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16. Abstract

Two gas dilution methods were evaluated for use in the calibration of analytical instruments used in air pollution studies at Lewis Research Center. Accuracy of the methods was established by the use of National Bureau of Standards - Standard Reference Material carbon monoxide - nitrogen mixtures. A dual isotope fluorescence carbon monoxide analyzer was used as the transfer standard. The methods are not new but some modifications are described. The rotary injection gas dilution method was found to be more accurate than the closed loop method. Results by the two methods differed by 5 percent. This could not be accounted for by the random errors in the measurements. The methods avoid the problems associated with pressurized cylinders. Both methods have merit and have found a place in instrument calibration work at Lewis.

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SUMMARY

Two gas-dilution methods were evaluated for use in the calibration of analytical instruments used to measure pollutants associated with engine exhaust gases. The primary purpose of the evaluation was to establish the accuracy with which gas mixtures can be prepared by these methods. For many years, statements of accuracy of analytical methods were based on wet chemical or statistical methods. In recent years the availability of Standard Reference Material gas mixtures, accurate to ±1 percent, has done much to standardize the field of calibration accuracy. The number of compounds and concentrations are limited, however. The methods described here are not new but some modifications were made in apparatus and procedure. Ten SRM carbon monoxide/nitrogen mixtures, including five concentrations between 10 and 1000 ppm were used to calibrate a dual isotope fluorescence carbon monoxide analyzer which served as the transfer standard. Two ranges of the instrument were used.

The concentrations of gas mixtures prepared by the rotary injection device (RID) were 2 percent high in the 0 to 100 ppm range and showed virtually no error in the 0 to 1000 ppm range. The random (root sum square) error band of this method overlapped the error band of the standard. This method is quite accurate but requires 1 to 2 hours to equilibrate.

Data obtained with mixtures prepared by the closed loop method were more scattered but results were consistently low, averaging 3 percent in the 0 to 100 ppm range and 6 percent in the 0 to 1000 ppm range. This method requires only a few minutes to equilibrate and is much faster.

The two methods differed from each other by about 5 percent at both levels, which exceeds the range of random errors involved in the measurements. The value of SRM's in resolving this kind of problem (which occurs frequently in calibration work) is gratefully acknowledged.

The methods are compatible with virtually any gas and can be used at concentrations to the low parts per billion level. They avoid the problems associated with pressurized cylinders. Both have merit and find a place in instrument calibration work at Lewis.

INTRODUCTION

A means of producing gas mixtures of a high degree of accuracy was needed to calibrate the instruments used in NASA programs to measure air pollution caused by auto and aircraft engines. In response to a national concern about air pollution, the Lewis Research Center has been making measurements of various exhaust gas components both at the source and in ambient air at altitudes currently used by commercial jet aircraft. A system of analytical instruments used for source emission measurements in laboratory tests is described in reference 1. Concentration of pollutants in exhaust gas range from about 10 to 1000 ppm. NASA's Global Air Sampling Program (GASP) uses commercially available instruments which have been modified for use on Boeing 747 commercial aircraft. The system of analytical instruments used in the GASP studies is described in reference 2. Concentration range of pollutants at altitudes of 20 000 to 40 000 feet is the order of 1 ppm to less than 1 ppb, thus requiring very sensitive methods of analysis. Modern technology is pushing the limits of measurement to ever greater sensitivity. Consequently, standard gas mixtures for calibration at lower and lower concentration levels are needed in order to realize the full potential of these instruments.

Pressurized cylinders of gas mixtures are preferred for the source emissions work where a supply of calibration gases must be on hand at the test site. The accuracy of gas mixtures available from vendors has, in general, been questionable and many factors involved in pressurized cylinders can lead to instability. In recent years, the National Bureau of Standards has made available a number of Standard Reference Material (SRM) gas mixtures accurate to ±1 percent (ref. 3) for a period of 1 year. These materials greatly facilitated the calibration of the source emission instruments and qualifying mixtures purchased from vendors as secondary standards. However, the number of compounds and concentrations available are limited. No SRM's were available for direct calibration of GASP instruments.

Two gas-dilution methods that avoid the problems of compressed gas cylinders and are suitable for virtually any concentration range were investigated.

