDIR	50.03	49.1	-1.86
Red Ball	EB0004947	GMIS	NDIR	48.56	48.5	-0.12
Scott-Marrin	CC37789	GMIS	UV Photo	50.41	50.3	-0.21
Specialty Air Technologies	CC86708	GMIS	Pulsed Fluor	56.92	56.59	-0.59
Specialty Gases of America	EB0018729	GMIS	NDUV	49.44	49.1	-0.69

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

<sup>b</sup> NIST SO<sub>2</sub> concentration calculated as an average of NDUV (against Low Reference) and NDIR (against Low Reference) analyses. See Table 18c for comparison of these two analyses.

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

**Table 15c:** Vendor and NIST Certified Concentrations – EPA Low Range – NO

Vendor	Cylinder#	Vendor Standard	Vendor Technique	NIST Chemi and NDUV, NO (ppm) <sup>b</sup>	Vendor (ppm)	%Diff. <sup>a</sup>
Air Liquide (CO)	ALM050278	NTRM	FTIR	50.43	50.1	-0.65
Air Liquide (MI)	AAL12922	NTRM	FTIR	48.94	50.2	<b>2.57</b>
Air Liquide (TX)	CC81064	NTRM	FTIR	49.80	49.9	0.21
Airgas (IL)	CC33482	NTRM	FTIR	52.19	51.49	-1.34
Airgas (NC)	CC323784	NTRM	FTIR	51.83	51.71	-0.23
Airgas (NJ)	CC5459	NTRM	FTIR	51.05	50.28	-1.51
Linde	CC-241882	GMIS	FTIR	50.63	50.4	-0.45
Liquid Technology Corp.	CC-251845	GMIS	FTIR	52.39	51.2	<b>-2.26</b>
Matheson	SX-16262	NTRM	FTIR	50.64	50.9	0.51
Praxair (CA)	SA13440	GMIS	Chemi	51.35	48.7	<b>-5.17</b>
Praxair (PA)	CC187418	GMIS	Chemi	50.21	49.9	-0.62
Red Ball	EB0004947	GMIS	NDIR	51.02	51.7	1.32
Scott-Marrin	CC37789	GMIS	Chemi	48.86	48.4	-0.93
Specialty Air Technologies	CC86708	GMIS	NDIR	49.84	50.26	0.85
Specialty Gases of America	EB0018729	GMIS	Chemi	50.57	51.0	0.85

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

<sup>b</sup> NIST NO concentration calculated as an average of chemi (against NO-CHEMI-LO curve using CO<sub>2</sub> correction factor, Equation 3) and NDUV (against Low Reference) analyses. See Table 18d for comparison of these two analyses.

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

**Table 16a:** Comparison of NIST Certified CO<sub>2</sub> Concentrations of 2008 audit WSs and Test cylinders of EPA High Range, with Uncertainty (k = 2)

Vendor / Sample ID	Cyl#	CO <sub>2</sub> against Curve, NDIR		CO <sub>2</sub> against Reference, NDIR		%Diff.
		Conc. (%)	± (%)	Conc. (%)	± (%)	
WS-EPA8-H1	CA08268	18.033	0.054	18.028	0.076	0.03
WS-EPA8-H2	SA10582	18.196	0.054	18.185	0.080	0.06
Airgas (IL)	CC40347	18.062	0.054	18.062	0.077	0.00
Matheson	SX45104	18.066	0.054	18.070	0.077	-0.02
Praxair	CC157996	17.723	0.053	17.725	0.075	-0.01
Spec. Gas of Amer.	EB0020538	18.084	0.054	18.083	0.077	0.01

**Table 16b:** Comparison of NIST Certified SO<sub>2</sub> Concentrations of 2008 audit WSs and Test cylinders of EPA High Range, with Uncertainty (k = 2)

Vendor / Sample ID	Cyl#	SO <sub>2</sub> against Curve, NDUV and / or NDIR <sup>a</sup>		SO <sub>2</sub> against Reference, NDIR		%Diff.
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	
WS-EPA8-H1	CA08268	998.4	4.2	999.8	6.6	-0.14
WS-EPA8-H2	SA10582	1000.1	4.2	1002.1	6.6	-0.20
Airgas (IL)	CC40347	988.8	4.2	988.0	6.5	0.07
Matheson	SX45104	981.5	4.1	981.9	6.5	-0.04
Praxair	CC157996	1028.9	4.3	1026.9	6.8	0.20
Spec. Gas of Amer.	EB0020538	949.4	4.0	951.4	6.3	-0.22

