PROCEEDINGS OF THE EPA/INDUSTRY QUALITY CONTROL SYMPOSIUM

GAS STANDARDS - MANAGEMENT AND TRACEABILITY PRACTICES

July 27, 1977

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July 27, 1977

9:00 a.m. - 4:00 p.m.

HELD AT:

Environmental Protection Agency
2565 Plymouth Road
Ann Arbor, Michigan
48105

Symposium Chairman:
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SUMMARY REPORT
EPA/INDUSTRY QUALITY CONTROL SYMPOSIUM
GAS STANDARDS - MANAGEMENT AND TRACEABILITY PRACTICES

INTRODUCTION

This report is a narrative synopsis of the proceedings, discussion and presentations made at the Quality Control Symposium at the Environmental Protection Agency (EPA) Laboratory, Ann Arbor, Michigan on July 27, 1977. The symposium was a joint effort by EPA and the automotive and specialty gas industries to discuss preparation and analytical techniques of calibration gas standards used in automotive emission testing and associated problems. Approximately sixty persons attended the symposium.

The symposium was chaired in such a manner so as to encourage maximum participation from audience attendees. Most topics were introduced by an informal five to ten minute presentation. The Chair then opened the floor to discussion hoping that elaboration on individual experiences would prove to be beneficial to other attendees.

The report is somewhat fragmentary since it generally follows the discussion which was not continuous in subject matter. Questions may be directed to the chairman or identified participants.

SYNOPSIS OF SYMPOSIUM

I. PRIMARY GAS STANDARDS

A. Gravimetric

Don Paulsell gave a summary of the gravimetric standards program carried out at EPA's test facility in Ann Arbor, Michigan. Their gas blends and ranges are:

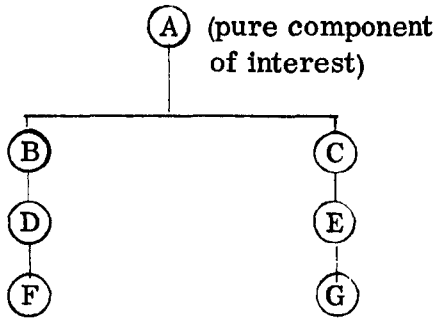
Gas Blend	Range
C_3H_8/Air	1 - 5000 ppm
C_3H_8/N_2	100 - 20,000 ppm
CO/N_2	10 ppm - 10%
CO_2/N_2	.15 - 15%
H_2/N_2	30 - 50%
H_2/He	30 - 50%
O_2/N_2	5 - 25%
$C_3H_8/O_2/N_2$	100 ppm in same O_2 concentrations as above
CH_4/Air	10 - 200 ppm

(In September, EPA started blending NO/N_2 mixtures.)

A. Gravimetric (Continued)

EPA recognizes their blends as primary standards and uses them to supplement NBS Standard Reference Materials where SRMs are not available. The blends are made in 200 cu in. cylinders at 1500 psi. They derive the lower concentrations from serial dilution.

A "tree" blending structure is used for the gravimetrics such as:



With such serial dilution, blends F and G can be compared. The results of this comparison tell much about the integrity of the other cylinders blended from A. A more extensive treatment can be found in the Appendix. Don stated that it is good practice to add at least 10 grams of the minor component since the uncertainty of the final determination is related to measurement error percentage based on the weight of the minor component. The uncertainty in EPA's balance is ±2 mg (0.05% of 10 grams).

The pure reagent gases used in the EPA gravimetrics are research grade (99.99+) purity.

When comparing their gravimetrics to NBS SRMs, EPA expects to correlate within ±1%. The new CO_2/N_2 SRMs matched their gravimetrics to ±0.1% on higher values and ±0.5% on lower ones.

Cylinders are purged with dry N_2. Steel cylinders are used for all blends except NO/N_2 and CO/N_2 below 0.5%. NO/N_2 cylinders are Luxfur Alrocked aluminum and are soaked with NO/N_2 for three weeks at a concentration near the desired gravimetric value. A Voland 2015CDN balance is used. The unit has manufacturer's specifications of 10 kg capacity and 1 mg readability.

A. Gravimetric (Continued)

Ernie Hughes of NBS noted the following:

- There is no way of checking a single gravimetric for possible bias. Several such preparations must be made by different operators on different balances in order to reduce some, but not necessarily all, of the sources of bias.
- Gravimetric blends are only good for relatively stable blends.
- There is some indication that in steel cylinders with rust present there may be CO depletion by action as a reducing agent with the iron oxide.
- NO is quite stable except when in the presence of water vapor. Instability problems of NO were greatly over-rated. The problems of NO/N_2 SRM issuance were more related to problems of analysis rather than instability.
- Purer reagents are becoming more available but they still need to be analyzed.
- Heavy hydrocarbons (C_5H_{12} and above) are too unstable for gravimetric blending.

Ted Eckman noted that General Motors has partially completed a gravimetric gas program. They have yet to be correlated with NBS SRMs.

B. Dynamic Blending

1. Mass Flow

Chuck Vaughn of Tylan Incorporated gave a short summary of mass flow technology. It is based on the principle of laminar gas flow through a small diameter capillary. For laminar flow the equation

$$W = \frac{K \rho \Delta P D^2}{\mu 1}$$

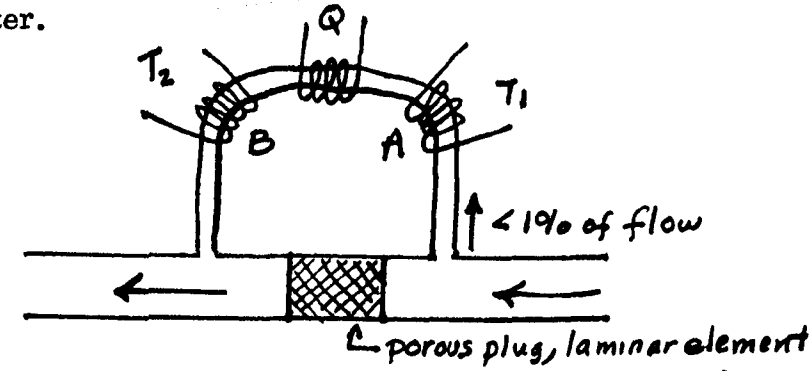
1. Mass Flow (Continued)

describes the mass flow ω through a capillary where,

K	=	Universal gas constant
ρ	=	density
ΔP	=	pressure drop
D	=	diameter
μ	=	viscosity
l	=	capillary length

Mass flow is sensitive to temperature and pressure.
μ varies proportionally with temperature.
ρ varies inversely with temperature and should be calculated using upstream pressure.

The diagram below is a simple representation of the Tylan flow meter.



Actual mass flow in the unit is measured by the heat transfer characteristic

Q	=	$C_p \Delta T$
Q	=	constant heat
$\omega \propto$		$\Delta t \; C_p$
Δt	=	the change in temperature from point A to B

C_p is the specific heat of the gas

Mass flow sensors are not universal for all gases and must be calibrated for each specific gas. General Motors noted that brief evaluations indicated Tylan's mass flow meters (and controllers) were extremely repeatable but had some difficulty with accuracy (traceable to inadequate calibration). Since that time Tylan reportedly improved calibrations.

2. Critical Flow Orifice

General Motors has fabricated a critical flow orifice console that is capable of producing any one of 66 typical blends of gases (CO_2/N_2, C_3H_8/Air, etc.) used in emission testing. It uses eleven reagent gases including oxygen and nitrogen.

EPA has built a cross-check bag blender that is based on partial times and a common CFO control. The bag blender is used for site-to-site correlation diagnostics. It is described in SAE Paper 770138 (See Appendix).

3. Flowmeters

No comments.

4. Other

Wosthoff pumps were mentioned. General Motors has two. Repeatability and accuracy appear to be good but the pump takes a long time to become stable. Hughes of NBS has experienced a cyclic output from them over a two-minute period. He has used them to make a 300 ppm blend of CO_2/N_2 using two-stage dilution.

II. ANALYZERS

Glenn Reschke of EPA gave a synopsis of most of the currently used exhaust emission analyzers. The presentation treated types of analyzers, application, precision, and limitations. A more complete summary is in the Appendix. Glenn noted that his data, particularly with respect to precision of NDIR, were based on instrument set-ups to obtain minimum noise and optimum absorption.

The major concern of participants with respect to analyzers was a general concern with inability to properly quantify accuracy and precision parameters.

III. DATA REDUCTION

Sandy Hunter of General Motors began the discussion on data reduction. She pointed out that data reduction is an integral part of gas correlation.

At General Motors, although specific data reduction techniques are not dictated by Federal regulations, hand drawn curves are not allowed for Federal tests. The most specific of the Federal regulations are heavy-duty regulations which state that a best fit of the equation $y = mx$ may be used for analyzers that are less than 2% nonlinear. All other curves

III. DATA REDUCTION (Continued)

are to be a best fit of one of the equations

$$y = Ax^4 + Bx^3 + Cx^2 + Dx + E$$

or $$y = \frac{X}{Ax^4 + Bx^3 + Cx^2 + Dx + E}$$

Best fit method is not defined in the regulations. Commonly used methods are Lagrangian, which forces the curve through the data point, and Gaussian or orthogonal regression, usually on a polynomial. Curves resulting from a regression typically do not pass directly through the data points.

One must decide on the model to describe the analyzer response. This has to be done by trying different models because the commonly expected response characteristics of an analyzer are usually not the true response. That is, flame ionization detectors and chemiluminescence analyzers are not truly linear and non-dispersive infrared analyzers do not respond exactly according to absorption theory.

Eric Zellin of EPA gave a detailed description of the data reduction program used at EPA (see Appendix). The program allows for gas cylinders or a calibrated gas blender to be used as the calibration gas source. Unknown gas concentrations can also be named. Software zero and span options are:

1. No software zero and span (used for light-duty testing).

2. Signal drift and offset correction (used for heavy-duty engine R & D).

3. Correction for linear signal drift and pressure (not used).

An orthogonal polynomial regression with degree option of 1 to 4 and the intercept either forced or not forced through the origin is used. Data points may be weighted by 1 or 1/concentration. The 1/concentration weighting factor is used to minimize "percent of point" deviations. Options currently used are:

Intercept forced through origin with a weighting of 1/concentration.

2nd degree fit for CL.

2nd or 3rd degree fit for FID.

4th degree fit for NDIR.

III. DATA REDUCTION (Continued)

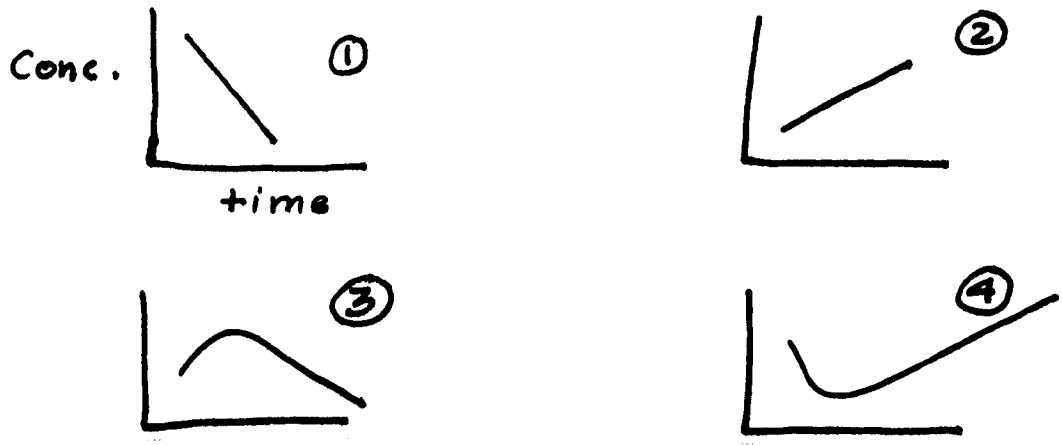
Unknown cylinder concentrations may be determined directly from the curve or by linear interpolation or extrapolation from nearby data points.

Several quality control warning checks are incorporated in the program. Data is entered in batch form. Personnel performing the calibration fill out data forms. Manual readings of a digital volt meter are used for analyzer output. Eric's presentation is included in the Appendix.

IV. STABILITY OF GASES

Steve Wechter, Airco Incorporated, Riverton, New Jersey defined stability as the absence of perceptible change over the useful life of the gas within the analytical accuracy of the analyzers. It can only be determined for a particular cylinder by reviewing historical data.

Four distinct types of unstability have been observed



Instabilities as above may change with pressure and temperature. Steve noted that many specialty gas manufacturers have proprietary methods for treating cylinders.

Ernie Hughes noted that NBS had slight difficulty with CO/Air in wax-lined cylinders. CO was being generated either by the oxidation of the wax lining or independently by the wax itself. He also has observed that NO/N_2 blends in aluminum cylinders (treated with Airco's Spectraseal process) were stable for more than one year whereas similar blends in moly-steel cylinders were not.

IV. STABILITY OF GASES (Continued)

Working gas lower pressure limits for Chrysler, Ford and GM were:

	NO_x	All Other Gases
Chrysler	400	100
Ford	300	100
GM	200	200

Temperature of cylinders being used are kept between 50-100°F. Extremely low temperature excursions (as low as -20°F) between usages were not thought to be a problem by any present.

V. ZERO GAS

Lower emission levels and CVS dilution has made the task of quantifying interference constituents in zero gas quite difficult. Many persons agreed that lower SRMs were needed to establish low levels of CO, CO_2, C_3H_8, and NO. With such low levels it is becoming more important not to set analyzer output at zero assuming that this truly represents the zero gas. Ernie Hughes of NBS said that this would be a topic of discussion in a forthcoming NBS-Automobile Industry meeting to determine future SRM needs.

The only facilities represented that volunteered to describe a zero air system from a source other than cylinders was the General Motors Vehicle Emission Laboratory at the Milford Proving Ground and the Ford Emission Test Laboratory, Allen Park. GM uses a CFO system which blends gasified liquid nitrogen and electrolytic oxygen. The system was made by Air Products and Chemicals Incorporated. The liquid nitrogen is supplied by the same company from an air separation plant in North Baltimore, Ohio. The electrolytic oxygen is furnished in twelve-cylinder cradles by Burdett Oxygen from Findlay, Ohio. The system has been virtually maintenance free for over three years. Typical product measures:

THC - less than 0.04 ppm THC
CO - less than .3 ppm
CO_2 - less than 10 ppm
NO - less than 0.1 ppm

Electrolytic oxygen must be used since oxygen from tonnage separation plants has a hydrocarbon content too high to be of use.

V. ZERO GAS (Continued)

Ford employs an ambient air scrubber system. It oxidizes HC and CO to CO_2 and then removes the CO_2 with a molecular sieve tower. They report that the product typically measures:

THC - less than 0.1 ppm
CO - less than 0.3 ppm
CO_2 - less than 4 ppm
NO - less than 0.1 ppm

It has, however, not always been maintenance free. Ford uses a Beckman Model GC-6800 process gas chromatograph to monitor the THC, CO, and CO_2 impurities from 4 to 6 times an hour.

When analyzing zero gas by gas chromatograph (gc), close attention must be paid to the impurities in the gc carrier gas. Such impurities will detract to the extent of their own magnitude on most detectors.

VI. GAS MANAGEMENT AND INVENTORY CONTROL

Don Paulsell discussed in detail a program of calibration gas management used at EPA, Ann Arbor. The substance of his presentation is included and expanded upon in the Appendix.

Chrysler, EPA, and GM route span gas through stainless steel tubing to the test sites from a single source. GM analyzes span gas to the analytical tolerance (±1%, 90 C.L.) of their Bench Master calibration gases. They feel that the accuracy of an analyzer on a particular day is going to be no better than the span gas value used to adjust its gain to its predetermined calibration curve. For span and calibration gases, many members present indicated that dedicated regulators are used.