One method employs a motor-driven rotary turncock of accurately known volume to inject pure gas into a diluent gas stream. For very dilute mixtures, either a second dilution stage is used or a mixture of accurately known concentration can replace the pure gas. This method employs the Gas Dosing Device of H. Wosthoff. O. H. G. (ref. 4) in a system similar to that described by Axelrod (ref. 5). The method will be referred to as the Rotary Injection Dilution method. In the second method, pure gas is injected by means of a syringe into a closed loop of known volume. This method is described in principle in reference 6 but specific details are not given. It will be referred to as the Closed Loop method.

The purpose of this work was to evaluate the absolute accuracy of these methods by the use of Standard Reference Materials. A carbon monoxide analyzer of the dual isotope fluorescence type was used as a transfer standard. This type of instrument is inherently stable and has multiple ranges suitable for calibration by available SRM's. Refinements in apparatus and procedure made at this laboratory are described. Random errors were estimated by statistical analysis of measured quantities. Although absolute accuracy of the methods below 10 ppm could not be established by direct use of SRM's, comparison of the methods was made with a nitrous oxide analyzer having full-scale range of 1 ppm.

APPARATUS AND PROCEDURE

Rotary Injection Gas Dilution Method

A schematic diagram of the rotary injection dilution apparatus is shown in figure 1. The gas injection device resembles a four-way stopcock to which pure and diluent gases are piped in such a way as to bypass the stopcock when the stopcock is in closed position. An impulse motor rotates the turncock from closed position to alignment with the pure gas line where the bore is quickly purged and filled. It then continues to alignment with the diluent gas line where the "slug" of pure gas is flushed into the diluent stream. Rotation continues to closed position, where it stops until the next impulse. The turncock used had a bore volume of 0.110 milliliter. A selector switch provides control of the number of impulses from 1 to 10 per minute. Diluent gas was missile grade nitrogen (99.95 percent N_2, 0.05 percent A, dew point, -150° F). Diluent gas is added in two parts, each being controlled by precision needle valves with back pressure regulators, and measured with mass flowmeters having ranges of 0 to 1000 and 0 to 20 000 SCCM. These were calibrated at 20° C, 760 torr, accurate to ±1.07 percent. Glass mixing bulbs were used to smooth out fluctuations caused by intermittent injections, so that the final concentration was uniform. One to three hours was allowed to equilibrate surfaces depending upon the gas and concentration. Glass, teflon, and stainless steel were the only materials used. Single dilution was used for 10 to 1000 ppm and double dilution for 0.01 to 10 ppm.

The concentration of a mixture prepared by the single dilution mode is calculated from the following equation:

$$C_{ppm} = \frac{V_c \times N_c \times 10^6}{F_1 + F_2} \tag{1}$$

where

V_c = volume of gas at 20 °C, 760 torr, injected per turn, milliliter

$= V_o \times A \times P/760 \times 293/T$

where

V_o = volume of turncock bore, milliliter

A = purity of "pure" gas, or concentration of "known" mixture

P = ambient pressure, torr

T = ambient temperature, °K

N_c = number of turns (injections) per minute

F_1 = flow of diluent gas, mass flowmeter 1, milliliter per minute

F_2 = flow of diluent gas, mass flowmeter 2, milliliter per minute

Random errors affecting the accuracy of the concentration calculated from equation (1) can be estimated by means of the Root Sum Square (RSS) method (ref. 7). The RSS equation becomes:

$$\frac{dC_{ppm}}{C_{ppm}} = \left[\left(\frac{dV_c}{V_c}\right)^2 + \left(\frac{dN_1}{N_1}\right)^2 + \left(\frac{F_1}{F_1+F_2}\right)^2\left(\frac{dF_1}{F_1}\right)^2 + \left(\frac{F_2}{F_1+F_2}\right)^2\left(\frac{dF_2}{F_2}\right)^2\right]^{1/2} \tag{2}$$

Volume of the turncock bore, V_o, was given by the manufacturer as 0.1036 ± 0.001 milliliter (1 percent error) and confirmed by a weight-of-mercury method. Purity of the "pure" gases was determined by mass spectrometric analysis. These were 95.4 ± 0.5 percent carbon monoxide and 98.0 ± 0.5 percent nitrous oxide. Pressure and temperature measurement errors were 0.1 percent. The total error of V_c was 1.7 percent. The mass flowmeters were calibrated by the Lewis laboratory flowmeter calibration facility with maximum errors of 1.07 percent (dF_1/F_1) and (dF_2/F_2). The blending rates $(F_1/(F_1 + F_2))$ and $(F_2/(F_1 + F_2))$ were variable factors. Also, N_1 has no error $(dN_1/N_1) = 0$. The random (RSS) errors (dC/C) were estimated from equation (2) to be 1.3 and 1.4 percent. In double dilution mode the concentration equation is:

$$C_{ppm} = \frac{V_c \times N_c \times V_D \times N_D \times 10^6}{F_1 \times F_2} \tag{3}$$

