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Project Summary

Stability Evaluation of Sulfur Dioxide, Nitric Oxide and Carbon Monoxide Gases in Cylinders

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The purpose of this project was to assess the stability of certain reactive gases used to calibrate/audit air quality analyzers as a function of time. The objective of the assessment was to determine if EPA's present guidelines suggesting recertification every 6 months could be relaxed to some longer time period. The reactive gases were contained in aluminum and steel cylinders and include: carbon monoxide in air (CO/air); carbon monoxide in nitrogen (CO/N_2); nitric oxide in nitrogen (NO/N_2); and sulfur dioxide in nitrogen (SO_2/N_2). The assessment included stability data for a total of 316 compressed gas cylinders, 300 aluminum and 16 steel. The 300 aluminum cylinders consisted of: 37 CO/air; 86 CO/N_2; 103 NO/N_2; and 74 SO_2/N_2. Time intervals covered by the stability data ranged from 10 to 58 months, with the average time period being in excess of 12 months.

Stability of each pollutant category (e.g., CO/air) was assessed by linear regression analysis of the measured concentration versus time in months for each cylinder. The average percent change of the median concentration within each pollutant category was calculated for time periods of 6, 12, 18 and 24 months. The criterion for judging a pollutant category to be stable over a specific time period was an average change of ±1 percent or less over that time period.

Based on the results of the analysis it was recommended that a recertification period of 18 months be adopted for reactive gases in aluminum cylinders as follows: CO/air at concentrations between 5 and 45 ppm; CO/N_2 at concentrations between 5 and 5,000 ppm; NO/N_2 at concentrations between 10 and 150 ppm; and SO_2/N_2 at concentrations between 9 and 375 ppm. It was also recommended that the present suggested recertification period of 6 months be retained for all other reactive gas/cylinder type combinations.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A model used to estimate the optimum time interval for recertification of a pollutant concentration in a cylinder would ideally include the following terms:

- the indicated stability of that pollutant at a specified concentration and in a particular cylinder type as a function of time;
- the precision, and potential for bias, of the certification process;
- the costs associated with recertification; and
- the costs associated with generating environmental data of poor quality (when used as a calibration or audit standard) and the cost associated with rejecting good quality data as bad (when used as an audit standard).

Due to limited resources this assessment of an acceptable recertification time period was limited to consideration of the first two items listed above. The stability data contained in this report were evaluated to determine if the recertification period stated in Section 1.2.5 of EPA Protocol No. 2 could be extended beyond six months for carbon monoxide (CO), nitric oxide (NO), and sulfur dioxide (SO_2) gases contained in aluminum steel cylinders. Traceability Protocol No. 2 provides procedures for establishing the true concentration of reactive gases using National Bureau of Standards (NBS) gaseous Standard Reference Materials (SRMs) or EPA/NBS-approved commercial Certified Reference Materials (CRMs).

Data Collection

Reactive gas stability data were solicited from federal, state, and local agencies, SLAMS Ambient Air Audit Centers, and selected specialty gas manufacturers. Also included in these data are reactive gas cylinders analyzed by the EPA-EMSL/QAD standards laboratory. Data were requested on reactive gas cylinders that had been analyzed over a time period of twelve months or longer.

Stability data were received for 37 CO/air, 86 CO/N_2, 103 NO/N_2, and 74 SO_2/N_2 for a total of 300 compressed gases in aluminum cylinders. Also, information on 15 CO/air and 13 CO/N_2 in steel cylinders was received. The analysis period covered by the reported data ranged from 10 to 58 months.

Procedures

Each pollutant/balance gas category (CO/air, CO/N_2, NO/N_2, SO_2/N_2) was divided into concentration ranges and cylinder construction (aluminum or steel) for analysis. The concentration ranges were selected according to natural gaps in the concentration distribution of the stability data and to allow for assuming constant variances over these relatively small concentration intervals.

