ANALYSIS OF PROTOCOL GASES

An On-Going Quality Assurance Audit
(Results Through Nov. 1995)

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1.0 INTRODUCTION

The National Exposure Research Laboratory (NERL) of the U.S. Environmental Protection Agency (EPA) operates a nationwide audit on the vendors of Protocol Gas Standards. The intent of this program is as follows:

1. Increase the acceptance and use of Protocol Gases as secondary standards by the air monitoring community.
2. Provide a quality assurance check for the vendors of these gases.
3. Assist users of Protocol Gases to identify vendors who can consistently provide accurately certified Protocol Gases.

For the first audits of nitric oxide, carbon monoxide, and sulfur dioxide, gas cylinders obtained through third parties were analyzed in triplicate by EPA and by a non-EPA laboratory. Each laboratory used its own SRMs and followed the Protocol Gas certification procedure. Because a statistical analysis showed that the results from EPA and the independent laboratory were indistinguishable, EPA is now the primary auditing laboratory. The other laboratory serves as the referee laboratory to resolve differences between EPA and the vendors.

2.0 PROCEDURE

Either directly or through third parties, EPA procures Protocol Gases from commercial sources, checks the accuracy of the vendors' certification of concentration, and examines the accompanying documentation for completeness and accuracy. The vendors are not aware that EPA is obtaining the gases for a check on the completeness of the documentation and accuracy of the certification of concentration.

Protocol Gases have a maximum allowable deviation of 2% from the certified value. Accuracy of the certification is checked using Standard Reference Materials (SRMs). If the difference between the EPA-determined and the vendor-determined concentration is more than 2%, or if the documentation is incomplete, EPA notifies the vendor immediately to resolve and correct the problem.

Results of EPA certification checks are placed on two bulletin boards, EMTIC (Emission Measurement Technology Information Center) and AMTIC (Ambient Monitoring Technology Information Center), of the Technology Transfer Network of the EPA Office of Air Quality Planning and Standards.

Bulletin board entries are organized in tables by gas mixture type and by vendor. Numerical data are supplemented by narrative footnotes explaining the results of any corrective action taken by the vendor. Thus the entries provide a continuous record of all audit activities.

Users who believe that their Protocol Gas has been certified incorrectly are encouraged to contact Ms. Avis Hines of NERL (919-541-4001) to request an EPA certification check. If EPA accepts the gas cylinder for testing, the results of these tests will also be posted on the bulletin boards.

3.0 REQUIRED DOCUMENTATION

The Protocol Gas procedure specifies two types of documentation that must accompany the gas cylinder: a Certificate of Analysis, which may be mailed separately or attached to the cylinder; and a cylinder tag which must be attached to the valve under the valve cap. Documentation is incomplete until the vendor provides every item shown in Tables A and B for the certificate and the tag, respectively. These tables reflect the requirements specified in the revised Protocol Gas guidance issued by this Laboratory in September 1993 (U.S. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards (Revised September 1993), EPA 600/R03/224).

Table A. REQUIRED DOCUMENTATION FOR A CERTIFICATE OF ANALYSIS

Cylinder ID number	Reference standard data
Certified concentration of analyte	Protocol statement
Balance gas	Analytical method used in assay
Cylinder pressure	All analyzer readings
Certificate date	Calculations to three significant figures
Expiration date	Name and signature of analyst and laboratory name
Certification period (months)	

TABLE B. REQUIRED DOCUMENTATION FOR A CYLINDER TAG

Cylinder ID number	Certification date
Expiration date	Protocol statement
Laboratory ID	Balance gas
Cylinder pressure	Analyte Concentration

4.0 RESULTS

This section of the audit report, organized by gas mixture type and by vendor, is updated whenever EPA conducts a new audit or receives corrective action reports from a vendor. It allows users of Protocol Gases to easily review the comparative performances of the vendors.

The standard of comparison used in reporting the certification of concentration check results is the relative percent difference between the vendor and the EPA values. Prior to this latest update only single component gases had been checked. With the inclusion of multi-component gases the reporting format used previously became unwieldy. Therefore, the tables were simplified to ensure they still provided information in a user-friendly form. This was accomplished by: (1) removing the vendor and the EPA concentration values from the tables and reporting the nominal value to the nearest 10 ppm; and (2) removing the cost information. (Since the prices of Protocol Gases are subject to change and differ markedly between vendors, users of these gases should obtain them through a competitive procurement procedure whenever possible.)