<sup>a</sup> Using EPA High SO<sub>2</sub> NDIR correction factor of 1.0025

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

Vendor / Sample ID	Cyl#	NO against Curve, Chemi <sup>a</sup> and / or NDIR <sup>b</sup>		NO against Reference, NDIR		%Diff.
		± (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	
WS-EPA8-H1	CA08268	893.2	4.7	893.9	6.1	-0.08
WS-EPA8-H2	SA10582	927.7	4.9	928.9	6.3	-0.13
Airgas (IL)	CC40347	876.3	4.6	875.7	6.0	0.08
Matheson	SX45104	877.7	4.6	875.8	6.0	0.21
Praxair	CC157996	890.4	4.7	889.3	6.0	0.12
Spec. Gas of Amer.	EB0020538	946.1	5.0	949.4	6.5	-0.35

<sup>a</sup> Using CO<sub>2</sub> correction factor (Equation 3)

<sup>b</sup> Using EPA High NO NDIR correction factor of 1.0162

**Table 17a:** Comparison of NIST Certified CO<sub>2</sub> Concentrations of 2008 audit WSs and Test cylinders of EPA Mid-Range, with Uncertainty ( $k = 2$ )

Vendor / Sample ID	Cyl#	CO <sub>2</sub> against Curve, NDIR		CO <sub>2</sub> against Reference, NDIR		%Diff.
		Conc. (%)	± (%)	Conc. (%)	± (%)	
WS-EPA8-M1	CC51188	12.181	0.037	12.183	0.061	-0.02
WS-EPA8-M2	CA08177	12.072	0.04	12.087	0.060	-0.12
Airgas (IL)	CC87345	12.020	0.036	12.030	0.060	-0.08
Airgas (IL)	SG9164934BAL	12.031	0.036	12.043	0.060	-0.10
Airgas (NC)	CC47476	11.833	0.035	11.846	0.059	-0.11
Spec. Gas of Amer.	EB0020755	12.003	0.036	12.005	0.060	-0.01

**Table 17b:** Comparison of NIST Certified SO<sub>2</sub> Concentrations of 2008 audit WSs and Test cylinders of EPA Mid-Range, with Uncertainty (k = 2)

Vendor	Cyl#	SO <sub>2</sub> against Curve, NDUV and / or NDIR <sup>a</sup>		SO <sub>2</sub> against Reference, NDIR		%Diff.
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	
WS-EPA8-M1	CC51188	515.5	2.8	516.6	3.5	-0.20
WS-EPA8-M2	CA08177	498.5	2.7	499.6	3.4	-0.22
Airgas (IL)	CC87345	524.8	2.8	525.7	3.6	-0.18
Airgas (IL)	SG9164934BAL	501.0	2.7	501.5	3.4	-0.10
Airgas (NC)	CC47476	503.6	2.7	504.3	3.4	-0.14
Spec. Gas of Amer.	EB0020755	446.5	2.4	447.0	3.0	-0.12

<sup>a</sup> Using EPA Mid SO<sub>2</sub> NDIR correction factor of 1.0002

**Table 17c:** Comparison of NIST Certified NO Concentrations of 2008 audit WSs and Test cylinders of EPA Mid-Range, with Uncertainty (k = 2)

Vendor	Cyl#	NO against Curve, Chemi <sup>a</sup> and NDIR <sup>b</sup>		NO against Reference, NDIR		%Diff.
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	
WS-EPA8-M1	CC51188	408.5	2.1	409.0	2.7	-0.13
WS-EPA8-M2	CA08177	399.3	2.1	399.8	2.6	-0.12
Airgas (IL)	CC87345	398.9	2.1	399.4	2.6	-0.14
Airgas (IL)	SG9164934BAL	392.2	2.1	392.5	2.6	-0.08
Airgas (NC)	CC47476	408.0	2.1	408.3	2.7	-0.06
Spec. Gas of Amer.	EB0020755	438.0	2.3	439.0	2.9	-0.23

<sup>a</sup> Using CO<sub>2</sub> correction factor (Equation 3)