Department of Transportation (DOT) regulations governing hydrostatic testing of cylinders were discussed briefly. Specialty gas manufacturers present said that cylinders must be tested every five years or each time it is filled - whichever is longer. No one seemed to have any information on the rumored weakening of CO/N_2 cylinders due to iron carbonyl formation.

Chrysler presented a viewgraph which outlined the traceability of their gas standards (see Appendix).

VII. STANDARD REFERENCE MATERIALS

A. Derivation From Primary Standards and Availability

Ernie Hughes, NBS, explained that the issuance of a new SRM or series of SRMs is predicated on basically two things: demonstrated need and money for development. First NBS surveys potential SRM users to determine the extent of need much in the same manner as a market survey. They then must obtain funding to do the necessary development. The funding may be obtained from other government agencies such as EPA in 1972 for the original emission SRMs or from outside sources such as the Motor Vehicle Manufacturers Association (MVMA) in 1975 for the recent issue of a series of low CO_2/N_2.

The development includes:

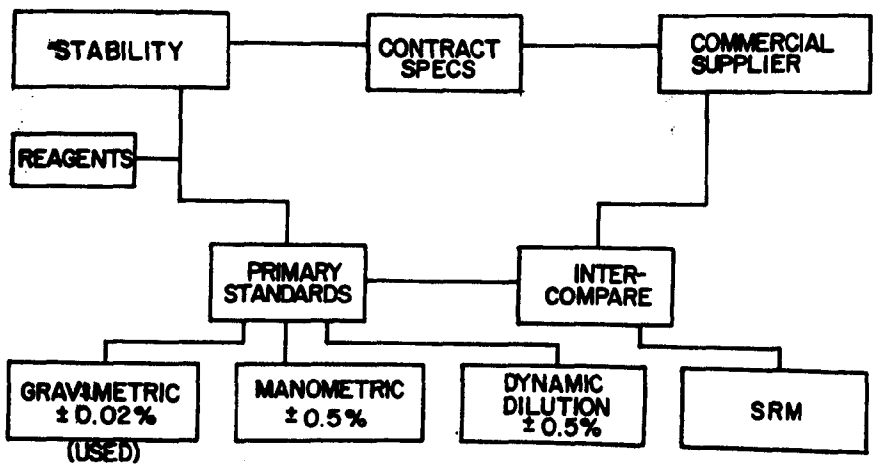
- Study of stability,
- Preparation of NBS in-house primary gravimetric, manometric, or dynamic standards,
- Specifications for commercial production of cylinders charged to nominal concentrations,
- Development of a comparator (analyzer) to compare primary standards to commercial nominals,
- Estimation of analytical error where:

$$\text{Variation} = a + \sqrt{b^2 + c^2}$$

$$\text{Upper limit} = 2\sqrt{a^2 + b^2 + c^2}$$

a = imprecision of gravimetric preparation
b = uncertainty of purity of reagents
c = intercomparison imprecision

SRM PROCESS



B. Future Needs

Don Strain, Chrysler Corporation, Highland Park, presented a list of SRMs that are needed for current and future needs. The list is included in the Appendix. Numerous questions came from the floor as to what is planned by NBS for future SRMs. Ernie said he was not surprised since he has at his office many letters requesting SRMs not now available. A meeting is being planned for October at NBS so that the Bureau and the mobile source industry can address the need for new SRMs. Ernie also noted that new SRMs of atmospheric level CO_2 are being developed for international ambient monitoring.

VIII. TRACEABILITY

Lynn Scott of Scott Environmental Technology Incorporated, Plumsteadville, Pennsylvania spoke of traceability. The stationary source office of EPA funded a private contractor, Scott Environmental Technology (SET) to define what gas traceability is. SET defined a protocol which EPA released. It generated much comment and EPA issued a paper which acknowledged the comments giving EPA's response. This latter document was essentially a hard line in favor of the protocol. However, EPA has since met with specialty gas manufacturers and other interested parties to work out a compromise position more agreeable to all. The SET protocol and EPA's response to comments are included in the Appendix.

Ted Eckman stated that MVMA currently is reviewing the stationary source protocol in the event that it comes into effect for mobile source. He said that it appears at this point that MVMA is not in favor of a protocol, but would favor a traceability requirement in the form of a performance standard.

Don Paulsell was asked what EPA meant by calibration gases being required to be ±1% traceable to SRMs. He said it was his interpretation that the statement addressed the amount of uncertainty introduced by the intercomparison of the SRM and the unknown gas. Curve fitting, analyzer performance, and the number of intercomparisons are all factors in the overall measure of uncertainty. For example, if the SRM cylinder had a stated value of 90 ppm, ±1%, a mobile source gas cylinder of the same stated value would have to analyze against it ±1% from the ±1% uncertainty band of the SRM. This will then assure that the calibration gas is named within ±2% of true value. Ernie Hughes agreed that there is nothing implied in an SRM certificate that there is a Gaussian distribution of probable true value across the ±1% but, that as far as NBS is concerned, the true value has equal chance of being anywhere in the ±1% band. Ernie noted that one cannot establish a 1% absolute traceability to a standard which has an uncertainty of ±1%.

EPA/INDUSTRY QUALITY CONTROL SYMPOSIUM

Gas Standards - Management and
Traceability Practice

Topics for Discussion

I. Primary Gas Standards
   - A. Gravimetric
   - B. Dynamic Blending
     1. Mass Flow
     2. Critical Flow Orifice
     3. Flowmeter
     4. Other
   - C. Volumetric
   - D. Other

II. Analyzer, Types and Limitations

III. Data Reduction
   - A. Curve Reduction Techniques
     1. Hand Drawn Plots
     2. Mathematical - Straight Line Segments, Least Squares Polynomial, Lagrangian, etc.

IV. Stability of Gases
   - A. Definition
   - B. Temperature and Time Limitations

V. Zero Gas
   - A. Requirements
   - B. Sources

VI. Gas Management and Inventory Control
   - A. Cylinders Needed
   - B. Gas Distribution
   - C. Quality Control - Integrity

VII. Standard Reference Materials (SRMs)
   - A. Derivation From Primary Standards and Availability
   - B. Future Needs

VIII. Traceability

APPENDIX

APPENDIX

1. Attendance List

2. EPA Gravimetric

   a. Gravimetric Inventory

   b. CO Gravimetric Blends

   c. CO_2 Gravimetric Blends

   d. CO_2 Gravimetric Blends

   e CFO Cross-Check Bag Blender

3. Analyzers (EPA)

   a. Analyzers for Gas Analysis

   b. Precision of Analyzers

   c. Limitations

4. EPA Exhaust Gas Analyzer Calibration Program

5. EPA Gas Management, Quality Assurance Paper

6. EPA Gas Management

   a. Curve Processing

   b. Curve Analysis

   c. Span Point Change Notice

7. Chrysler Corporation - Calibration Gas Program

8. SRMs, Existing and Future Needs

9. Protocol for Establishing Traceability of Calibration Gases Used With Continuous Source Emission Monitors

10. Discussion of Comments Received on Draft Protocol for Establishing Traceability of Calibration Gases Used With Continuous Source Emission Monitors

EPA/INDUSTRY QUALITY CONTROL SYMPOSIUM
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EPA 2a

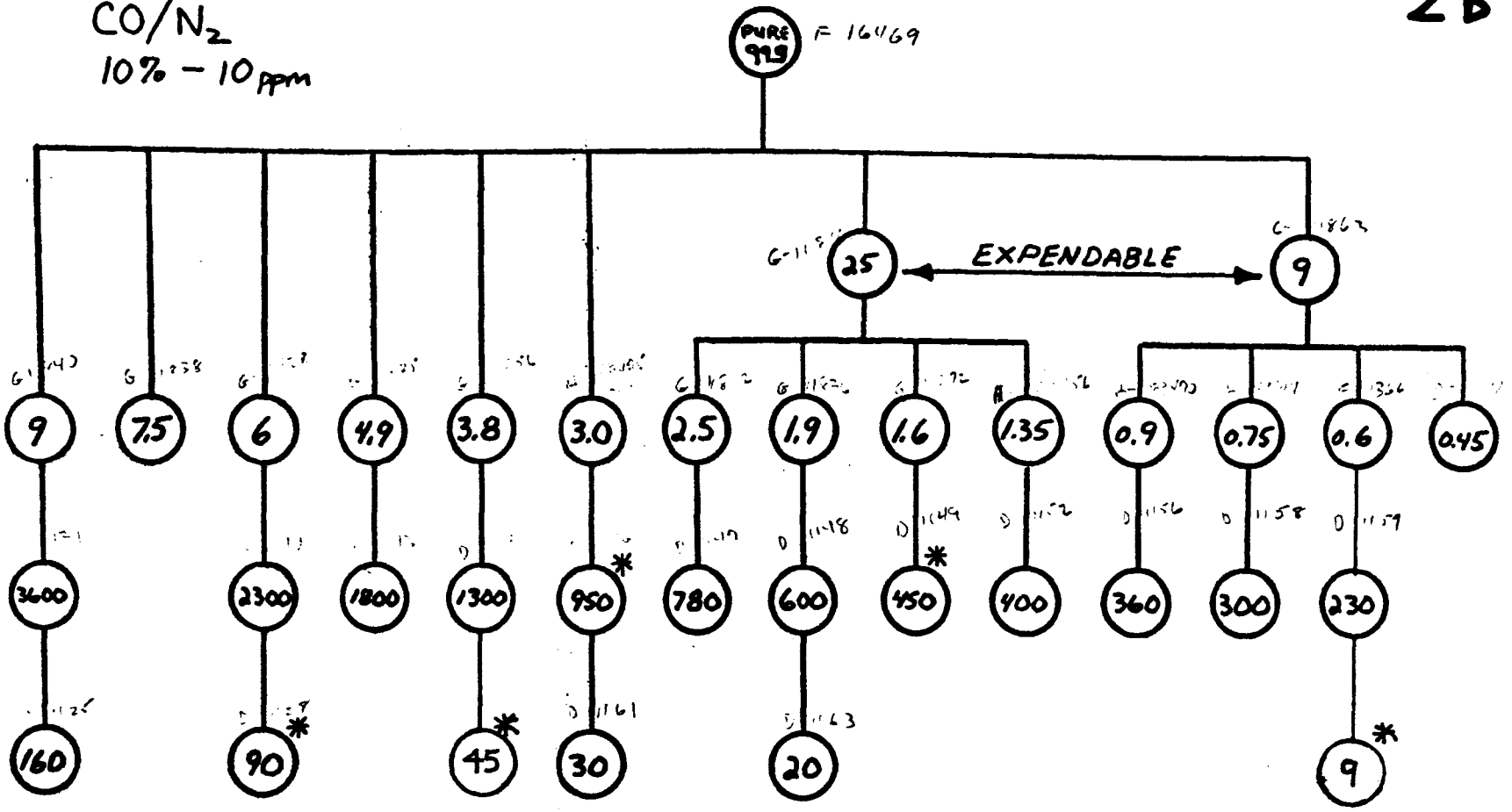
EPA GRAVIMETRIC INVENTORY

GAS BLEND	EPA RANGE	NBS SRMS
C_3H_8 / AIR	1 - 5000 ppm	3, 10, 50, 100, 500 ppm
C_3H_8 / N_2	100 - 20,000 ppm	N/A
CO / N_2	10 ppm - 10 %	10, 50, 100, 500, 1000 ppm
CO_2 / N_2	.15 - 15. %	.5, 1., 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 7.0, 14.0 %
NO_x / N_2	10 - 5000 ppm	50, 100, 250, 500, 1000 ppm
H_2 / N_2	30, 35, 40, 45, 50 %	N/A
H_2 / He	" %	N/A
O_2 / N_2	0, 5, 10, 15, 20, 25 %	21 %
C_3H_8 / O_2 / N_2	100 ppm IN SAME O_2 % AS ABOVE	N/A
CH_4 / AIR	10 - 200 ppm	

CO GRAVIMETRIC BLENDS EPA

2b

CO/N_2
10% – 10 ppm



* = NBS SRM

EPA
2c

FOLD TO FIT

CO_2/N_2 GRAVIMETRIC BLENDS. (CONCENTRATIONS = % CO_2)

	CYLINDER No.	[1] NOMINAL CONC. % CO_2	[2] ACTUAL CONC.	[3] EXISTING BLENDS % CO_2	[4] CYL TYPE	PARENT BLEND % CO_2	[6] P_1 (PSIA)	[7] P_1 (PSIG)	[8] M_1 (GMS)	[9] P_2 (PSIA)	[10] P_2 (PSIG)	[11] M_2 (GMS)	[12] TOTAL MASS (GMS)
1		PURE –	99.99%	Coleman CO_2 +		ZERO N_2	(< 1.0 ppm CO_2)						
2	G-11839	14.00		13.9961	STEEL	PURE	212.0	197.7	96.5	1514.3	1500	376.4	472.9
3	G-11854	11.50		11.6910			174.2	159.9	79.2			387.3	466.5
4	G-11868	8.50		8.6350			128.7	114.4	58.6			400.4	459.0
5	G-11850	6.75		6.7680			102.2	87.9	46.5			408.1	454.6
6	G-11845	6.00		15.6220			90.9	76.6	41.3			411.4	452.7
7	G-11862	5.00		5.0190			75.7	61.4	34.5			415.7	450.2
8	H-89462	3.75		3.7530			56.8	42.5	25.8			421.2	447.0
9	G-11853	3.00		3.0450			45.4	31.1	20.7			424.5	445.2
10	G-11866	2.45		2.4530			37.1	22.8	16.9			426.9	443.8
11	G-11847	1.95		1.9680		PURE	29.5	15.2	13.4			429.1	442.5
12	G-11858	1.45		1.6820		14.00	156.8	142.5	49.0			392.3	441.3
13	H-89464	.95		1.0750		11.50	125.1	110.8	38.5			401.5	440.0
14	G-11870	.75		0.8340		8.50	133.6	119.3	40.5			399.0	439.5
15	H-89465	.60		0.6200		6.00	151.4	137.1	45.2			393.9	439.1
16	G-11851	.45		0.4230		5.00	136.3	122.0	42.5			398.2	440.7
17	G-11843	.30		0.2300		3.00	151.4	137.1	44.5			393.9	438.4
18	Cylinder NEEDED	.15		NONE		1.95	116.5	102.2	34.0	1514.3	1500	404.0	438.0
19													
20													
21													
22													
23													
24													
25													
26													
27													
28													
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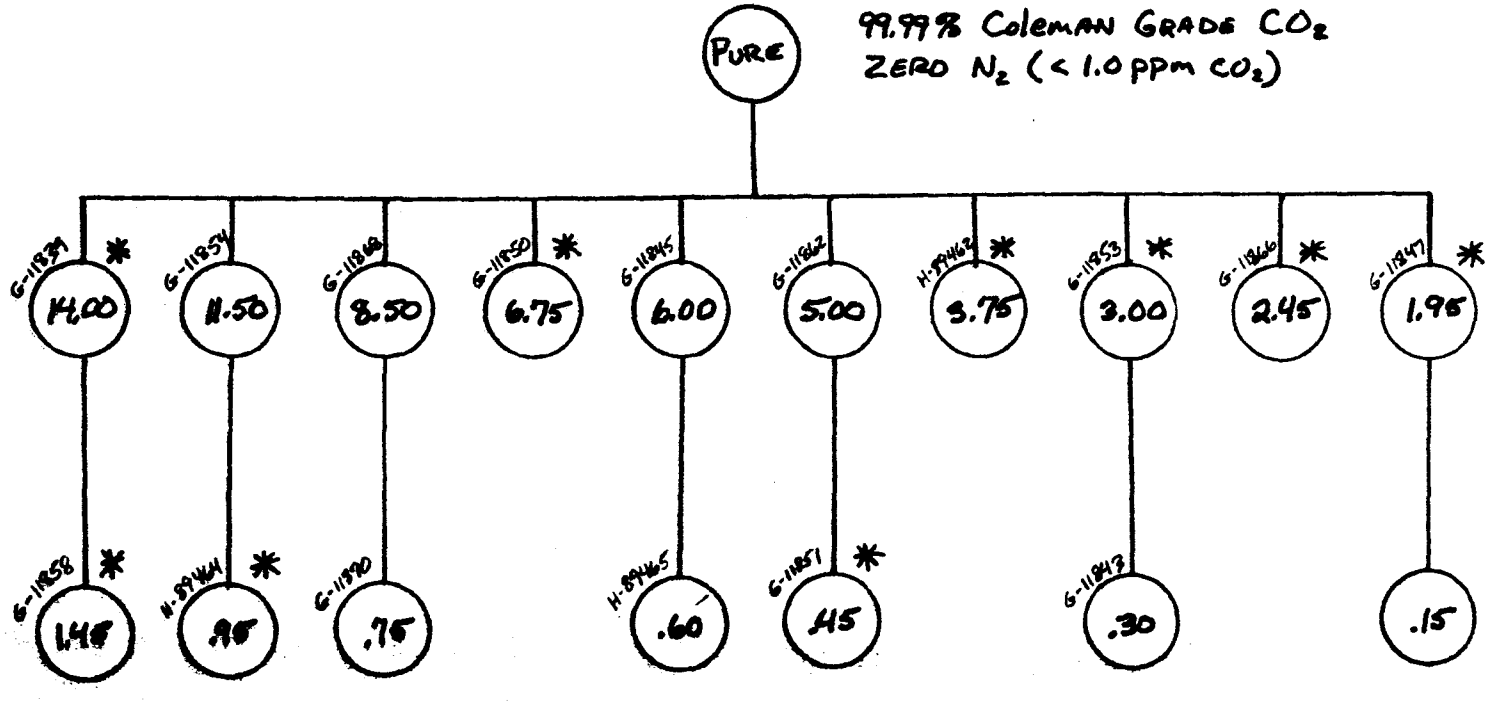
30													
31													

EPA 2d.