The tables summarize audit results for each gas mixture type and include footnotes which describe corrective actions taken by the vendors. In each table each vendor has been assigned an acronym and a footnote letter. If a vendor has more than one plant, each plant is assigned its own acronym and footnote. Notes may not be necessary for every vendor on every audit. The following acronyms have been assigned to each vendor:

ACRONYM	VENDOR
AGA-OH	AGA Gas, Inc. Maumee, OH
AL-CA	Air Liquide Long Beach, CA
APC-NC	Air Prod. and Chem Durham, NC
APC-IL	Air Prod. and Chem Chicago, IL
AIG-MI	Airco Industrial Gases Royal Oak, MI
AIG-NC	Airco Industrial Gases Research Triangle Park, NC
AIG-NJ	Airco Industrial Gases Riverton, NJ
ASG-PA	Alphagaz Spec. Gas Div. Morrisville, PA
ASG-CA	Alphagaz Spec. Gas Div.

	Long Beach, CA
MGP-OH	Matheson Gas Products Twinsburg, OH
LCC-PA	Liquid Carbonic Cylinder Gas Products Bethlehem, PA
MGP-NJ	Matheson Gas Products East Rutherford, NJ
MGI-PA	MG Industries Gas Products Valley Forge, PA
MGI-PA	MG Industries Gas Products Morrisville, PA
NSG-NC	National Specialty Gases Durham, NC
SMG-CA	Scott Marrin Gases Riverside, CA
SSG-NC	Scott Specialty Gases Durham, NC
SSG-NJ	Scott Specialty Gases Plainville, NJ
SSG-PA	Scott Specialty Gases Plumsteadville, PA

When using the data in the following tables for procuring Protocol Gases readers should bear in mind the following points. First, the information in the footnotes may be important and should not be ignored. Second, if the difference between EPA's value and a manufacturer's value differs by 2% or less, then (because of the uncertainties in the total measurement system) statistically there is no difference between the two values. Thus, a difference of 2.0% is the same as one of 0.57%. Third, EPA has not assigned a rating to the vendors concerning who is the best, who is approved, who is not approved, etc. The information is presented without making such judgments.

TABLE I. NO Protocol Gas Results

Vendor	NO	Nominal ppm	Date Certified	Date Checked	% Difference (Vendor-EPA)	Complete Doc.	Notes
APC-NC	40		4-92	7-92	2.0	Yes	
AIG-MI	40		5-92	7-92	-0.5	No	a
ASG-PA	40		4-92	7-92	-0.7	No	b
MGP-NJ	40		4-92	7-92	0.7	No	c
MGI-PA	40		4-92	7-92	0.2	No	d
NSG-NC	40		4-92	7-92	-1.7	Yes	
SMG-CA	40		4-92	7-92	0.0	Yes	
SSG-NC	40		4-92	7-92	-0.7	No	e

a. Documentation problems corrected.
b. Documentation problems corrected.
c. Documentation problems corrected.
d. Documentation problems corrected.
e. Documentation problems corrected.

TABLE II. SO_2 Protocol Gas Results

Vendor	Nominal ppm SO_2	Date Certified	Date Checked	% Difference (Vendor-EPA)	Complete Doc.	Notes
APC-NC	50	9-92	12-92	-3.8	No	a
APC-NC	10	5-95	9-95	-4.6	Yes	k
AIG-NJ	50	9-92	12-92	-0.7	No	b
AIG-NC	50	6-93	7-93	1.3	Yes	
AGA-OH	20	7-92	7-93	0.8	Yes	
AGA-OH	50	2-95	9-95	-16.3	No	j
ASG-PA	50	8-92	12-92	1.1	No	c
MGP-OH	50	9-92	12-92	-3.9	No	d
MGP-NJ	50	5-93	5-93	3.1	Yes	i
MGI-PA	50	12-92	2-93	-5.5	No	e
MGI-PA	99	8-94	2-95	-0.8	Yes	
NSG-NC	50	8-92	12-92	-3.6	Yes	f
SMG-CA	50	8-92	12-92	-0.2	No	g
SMG-CA	100	10-92	9-93	1.1	Yes	
SSG-NC	50	7-92	12-92	0.6	Yes	
SSG-NJ	50	7-93	5-94	0.4	No	h

a. Vendor replaced calibration standard and reported (3/93) new value of 5
b. Prior to receiving EPA results, vendor notified all recent purchasers t
c. Documentation problems corrected.
d. Vendor replaced calibration standard and reported (2/93) new value of 5
e. Vendor found error on part of analyst (3/93). Analyst given additional training. Documentation problems corrected.
f. Vendor replaced calibration standard. No re-analysis done. D
g. Documentation problems corrected.
h. Documentation problems corrected.
i. Vendor replaced pulsed fluorescence detector with a NDIR detector and reported a new value of 52.6 ppm (1.3% difference).
j. Vendor has not responded to notification of protocol results.
k. Mixture was recertified and returned to customer. No corrected value o