<sup>b</sup> Using EPA Mid NO NDIR correction factor of 1.0022



**Table 18a:** Comparison of NIST Certified CO<sub>2</sub> Concentrations of 2008 audit WSs and Test cylinders of EPA Low Range, with Uncertainty (k = 2)

Vendor	Cyl#	CO <sub>2</sub> against Curve, NDIR		CO <sub>2</sub> against Reference, NDIR		%Diff.
		Conc. (%)	± (%)	Conc. (%)	± (%)	
WS-EPA8-L1	CA08181	5.119	0.015	5.108	0.021	0.21
WS-EPA8-L2	ALM054809	5.014	0.015	5.007	0.021	0.14
Air Liquide (TX)	CC81064	4.961	0.015	4.959	0.021	0.02
Airgas (NC)	CC323784	5.025	0.015	5.019	0.021	0.12
Liq. Tech.	CC251845	4.990	0.015	4.989	0.021	0.04
Scott-Marrin	CC37789	5.021	0.015	5.017	0.021	0.08
Spec. Air	CC86708	5.006	0.015	5.005	0.021	0.03

**Table 18b:** Comparison of NIST Certified SO<sub>2</sub> Concentrations of 2008 audit WSs and Test cylinders of EPA Low Range, with Uncertainty (k = 2)

Vendor	Cyl#	SO <sub>2</sub> against Curve, NDUV and NDIR <sup>a</sup>		SO <sub>2</sub> against Reference, NDUV and NDIR		%Diff.
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	
WS-EPA8-L1	CA08181	51.14	0.31	51.22	0.43	-0.15
WS-EPA8-L2	ALM054809	51.51	0.31	51.45	0.43	0.11
Air Liquide (TX)	CC81064	48.70	0.30	48.71	0.40	-0.02
Airgas (NC)	CC323784	50.76	0.31	50.83	0.42	-0.12
Liq. Tech.	CC251845	48.99	0.30	49.00	0.41	-0.02
Scott-Marrin	CC37789	50.52	0.31	50.41	0.42	0.22
Spec. Air	CC86708	56.99	0.35	56.93	0.47	0.11

<sup>a</sup> Using EPA Low SO<sub>2</sub> NDIR correction factor of 0.9884

**Table 18c:** Comparison of NDIR and NDUV Analysis of SO<sub>2</sub> (against Reference) at Low Range, with uncertainty (k=2)

Vendor	Cyl#	SO <sub>2</sub> against Reference, NDIR		SO <sub>2</sub> against Reference, NDUV		NIST Certified SO <sub>2</sub>		
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	%Diff.	Mean (ppm)	± (ppm)
Air Liquide (CO)	ALM050278	50.56	0.43	50.63	0.41	-0.14	50.60	0.42
Air Liquide (MI)	AAL12922	49.61	0.43	49.56	0.40	0.10	49.58	0.41
Air Liquide (TX)	CC81064	48.66	0.42	48.76	0.39	-0.20	48.71	0.40
Airgas (IL)	CC33482	48.97	0.42	48.97	0.39	0.00	48.97	0.41
Airgas (IL)	XC024418B	50.01	0.43	50.06	0.40	-0.10	50.03	0.42
Airgas (NC)	CC323784	50.84	0.44	50.80	0.41	0.08	50.82	0.42
Airgas (NJ)	CC5459	50.11	0.43	50.07	0.40	0.07	50.09	0.42
Linde	CC-241882	49.55	0.43	49.68	0.40	-0.26	49.62	0.41
Liquid Technology Corp.	CC-251845	49.07	0.42	48.92	0.39	0.31	48.99	0.41
Matheson	CC-176947	51.36	0.44	51.38	0.41	-0.04	51.37	0.43
Matheson	SX-16262	51.85	0.45	51.79	0.41	0.11	51.82	0.43
Praxair (CA)	SA13440	51.69	0.44	51.66	0.41	0.06	51.67	0.43
Praxair (PA)	CC187418	50.01	0.43	50.05	0.40	-0.09	50.03	0.42
Red Ball	EB0004947	48.59	0.42	48.53	0.39	0.13	48.56	0.40
Scott-Marrin	CC37789	50.35	0.43	50.46	0.40	-0.22	50.41	0.42
Specialty Air Technologies	CC86708	56.98	0.49	56.88	0.46	0.17	56.92	0.47
Specialty Gases of America	EB0018729	49.54	0.43	49.34	0.39	0.40	49.44	0.41
Specialty Gases of America	EB0020540	50.40	0.43	50.34	0.40	0.12	50.37	0.42