CO_2/N_2 GRAVIMETRIC BLENDS
($\%\ CO_2$)

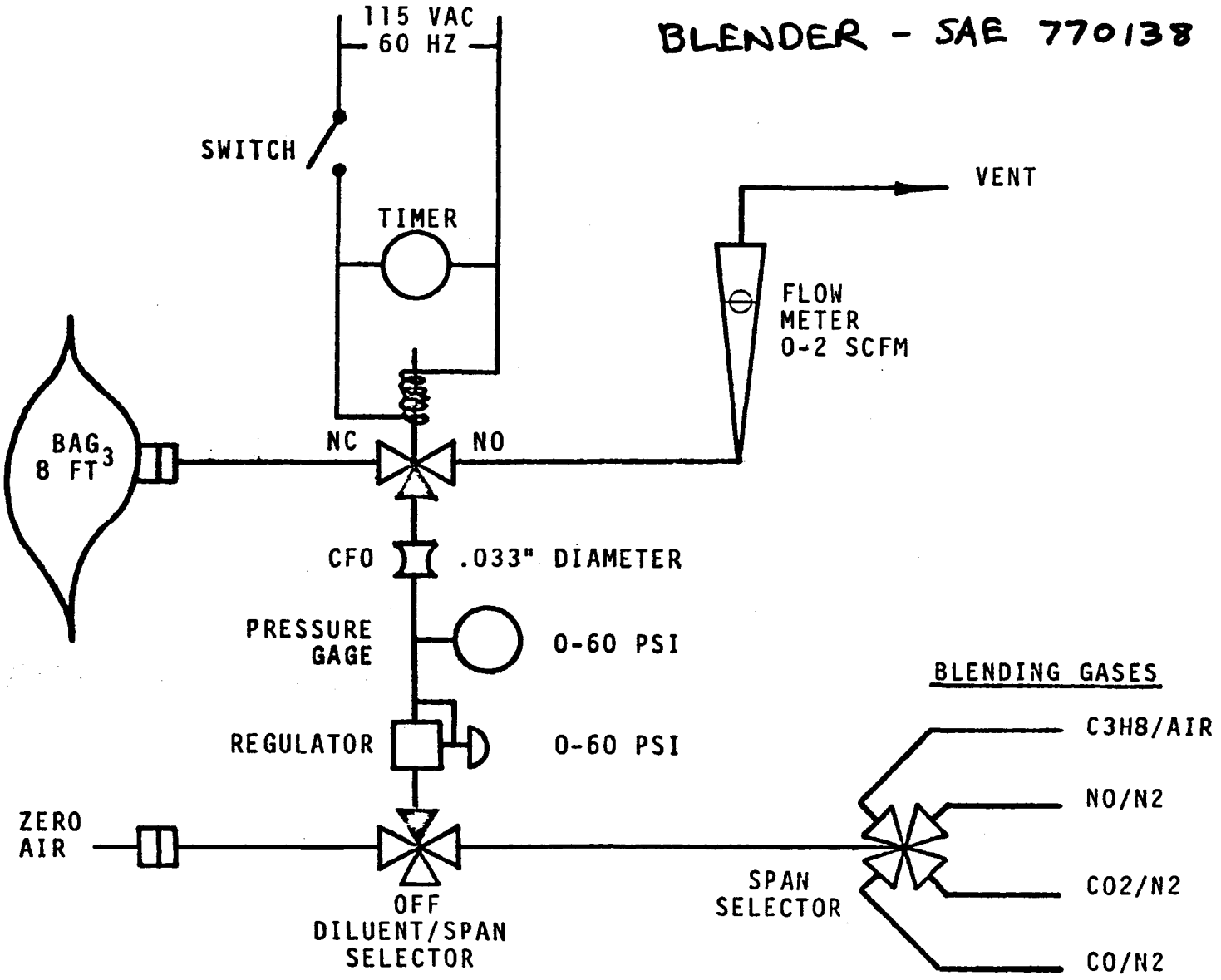


* = NBS SRM

EPA

CFO CROSSCHECK BAG BLENDER - SAE 770138

2e



EPA

3a.

ANALYZERS FOR GAS ANALYSIS

GAS BLEND	PRIMARY	OTHER
PROPANE/AIR PROPANE/N_2	FLAME IONIZATION DETECTOR (FID)	GAS CHROMATOGRAPH W/FID OR THERMO-CONDUCTIVITY DETECTOR (TC)
CO/AIR CO/N_2	NON-DISPERSIVE INFRARED (NDIR)	GC W/TC OR METHANATOR & FID, CORRELATION SPECTROMETER
CO_2/AIR CO_2/N_2	NDIR	GC W/TC OR METHANATOR & FID, CORRELATION SPECTROMETER
NO/N_2	CHEMILUMINESCENT ANALYZER (CL)	NON-DISPERSIVE ULTRAVIOLET NDUV, NDIR, CORRELATION SPECTROMETER

EPA

36.

PRECISION OF ANALYZERS

$$\text{PRECISION OF MEAS.} \approx \frac{2 \times \text{PRECISION OF ANALYZER}}{\sqrt{\text{NO. OF READINGS}}}$$

ANALYZER	PRECISION (1σ)*	RANGE
FID	≈ 0.05 PPM	0-25 PPM PROPANE
NDIR-CO	≈ .2 PPM	0-500 PPM CO
NDIR-CO_2	≈ .004% CO_2	0-4% CO_2
CL-NOx	≈ 0.3 PPM	0-100 PPM NO

* PRECISION WITH A 3 SECOND ELECTRONIC TIME CONSTANT
PRECISION OF ANALYZER DOES NOT INCLUDE PRECISION OF READOUT DEVICE.

EPA
3c

LIMITATIONS

ANALYZER	AREA OF CONCERN
FID	PRESSURE REGULATOR TYPE OF FUEL
NDIR	0.1% FS → 0.4" H_2O PRESSURE → 0.3° C. DEMODULATOR PHASING (NOISE) STABILITY (POWER INTERRUPTION)
CL	PRESSURE REGULATOR NOx CONVERTER O_3 GENERATOR - VOLTAGE SENSITIVE
GC	MAY NOT MEASURE HC IMPURITIES

A Description of the EPA Exhaust Gas Analyzer Calibration Program

I. Background.

A. Curve fitting techniques examined by EPA.

1. Least squares regression techniques.

a. Beers-Lambert equation:

$$y = \frac{\ln (1 - K_1 x)}{K_2}$$

where y = gas concentration,
x = instrument deflection.

b. Quadratic polynomial with a zero intercept:

$$y = a_3 x^2 + a_2 x + 0$$

c. Cubic rational polynomial:

$$y = \frac{x}{a_4 x^3 + a_3 x^2 + a_2 x + a_1}$$

d. Fourth-degree polynomial:

$$y = a_5 x^4 + a_4 x^3 + a_3 x^2 + a_2 x + a_1 .$$

2. Interpolation techniques.

   a. Piecewise linear interpolation.

   b. Piecewise Lagrangian interpolation.

   c. Cubic spline fitting.

B. History of EPA calibration software.

1. Before January 1974. EPA used quadratic polynomial curves with a zero intercept.

2. January 1974. EPA examined several regression techniques and concluded that curves with two coefficients were not sufficiently accurate.

3. January 1974 to June 1976. EPA used a cubic rational polynomial for calibration.

   a. Advantages.

      (1). Accurate.

      (2). Good for highly nonlinear instruments.

   b. Disadvantages.

      (1). The equation is difficult to analyze mathematically.

      (2). Statistical literature is less complete for this equation than some others.

      (3). The curve can be discontinuous in the region of interest.

      (4). The computer software required double precision arithmetic.

      (5). The computer program used special system dependent software.

4. January 1975. Clark Chapin developed a computer program used by EPA contractors. It used fourth-degree polynomial equations with a zero constant term.

5. January 1975 to December 1975. EPA made a brief examination of interpolation techniques. They were compared against least square regression curves.

6. June 1976 to present. EPA implemented calibration software that used fourth-degree polynomial equations with and without a zero constant term.

II. Features supported by the present EPA exhaust gas analyzer program.

A. Calibration gas sources.

1. Gas cylinders.

2. Calibrated Brooks gas blender.

B. Curve fitting options.

1. Software zero and span.

a. No software zero and span (light duty testing).

b. Correction for linear instrument signal drift and offset (heavy duty engine R&D testing).

c. Correction for linear signal drift and pressure (not used now).

d. Correction for linear signal drift, pressure, and temperature (not supported, but easily added).

2. Orthogonal polynomial regression.

a. Degree of fit: 1 to 4.

b. Intercept

(1). Forced through the origin.

(2). Not forced through the origin.

c. Data points weighted.

(1). Weighting factor of 1.

(2). Weighting factor of 1 / Concentration.

C. Determine concentration of unknown cylinders.

1. From the calibration curve.

2. From a linear interpolation/extrapolation from nearby data points.

D. Quality control warning conditions.

1. Illegal input data.

2. Negative slope at the origin.

3. Two inflection points over the range of deflection of a valid calibration curve (possible maximum or minimum in the curve).

4. Fewer than 8 data points for a fourth-degree fit.

5. Low-point deflection less than 10% of full-scale when the data points are given a 1 / Concentration weighting.

6. Curve nonlinearity exceeds 15% of full-scale.

E. Curves are stored in an instrument data base.

1. The data base will be used for all instruments.

2. Curves may be identified two ways:

a. By individual instrument identification.

(1). Instrument ID number.

(2). Calibration curve function (concentration, Oxygen correction, etc.).

(3). Standard instrument range.

(4). Test date and time.

b. By location.

(1). Test site name.

(2). Usage (How the instrument is used when a site has more than one instrument of the same type).

(3). Calibration curve function.

(4). Standard instrument range.

(5). Test date and time.

3. A variation of the instrument identification nomenclature can be used to identify instruments connected to a real time data acquisition system.

F. Other features of the program.

1. Written in IBM Fortran IV.

2. Uses double precision arithmetic (single precision should work, but with less accuracy).

3. Does not use special system dependent software except for file storage.

4. Implements standard EPA codes for

a. Temperature units.

b. Pressure units.

c. Instrument ranges.

d. Gas types.

5. Somewhat large and expensive to run.

6. Cylinder results are stored in an output file for further quality control processing.

III. Future.

A. Implement a gas cylinder data base.

B. Make a thorough comparison of curve fitting techniques.

References

The Use of NBS Reference Gases in Mobile Source Emission Testing, C. Don Paulsell, August 1975.

The remaining references are all internal EPA documents.

Orthogonal Polynomial Calibration, Eric Zellin, August, 1976.

Software Zero and Span for a Laboratory Computer System, Eric Zellin, August 1975.

Computer program documentation

Gas Analyzer Calibration Program Documentation

Software Zero and Span Documentation

EPA Instrument Data Base System Documentation

5.

Quality Assurance

Position Paper

On

Calibration Gas Management

by

Don Paulsell

March, 1976

Environmental Protection Agency
Office of Air and Waste Management
Mobile Source Air Pollution Control
Program Management Division
Quality Assurance Program
Ann Arbor, Michigan

Introduction: This paper discusses five areas of calibration gas management which can be developed into a system that documents the quality control and quantifies the integrity of any gas analysis made in the EPA Mobile Source Emissions Laboratory. These areas encompass such topics as standards traceability, analysis instrumentation, calibration correlation, gas inventory control, and data processing and documentation provisions.

Gas Inventory Management

Before the system can deal with the questions of quality control in gas standards, the total number of standards required to perform the job must be determined. For mobile source emission analysis work, the instrumentation ranges have been standardized for all components measured and are shown in Table A. (These range codes are scheduled for implementation in April 1976.) The instruments used in gas analyses are both linear and non-linear in their response characteristics. The current Federal Register requirements call for two point linear and eight point nonlinear calibration curves.

Future requirements range from three point linear and six point nonlinear to six point general calibration curves.

Tables B-1 through B-5 show the ranges normally used in both light duty and heavy duty sample analyses for each component. These tables also illustrate how a sequential arrangement of secondary standards permit 8, 6, 4, 3, and 2 point calibrations on the applicable instruments. In some cases, 11 and 12 point curves can be run to improve the confidence level of the lower end of the calibration curve.

Therefore, the achievement of the sequential ordering of secondary standards becomes the focal point of the gas inventory management.

The sequential ordering of gas standards also provides the advantages of maximum calibration coverage from the minimum number of cylinders. Use of a singular concentration on several ranges provides good range to range correlation. This, in turn, facilitates the monitoring of all cylinders concentrations relative to their adjacent bottles by use of analyzer curve fit deviations obtained whenever a curve calibration is done.

Tables B-1 through B-5 also show the nominal values of the working span gases needed for the systems in use. The number of cylinders which must be inventoried is a function of the number of systems in use and the relative consumption rates of the ranges used. The total number of cylinders needed has been estimated in Table C-1.

The use of a formalized inventory control program to monitor the usage rates and the cylinder receiving and shipping records will provide the information needed to prevent excess stock of some concentrations and shortages of others. Such a program has been attempted in the MSAPC, but the failure to update the computer file has caused the system to be inoperative.

Figure 1 illustrates a cylinder inventory tag which could be used to improve the flow of information about cylinder inventory. This tag could be printed with two removable carbon copies over the heavy gauge paper tag that would be permanently attached to the cylinder while it was inventoried at the MSAPC Laboratory. When the cylinders are shipped from the building, the shipping date is entered and the tag is removed and processed to remove the cylinder from the data file.