TABLE III. CO Protocol Gas Results

Vendor	Nominal ppm CO	Date Certified	Date Checked	% Difference (Vendor-EPA)	Complete Doc.	Notes
APC-NC	40	1-93	4-93	0.3	No	a
AIG-NJ	40	1-93	4-93	-0.3	No	
APC-IL	9	12-94	2-95	-0.8	Yes	
ASG-PA	40	1-93	4-93	-0.7	Yes	
MGP-OH	40	1-93	4-93	0.3	No	b
MGP-NJ	40	5-93	6-93	-0.6	Yes	
MGI-PA	40	1-93	4-93	-1.2	No	c
NSG-NC	40	12-92	4-93	1.0	No	d
SMG-CA	40	1-93	4-93	-0.5	Yes	
SSG-NC	40	1-93	4-93	0.0	Yes	

a. Certificate missing; sent when EPA requested but did not agree with cylinder tag; second certificate matched cylinder tag but calibration standard identified as having gone out of calibration in January 1992; sent third certificate with corrected calibration date.
b. Certificate sent only after EPA requested it.
c. Documentation problems corrected.
d. Certified only for six months rather than the 24 months allowed.

TABLE IV. Mixture NO/SO_2 Protocol Gas Results

Note: The first group of multi-blend Protocol Gases was checked November 1993 through May 1994. The results are listed in Table IV. Initially, the results for five of these mixtures were disappointing, but in four of these five cases incorrectly certified SRM's caused the inaccurate certifications. Once the vendors had obtained the correct certified value for their SRM's, their revised SO_2 concentrations differed by less than 1% from the EPA-determined value. All vendors supplied complete documentation.

	Nominal ppm		Date	Date	% Difference (Vendor-EPA)		Complete	
Vendor	NO	SO_2	Certified	Checked	NO	SO_2	Doc.	Notes
AGA-OH	400	300	11-93	12-93	1.5	-1.7	Yes	
	900	1500	11-93	12-93	2.0	0.7	Yes	
AIG-NJ	400	300	9-93	11-93	1.6	0.3	Yes	
	900	1500	9-93	11-93	0.5	2.4	Yes	a
ASG-CA	400	300	9-93	11-93	3.2	-2.7	Yes	
	900	1500	9-93	11-93	-0.6	1.4	Yes	b
LCC-PA	400	300	8-93	11-93	0.5	2.5	Yes	
	900	1500	8-93	11-93	-0.1	-0.5	Yes	c
MGP-OH	400	300	10-93	12-93	-1.7	1.7	Yes	
	900	1500	10-93	12-93	0.4	-1.4	Yes	
MGI-PA	400	300	9-93	11-93	0.5	-0.6	Yes	
	900	1500	10-93	11-93	0.7	-0.8	Yes	
NSG-NC	400	300	9-93	11-93	0.0	-4.3	Yes	
	900	1500	9-93	11-93	0.3	-1.9	Yes	d
SMG-CA	400	300	11-93	12-93	1.5	-1.4	Yes	
	900	1500	11-93	12-93	0.6	-0.7	Yes	
SSG-NC	400	300	9-93	11-93	-1.2	-3.2	Yes	
	900	1500	9-93	11-93	-0.1	-0.7	Yes	e

a. Manufacturer used corrected value for NIST SRM, and reported (1-94) a new value of 1468 ppm SO_2 (0.1% difference).
b. Manufacturer reported a new NO value (4-94) of 401 ppm NO (-2.4% difference), and no change for the SO_2 value.
c. Manufacturer used corrected value for NIST SRM, reanalyzed the gas and reported (2-94) a new value of 311.4 ppm SO_2 (-1.3% difference).
d. Manufacturer purchased new analyzer and reanalyzed cylinder, reported a new value (5-94) 302 ppm SO_2 (0.7% difference).
e. Manufacturer used corrected value for NIST SRM, reanalyzed the gas and reported (1-94) a new value of 302.9 ppm SO_2 (-1.7% difference).