The RSS error equation is:

$$\frac{dC_{ppm}}{C} = \left[\left(\frac{dV_c}{V_c}\right)^2 + \left(\frac{dN_c}{N_c}\right)^2 + \left(\frac{dV_D}{V_D}\right)^2 + \left(\frac{dN_D}{N_D}\right)^2 + \left(\frac{dF_1}{F_1}\right)^2 + \left(\frac{F_2}{F_2}\right)^2\right]^{1/2} \tag{4}$$

The volume of V_D, the second-stage turncock bore, was 0.1029 ± 0.001 milliliter. Random error estimated from equation (4) was 2.1 percent.

Closed-Loop Method

The Closed-Loop method is described in only a general way in reference 6; specific details as to apparatus are left to the user. The apparatus used here is shown schematically in figure 2. The "loop" is made up of a rubber septum (for syringe injection of pure gas), a circulation pump (stainless steel bellows with 6 liters/min capacity), a mixing bottle (stainless steel, 1 or 3 liters in volume), the test instrument absorption cell and connecting tubing. Loop pressure was measured with a 0.to 15 psia transducer. An iron-constantan thermocouple was used for temperature measurement. A valved connection was provided for a vacuum pump. A four-way valve was included for convenience in purging the system.

Preparation of Calibration Gas Mixtures

After thorough purging with nitrogen, the loop was closed and the pressure adjusted to 14.7 psia by allowing excess gas to escape through the needle valve. Adjustment to the instrument's zero potentiometer was made if needed. A strip chart recorder was used to monitor instrument output with time. An appropriate amount of "pure" gas was injected into the loop, through the rubber septum, with a syringe. The pump was started and run for 2 to 3 minutes to thoroughly mix the gases, as indicated by a constant output of the instrument and a "plateau" on the strip chart recording. The pump was then stopped to allow the pressure to equalize in the loop. Several minutes were allowed for the instrument output to stabilize and the recorder to reach a new plateau. This value was recorded. Concentration of the mixture was calculated from the following equation

$$C_{ppm} = \frac{V_N \text{ (microliter)}}{V_L \text{ (liter)}} \tag{5}$$

where V_N is the volume of pure gas at 14.7 psia injected by syringe. Since the syringe was filled at ambient pressure and discharged into the loop at 14.7 psia, a correction was applied to the volume measured from displacement of the plunger. A correction for purity of the "pure" gas was also applied.

$$V_N = \left[V_X - V_Y\left(1 - \frac{P_A}{14.7}\right)\right] \times A \tag{6}$$

where

V_X = volume displaced by plunger, microliter

V_Y = volume to which syringe was filled, microliter

P_A = ambient pressure, psia

A = purity (CO, 95.4 percent, N_2O, 98.0 percent)

The random error in equation (5) was estimated from the following RSS equation:

$$\frac{dC_{ppm}}{C_{ppm}} = \left[\left(\frac{dV_N}{V_N}\right)^2 + \left(\frac{dV_L}{V_L}\right)^2\right]^{1/2} \tag{7}$$

The error in V_N was taken as the sum of the errors in the syringe, the pressure measuremant, and gas purity measurement. The 500-microliter syringe used here was calibrated by using mercury as the fluid. The volume displaced by the plunger was compared to the volume calculated from the weight and density of the expelled mercury. The average difference of four determinations was 0.2 percent or 1 microliter. However, the scale can be read to only 2 microliters so this value was used. The relative error depends on the volume injected. The volumes injected were between 100 and 475 microliters; therefore, dV_X/V_X varied from 2 to 0.4 percent. Values for V_Y were between 200 and 500 microliters, therefore, $dV_X/V_Y = 1$ to 0.4 percent. Values for dV_N/V_N were between 3.6 and 1.4 percent.