If the data file is updated regularly, the supporting inventory program can provide information about cylinder demurrage charges and gas blends which need to be ordered.

Figure 1 also illustrates additional information which could be kept with the cylinder.

Gas Standards Correlation

Once the nominal concentrations and quantities of gases have been established and inventoried, the true value of the gas concentration must be determined. The process of "naming" a mixture is actually a correlation test between two known standards and the unknown.

The accuracy and integrity of this naming process is dependent upon the gases which are used for the known values. Specific quality control provisions must be used in the naming process to assure the most precise analysis.

The MSAPC conducted an interagency agreement with NBS in 1972 to develop several gas mixtures for light duty vehicle testing and to make these certified values available to the public. Reviewing the values shown in Tables B-1 to B-5, one observes these NBS standards do not adequately cover the spectrum of gas mixtures used in mobile source testing.

The MSAPC has developed the capability to blend gas mixtures on a gravimetric basis and therefore, has the ability to duplicate and extrapolate the work of NBS. Tables B-1 to B-5 show the values of the gravimetric blends which are to be maintained as primary blends.

In the process of gas correlation, the relationship between the NBS standards and the MSAPC primary blends must be quantified and assured. If the MSAPC gravimetrics correlate at the NBS points and also correlate with themselves, the two sets of primary standards can be accepted as equivalent.

The next step in the gas correlation process is to quantify the relationship between the primary blends and the secondary standards. This is done in three steps.

First, each secondary standard must be "named" with respect to the two closest bracketing primary blends. The second step is to "name" each secondary standard relative to its adjacent secondary standards. The final step is to correlate all primary and secondary mixtures in groups of ten sequential secondary values. Each group of ten overlaps by five on the next group. The three values obtained from these steps should agree within 1% and the average of the three is the best name which can be placed on the secondary mixture.

There are two additional techniques which can be used to monitor the secondary standards on a continuous basis. The first technique involves a control chart for each secondary, using the deviations from the best fit curves obtained during all analyzer calibrations. The sequential arrangement of secondary standards provides for overlap on different instrument ranges; the use of 8 to 12 data points per curve provides an excellent data base for improving the confidence on the secondary name and for monitoring the cylinder for deterioration. For example, if 20 calibration curves have used the 240ppm CO/N2 secondary standard as low, mid, and high scale data points, and the average curve fit value is 239ppm, then 239ppm is the best statistical value for that secondary.

The second technique which can be used to verify the integrity of a set of secondary standards from the highest to lowest value is to make a one-step dilution of a 10:1 ratio by the gravimetric method or by use of the critical flow orifice bag blender. This blend is then correlated to the closest two secondary standards bracketing the blended concentration. The calculated and indicated values should agree within 2%.

A final comment needs to be made with respect to the accuracy limitations of the two point straight line fit between the known standards, from which the unknown value is calculated. It is apparent that an error is caused in the analysis if the instrument response is not linear. Quality control provisions have been developed to limit the level of uncertainty associated with a gas correlation on a nonlinear instrument.

The QC provisions are:

1. Use an instrument with minimum nonlinearity, less than 10%.

2. Perform the analysis in the upper half of the range output.

3. Bracket the unknown with the closest available standards. The interval should not exceed 15 percent of full scale for nonlinearities of 10%.

These criteria are easily met by the FID and chemiluminescent analyzers; therefore, the 15 division interval limit can be extended to about 30, but the upper half of the range should still be used. Additional discussion regarding the analysis instrumentation will be the subject of the next section.

Analysis Instrumentation

The use of the linear interpolation between known concentrations to calculate the value of the unknown gas provides a simple method which can be used on any instrument that will respond to the component of interest.

Any of the analyzers used in mobile source testing that are in good operating condition and meet the QC criteria outlined earlier can be used for gas naming.

The FID is used for analyzing all the hydrocarbon mixtures rather than the NDIR n-Hexane analyzer. The CL (Chemiluminescent) analyzer is used for correlating NO/N2 mixtures. These mixtures must be named as both NO/N2 and NOX/N2 to assure the criteria on NO2 content, (less than 5% of value). Therefore, the converter efficiency test should also be verified before NOX/N2 correlations are done.

Daily use of the analyzer systems for vehicle testing normally precludes their use for conducting gas correlation programs. Since gas correlation is an ongoing activity, the functional groups responsible should maintain an analyzer system that can be used at any time.

As part of the MSAPC/NBS interagency agreement on gas standards, a comparator was developed to name HC, CO, and CO2 binary blends. This comparator utilized a hot nickel catalyst to convert CO and CO2 to CH4, to permit their responses to be detected using a FID. This unit has the inherent advantages of linear behavior and a broad range of sensitivities. It is recommended that this type of comparator be used as a supplemental method to verify gas mixture concentrations when discrepancies are detected or the other analyzers do not meet the linearity criteria.

Analyzer Calibrations

Once the process of correlating the primary and secondary gases has been done, the secondary gases are ready for use in instrument calibration. Tables B-1 to B-5 illustrate which secondary gases are to be used on each standard range.

In general, the nonlinear CO and CO2 analyzers have 8 point curves shown, but in some cases, 12 point curves can be performed between 15 and 100 percent of fullscale. Whenever possible, this should be done in order to improve the confidence of the lower portion of the curve. As mentioned earlier, calibration data are also used to assess the consistency of a secondary value as well as to detect any deterioration. This is another reason for including all the secondary mixtures on a curve.

The MSAPC uses a fourth degree polynomial equation, forced thru zero, to define nonlinear analyzer response curves. This equation is also weighted to minimize the percent of point deviations. For this reason, the lowest data point used in a calibration should normally be at 15 percent of full scale and should never be below 10 percent.

During the calibration process, all the working span gases that are plumbed to the analyzer and that respond in the 15-100 percent of full scale interval should be flowed and the analyzer response recorded. The point is not included as a data point for the curve fit, but is entered as a point to be named from the two adjacent secondary standards as well as from the curve fit. These two values as well as the original name placed on the cylinder should agree within a band of ± 1% of the average value of the three readings.

The span points for all the instrument ranges should be updated by computer on a monthly basis. If the working gas is changed during the month, its value must be verified against the previous working gas and a new list of span points should be printed and posted. If the previous working gas is completely empty, the secondary standards should be brought to an analyzer to verify the value of the new working gas. All systems using that gas would then get a new update on the span points.

This part of the program should also be interfaced with the gas inventory program to alert the inventory controller that a cylinder has been put into use and should be replenished.

There are two additional techniques which are available for validating and correlating analyzer calibrations.

The first technique is the daily cross check sample. This procedure has been specified in TPM-401. The schedule is repeated every two weeks and all normally used ranges are checked at low, mid and high scale values. The correlation blends are made by use of a precise critical flow orifice dilution device. The parent blends for this device are named as secondary values from the primary blends. Therefore, the data analysis not only indicates how each analyzer relates to the average response of all systems, but also shows how each system and the average of all systems relate to a theoretically absolute value.

As part of the bag analysis, the span points used in the analysis are recorded and compared to the values on file for that range. This provision will flag any curve that has received a new span point which has not been implemented. Conversely, if a bottle has been changed to a new concentration and the computer file has not been updated, the error will show up in the analysis.

The second technique which has been evaluated for checking analyzer calibrations involves the use of a precision blending device. This device is used to precisely dilute a span gas with zero gas to generate a series of data points which define the curve shape. The analyzer calibration data analysis program has provisions for using this type of device. A precision dilution device can also be used in the correlation of secondary standards using a primary blend as one input to the device.

Data Processing Provisions

So far this paper has discussed how to establish a gas inventory, how to correlate all standards and to document their traceability to an NBS SRM, how to employ the analysis instrumentation in the naming process, and how to properly calibrate the instruments to assure range to range correlations. This section of the paper deals with an aspect of quality control that interfaces with all these steps.

Data processing and analysis programs are a vital component of the calibration gas management process. The volume of data handled and the necessity to correlate data from one system to another make automatic data processing a prerequisite to efficient quality control in this area.

Figure 2 illustrates how all the forementioned procedures and techniques combine in a consolidated scheme whose focal point is the data analysis programs. Each of the particular programs used must incorporate quality control provisions wherever possible to automatically monitor and validate calibration gas data.

Without elaborating extensively on the details of each data analysis program, the following paragraph summarize the capabilities of each one.

(A) Gravimetric Blending TPM - 101

This procedure explains how gravimetric blends are prepared from pure components or other gravimetric blends. The data analysis program calculates the mass ratio concentration from the gravimetric masses of the input data. These data are printed out and are also stored in a file for retrieval of mass ratio values for use in the computation of a stepwise dilution. These cylinders and their values are also entered into the inventory data base.

(B) Gas Analysis TPM - 102

This procedure is the two point linear bracketing technique used to name a secondary standard from a primary blend. All working gases and secondary standards must have this relationship established as a reference point.

The calibration curve analysis program has the capabiltity to crosscheck the working gas value to the secondary standards used to generate the curve.

The importance of having the relationship between primary and secondary gases quantified becomes apparent if an error is discovered in any of the concentrations. The data can be corrected or compared without having to repeat the actual analysis.

(C) Analyzer Calibrations TPM - 203

The use of sequential secondary standards provides the means to perform calibrations which use as many as 12 data points. The analysis program can handle as many as 20 points, some of which can be non data points, in which case they are named from the best fit curve.

The program also names (verifies) the working gas concentration and determines the set point. The best fit values for each secondary standard are output to the inventory file for later analysis. This provides comparative data on adjacent secondary gases in both the two point configuration as well as the best fit curve value. When 20 curve values are received on a secondary, the average can be determined or longterm deterioration can be assessed.

(D) Span Set and Curve Check

No standard test procedure has been written to perform this function. At the present time, span set points are determined by simply flowing the span gas at the time of calibration. The highest secondary is essentially used as the span point in this case.

This technique is adequate in most calibrations, but when several analyzers are spanned from the same source, and each analyzer names the source as a different value, the confidence of the span point is questionable.

This function provides the mechanism to quantify the accuracy of the set point. It also provides the means to change a span cylinder and to determine new set points for all systems using the gas.

(E) Analyzer Correlation

This procedure has been computerized to provide a daily assessment of site-to-site analysis correlation. It statistically quantifies the variability of each instrument and indicates when a system is consistently high or low.

The program also provides quality control comments about when calibrations are due and when a system differs from expected behavior.

(F) Sample Analysis

The purpose of all the forementioned procedures is to assure that the highest degree of accuracy is obtained during a vehicle sample analysis and that all sites produce the same value for a sample. From gas naming to calibrations to verifications, the data processing programs are providing the instrument file data needed to determine the value of the unknown sample.

Conclusions and Recommendations

The previous five sections of this paper have discussed the aspects of quality control which must be achieved in the following areas of calibration gas management.

A. Gas Inventory Management
B. Gas Standards Correlation
C. Analysis Instrumentation
D. Analyzer Calibrations and correlations
E. Data Processing Provisions

Some of these areas are more well developed than others within the MSAPC. However, none of them have been completely addressed with regard to quality control. As an initial outline of the tasks which need work to further those quality control objectives, the following actions are recommended.

1. Establish and maintain the gravimetric blends shown in Tables B-1 to B-5.

2. Sequentially arrange the secondary standards shown in Tables B-1 to B-5 on six bottle carts as shown in Table C-2.

3. Obtain any secondary values which have not been inventoried.

4. Evaluate the characteristics of instrumentation for use in gas standards correlations.

5. Correlate all gravimetric and secondary standards by two point and overlapping curve techniques.

6. Calibrate and verify the precision blender for curve checks and gas correlations.

7. Develop a reliable and accurate inventory control program.

8. Develop and implement more comprehensive working gas implementation and monitoring procedures.

9. Establish a continuous monitoring program for gravimetric, NBS, and secondary standards.

FIGURE 1 - Gas Cylinder Inventory Control Record

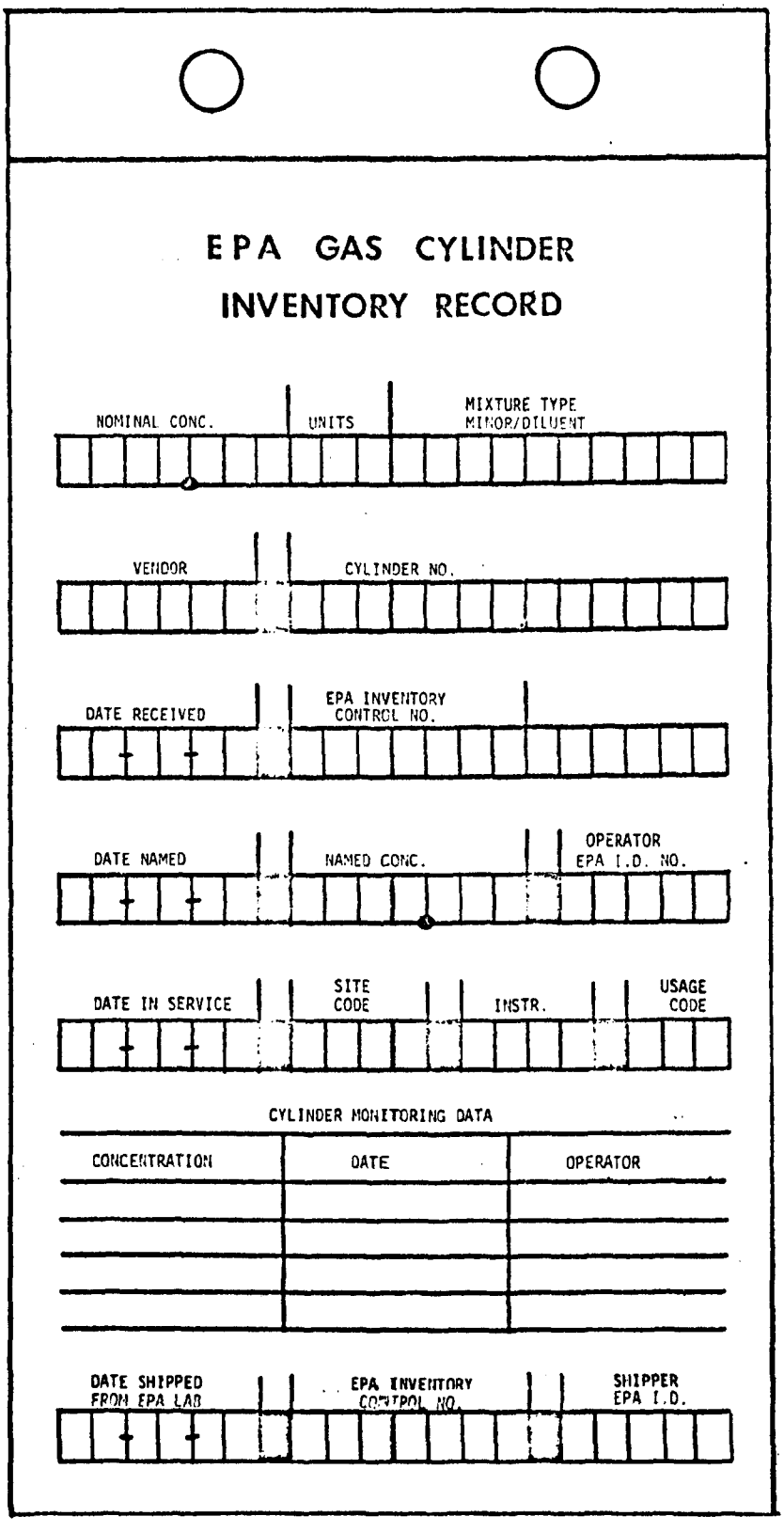


TABLE A — INSTRUMENT LABORATORY STANDARD RANGE CODES

LSR CODES FOR GAS ANALYZERS

RANGE CODE	CONCENTRATION (PPM)	PERCENT (%)	
28	0 - 1,000,000	1 - 100	
27	0 - 500,000	0 - 50	
26	0 - 250,000	0 - 25	
25	0 - 100,000	0 - 10	
24	0 - 50,000	0 - 5	(4) OPTIMIZES
23	0 - 25,000	0 - 2.5	(2) FOR FUEL
22	0 - 10,000	0 - 1.0	ECONOMY
21	0 - 5,000	0 - .5	TESTS
20	0 - 2,500		
19	0 - 1,000		
18	0 - 500		
17	0 - 250		
16	0 - 100		
15	0 - 50		
14	0 - 25		
13	0 - 10		
12	0 - 5		
11	0 - 2.5		
10	0 - 1.0		
09	0 - .5		
07	0 - .10		
06	0 - .050		
05	0 - .025		
04	0 - .010		
03	0 - .0050		
02	0 - .0025		
01	0 - .0010		