TABLE V. Mixture NO/CO_2 Protocol Gas Results

Vendor	Nominal ppm NO	Nominal ppm CO_2	Date Certified	Date Checked	% Difference (Vendor-EPA) NO	% Difference (Vendor-EPA) CO_2	Complete Doc.	Notes
AIG-NJ	910	18%	7-93	5-94	-2.9	---	Yes	a
AIG-NJ	540	18%	8-93	5-94	-2.2	---	Yes	b
MGI-PA	880	18%	? ?	5-94	1.4	---	No	c
MGI-PA	900	18%	? ?	5-94	1.8	---	No	d

a. Client owned cylinder, has not been returned to vendor for recertification. CO_2 concentration well within 2%; exact value not determined.
b. Client owned cylinder, has not been returned to vendor for recertification. CO_2 concentration well within 2%; exact value not determined.
c. CO_2 concentration well within 2%; exact value not determined.
d. CO_2 concentration well within 2%; exact value not determined

TABLE VI. Mixture $NO/SO_2/CO_2$ Protocol Gas Results

Vendor	Nominal ppm NO	Nominal ppm SO_2	Nominal ppm CO_2	Date Cert.	Date Checked	% Difference (Vendor-EPA) NO	% Difference (Vendor-EPA) SO_2	% Difference (Vendor-EPA) CO_2	Comp. Doc.	Notes
APC-IL	550	500	18%	4-94	5-94	-0.9	-0.2	---	Yes	a
SSG-PA	570	530	18%	4-94	5-94	0.4	-0.2	---	Yes	b

a. CO_2 concentration well within 2%; exact value not determined.
b. CO_2 concentration well within 2%; exact value not determined.

Table VII. Mixture $NO/SO_2/CO_2$ Protocol Gas Results

Note: This second group of multi-blend Protocol Gases was checked April 1995 through June 1995. The results are listed in Table VII.

Vendor	Nominal Conc. $NO/SO_2/CO_2$ ppm ppm %	Date of Cert	Date Checked	% Difference (Vendor - EPA) NO	SO_2	CO_2	Comp. Doc	Notes
AGA-OH	400/300/18	4-95	6-95	-1.1	-1.1	-1.0	Yes	
	900/1300/12	4-95	6-95	-1.1	1.9	1.0	No	a
AL-CA	400/300/18	3-95	6-95	-0.8	0.0	0.5	Yes	
	900/1300/12	3-95	6-95	-0.4	-0.7	1.0	Yes	
APC-NC	400/300/18	3-95	6-95	-0.5	-2.0	1.0	Yes	
	900/1300/12	5-95	6-95	-0.5	-0.6	0.0	Yes	
AIG-NJ	400/300/18	2-95	6-95	0.0	-0.2	-0.2	Yes	
	900/1300/12	3-95		-1.5	-0.5	-2.0	Yes	
LCC-PA	400/300/18	6-95	6-95	-4.9	-0.8	0.9	No	
	900/1300/12	4-95	6-95	-4.5	-0.3	2.0	No	b
MGP-OH	400/300/18	2-95	6-95	0.8	-7.2	1.0	Yes	
	900/1300/12	3-95	6-95	0.8	-3.4	0.0	Yes	c
MGI-PA	400/300/18	2-95	6-95	-0.3	0.7	1.6	Yes	
	900/1300/12	3-95	6-95	-0.3	-0.6	0.0	Yes	
NSG-NC	400/300/18	3-95	6-95	-2.4	-1.6	-0.5	Yes	
	900/1300/12	3-95	6-95	-0.1	-0.9	2.0	Yes	d
SMG-CA	400/300/18	3-95	6-95	-1.3	0.5	0.0	No	
	900/1300/12	3-95	6-95	-0.7	1.6	-1.7	Yes	e
SSG-NC	400/300/18	2-95	6-95	-0.1	1.6	-0.2	Yes	
	900/1300/12	3-95	6-95	1.0	1.7	0.0	Yes	

a. Documentation problems corrected promptly.

b. Documentation problems corrected promptly. Manufacturer corrected analytical problems and reported new values (9-95) 388 ppm NO (-2.0% difference) and 883.0 ppm NO (-0.7% difference).

c. Manufacturer used FTIR technique, determined problem with SO_2 caused by masking effect of the SO_2 by CO_2. Analytical problems were corrected. Vendor reported new values (9-95) 235 ppm SO_2 (0.1% difference) and 1259 ppm SO_2 (-0.4% difference), respectively.

d. Manufacturer reported inadequate numbers for their GMIS standards used for certification. Vendor reanalyzed gas using SRMs and a dilution

system. Vendor reported a new value (9-95) 364 ppm NO (0.4% difference).

e. Documentation problems corrected promptly.