Gas Tight Syringes

Gas tight syringes are made with teflon tipped plungers to prevent leakage around the plunger. Scratches from wear or imperfections in the barrel or teflon tip may cause leakage. To insure against this source of error, the plunger was sealed with a small plug of mercury. By drawing a small amount of mercury into the syringe, holding vertical and tapping, the mercury was brought into contact with the plunger and served as a gas tight seal. With this technique, ordinary syringes (without teflon tip) were made gas tight and used as references if a teflon tipped syringe was suspected of leaking. Care was taken not to "bottom out" the plunger when mercury was used.

Loop Volume Measurement

Total loop volume was measured by the "pressure change - known volume" method. The "known volume" was a 500-milliliter gas sampling bottle with stopcocks at each end, connected directly to the loop. It's volume was determined from the weight and density of water (distilled water at room temperature for 24 hr) required to fill it, including one stopcock bore. Measurement accuracy is 0.03 percent. The loop volume was measured as follows: The loop was first evacuated to the limit of the vacuum pump (0.02 psia) and closed off. Next, the "known volume" was filled with filtered and dried air at ambient pressure, closed off, the barometric pressured noted, and then expanded into the closed loop. Final pressure was measured with the pressure transducer and noted. Loop volume was calculated from the following equation:

$$V_L = V_o \times \frac{P_1 - P_F}{P_F - P_1} \qquad (8)$$

where

V_L = total volume of loop, milliliter

V_o = "known volume", milliliter

P_1 = initial pressure in V_o, barometric pressure, psia

P_F = final pressure in V_o and loop, psia

P_2 = initial pressure in loop, psia

Accuracy of the loop volume measurements was estimated from the following RSS equation:

$$\frac{dV_L}{V_L} = \left\{\left[\frac{d(P_1 - P_F)}{P_1 - P_F}\right]^2 + \left[\frac{d(P_F - P_2)}{P_F - P_2}\right]^2 + \left(\frac{dV_o}{V_o}\right)^2\right\}^{1/2} \qquad (9)$$

The pressure transducer was accurate to 0.01 psia and pressure differences were considered accurate to 0.02 psia. For the three loop volumes for this work (1, 3, and 10 liters), equation (9) yields accuracies of 0.5, 1.0, and 3.3 percent, respectively. The random errors estimated from equation (7) were between 2 and 7 percent. Specific values are given in the results.

Instrument Used for Transfer Standard

The instrument used to compare the two dilution methods described above to Standard Reference Materials gas mixtures was a Beckman Dual Isotope Fluoroscence (DIF) 7000 infrared carbon monoxide analyzer (ref. 8). This instrument was particularly suitable because its ranges matched the SRM's available and because of its inherent stability. The modulated single beam principle employed is self-compensating for many variables that normally cause drift in double-beam spectrometers. Reported span drift is 1 percent per month. Calibrations made here with SRM's repeated 5 months apart were within 1 percent without any adjustments being required.

Standard Reference Material (SRM) Gases

The 10 SRM's available for this work are listed in table I by NBS identification number, composition, and instrument response on the 100 and 1000 ppm ranges. The SRM's provided calibration points at three concentration levels on each of these ranges (10, 50, and 100, and 100, 500, and 1000 ppm, respectively). However, they fall in the lower third of the 300 and 3000 ppm ranges which were not adequate for calibration and these ranges were not used. Where more than one cylinder of the same nominal concentration was available, instrument responses were the same, with one exception. A 4-percent difference occurred between the two cylinders of 957 ppm, and was consistently reproduced.

In hopes of resolving this discrepancy, one of these cylinders was returned to NBS for reanalysis, along with four others (one of each concentration), as all the SRM's were approaching the end of their 1-year guarantee period. The reanalyzed values are shown in parentheses in table I. The 957 ppm value was confirmed and, therefore, the data obtained with this cylinder was retained in table I; the other was excluded from calculations.

After the first cylinder was returned to Lewis, comparison was made again, by a different operator and a different type spectrometer. A difference of 2.9 percent was found. The second cylinder will be returned to NBS for analysis. Reanalysis values for the other cylinders were only 0.4 percent lower so the original values were retained for this work.

The SRM calibration data in table I were fitted to appropriate lines. The 100-ppm range data fitted the straight line equation:

$$Y = 0.9396\,X + 0.6106 \qquad (10)$$

where

Y = concentration, ppm

X = response, mv

The correlation coefficient was 0.9999.

The instrument is not linear in the 1000-ppm range. The data were fitted to the parabolic curve:

$$Y = 9.3028\,X + 0.008357\,X^2 \qquad (11)$$

where Y and X have the same meanings as in equation (10). The correlation coefficient was 0.9907.