C3H8/AIR CALIBRATION GASES TABLE B - 1

Working Span Gases	No. of Cyls.	EPA NBS SRMs	EPA Primary Blends	EPA Secondary Standards	FULL SCALE CONCENTRATIONS AND % OF FULL SCALE VALUES																	
					10	%FS	40 13	%FS	25	%FS	100 33	%FS	50	%FS	100	%FS	400 133	%FS	250	%FS	1000 333	%FS	PPMC 500	%FS	1000	%FS
			2	1.5	x	15																				
		2.83	3	3.0	x	30	x	22																		
				3.75			x	28	x	15																
			5	4.5	x	45					x	14														
				6.0	x	60	x	45																		
			7	7.5	x	75	x	56	x	24			x	15												
9		9.52	9	9.5	x	95	x	71			x	28														
12				12.0			x	90	x	48																
			15	15.0					x	60	x	45	x	30	x	15										
				19.0					x	76	x	57					x	14								
23			23	22.5					x	90	x	67	x	45												
30				30.0							x	90	x	60	x	30										
				37.5									x	75			x	28	x	15						
45		46.5	45	45.0									x	90	x	45					x	14				
				60.0											x	60	x	45								
			70	75.0											x	75	x	56	x	30			x	15		
90		93.6	95	95.0											x	95	x	71			x	28				
120				112													x	84	x	45						
			150	150															x	60	x	45	x	30	x	15
				180															x	72	x	54				
230				225															x	90	x	68	x	45		
300			300	300																	x	90	x	60	x	30
				375																			x	75		
450		477.	450	450																			x	90	x	45
				600																					x	60
				750																					x	75
900			900	900																					x	90
			1200	1200																						

NOTE: All concentration values are listed as PPM Propane.

C3H8/N2 CALIBRATION STANDARDS

TABLE B - 2

Working Span Gases	No. of Cyls.	EPA Primary Blends	EPA Secondary Standards	FULL SCALE CONCENTRATIONS AND % OF FULL SCALE VALUES																									
				40				100						400				1000				4000		10000		40000		PPMC	
				13.3	%FS	25	%FS	33	%FS	50	%FS	100	%FS	133	%FS	250	%FS	333	%FS	500	%FS	1000	%FS	1333	%FS	3333	%FS	13333	%FS
		4	4	x	30	x	16																						
		8	8	x	60	x	32	x	24	x	16																		
12		12	12	x	90	x	48	x	36	x	24																		
		20	20			x	80	x	60	x	40	x	20	x	15														
30			30					x	90	x	60	x	30	x	22														
		40	40							x	80	x	40	x	30	x	16												
		80	80									x	80	x	60	x	32	x	24	x	16								
120		120	120											x	90	x	48	x	36	x	24								
		200	200													x	80	x	60	x	40	x	20	x	15				
300			300															x	90	x	60	x	30	x	22				
		400	400																	x	80	x	40	x	30				
		800	800																			x	80	x	60	x	24		
1200		1200	1200																					x	90	x	36		
1800*		2000	2000																							x	60	x	15
3000			3000																							x	90	x	22
		4000	4000																									x	30
		8000	8000																									x	60
12000		12000	12000																									x	90
		15000	15000																										
18000*		20000	20000																										

NOTE: All concentration values are listed as PPM Propane.
NBS SRMs have not been developed for C3H8/N2.

* Span gases for 1000and 10,000 ppm N-Hexane
NDIR analyzers for heavy duty engine testing.

CO/N2 CALIBRATION GASES TABLE B - 3

Working Span Gases	No. of Cyls.	EPA NBS SRMs	EPA Primary Blends	EPA Secondary Standards	FULL SCALE CONCENTRATIONS AND % OF FULL SCALE VALUES																	
					50	%FS	100	%FS	250	%FS	500	%FS	1000	%FS	2500	%FS	5000	%FS	1.0	%FS	2.0	%FS	4.0	%FS	10	%FS
		9.72	9	8	x	16																		
				13	x	26																		
			20	20	x	40	x	20																
				25	x	50	x	25																
			30	30	x	60	x	30																
				35	x	70	x	35	x	14														
				40	x	80	x	40																
45		47.1	45	48	x	96	x	48	x	19														
				75			x	75	x	30	x	15												
		94.7	90	95			x	95	x	38														
				130					x	52	x	26												
			160	160					x	64			x	16										
				200					x	80	x	40												
230			230	240					x	96	x	48	x	24										
			300	300							x	60												
			360	360							x	72	x	36	x	14								
			400	420							x	84	x	42										
450		484.	450	490							x	98	x	49										
			600	650									x	65	x	26								
			780	800									x	80			x	16						
900		956.	950	950									x	95	x	38								
			1300	1250											x	50	x	25						
				1500											x	60			x	15				
			1800	1750											x	70								
				2000											x	80	x	40						
2300			2300	2400											x	96	x	48	x	24				
				3000													x	60			x	15		
			3600	3500													x	70						
				4000													x	80	x	40				
4500			4500	4750													x	95	x	48	x	24		
			.60	.60															x	60			x	15
				.70															x	70				
			.75	.80															x	80	x	40		
.90			.90	.95															x	95	x	47	x	24
				1.20																	x	60		
			1.35	1.40																	x	70		
			1.60	1.60																	x	80	x	40	x	16
1.80			1.90	1.90																	x	95	x	48		
			2.50	2.40																			x	60	x	24
				2.80																			x	70		
			3.00	3.20																			x	80		
3.60			3.80	3.80																			x	95	x	38
			4.90	5.00																					x	50
			6.00	6.00																					x	60
				7.00																					x	70
			7.50	8.00																					x	80
9.00			9.00	9.50																					x	95

CO_2/N_2 CALIBRATION GASES

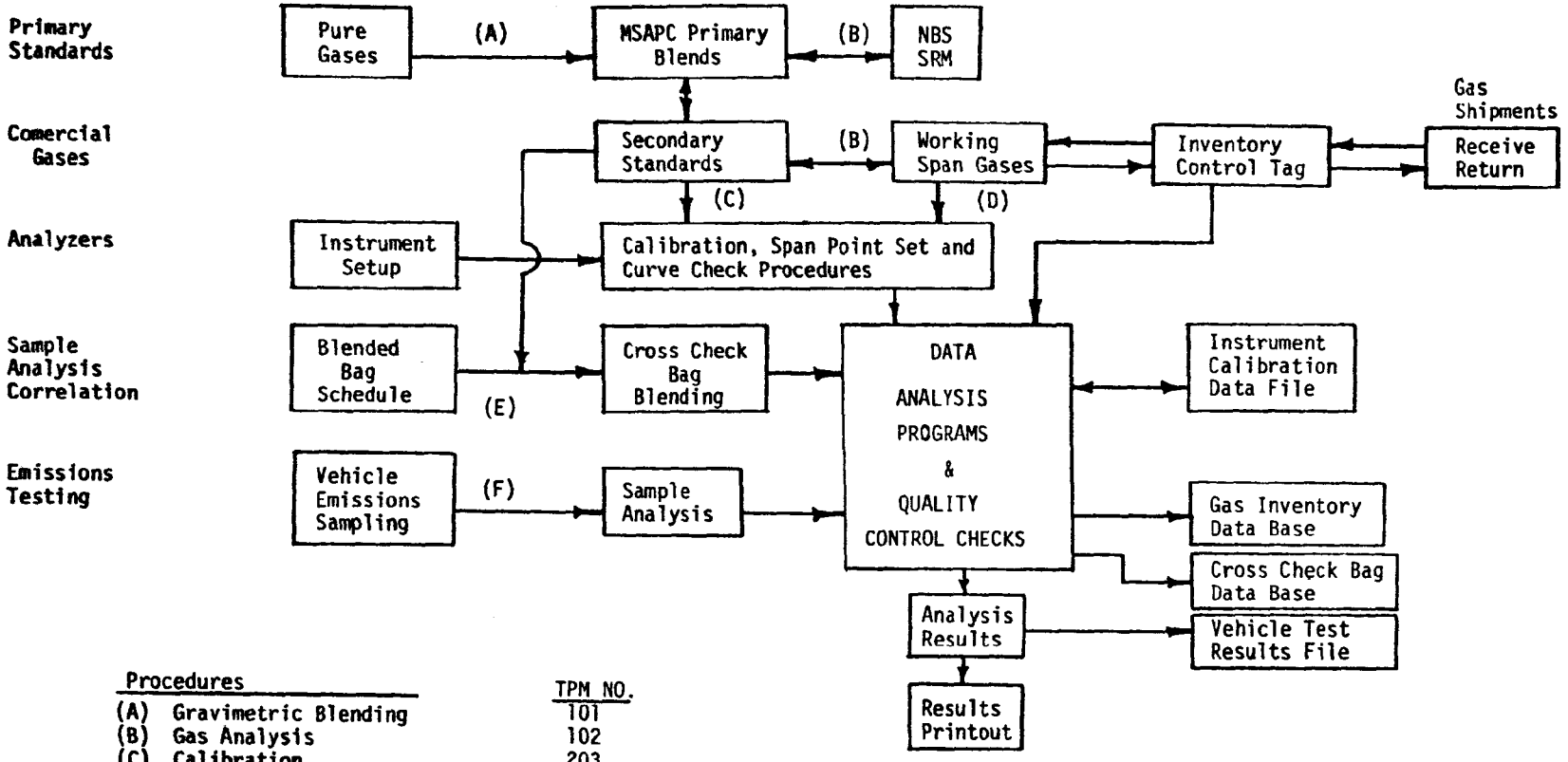
TABLE B - 4

Working Span Gases	No. of Cyls.	EPA NBS SRMs	EPA Primary Blends	EPA Secondary Standards	FULL SCALE CONCENTRATIONS AND % OF FULL SCALE VALUES											
					1.0	%FS	2.0	%FS	3.0	%FS	4.0	%FS	5.0	%FS	10.	%FS	15.	%FS
				.15	x	15												
			.230	.25	x	25												
			.423	.40	x	40	x	20										
				.50	x	50	x	25	x	17								
			.620	.60	x	60												
				.70	x	70					x	18						
			.834	.80	x	80	x	40	x	27			x	16				
.90		.922	1.02	.95	x	95	x	47										
			1.22	1.20			x	60	x	40	x	30	x	24				
			1.45	1.40			x	70										
			1.68	1.60			x	80	x	47	x	40			x	16		
1.80			1.97	1.90			x	95	x	63	x	48	x	38				
			2.20	2.10					x	70								
			2.45	2.40					x	80	x	60	x	48	x	24	x	16
2.70			2.75	2.90					x	97	x	73	x	58				
			3.04	3.35							x	84	x	67	x	34		
3.60			3.75	3.90							x	98	x	78	x	39	x	23
4.50			5.02	4.75									x	95	x	47		
				6.00											x	60	x	40
		7.02	6.77	7.50											x	75	x	50
9.00			8.63	9.00											x	90	x	60
				10.50													x	70
			11.69	12.00													x	80
13.5		14.02	13.86	14.30													x	95
			15.68															

NOX/N2 CALIBRATION GASES TABLE B - 5

Working Span Gases	No. of Cyls.	EPA NBS SRMs	EPA Primary Blends	EPA Secondary Standards	FULL SCALE CONCENTRATIONS AND % OF FULL SCALE VALUES													
					10 %FS	25 %FS	40 %FS	50 %FS	100 %FS	250 %FS	400 %FS	500 %FS	1000 %FS	2500 %FS	4000 %FS			
				1.5	x 15													
			3	3.0	x 30													
				3.75		x 15												
				4.5	x 45													
			6	6.0	x 60		x 15											
				7.5	x 75	x 30		x 15										
9			9	9.0	x 90													
				12.0		x 48	x 30											
			15	15.0		x 60		x 30	x 15									
				18.0		x 72	x 37											
23			23	23.0		x 92	x 57	x 46										
				30.0			x 75	x 60	x 30									
36				36.0			x 90	x 72		x 14								
45		45.9	45	45.0				x 90	x 45									
				60.0					x 60		x 15							
				75.0					x 75	x 30		x 15						
90		93.7	90	90.0					x 90									
				112.0						x 45								
				120.0							x 30							
			135	150.0						x 60		x 30	x 15					
				180.0						x 72	x 45							
230		252	240	235.0						x 94	x 59	x 47						
				300.0							x 75	x 60	x 30					
360				360.0							x 90	x 72		x 15				
450		478	480	450.0								x 90	x 45					
				600.0									x 60		x 15			
			700	750.0									x 75	x 30				
900		995	960	900.0									x 90					
			1200	1200.0										x 48	x 30			
				1500.0										x 60				
			1800	1800.0										x 72	x 45			
				2100.0										x 84				
2400			2400	2400.0										x 96	x 60			
			3000	3000.0											x 75			
3600			3800	3600.0											x 90			

FIGURE 2 - CALIBRATION GAS MANAGEMENT PROCESS



Procedures	TPM NO.
(A) Gravimetric Blending	101
(B) Gas Analysis	102
(C) Calibration	203
(D) Span Set and Curve Check	-
(E) Analyzer Correlation	401
(F) Sample Analysis	707

TABLE C-1 GAS CYLINDER INVENTORY

CALIBRATION GASES

	C3H8/AIR	C3H8/N2	CO/N2	CO2/N2	NOX/N2	O2/N2	TOTAL CYLINDERS
NBS SRMs	5	0	5	3	5	0	18
MSAPC Primary Blends	15	17	31	20	17	8	108
MSAPC Secondary Calibration Gases	28	20	47	24	35	6	160
Six Bottle Carts (Normally Used)	4	3	8	4	6	1	26
Working Gases							
On-Line	28	4	40	28	24	0	124
In Stock	40	6	60	40	36	6	188

FUELS AND ZERO GASES

	N2	AIR	H2/N2	H2/HE	H2	O2	
On-Line	6+TANK	8	8	2	1	2	27
In Stock	20	20	10	4	3	4	61

TOTAL "A" SIZE CYLINDERS	560
TOTAL CYLINDERS	688
TOTAL SIX BOTTLE CARTS	26

CALIBRATION GAS STORAGE CARTS

C3H8 / AIR
ppmp

	3.7	7.5	15.	30.	60.	112.	225.	450.	900.
1.5	4.5	9.5	19.	38.	75.	150.	300.	600.	1200.
3.0	6.0	12.0	22.	45.	95.	180.	375.	750.	