Stability of the reactive gases was assessed by calculating a linear regression equation of concentration versus time in months from the initial analysis for each cylinder. The slope of the resultant regression equation was in units of ppm change per month. When the slope was multiplied by a number of months, the product equaled a change in pollutant concentration (ppm) for that specific number of months. Also calculated for each pollutant category were the average slope, the standard deviation of the slopes, and, based upon the median concentration in each concentration interval, an average percent change for 6, 12, 18, and 24 months, and the standard deviation of the percent change for an 18 month period (Table 1). Within a specific pollutant category, the average percent change ($\bar{P}$) was used as a measure of stability. Two times the standard deviation of the percent change (s_p) represented the approximate 95 percent probability limits for the percent change of individual pollutant cylinders in the category. The pooled standard deviation for analysis results for a pollutant cylinder category was used to estimate the range of error that can be expected for the pollutant concentration, based on one analysis.

The following variables and formulas were used to calculate the stability of the reactive gases:

X = Median concentration of a concentration range or pollutant category, ppm.

$\bar{m}$ = Average slope for all cylinders in a concentration range ppm change/month.

s_m = Standard deviation of the slope calculated for each concentration range, ppm change/month.

T = Time since the original analysis, months.

$\bar{P} = 100(\bar{m})(T)/X$, average percent change for a median concentration over a specified time period, percent.

$s_p = 100(s_m)(T)/X$, standard deviation of percent change at the median concentration, over time period T, percent.

$\pm 2\ s_p$ = 95% probability limits for the percent change of a reactive gas concentration, percent.

s_y = standard deviation of the measured concentrations for a specific cylinder, ppm.

$s_{yp} = [((n_1-1)\ s_{y1}^2 + \cdots + (n_k-1)\ s_{yk}^2)/(n_1 + \cdots + n_k-k)]^{1/2}$, pooled standard deviation of the measured concentrations across cylinders within a pollutant cylinder category, ppm.

Results

Results of the analysis of stability data for thirty-seven aluminum cylinders containing carbon monoxide with a balance gas of air are presented here as an

Table 1. Summary of Reactive Gases Contained in Aluminum and Steel Cylinders[a]

Pollutant Category	Number of Standards	Concentration Range (ppm)	Median, X Concentration (ppm)	Slope, m (ppm/month)		Average Percent Change, $\bar{P}$				s_p (18 mo)
				$\bar{m}$	s_m	6 mo	12 mo	18 mo	24 mo	(%)
			Aluminum Cylinders							
CO/Air	10	5-11	7	-0.004	0.013	-0.3	-0.7	-1.0	-1.4	3.3
CO/Air	22	17-45	30	0.000	0.017	0.0	0.0	0.0	0.0	1.0
CO/N_2	16	5-15	10	+0.001	0.010	+0.0	+0.1	+0.2	+0.2	1.8
CO/N_2	17	19-46	30	+0.006	0.018	+0.1	+0.2	+0.4	+0.5	1.1
CO/N_2	16	100-1000	500	-0.112	0.268	-0.1	-0.3	-0.4	-0.5	1.0
CO/N_2	26	2500-5000	3750	+0.009	4.922	0.0	0.0	0.0	0.0	2.4
NO/N_2	7	10-22	16	-0.003	0.014	-0.1	-0.2	-0.3	-0.5	1.6
NO/N_2	25	43-55	49	-0.025	0.070	-0.3	-0.6	-0.9	-1.2	2.6
NO/N_2	71	80-113	97	-0.009	0.112	-0.1	-0.1	-0.2	-0.2	2.1
SO_2/N_2	10	9-22	15	-0.003	0.020	-0.1	-0.2	-0.4	-0.5	2.4
SO_2/N_2	21	45-56	51	+0.007	0.070	0.0	+0.2	+0.2	+0.3	2.5
SO_2/N_2	33	78-110	94	-0.039	0.115	-0.2	-0.5	-0.7	-1.0	2.2
SO_2/N_2	10	152-375	264	+0.061	0.103	+0.1	+0.3	+0.4	+0.6	0.7
			Steel Cylinders							
CO/Air	5	9-11	10	-0.028	0.020	-1.7	-3.4	-5.0	-6.7	3.6
CO/N_2	9	19-43	31	-0.032	0.029	-0.6	-1.2	-1.9	-2.5	1.7
CO/N_2	2	1000	1000	0.153	0.095	-0.1	-0.2	-0.3	-0.4	0.2