**Table 18d:** Comparison of NIST Certified NO Concentrations of 2008 audit WSs and Test cylinders of EPA Low Range, with Uncertainty ( $k = 2$ )

Vendor	Cyl#	NO <sup>a</sup> against Curve, Chemi		NO against Reference, NDUV		%Diff.
		Conc. (ppm)	± (ppm)	Conc. (ppm)	± (ppm)	
WS-EPA8-L1	CA08181	50.79	0.34	50.80	0.44	-0.03
WS-EPA8-L2	ALM054809	51.35	0.34	51.28	0.44	0.14
Air Liquide (TX)	CC81064	49.82	0.33	49.77	0.43	0.10
Airgas (NC)	CC323784	51.80	0.34	51.86	0.45	-0.12
Liq. Tech.	CC251845	52.33	0.35	52.45	0.45	-0.23
Scott-Marrin	CC37789	48.95	0.32	48.77	0.42	0.36
Spec. Air	CC86708	49.87	0.33	49.80	0.43	0.14
Air Liquide (CO)	ALM050278	50.37	0.33	50.48	0.43	-0.21
Air Liquide (MI)	AAL12922	48.95	0.32	48.93	0.42	0.04
Airgas (IL)	CC33482	52.17	0.34	52.21	0.45	-0.09
Airgas (IL)	XC024418B	51.11	0.34	51.10	0.44	0.02
Airgas (NJ)	CC5459	51.10	0.34	51.00	0.44	0.20
Linde	CC-241882	50.58	0.33	50.67	0.44	-0.18
Matheson	CC-176947	51.03	0.34	51.05	0.44	-0.03
Matheson	SX-16262	50.64	0.33	50.64	0.44	0.01
Praxair (CA)	SA13440	51.39	0.34	51.31	0.44	0.16
Praxair (PA)	CC187418	50.23	0.33	50.19	0.43	0.07
Red Ball	EB0004947	50.99	0.34	51.06	0.44	-0.13
Spec. Gases of America	EB0018729	50.59	0.33	50.56	0.43	0.06
Spec. Gases of America	EB0020540	50.06	0.33	50.06	0.43	0.00

<sup>a</sup> Using CO<sub>2</sub> correction factor (Equation 3)

**Table 19a:** Comparison to Working Standards from 2008 Audit for CO<sub>2</sub>, with uncertainty (k=2)

Sample ID	Certification in 2008		Current Analysis Vrs Reference		
	CO <sub>2</sub> Conc. (%)	± (%)	CO <sub>2</sub> Conc. (%)	± (%)	%Diff.
WS-EPA8-L1	5.111	0.022	5.108	0.021	0.06
WS-EPA8-L2	5.011	0.015	5.007	0.021	0.08
WS-EPA8-M1	12.186	0.038	12.183	0.061	0.02
WS-EPA8-M2	12.073	0.050	12.087	0.060	-0.12
WS-EPA8-H1	18.038	0.076	18.028	0.076	0.06
WS-EPA8-H2	18.208	0.054	18.185	0.080	0.13

**Table 19b:** Comparison to Working Standards from 2008 Audit for SO<sub>2</sub>, with uncertainty (k=2)

Sample ID	Certification in 2008		Current Analysis Vrs Reference		
	SO <sub>2</sub> Conc. (ppm)	± (ppm)	SO <sub>2</sub> Conc. (ppm)	± (ppm)	%Diff.
WS-EPA8-L1	51.35	0.28	51.22	0.43	0.25
WS-EPA8-L2	51.61	0.20	51.45	0.43	0.31
WS-EPA8-M1	515.1	2.4	516.6	3.5	-0.29
WS-EPA8-M2	497.2	3.0	499.6	3.4	-0.49
WS-EPA8-H1	998.0	6.0	999.8	6.6	-0.18
WS-EPA8-H2	1003.5	4.6	1002.1	6.6	0.14