C3H8 / N2
ppmp

20.	80.	300.	1.2K	3K	12K
30.	120.	400.	1.6K	4K	16K
40.	200.	800.	2K	8K	20K

CO / N2
ppm

8.	25.	35.	95.	200.	360.	650.	1250	1500	3500
13.	30.	48.	130.	240.	420.	800.	1750	2000	4000
20.	40.	75.	160.	300.	490.	950.	2400	3000	4750

CO / N2
%

.60	.95	1.6	2.8	5.0	8.0
.70	1.2	1.9	3.2	6.0	9.5
.80	1.4	2.4	3.8	7.0	

CO2 / N2
%

.15	.50	.80	1.4	2.1	3.4	6.0	10.5
.25	.60	.95	1.6	2.4	3.9	7.5	12.0
.40	.70	1.2	1.9	2.9	4.8	9.0	14.3

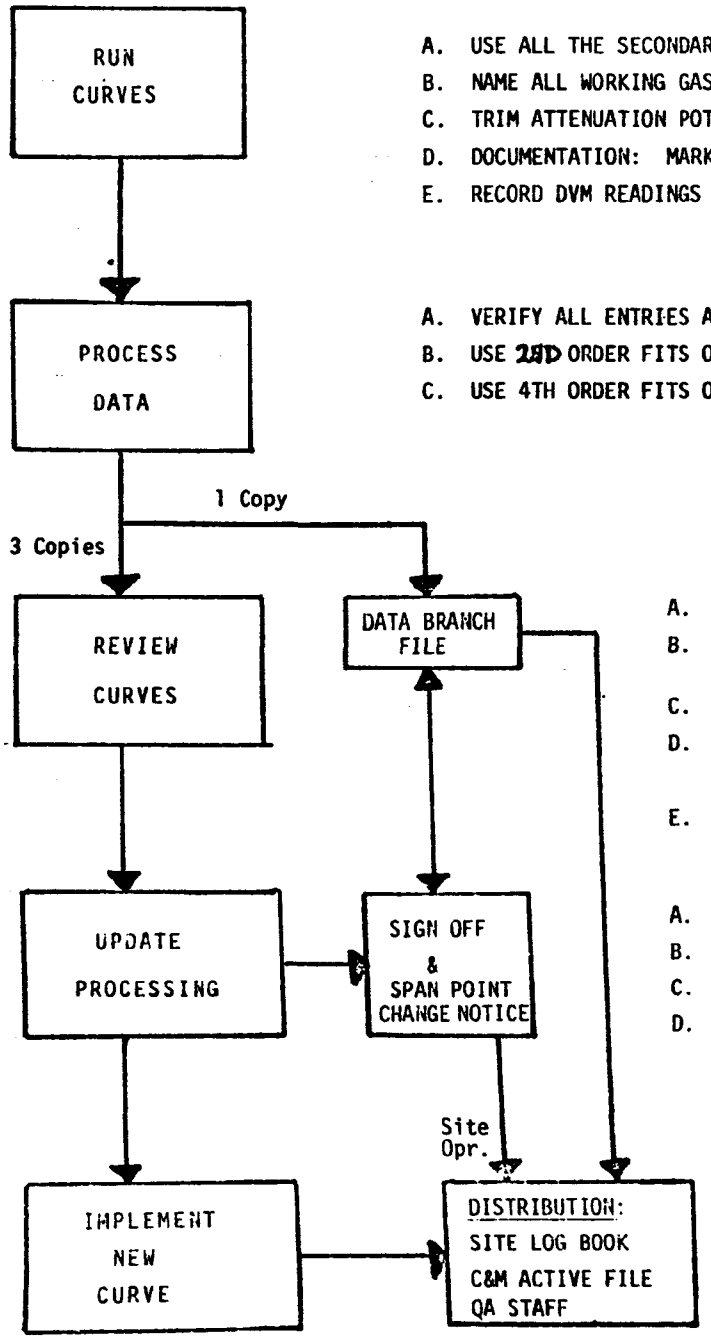
NOX / N2
ppm

	3.8	7.5	15	30	60	112	180	360	750	1500	2400
1.5	4.5	9.0	18	36	75	120	235	450	900	1800	3000
3.0	6.0	12	23	45	90	150	300	600	1200	2100	3600

CALIBRATION CURVE PROCESSING

EPA

6a.



A. USE ALL THE SECONDARY STANDARDS BETWEEN THE TOP VALUE AND 15-20 DIVISIONS
B. NAME ALL WORKING GAS WHICH WILL FIT ON 15-100 INTERVAL
C. TRIM ATTENUATION POTS TO CORRELATE RANGES WHERE APPLICABLE
D. DOCUMENTATION: MARK STRIP CHARTS WITH SITE, DATE, GAS, RANGE, CYL.#, AND CONCENTRATION, ANALYZER PID
E. RECORD DVM READINGS AND CHECK RECORDER CALIBRATION

A. VERIFY ALL ENTRIES AGAINST STRIP CHART (USE DVM VALUES)
B. USE 2ND ORDER FITS ON FIDs AND CLs (01 01 2 2) IF NONLINEAR, USE ORDER ≤(# POINTS - 2)
C. USE 4TH ORDER FITS ON NDIRs (01 01 4 2)

A. VERIFY ALL DATA
B. CHECK DATA POINT DEVIATIONS %PT < 1.0%
AVG%PT < .5%
C. LINEARITY < 10%
D. CHECK QC COMMENTS
1. NO INFLECTIONS, MAX OR MINS.
E. CURVE SHIFT ANY%PT > 2%
AVG%PT > 1%

A. CALCULATE SET POINT BASED ON CYL. CONC. (SEE SPCN)
B. SIGN CURVE SHEET, SPCN, AND SPECIFY EFFECTIVE DATE/TIME
C. RETURN BOTH SHEETS TO DATA BRANCH FOR UPDATE
D. DATA BRANCH WILL MARK OFFICIAL UPDATE DATE/TIME

A. POST SPCN ON ANALYZER
B. CONFIRM USE OF NEW SPAN POINT ON CROSSCHECK
C. NOTIFY DATA VALIDATION OF CHANGE
D. DATA VALIDATION SIGNOFF OF NEW SET POINT

EPA

6b

**** PROCESSED: 14:33:57 12-15-76

****
****
*** ***
*** ANALYZER CALIBRATION CURVE ANALYSIS ***
*** ***
****
****

```
 AAA      000      000     22222
 AAAAA    00000    00000   2222222
AA   AA  00   00  00   00       22
AAAAAAA  00   00  00   00     222
AAAAAAA  00   00  00   00   222
AA   AA   00000    00000   2222222
AA   AA    000      000    2222222
```

END CALIB AT TIME : 0: 0
CALIBRATION DATE :12-15-76
TEST SITE NUMBER : A002
GAS ANALYZED :CO2
DILUENT GAS :NITROGEN
CONCENTRATION UNIT: PCT
STANDARD LAB RANGE: 23
OPERATOR ID NO : 17228

ANALYZER VENDOR :MSA
INSTRUMENT NAME : CO2A
EPA DECAL ID NO : 109642
SIGNAL LEAD :CO2A-C
HARDWARE RANGE :
USAGE : RAGA
CALIB GAS SOURCE :
BLENDER DECAL ID :

SAMPLE FLOW RATE : 6.0 SCFH
MONITOR SET POINT : 5.5 IN H2O
ZERO GAIN SETTING : 0.0
SPAN GAIN SETTING : 0.0
TUNE READING : 0.0
FID AIR PRESSURE : 0.0
FID FUEL PRESSURE : 0.0
FID SAMP PRESSURE : 0.0

VALID DEFL. UPPER LIMIT : 110.000
VALID DEFL. LOWER LIMIT : -10.000
RANGE CHANGE UPPER LIMIT : 100.000
RANGE CHANGE LOWER LIMIT : 20.000
FULL-SCALE (100%) DEFL. : 100.000
FULL-SCALE (100%) VOLTAGE: 10.000
FULL-SCALE (100%) CONC. : 2.5
RECORDER TYPE :DVM

PREVIOUS FILE COMMENT: 0 2.5 PERCENT CO2 INST RANGE 2
FILE COMMENT : 0-2.5 PERCENT CO2
OPERATOR COMMENT : 0-2.5 PERCENT CO2

CYLINDER NUMBER	BLENDER METER READINGS SPAN	BLENDER METER READINGS DILUENT	BLEND RATIO	CONCENTRATIONS CYLINDER (BLENDED)	CONCENTRATIONS CALCULATED	ANALYZER SIGNAL MEASURED X	ANALYZER SIGNAL CORRECTED X	CALIBRATION DATA POINT	CURVE FIT DEVIATIONS % POINT	CURVE FIT DEVIATIONS % FULL-SCALE	CURVE FIT DEVIATIONS % FROM LAST CALIBRATION
	X			0.0			M ------ C				
		X		0.0							
A-9156	0.0	0.0	0.0	2.4060	2.4064	97.200	97.200	X	0.015	0.015	0.059
A-7319	0.0	0.0	0.0	2.2440	2.2514	91.900	91.900		0.0	0.0	0.0
A-8599	0.0	0.0	0.0	1.8950	1.8944	79.200	79.200	X	-0.032	-0.024	0.416
A-8866	0.0	0.0	0.0	1.6890	1.6870	71.500	71.500	X	-0.117	-0.079	0.506
A-9526	0.0	0.0	0.0	1.3800	1.3836	59.800	59.800	X	0.263	0.146	0.588
A-12238	0.0	0.0	0.0	1.1820	1.1836	51.800	51.800	X	0.132	0.063	0.614
A-6256	0.0	0.0	0.0	0.9857	0.9817	43.500	43.500	X	-0.410	-0.162	0.624
A-4570	0.0	0.0	0.0	0.7886	0.7863	35.250	35.250	X	-0.043	-0.014	0.625
A-7631	0.0	0.0	0.0	0.7591	0.7571	34.000	34.000		0.0	0.0	0.0
A-9062	0.0	0.0	0.0	0.6088	0.6105	27.650	27.650	X	0.272	0.067	0.624
A-4610	0.0	0.0	0.0	0.4845	0.4856	22.150	22.150		0.0	0.0	0.0
A-4631	0.0	0.0	0.0	0.3893	0.3890	17.840	17.840	X	-0.082	-0.013	0.634
A-2391	0.0	0.0	0.0	0.2445	0.2449	11.320	11.320		0.0	0.0	0.0
MM-388	0.0	0.0	0.0	2.2680	2.2716	92.600	92.600		0.0	0.0	0.0
								AVERAGE DEVIATION	0.152	0.065	0.521

NONLINEARITY = 4.2 PERCENT

ANALYSIS OF "CYLINDERS TO BE NAMED"

CYLINDER NUMBER	NOMINAL CONCENTRATION (NC)	LINEAR FIT SIGNAL LOW	LINEAR FIT SIGNAL HIGH CYLINDER	LINEAR FIT CALC. CONC. (LC)	CURVE FIT CALC. CONC. (CC)	CONCENTRATION RATIOS NC/CC	CONCENTRATION RATIOS LC/CC
MM-388	2.268	79.200	97.200 92.600	2.275	2.272	0.99840	1.00166

EPA

6b

**** PROCESSED: 14:33:57 12-15-76

****
****
*** ***
*** ANALYZER CALIBRATION CURVE ANALYSIS ***
*** ***
****
****

```
 AAA      000      000     22222
AAAAA    00000    00000   2222222
AA   AA  00   00  00   00      22
AAAAAAA  00   00  00   00    222
AAAAAAA  00   00  00   00  222
AA   AA  00000    00000   2222222
AA   AA   000      000    2222222
```

END CALIB AT TIME : 0: 0	ANALYZER VENDOR :MSA	ZERO SPAN TYPE : 1	
CALIBRATION DATE :12-15-76	INSTRUMENT NAME : CO2A	CURVE FORM : 1	
TEST SITE NUMBER : A002	EPA DECAL ID NO : 109642	DEGREE FIT : 4	
GAS ANALYZED :CO2	SIGNAL LEAD :CO2A-C	WEIGHTING FACTOR : 2	
FULL-SCALE CONC : 2.5	HARDWARE RANGE :		
CONCENTRATION UNIT: PCT	USAGE : BAGA		
STANDARD LAB RANGE: 23	OPERATOR ID NO : 17228		

EQUATIONS AND COEFFICIENTS

$$X_C = X_M$$

$$(A5*X_C^4 + A4*X_C^3 + A3*X_C^2 + A2*X_C + A1) = \text{PCT CO2/NITROGEN}$$

CALIBRATION P(BARO) = 0.0

A1 = 0.0
A2 = 0.2135274E-01
A3 = 0.2373872E-04
A4 = 0.8000588E-07
A5 = 0.3711790E-09

CALIBRATION TABLE PERCENT FULL-SCALE CHART DEFLECTION VS PCT CO2/NITROGEN

0.	0.0																
1.	0.0214	11.	0.2379	21.	0.4597	31.	0.6875	41.	0.9219	51.	1.1639	61.	1.4141	71.	1.6738	81.	1.9438	91.	2.2254
2.	0.0428	12.	0.2598	22.	0.4822	32.	0.7106	42.	0.9458	52.	1.1885	62.	1.4397	72.	1.7003	82.	1.9714	92.	2.2543
3.	0.0643	13.	0.2818	23.	0.5047	33.	0.7338	43.	0.9697	53.	1.2132	63.	1.4653	73.	1.7269	83.	1.9992	93.	2.2832
4.	0.0858	14.	0.3038	24.	0.5274	34.	0.7571	44.	0.9937	54.	1.2380	64.	1.4910	74.	1.7536	84.	2.0270	94.	2.3123
5.	0.1074	15.	0.3259	25.	0.5501	35.	0.7804	45.	1.0178	55.	1.2629	65.	1.5168	75.	1.7805	85.	2.0550	95.	2.3416
6.	0.1290	16.	0.3481	26.	0.5728	36.	0.8038	46.	1.0419	56.	1.2879	66.	1.5427	76.	1.8074	86.	2.0831	96.	2.3709
7.	0.1507	17.	0.3703	27.	0.5956	37.	0.8273	47.	1.0661	57.	1.3130	67.	1.5687	77.	1.8345	87.	2.1113	97.	2.4005
8.	0.1724	18.	0.3925	28.	0.6185	38.	0.8508	48.	1.0904	58.	1.3381	68.	1.5948	78.	1.8616	88.	2.1397	98.	2.4301
9.	0.1942	19.	0.4149	29.	0.6414	39.	0.8745	49.	1.1148	59.	1.3634	69.	1.6211	79.	1.8889	89.	2.1681	99.	2.4599
10.	0.2160	20.	0.4372	30.	0.6644	40.	0.8982	50.	1.1393	60.	1.3887	70.	1.6474	80.	1.9163	90.	2.1967	100.	2.4898

QUALITY CONTROL COMMENTS

THIS CURVE HAS BEEN REVIEWED AND APPROVED FOR OFFICIAL UPDATE. PLEASE UPDATE THE CALIBRATION FILE.

AUTHORIZED SIGNATURE:_____

EFFECTIVE DATE AND TIME:__-__-__ __:__
MON DAY YEAR HR MIN

*** CURVE ON FILE AS A PENDING CALIBRATION.

EPA 6c.

SPAN POINT CHANGE NOTICE

Complete This Form for Each New Span Bottle or Curve Update.