[a]See Procedures section for definition of terms.

example. The same type of information is contained in the subject report for the other reactive gased included in this study. This stability data (cylinder number, date of initial analysis, initial concentration, time in months (T) since the initial analysis, and the analyzed concentration in ppm are contained in Table 2. Also contained in this table are the linear regression coefficients: slope (m), intercept (b) calculated from the analyzed concentrations versus time in months since the initial analysis, the standard deviation (s_y) of the y axis values (measured CO concentrations), and summary statistics for each category. The CO/air data were divided into two concentration ranges, 5 to 11 and 17 to 45 ppm for analysis.

Concentration Range 5 to 11 ppm

For CO/air in aluminum cylinders, there were 10 cylinders with measured concentrations ranging from 5 to 11 ppm (see Table 2). The 10 calculated regression equation slopes included seven negative, two positive and one zero values. The average slope was $\bar{m} = -0.004$ ppm change/month and the standard deviation of the slopes about that average was $s_m = 0.013$ ppm change/month (see summary statistics in Table 3). A Student's t-test indicated that average slopes of 0.004 ppm change/month or larger could be expected to occur more than 20 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the mean slope was zero.

The approximate 95 percent probability interval for the uncertainty (excluding bias) of a CO/air concentration estimated by one analysis is $\pm 2\ s_{yp} = 0.48$ ppm or ± 10 percent at a concentration of 5 ppm.

Concentration Range 17 to 45 ppm

There were 22 cylinders with measured CO/air concentrations ranging from 17 to 45 ppm (see Table 2).

The calculated regression equation slopes include thirteen negative, eight positive and one zero values. The average slope was $\bar{m} = -0.000$ ppm change/month and the standard deviation of the slopes

Table 2. *Stability Data for CO/Air in Aluminum Cylinders*[a]