**Table 19c:** Comparison to Working Standards from 2008 Audit for NO, with uncertainty (k=2)

Sample ID	Certification in 2008		Current Analysis Vrs Reference		
	NO Conc. (ppm)	± (ppm)	NO Conc. (ppm)	± (ppm)	%Diff.
WS-EPA8-L1	50.85	0.34	50.80	0.44	0.10
WS-EPA8-L2	51.45	0.26	51.28	0.44	0.34
WS-EPA8-M1	408.4	2.2	409.0	2.7	-0.15
WS-EPA8-M2	399.5	2.8	399.8	2.6	-0.07
WS-EPA8-H1	895.8	6.0	893.9	6.1	0.22
WS-EPA8-H2	929.8	5.0	928.9	6.3	0.10

**Table 20a:** 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 <sub>2</sub>	High	NDIR	0.15	0.00	0.00	0.15
SO <sub>2</sub>	High	NDIR	0.20	0.05	0.16	0.26
SO <sub>2</sub>	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 <sub>2</sub>	Mid	NDIR	0.15	0.00	0.00	0.15
SO <sub>2</sub>	Mid	NDIR	0.20	0.10	0.16	0.27
SO <sub>2</sub>	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 <sub>2</sub>	Low	NDIR	0.15	0.00	0.00	0.15
SO <sub>2</sub>	Low	NDUV	0.20	0.20	0.00	0.28
SO <sub>2</sub>	Low	NDIR	0.20	0.20	0.17	0.33
NO	Low	Chemi	0.20	0.20	0.17	0.33

**Table 20b:** Uncertainty of Audit Samples as a function of Component Analyzed and EPA Range (at k =1)

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

**Table 21a:** Vendor Reanalysis of samples that failed the “2 % Tag Rule” (SO<sub>2</sub> and NO)

Vendor	Cylinder #	Component	Vendor Concentrations			NIST		
			Original (ppm)	Re-Analysis (ppm)	%Diff. <sup>a</sup>	Conc. (ppm)	%Diff. to Original <sup>b</sup>	%Diff. to Re-Analysis <sup>c</sup>
Air Liquide (MI)	AAL12922	NO	50.2	48.63	<b>-3.13</b>	48.94	<b>2.57</b>	-0.63
Airgas (NC)	CC201169	NO	927.8	911.3	-1.78	907.6	<b>2.22</b>	0.41
Liquid Technology	CC-251845	NO	51.2	52.2	1.95	52.39	<b>-2.26</b>	-0.36
Liquid Technology	EB-0019812	SO <sub>2</sub>	485	494	1.86	497.4	<b>-2.50</b>	-0.69
Liquid Technology	EB-0019812	NO	406	396	<b>-2.46</b>	396.0	<b>2.53</b>	0.00
Liquid Technology	CC-231468	SO <sub>2</sub>	975	1002	<b>2.77</b>	1004.1	<b>-2.90</b>	-0.21
Liquid Technology	CC-231468	NO	913	890	<b>-2.52</b>	890.3	<b>2.55</b>	-0.03
Matheson	SX-16262	SO <sub>2</sub>	49.2	52.0	<b>5.69</b>	51.82	<b>-5.05</b>	0.35
Matheson	SX-45104	SO <sub>2</sub>	947	971	<b>2.53</b>	981.9	<b>-3.56</b>	-1.11
Matheson	SX-45104	NO	901	880.6	<b>-2.26</b>	875.8	<b>2.88</b>	0.55
Praxair (CA)	SA13440	NO	48.7	51.3	<b>5.34</b>	51.35	<b>-5.17</b>	-0.10

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

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

<sup>c</sup> % 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



**Table 21b:** Vendor Reanalysis of samples that failed the “2 % Tag Rule” (CO<sub>2</sub>)

Vendor	Cylinder #	Component	Vendor Concentrations			NIST		
			Original (%)	Re-Analysis (%)	%Diff. <sup>a</sup>	Conc. (%)	%Diff. to Original <sup>b</sup>	%Diff. to Re-Analysis <sup>c</sup>
Airgas (IL)	CC87345	CO <sub>2</sub>	12.35	12.11	-1.94	12.030	<b>2.66</b>	0.67
Liquid Technology	CC-251845	CO <sub>2</sub>	5.15	4.96	<b>-3.69</b>	4.989	<b>3.24</b>	-0.58

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

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

<sup>c</sup> % 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

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