RESULTS

Rotary Injection Dilution Device Data

Composition of gas mixtures prepared by the rotary injection gas dilution device are shown in table II together with instrument response. Four concentrations were made in the 100-ppm range with one setting of the nitrogen flow rates and simply changing the number of injections of carbon monoxide per minute. In order to produce mixtures in the 1000-ppm range, it was necessary to reduce nitrogen flow, F_2, to a rate too low to read accurately on the 20 000 SCCM flowmeter. This flow was determined by setting F_1 at 200 SCCM, the number of turns to one, and adjusting F_2 to give 95.2 millivolts on the recorder trace, corresponding to 88.4 ppm. From this, F_2 was calculated to be 892 SCCM. These flows were held constant and the number of injections per minute was varied to produce four concentrations in the 1000-ppm range.

To compare the results, a SRM concentration (C_s) was calculated from the instrument response and the SRM calibration line equation appropriate for the scale. These values are given in columns 9 and 10. The individual differences are expressed as fractions in column 11, being the ratio of the differences between the SRM and RID concentrations to the SRM concentration. The comparisons are shown graphically in figures 3 and 4. Random errors calculated from equation (2) are given in column 6 and shown in figures 3 and 4 as vertical lines above and below the data points.

Closed Loop Method Data

Gas mixtures prepared by the Closed Loop method and corresponding instrument responses are given in table III. Data for the 100-ppm range were obtained by injecting 100 microliters of CO several times, so as to produce several steps up the scale. Also 300 microliters were injected repeatedly, with nitrogen purges-in between, to repeat a single concentration. The repeatability of syringe injections indicated by these responses was 0.8 percent; in good agreement with syringe accuracy. The volumes of pure gas injected, as determined from equation (6), are shown in column 3.

Data for the 1000-ppm range were produced similarly, using loop volumes of 3.0 and 1.0 liters. Accuracy of the prepared concentrations as calculated from equation (7) are shown in column 5. These results are compared to the SRM calibration curves in the same way as the RID data. SRM concentration (C_s) and fractional differences are given in columns 8 and 9, and shown graphically in figures 3 and 4.

In the 0 to 100 ppm range (fig. 3) the RID data points are within 2 percent of the SRM calibration with about 1 percent scatter. The lines representing random errors of the data points overlap the SRM error range. The closed loop data points are consistently negative between about -1.6 and -5.2 percent, averaging $-3\frac{1}{2}$ percent. A few of the random error lines overlap the SRM error band.

In the 0 to 1000 ppm range (fig. 4) the RID data points are within the SRM error band except one point in the low 10 percent of the scale. The closed loop data points are again all negative, scattered between -3.9 and -7.8 percent, the average being 5.9 percent. Largest differences occurred with both methods in the lower 10 percent of the scale. The two test methods differ by 5 percent in both ranges.

Comparison of Test Methods in 1 ppm Range

Some of the instruments used in the GASP program require accurate calibration at 1 ppm and less. Although the accuracy of the methods could not be determined with SRM's at these low concentrations, it would not be expected to change significantly. Therefore, a comparison of the two methods was made with a nitrous oxide analyzer having 0 to 1 ppm full-scale range. This instrument was especially made for the NASA-GASP evaluation. It is an infrared spectrometer with a 20-meter pathlength cell. The RID method was used in double dilution mode. The Closed Loop method was modified by increasing the total loop volume to 10 liters and a 10-microliter, gas-tight syringe was used to inject nitrous oxide gas. The mixtures prepared, corresponding instrument responses and the random errors calculated from equations (4) and (7) are given in table IV. The data were treated as straight lines without intercepts (ref. 9). The calculated slopes were 10.5 and 10.0 volts per ppm for the RID and Closed Loop methods, respectively. The ratio of the slopes indicate 5 percent difference between the two methods, the same as occurred at the higher concentration levels.

DISCUSSION OF RESULTS

The results show that gas mixtures made by the RID method were accurate within 2 percent compared to Standard Reference Materials. This result is in agreement with estimates of the accuracy based on the RSS evaluation of random errors involved and, also, evaluations based on wet chemical tests reported in reference 5. The method is compatible with virtually any gas and in any concentration range. The intermittent nature of solute gas introduction necessitates relatively large mixing volumes and, consequently, requires several hours to purge and equilibrate surfaces. This restricts the number of calibration points obtainable in a given time.