SECTION A

	ANALYZER SITE NO.	A001	A002	A003	
CURRENT SPAN DATA	GAS TYPE	CO_2	CO_2	CO_2	
	RANGE NO.	24	24	24	
	SPAN CYL. NO.	A3480	A3480	A3480	
	BOTTLE CONC. Y3	4.570	4.570	4.570	
	SPAN SET POINT	93.8	92.1	93.3	

SECTION B

CURVE DATA	CURVE	X2	94.0	93.0	94.0	
		X1	93.0	92.0	93.0	
	BRACKET	ΔX	1.0	1.0	1.0	
	DATA POINTS	Y2	4.5895	4.6233	4.6137	
		Y1	4.5084	4.5611	4.5473	
		ΔY	0.0811	0.0622	0.0664	
	NEW CURVE SET POINT (See Eq. B) USE Y3 FROM SEC. A					
	CURVE PROCESSED: (TIME/DATE)					

SECTION C

SPAN BOTTLE DATA	SPAN CYL. NO	A1032	A1032	A1032	
	BOTTLE CONC.(1) Yb	4.570	4.570	4.570	
	CHECK RESPONSE(2) Xc	93.8	92.1	92.8	
	CALC. BOTTLE CONCENTRATION Yc (See Eq. C.)	4.573	4.567	4.534	
	% DIFF. $\frac{Yc - Yb}{Yb} \times 100$ USE Yb SEC. C	.07 %	-.07 %	-.79 %	
	NEW SPAN SET POINT X3 (See Eq. A) USE Yb FROM SEC. C	93.8	92.1	93.3	

SECTION D

SIGNOFF	CALCULATED BY:	[signature]			
	VERIFIED BY:	M. Morris			
	UPDATE EFFECTIVE (TIME/DATE)	0700 7-27-77			

NOTES:

(1) Cylinder Labels Are Generated Using secondary Standards and Are Not To Be Changed Unless Approval Has Been Documented.

(2) Set up Analyzer With Current Span Data Or Secondary Stds.

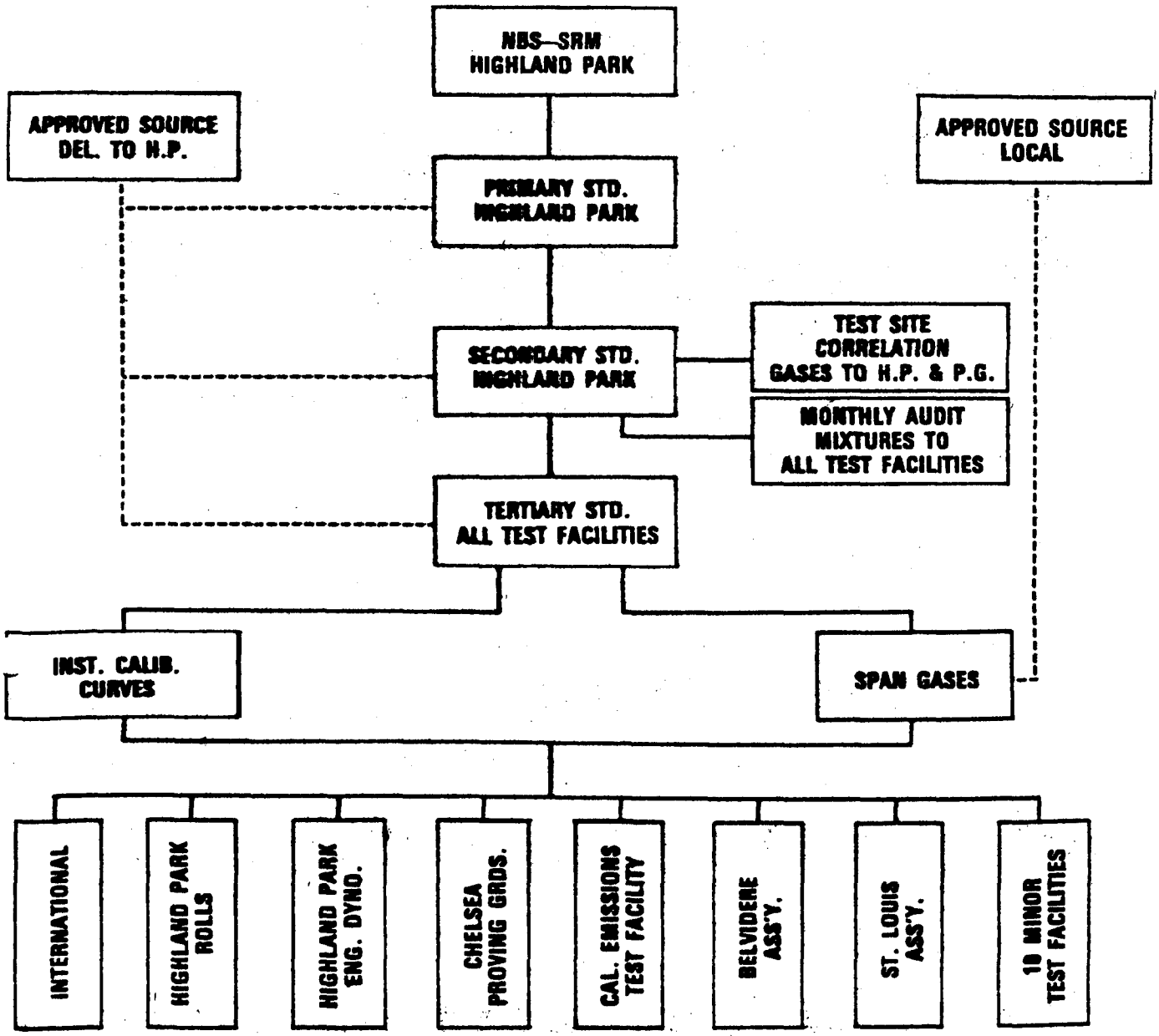
EQUATIONS:

(A) $X3 = X1 + (\Delta X/\Delta Y)(Yb - Y1)$

(B) $X3 = X1 + (\Delta X/\Delta Y)(Y3 - Y1)$

(C) $Yc = Y. + (\Delta Y/\Delta X)(Xc - X1)$

CHRYSLER CORPORATION
CALIBRATION GAS PROGRAM



APPROVED SOURCE: DEMONSTRATED CAPABILITIES

1.) BLEND TOLERANCE
2.) ANALYTICAL ACCURACY
3.) STABILITY
4.) IMPURITY LEVELS
5.) CONSISTENCY
6.) DELIVERY

CORRELATION GASES: MIXTURE OF $C_3H_8 + CO + CO_2 + O_2$ IN N_2 FLOW BLENDED ON A DEMAND BASIS WITH A MIXTURE OF NO IN N_2.

AUDIT MIXTURES: NO IN N_2 AND $C_3H_8 + CO + CO_2$ IN N_2 OR AIR AND SHIPPED IN DISPOSABLE COMPRESSED GAS CONTAINERS.

NITRIC OXIDE in NITROGEN

Existing SRM's - 50, 100, 250, 500, and 1000 PPM
Needed SRM's - 5, 10, 20, 30, 1500, 2000, 2500, 3000, 4000, and 5000 PPM to better define the lower concentrations and cover heavy duty testing.

CARBON MONOXIDE in NITROGEN

Existing - 10, 50, 100, 500, and 1000 PPM
Needed - 250, 1500, 2000, 2500, 3000, 4000, 5000, PPM and 1, 1.5, 2, 2.5, 3, 4, 5, 6, 7% to fill in the gap between 100 and 500 PPM and cover heavy duty testing.

PROPANE IN AIR

Existing - 3, 10, 50, 100, and 500 PPM
Needed - 250 PPM to fill in the gap between 100 and 500 PPM

PROPANE in NITROGEN

Existing - None
Needed - 250, 500, 1000, 2000, 4000, 8000, 14000 and 20000 PPM to cover heavy duty testing. If propane in air SRM's are available they could be used provided a G.C. procedure is used for comparative analysis to eliminate oxygen synergism.

METHANE in AIR

Existing - 1 and 10 PPM
Needed - 5, 20, 40, 60, 100 PPM cover NMHC analysis for both bag and raw exhaust.

CARBON DIOXIDE in NITROGEN

Existing - 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 7.5, 15%
Needed - 100, 200, 400, 600, 800, 1000 PPM and 5, 10, 12.5% to provide for analysis of the ambient and sample bags accurately in the PPM range. This is becoming more important due to fuel economy and dilution factor calculations.

SULFUR and AMMONIA - ?

9

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PROTOCOL FOR ESTABLISHING TRACEABILITY OF CALIBRATION GASES USED WITH CONTINUOUS SOURCE EMISSION MONITORS

Prepared For:

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February 28, 1977

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TABLE OF CONTENTS

1.0 INTRODUCTION

Performance standards for new and existing stationary sources require the installation and operation of continuous monitoring systems for specified pollutants. Extractive continuous monitoring systems for gases must be calibrated daily at zero and 90% of full scale concentration. The gases used for calibration must be certified by the gas vendor to be traceable to National Bureau of Standards (NBS) Standard Reference Materials (SRM) where available (40 CFR 60.13(d) (1)). The term traceable is not defined. As a result, traceability and other requirements for the calibration of continuous monitors have been interpreted in various ways by gas vendors and monitoring system operators.

This protocol defines the procedures to be followed in the analysis of calibration gases and in assuring their stability. It also specifies the time period during which they may be used for field calibration of continuous monitoring systems. The protocol is designed to achieve calibration gases which will be stable and accurate within 6% during the entire designed use period. Calibration gases for stationary sources shall be considered traceable to NBS, SRM if they are manufactured according to the procedures described herein, and they are within the stated use period. Consideration has been given to the degree of stringency required to achieve the desired accuracy without causing excessive costs to the vendor or user.

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2.0 CALIBRATION GASES REQUIRING TRACEABILITY AND NBS, SRM AVAILABILITY

2.1 SOURCE CATEGORIES AND POLLUTANTS REQUIRING CONTINUOUS SOURCE EMISSION MONITORS

Performance standards for stationary sources require continuous monitoring for the following gases in one or more specified source types: sulfur dioxide, nitric oxide, nitrogen dioxide, oxygen, and carbon dioxide. The sources and pollutants requiring monitoring are shown in Table 1.

TABLE 1
SOURCE CATEGORIES AND POLLUTANTS REQUIRING CONTINUOUS SOURCE EMISSION MONITORS

Pollutant	Source	EPA Regulation	Monitor Mid-Range And Span Gas Concentrations, ppm (4)
SO_2	Steam Generation	SPNSS (1)	Oil-500, 900; Coal-750, 1350
	Steam Generation	SIP (2)	Coal-500-2000 (3)
	Petro. Refinery	SPNSS	50, 90
	Sulfuric Acid Plant	SPNSS	500, 900
	Sulfuric Acid Plant	SIP	2000 to 3500 (3)
	Primary Smelters: Copper, Lead & Zinc	SPNSS	1600, 1800
NO	Steam Generation	SPNSS	Gas & Oil - 250, 450 Coal - 500, 900
	Steam Generation	SIP	Coal - 400 to 1500 (3)
NO_2	Nitric Acid Plant	SPNSS	250, 450
	Nitric Acid Plant	SIP	200 to 1000 (3)
O_2	Steam Generation	SPNSS	EPA Regulation 40 CRF 60 (SPNSS) does not require a specific setting for monitor full scale.
CO_2	Steam Generation	SPNSS	

(1) Standards of Performance for New Stationary Sources.

(2) Existing Sources Under State Implementation Plans.

(3) This is the Range of Typical Operation. Mid-range and span gas concentrations need will depend on State Regulations. However, the concentrations will be within the range shown.

(4) Required setting for monitor full scale (called span value) is specified in SPNSS (40 CFR 60). Span is 90% and mid-range is 50% of the monitor full scale.

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2.2 CURRENTLY AVAILABLE AND PLANNED NBS, SRM

Of the gaseous pollutants listed in Table 1, NBS, SRM are available for nitric oxide, oxygen, sulfur dioxide and carbon dioxide. NBS, SRM for nitrogen dioxide are under development. The required mid-range and span gas concentrations required for calibration of continuous source emission monitors are compared to available and planned NBS, SRM in Table 2.

TABLE 2
MID-RANGE AND SPAN GAS CONCENTRATIONS
REQUIRED FOR CONTINUOUS MONITORING VS. AVAILABLE OR PLANNED SRM

Required Gas Mixture	Required Concentration	Available SRM No.	Available SRM Conc.(2)	Planned SRM Conc.
Sulfur Dioxide In Air or N_2, ppm	50			
	90			
	500	1661	500	
	750			
	900	1662	1000	
	1800	1663	1500	
	3500 (1)	1664	2500	
Nitric Oxide in N_2, ppm	250	1685	250	
	450,500	1686	500	
	900	1687	1000	
	1500 (1)			
Nitrogen Dioxide in Air, ppm	250			250
	450			500
	1000 (1)			1000
Oxygen in N_2, Mol. %	NA (3)			2
				10
		1609	21	
Carbon Dioxide in Air or N_2, mol. %	NA (3)	1674	7.2	
		1675	14.2	

(1) Estimated maximum for existing sources under State Implementation Plans

(2) Nominal concentration, subject to variation. The SRM standards are in the following gas matrix: SO_2 in N_2, NO in N_2, NO_2 in air, O_2 in N_2 and CO_2 in N_2.

(3) Not Applicable. EPA regulation 40 CFR 60 (SPNSS) does not require a specific setting for monitor full scale.

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2.3 RESPONSIBILITY FOR TRACEABILITY

The gas manufacturer is responsible for establishing traceability for new calibration gases. This responsibility has been placed on the gas manufacturer by 40 CFR 60.13(d) (1) which states, "Span and zero gases certified by their manufacturer to be traceable to National Bureau of Standards reference gases shall be used whenever these reference gases are available."

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3.0 TRACEABILITY PROTOCOL FOR CALIBRATION GASES

3.1 OVERVIEW OF TRACEABILITY PROCEDURE

The traceability procedure described in this section is intended to minimize systematic and random errors during the analysis of calibration gases and to establish the true concentrations by means of NBS, SRM. The term calibration gases, as used in the procedure, refers to gas mixtures in cylinders sold by gas manufacturers for calibration of source emission monitors. The procedure provides for a direct comparison between the calibration gas and an NBS, SRM or a gas manufacturers' primary standard (GMPS) which is referenced to NBS, SRM. All comparisons will be made using instruments calibrated periodically with applicable NBS, SRM.

This procedure is applicable to any continuous, semi-continuous or periodic analysis instrument which meets the performance requirements in the following sections. A manual wet chemical method may be substituted for an instrument, if such method meets the performance requirements. For wet chemical methods, all steps prescribed in Sections 3.2 and 3.3 must be performed with the word "method" substituted for "instrument".

3.2 PROCEDURE FOR INSTRUMENT CALIBRATION

The following procedures for periodic multipoint calibration and daily instrument span checks are prescribed to minimize systematic error. Separate procedures for instrument span checks are described for linear and non-linear instruments. For this purpose, a linear instrument is defined as one which yields a calibration curve which deviates by 2% or less from a straight line drawn from the point determined by zero gas to the highest calibration point. To be considered linear, the difference between the concentrations indicated by the calibration curve and the straight line must not exceed 2% of full scale at any point on the curve.

3.2.1 Multipoint Calibration

A multipoint calibration curve is prepared monthly using all available SRM in the range over which the instrument is to be used and zero gas. The zero gas must not contain more than 0.2% of the full scale concentration of the component being analyzed. In addition, zero gas must be

free of any impurity that will give a response on the analytical instrument.

For most gases, there are not enough SRM available or planned to fully define the calibration curve. The additional data points needed can be obtained best by diluting the highest SRM with zero gas using a calibrated flow system. The accuracy of the dilution achieved is then checked by comparison of the response for the lower SRM(s) to the calibration curve prepared from data points obtained by the dilution technique.

The multipoint calibration is accomplished by diluting the highest SRM with zero gas using a calibrated flow system. Obtain the instrument response for 6 points representing 0, 10, 30, 50, 75 and 100% of the SRM concentration.

Plot the data and construct the calibration curve. Obtain the instrument response for the other (lower) SRM's without dilution. Compare the apparent concentrations from the calibration curve to the true concentration of each lower SRM. If the difference between the apparent concentration and the true concentration of any lower SRM(s) exceeds 2% of the true concentration, repeat the multipoint calibration procedure. Test the calibration curve for linearity as defined above and proceed to either 3.2.2.1 or 3.2.2.2.