Analysis No.	*Initial Analysis*		*Subsequent Analysis*										*Regression Coefficients*		*Standard Deviation*
Cylinder No.	*Date*	*Conc. (ppm)*	*Time T (months)*	*Conc. (ppm)*	*Time T (months)*	*Conc. (ppm)*	*Time T (months)*	*Conc. (ppm)*	*Time T (months)*	*Conc. (ppm)*	*Time T (months)*	*Conc. (ppm)*	*m (ppm/mo)*	*b (ppm)*	*s_y (ppm)*
BAL695-8	05-13-80	5.1	10	5.6	18	5.4							+0.018	5.20	0.25
BAL1180-9	01-24-80	5.6	9	5.6	19	5.4	40	5.5					-0.003	5.58	0.10
CAL6857-1	05-01-81	9.2	4	8.7	10	9.0	16	9.2	19	9.6	24	9.2	+0.018	8.93	0.29
CC3384-11	05-01-81	9.7	17	9.7									0.000	9.70	0.00
BAL1193-10	01-24-80	10.1	9	10.1	19	10.0	40	10.0					-0.003	10.10	0.06
AAL1053-5	11-04-80	10.6	10	10.0	23	10.3							-0.011	10.42	0.30
AAL420-6	11-04-80	10.6	10	10.1	23	10.3							-0.012	10.46	0.25
AAL1508-3	11-04-80	10.7	10	10.1	23	10.3							-0.016	10.54	0.31
AAL1710-4	11-04-80	10.7	10	10.2	23	10.3							-0.016	10.58	0.27
AAL459-7	11-04-80	10.7	10	10.1	23	10.3							-0.016	10.54	0.31
Summary Statistics: $\bar{m} = -0.004$ ppm change/month; $s_m = 0.013$ ppm change/month; $s_{yp} = 0.24$ ppm															
CC10574-32	09-01-80	17.9	8	18.0	25	17.9							-0.001	17.94	0.06
CC15074-19	05-01-81	18.0	17	17.9									-0.006	18.00	0.07
BAL1187-27	05-13-80	18.1	10	18.5	18	18.3							+0.012	18.19	0.20
CC4222-18	12-01-81	18.2	10	18.3									+0.010	18.20	0.07
CAL6997-16	05-01-81	18.9	4	19.2	10	18.8	16	19.4	19	19.9	24	19.0	+0.018	18.98	0.41
BAL1172-28	01-24-80	19.6	9	19.6	19	19.4	40	19.4					-0.006	19.60	0.12
SGCC27593-12	01-13-82	20.1	2	20.2	5	20.1	8	20.2	14	20.6	16	20.6	+0.034	20.05	0.24
BAL1190-29	01-24-80	29.6	9	29.7	19	29.4	40	29.7					+0.001	29.58	0.14
SGCC27603-53	01-13-82	29.0	2	29.0	5	29.1	8	29.0	14	29.3	16	29.4	+0.025	28.95	0.17
SGCC27774-13	01-13-82	40.2	2	40.4	5	40.4	8	40.3	14	40.4	16	40.6	+0.015	40.27	0.13
AAL2644-21	11-04-80	40.6	10	40.4	23	40.5							-0.004	40.54	0.10
AAL785-23	11-04-80	40.8	10	40.5	23	40.6							-0.008	40.72	0.15
AAL1707-25	11-04-80	40.8	10	40.6	23	40.7							-0.004	40.74	0.10
AAL4338-22	11-04-80	40.9	10	40.6	23	40.7							-0.008	40.82	0.15
AAL1990-24	11-04-80	41.2	10	40.9	23	41.0							-0.008	41.12	0.15
SGAL3235-14	01-29-82	41.8	10	41.7									-0.010	41.80	0.07
CC15150-31	09-01-80	41.9	8	41.8	25	41.7							-0.008	41.88	0.10
BAL1001-26	05-13-80	42.8	10	42.8	18	42.6							-0.011	42.83	0.12
BAL1181-17	05-01-81	43.1	4	43.2	10	42.2	16	43.3	19	43.7	24	43.5	+0.026	42.86	0.52
SGAL639-15	02-03-82	43.8	11	43.8									0.000	43.80	0.00
BAL1171-30	01-24-80	44.9	9	45.1	19	44.2							-0.038	45.09	0.47
AAL5920-20	06-11-81	45.1	9	45.1	19	44.7							-0.021	45.17	0.23
Summary Statistics: $\bar{m} = 0.000$ ppm change/month; $s_m = 0.017$ ppm change/month; $s_{yp} = 0.33$ ppm															

[a]*See Procedures section for definition of terms.*

about the average was s_m = 0.017 ppm change/month (see summary statistics in Table 2). Based on $\bar{m}$ = 0.000 ppm change/month there was no reason to reject the hypothesis that the true mean slope was zero.

The approximate 95 percent probability interval for the uncertainty (excluding bias) of a CO/air concentration estimated by one analysis is $\pm 2\ s_{yp}$ = 0.66 ppm or ±2.2 percent at the median concentration of 30 ppm.

Discussion

For reactive gases in aluminum cylinders the average percent change ($\bar{P}$), based on the average slope ($\bar{m}$), was 1 percent or less for all pollutant categories for an eighteen month period. For this reason, an eighteen month recertification time period is being recommended for reactive gases contained in aluminum cylinders. The average percent change and the 95 percent probability interval of the percent change have been summarized in Table 3.