Results obtained with the Closed Loop method were at least 5 percent low compared to SRM's. Accuracy based on RSS evaluation of the random errors was not more than 2 percent and does not account for the difference. If surface adsorption were a significant factor, it would be more pronounced in the 100- than in the 1000-ppm range. Since the differences are practically the same for both ranges, this explanation was ruled out. The inaccuracy is more likely associated with the manual use of syringes. Response time for this method is only a few minutes, once the loop volume determination has been made. This is an advantage when many points are needed to establish a calibration curve. The method is limited to instruments that do not destroy the sample, such as spectrophotometers.

Comparison of the two methods at low concentration levels (below 1 ppm) by means of a nitrous oxide analyzer indicated the same difference (5 percent) found at the higher concentration levels. This does not prove that the accuracies are unchanged, but does provide some assurance that this is the case.

Both methods appear useful for calibration of analytical instruments. Relative inaccuracy of 5 percent is acceptable in many cases and the use of two independent methods is more likely to reveal the presence of systematic errors than relying on a single method. The methods are compatible with virtually all air pollutant gases, and can be used at concentrations to the low parts per billion level. Problems associated with pressurized cylinders are avoided.

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TABLE I. - NATIONAL BUREAU OF STANDARDS

STANDARD REFERENCE MATERIALS (SRM) USED FOR CALIBRATION

NBS Identification No.	Composition and Probable Error PPM	Instrument Response 20°C, 760 mm-hg.	
		100 PPM Range MV	1000 PPM Range MV
1677	9.74 ± 0.14 CO/N_2	9.7	
1677A	9.82 ± 0.14 CO/N_2 (9.78)*	9.8	
1677A	9.82 ± 0.14	9.8; 9.6	
1678	47.1 ± 0.5 CO/N_2	49.5	
1678A	46.3 ± 0.5 CO/N_2 (46.1)*	49.0	
1679	94.7 ± 0.9 CO/N_2 (94.4)*	100.2; 99.9	10.0
1680	484 ± 5.0 CO/N_2 (482)*		49.8
1680	484 ± 5.0 CO/N_2		49.7
1681	957 ± 9.0 CO/N_2 (957)*		94.8
1681	957 ± 9.0 CO/N_2		90.9**
	Slope, PPM/Mv	0.9396	
	Intercept, PPM	0.6106	
	Correlation Coefficient	0.9999	

*Returned to NBS and reanalyzed

**Not included in calculations

TABLE II. - ROTARY INJECTION DILUTION DEVICE TEST DATA

1	2	3	4	5	6	7	8	9	10	11
No. turns per minute	V_c ml	F_1 ml/min	F_2 ml/min	C_C CO/N_2 PPM	RSS RANDOM ERROR %	INSTRUMENT RESPONSE 20°C, 760 TORR		C_S		$\frac{C_S - C_C}{C_S}$
						100 PPM RANGE MV	1000 PPM RANGE MV	100 PPM RANGE PPM	1000 PPM RANGE PPM	
5	.0966	492	4970	88.4	1.4	95.2		90.06 ①		.018
4	"	"	"	70.7	"	76.3		72.30		.022
2	"	"	"	35.4	"	37.5		35.84		.012
1	"	"	"	17.7	"	18.4		17.90		.011
1	"	200	892	88.4	1.3	95.2		90.06		.018
1	"	"	"	88.4	"		9.63		90.36 ②	.022
2	"	"	"	177	"		18.95		179.3	.013
4	"	"	"	354	"		36.99		355.5	.004
10	"	"	"	884	"		87.65		879.6	-.005

① Equation (10).
② Equation (11).

TABLE III. - CLOSED LOOP METHOD TEST DATA

1	2	3	4	5	6	7	8	9
LOOP VOLUME LITERS	VOLUME INJECTED		C_C CO/N_2 PPM	RSS %	INSTRUMENT RESPONSES		C_S PPM	$\frac{C_S - C_C}{C_S}$
	PLUNGER 1	CORR'D 1			100 RANGE MV	1000 RANGE MV		
3.261	100	92.2	27.0	2.3	27.5		26.4 ①	-.021
	"	94.8	54.7	"	56.0		53.2	-.028
	"	"	82.4	"	84.8		80.3	-.026
	"	"	27.7	"	27.5		26.4	-.047
	"	"	55.4	"	56.0		53.2	-.041
	"	"	83.1	"	83.5		79.1	-.051
	300	292	85.4	1.3	86.5		81.9	-.043
	"	290	84.8	"	87.8		83.1	-.020
	"	"	"	"	88.0		83.3	-.018
	"	"	"	"	86.9		82.3	-.031
3.317	100	96.0	27.6	2.3	28.0		26.9	-.025
	"	"	55.2	"	56.2		53.4	-.033
	"	"	82.8	"	84.3		79.8	-.037
	175	171	49.2	1.6	49.1		46.7	-.052
	"	"	98.4	"	99.0		93.6	-.051
3.261	300	290	84.8	1.3		8.4	78.7 ②	-.077
	400	388	113	1.2		11.2	105.2	-.074
	"	"	226	"		22.4	212.6	-.063
	"	"	339	"		33.6	322.0	-.053
	"	"	452	"		44.8	433.5	-.043
	2(400)	2(388)	678	"		66.0	650.4	-.042
3.317	2(175)	2(171)	98.4	1.1		9.9	92.9	-.059
	475	465	232	"		22.9	217.4	-.067
	"	"	366	"		36.1	346.7	-.056
	2(475)	2(465)	633	"		61.8	606.8	-.043
	475	465	767	"		73.6	730.0	-.051
	"	"	901	"		85.7	858.6	-.049
1.037	400	389	358	0.7		35.5	340.8	-.051
	"	"	716	"		69.7	689.0	-.039
	300	291	984	0.8		93.3	940.7	-.046

① Equation (10).

② Equation (11).

TABLE IV. - COMPARISON OF TEST METHODS WITH 1 PPM NITROUS OXIDE ANALYZER

ROTARY INJECTION METHOD

N_1 Turns Min.	N_2 Turns Min.	F_1 SCCM	F_2 SCCM	CONC PPM	Instrument Response V	RSS Error
9	9	490	3100	0.50	5.41	2.1%
9	9	500	3100	0.49	5.21	
10	10	500	3100	0.60	6.25	
8	8	500	3100	0.39	3.86	
		Slope			10.49	
		Standard Deviation of Slope			0.17	

CLOSED LOOP

Loop Vol. Liters	Vol. N_2O Injected By 10 μ Liter Syringe μL.	Conc. N_2O PPM	Instrument Response Volts	RSS Error
9.821	9.0	0.88	9.35	
	9.0	0.87	8.90	
	5.0	0.48	4.70	
	5.0	0.48	4.70	
	3.0	0.29	2.88	
	3.0	0.29	2.80	
	9.0	0.87	8.55	
	9.0	0.90	8.74	
	9.0	0.86	8.56	1.0%
	Slope		10.0	
	Standard Deviation of Slope		0.11	

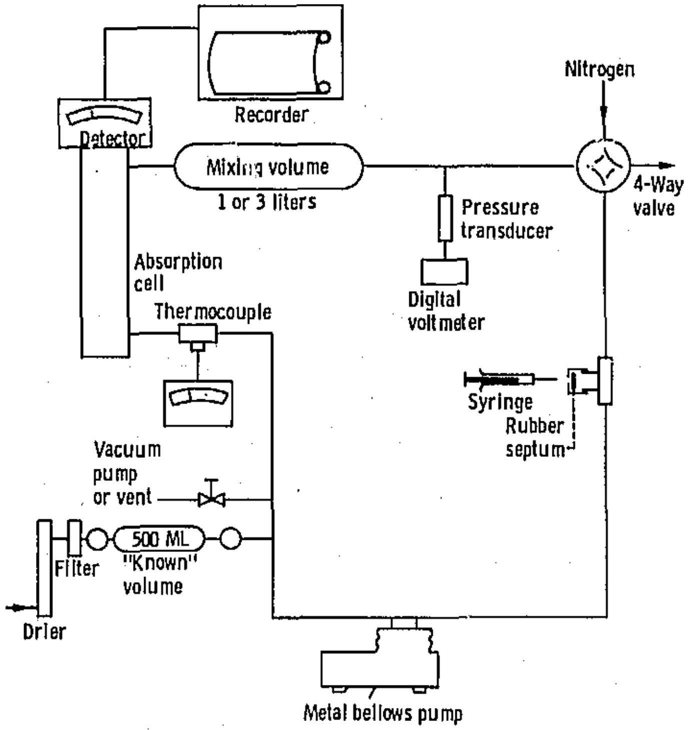

Figure 2. - Apparatus; closed loop method.