The average percent change for CO/air and CO/N_2 gases contained in steel cylinders approaches or is less than 1 percent for the 6 month period only. The average percent change and the 95 percent probability limits for the percent change for CO contained in steel cylinders for an 18 month period have been calculated in Table 3.

Conclusions and Recommendations

Data contained in this report, indicate that reactive gases (CO/air, CO/N_2, NO/N_2, SO_2/N_2) contained in aluminum cylinders, will remain stable for at least eighteen months. However, it is desirable that a pollutant gas being used as a calibration or audit standard be analyzed at least twice within its useful lifetime. A pollutant gas user should take into account the consumption rate of the gas and plan for a second analysis before the cylinder is empty. This second analysis will provide assurance of the stability of the standard over its period of use.

It is recommended that the present requirement for reanalysis of reactive gases every six months be extended to eighteen months for the following:

- Carbon monoxide in air in aluminum cylinders at concentrations between 5 ppm and 45 ppm. NOTE: To ensure uncertainties of less than 10 percent in measured concentrations near 5 ppm, it may be necessary to use the average of two Protocol No. 2 analyses.
- Carbon monoxide in nitrogen in aluminum cylinders at concentrations between 5 ppm and 5,000 ppm. NOTE: To ensure uncertainties of less than 10 percent in measured concentrations near 5 ppm, it may be necessary to use the average of two Protocol No. 2 analyses.
- Nitric oxide in nitrogen in aluminum cylinders at concentrations between 10 ppm and 150 ppm.
- Sulfur dioxide in nitrogen in aluminum cylinders at concentrations between 9 ppm and 375 ppm.

The data contained in this report, indicates that CO/air and CO/N_2 contained in steel cylinders will remain stable for no more than six months. Even though this conclusion was based upon a relatively small data set, it is recommended that the present requirement for reanalysis every six months remain unchanged for the following:

- Carbon monoxide in air contained in steel cylinders.
- Carbon monoxide in nitrogen contained in steel cylinders.

Current recertification requirements should remain unchanged for reactive gases and cylinder types not considered in this report.

Table 3. *Average Percent Change and Probability Limits of Reactive Gases Contained in Aluminum and Steel Cylinders for Eighteen Months*

Pollutant/Balance Gas	Concentration Range (ppm)	Concentration Median (ppm)	$\bar{P} \pm 2\ s_p$* (Percent)
	Aluminum Cylinders		
CO/Air	5 to 11	7	-1.0 ± 6.6
CO/Air	17 to 45	30	0.0 ± 2.0
CO/N_2	5 to 15	10	+0.2 ± 3.6
CO/N_2	14 to 46	30	+0.4 ± 2.2
CO/N_2	100 to 1000	500	+0.4 ± 2.0
CO/N_2	2500 to 5000	3750	-0.0 ± 4.8
NO/N_2	10 to 22	16	0.3 ± 3.2
NO/N_2	43 to 55	49	-0.9 ± 5.2
NO/N_2	80 to 113	97	-0.2 ± 4.2
SO_2/N_2	9 to 22	15	-0.4 ± 5.0
SO_2/N_2	45 to 56	51	-0.2 ± 5.0
SO_2/N_2	78 to 110	94	+0.7 ± 4.4
SO_2/N_2	152 to 375	264	-0.4 ± 1.4
	Steel Cylinders		
CO/Air	9 to 11	10	-5.0 ± 7.2
CO/N_2	10 to 43	31	-1.9 ± 3.4
CO/N_2	1000	1000	-0.3 ± 0.4

*$\bar{P}$ = *Average percent change at the nominal concentration over a specified time period, percent.*
s_p = *Standard deviation of the percent change at the median concentration over the time period, percent.*

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The complete report, entitled "Stability Evaluation of Sulfur Dioxide, Nitric Oxide and Carbon Monoxide Gases in Cylinders," (Order No. PB 85-122 646; Cost: $20.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
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