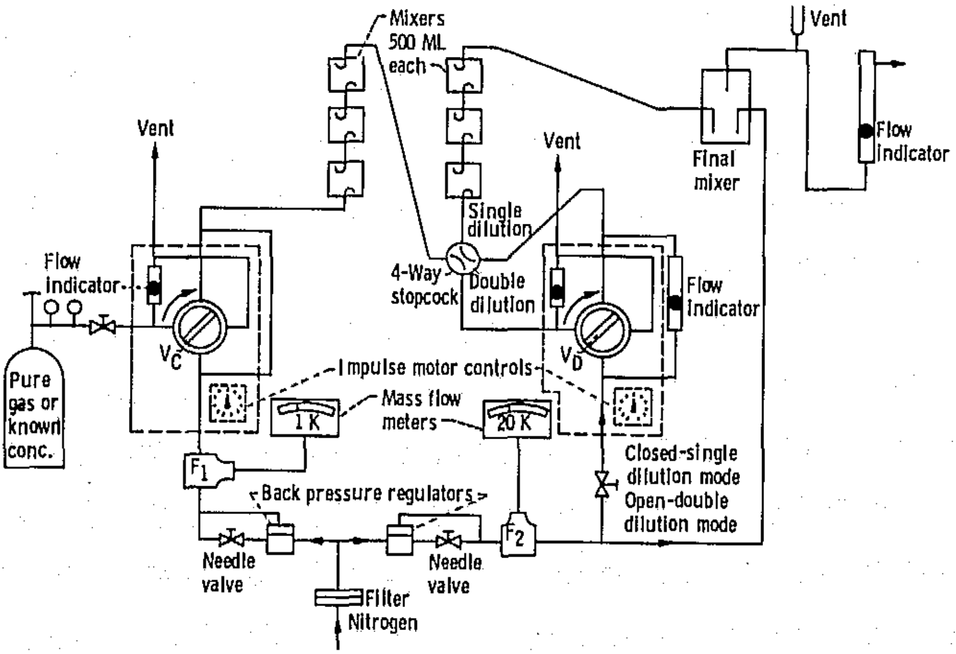

Figure 1. - Rotary injection dilution device.

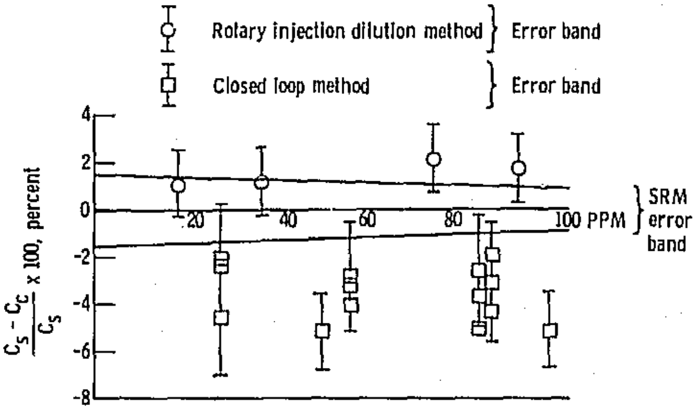

Figure 3. - Comparison of test method concentration to standard reference materials, 0 to 100 PPM.

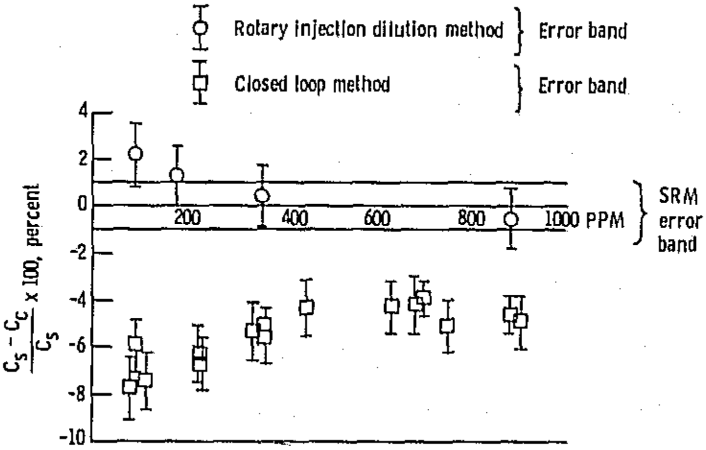

Figure 4. - Comparison of test method concentrations to standard reference materials, 0 to 1000 PPM.