3.2.2 Instrument Span Check

3.2.2.1 Linear Response Analytical Instrument

At the start of each day that calibration gases are to be analyzed, check instrument response to the highest SRM (or GMPS) in the range to be used and to zero gas. Adjust response to the value obtained in the most recent multipoint calibration. Calibration gases analyzed with a linear instrument must not have a concentration greater than 15% above the highest available SRM concentration.

3.2.2.2 Non-Linear Response Analytical Instrument

At the start of each day that calibration gases are to be analyzed, check instrument response to two or more SRM (or GMPS) in the range of calibration gases to be analyzed and to zero gas as follows. First, set the instrument zero with zero gas and then adjust the instrument

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response to the highest SRM (or GMPS) to the value obtained in the most recent multipoint calibration. Next, obtain the response to the SRM (or GMPS) nearest in concentration to mid-range. If the response to the lower standard varies by greater than 2% from the response obtained in the most recent multipoint calibration, a full multipoint calibration must be performed as in 3.2.1. Otherwise proceed to 3.3. Calibration gases analyzed with a non-linear instrument must not have a concentration greater than the highest available SRM concentration.

3.3 PROCEDURE FOR ANALYSIS OF CALIBRATION GASES

The following procedure is designed to assure the precision and accuracy of calibration gas cylinder analyses. The analyses involve the direct comparison of the calibration gas to an SRM or gas manufacturer's primary standard (GMPS) in order to compensate for variations in instrument response between the time of daily span check and the time of analysis. Significant variations in response often result from changes in room temperature, line voltage, etc. Analyses are performed in triplicate to expose erroneous data points and excessive random variations in instrument response.

1. Analyze each calibration gas cylinder directly against the nearest SRM (or GMPS) by alternate analyses of the SRM and calibration gas in triplicate (3 pairs). Adjust the instrument span if necessary prior to the analysis, but do not adjust the instrument during the triplicate analyses. The response to zero gas shall be obtained with sufficient frequency that the change in successive zero responses does not exceed 1% of full scale.

2. For each of the six analyses, determine the apparent concentration of the standard or calibration gas from the calibration curve.

3. For each pair of analyses (one standard and one calibration gas), calculate the true concentration of the calibration gas by:

$$\text{True Conc. of Cal. Gas} = \text{Apparent Conc. of Cal. Gas} \times \frac{\text{True Conc. of Std.}}{\text{Apparent Conc. of Std.}}$$

4. Determine the mean of the three values for true concentration of the calibration gas.

5. If any one value differs from the mean by greater than 1.5%, discard the data, reset the instrument span if necessary and repeat steps 1 to 4.

A detailed example of the calculation procedure is given in the Appendix.

3.4 USE OF GAS MANUFACTURER'S PRIMARY STANDARDS

Gas manufacturer's primary standards (GMPS) are gas mixtures prepared in pressurized containers and analyzed against SRM. Their purpose is to conserve SRM's where large quantities of calibration gas cylinders are analyzed. GMPS may be substituted for SRM for instrument span checks (Section 3.2.2) and calibration gas analysis (Section 3.3) if the following conditions are met. In no case may GMPS be substituted for SRM for the required multipoint calibrations (Section 3.2.1).

1. GMPS must have been analyzed against SRM as described in 3.2 and 3.3 within 30 days of their use for calibration gas analysis. It is preferred that GMPS be analyzed on the days that multipoint calibrations are performed.

2. GMPS must not have changed in concentration by more than 1% per month (average) for the three-month period prior to their use for calibration gas analysis.

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4.0 CALIBRATION GAS STABILITY

4.1 STABILITY CRITERIA

All calibration gases analyzed by this protocol and shipped to users must have a minimum shelf life of six months at 6% accuracy. Separate procedures are given below for reactive gases and non-reactive gases.

4.1.1 Non-Reactive Gases

Carbon dioxide and oxygen calibration gases can be used for periods up to one year from the date of manufacturer's last analysis. For use beyond one year, cylinders must be re-analyzed by the manufacturer or user using the procedure given in 3.0.

4.1.2 Reactive Gases

The stability of nitric oxide and sulfur dioxide calibration gases (and nitrogen dioxide when SRM are available) will be verified by the gas manufacturer prior to shipment to the user. The stability of each cylinder must be verified by performing two or more analyses as per 3.3 in addition to the initial analysis, over a period of sixty days or longer. It is preferred that analyses be performed at 30 day intervals, and at least one analysis must be performed in the middle third of the stability test period. The cylinder has acceptable stability if its concentration does not change by more than 1% per thirty days based on the slope of the best fit straight line through the data points. The procedure for calculating the rate of change is given in the Appendix. The gas concentration to be reported to the user is the mean concentration at the last analysis.

Nitric oxide and sulfur dioxide calibration gases can be used for the number of months calculated from six divided by the average percent concentration change reported by the manufacturer per thirty day period or for one year whichever is less. For use beyond this period, cylinders must be re-analyzed as per 3.0.

4.1.3 Minimum Cylinder Pressure

No calibration gas shall be used below a cylinder pressure of 200 pounds per square inch as shown by the cylinder gas regulator.

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4.2 RE-ANALYSIS REQUIREMENTS OF EPA REGULATION

40 CFR 60.13(d) (1) states, "Every six months from date of manufacture , span and zero gases shall be re-analyzed by conducting triplicate analyses with Reference Method 6 for SO_2, 7 for NO_x, and 3 for O_2, and CO_2, respectively. The gases may be analyzed at less frequent intervals if longer shelf lives are guaranteed by the manufacturer." With the completion of this protocol, EPA will revise the re-analysis requirements of calibration gases to be consistent with the recommendations shown in Section 4.1.

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5.0 SUBMISSION OF CALIBRATION GAS ANALYSIS DATA TO USERS

Each calibration gas cylinder shipped by a gas manufacturer to a user shall contain the following minimum traceability information on a gummed label affixed to the cylinder wall and/or a tag attached to the cylinder valve:

1. Cylinder number
2. Mean concentration of trace component, ppm or mol %
3. Balance gas
4. Last analysis date
5. Expiration date of use period
6.* Stability in % change per thirty days
7.* Duration of stability test period, months
8. Analyst name or identification number

In addition, the manufacturer shall submit a written analysis report to the user which certifies that the gas has been manufactured according to the protocol, and which contains the following information:

1. Cylinder number
2. Mean concentration of trace component, ppm or mol %
3. Replicate analysis data
4. Balance gas
5. NBS, SRM number(s) used as primary standard(s)
6. Analytical principle used
7. Last analysis date
8. Expiration date of use period
9.* Stability in % change per thirty days
10.* Duration of stability test period, months
11. Analyst name or identification number

---

*Required only for sulfur dioxide and nitric oxide (and for nitrogen dioxide when SRM are available).

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6.0 REFERENCES

1. Requirements For Submittal of Implementation Plans and Standards for New Stationary Sources - Emission Monitoring, Federal Register 40, Number 194, October 6, 1975, pages 46240-46270.

2. Part 60 - Standards of Performance for New Stationary Sources - Emission Monitoring Requirements and Revisions to Performance Testing Methods, Federal Register 40, Number 246, December 22, 1975, pages 59204 and 59205.

3. Part 60 - Standards of Performance for New Stationary Sources - Primary Copper, Zinc and Lead Smelters, Federal Register 40, Number 10, January 15, 1976, pages 2332-2341.

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A.1 DETERMINATION OF MEAN CONCENTRATION

Problem:

A calibration gas containing approximately 9% CO_2 in nitrogen is to be analyzed with the concentration reported as traceable to SRM. The most recent multipoint calibration curve for the non-dispersive infrared instrument (non-linear) as obtained by the procedure given in Section 3.2.1 is shown in Figure A-1. The instrument span check (Section 3.2.2) was performed earlier in the day. The calibration gas was analyzed in triplicate against the nearest SRM, which contained 7.2% CO_2. The responses were as follows:

Replicate No.	SRM Response	Cal. Gas Response
1	65.6	74.7
2	65.3	74.2
3	65.0	74.8

Solution:

From the calibration curve determine the apparent concentrations for each of the six data points and tabulate as shown below. Calculate the true concentration of the gas cylinder for each of the three replicates from the equation:

$$\text{True Conc. of Cal. Gas} = \text{Apparent Conc. of Cal. Gas} \times \frac{\text{True Conc. of Std.}}{\text{Apparent Conc. of Std.}}$$

For Replicate 2

$$\text{True Conc.} = 8.81 \times \frac{7.20}{7.17} = 8.85\%$$

Calculate the mean of the three concentration values and the maximum deviation from the mean.

Replicate No.	SRM Resp.	Apparent SRM Conc.	Cyl. Resp.	Apparent Cyl. Conc.	True Cyl. Conc.
1	65.6	7.20	74.7	8.86	8.86
2	65.3	7.17	74.2	8.81	8.85
3	65.0	7.13	74.8	8.88	8.97
					Mean = 8.89

$$\text{Maximum deviation} = \frac{8.97 - 8.89}{8.89} \times 100 = 0.9\%$$

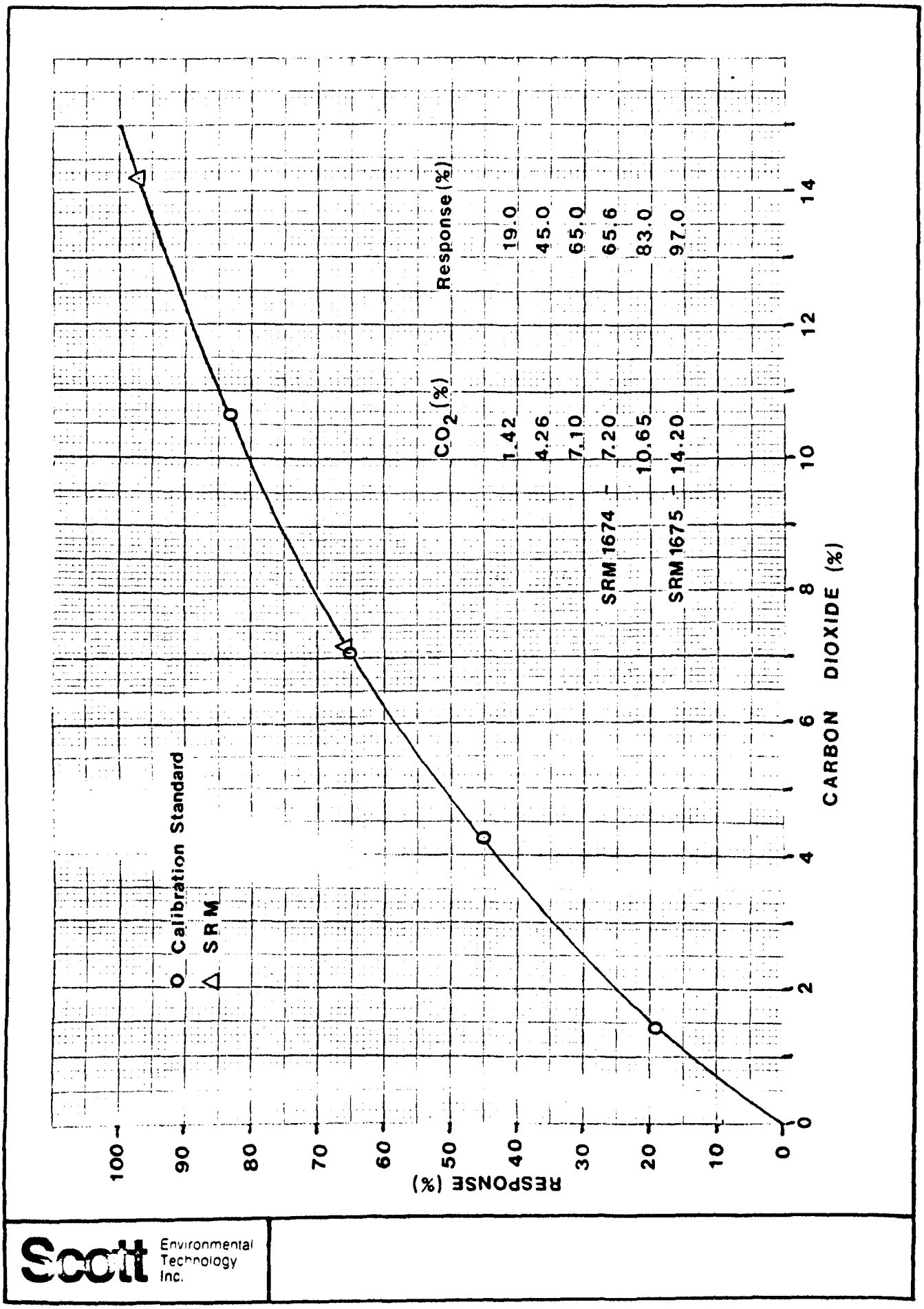

Figure A-1 Multipoint Calibration Curve

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Since the maximum deviation from the mean is less than 1.5%, the analysis is satisfactory. If the third replicate had shown a true concentration of 9.08%, then the maximum deviation (0.15%) would have been 1.7% of the mean of 8.93% and the analysis would have had to be repeated.

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A.2 DETERMINATION OF STABILITY

Problem:

A calibration gas cylinder has been analyzed per Section 3.3 with the following results for three analyses:

Date	Conc.
3/15	104.3
4/12	103.7
5/16	103.4

What is the concentration change per 30 day period?

Solution:

For a linear regression the slope of the best fit line is given by:

$$b = \frac{\Sigma(x_i - \bar{x})y_i}{\Sigma(x_i - \bar{x})^2}$$

where,

b = slope of best fit straight line

x_i = individual data values for days after initial analysis

$\bar{x}$ = mean of all x_i points

y_i = individual data values for component concentration

Tabulate the data as follows:

x_i	y_i	$x_i - \bar{x}$	$y_i(x_i - \bar{x})$	$(x_i - \bar{x})^2$
0	104.3	-30	-3129.0	900
28	103.7	- 2	- 207.4	4
62	103.4	+32	+3308.8	1024
			- 27.6	1928

$$\bar{x} = \frac{\Sigma x_i}{n} = \frac{90}{3} = 30$$

$$b = \frac{\Sigma(x_i - \bar{x})y_i}{\Sigma(x_i - \bar{x})^2} = \frac{-27.6}{1928} = -0.0143 \text{ ppm/day}$$

From b, determine the % loss per 30 days by:

$$\% \text{ loss/30 days} = \frac{\text{loss per day} \times 30}{\text{final conc.}} \times 100 = \frac{0.0143 \times 30}{103.4} \times 100 = 0.41\%$$

The loss is less than 1.0% and the cylinder has acceptable stability.

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DISCUSSION OF COMMENTS
RECEIVED ON
DRAFT PROTOCOL FOR ESTABLISHING TRACEABILITY
OF CALIBRATION GASES USED WITH
CONTINUOUS SOURCE EMISSION MONITORS

Prepared For:

Darryl J. Von Lehmden
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Environmental Monitoring & Support Laboratory
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March 8, 1977

SCOTT ENVIRONMENTAL TECHNOLOGY, INC.
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SET 1500 05 0277

1.0 INTRODUCTION

The draft protocol submitted in September 1976 has been revised based on comments submitted by gas manufacturers, EPA personnel, NBS personnel and other persons associated with regulatory agencies and private industry. These comments are addressed as they apply to the protocol on a section by section bases. The various positions taken by the commentators are identified, the pros and cons of the alternatives are discussed, and the rationale for the position taken in the protocol is presented.

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2.0 COMMENTS ON INDIVIDUAL PROTOCOL SECTIONS

2.1 INTRODUCTION OF PROTOCOL

The comments related to the introduction addressed the need for a definition of traceability and the areas covered by the protocol as stated at the beginning of the second paragraph. In order to clarify the meaning of gas traceability, a sentence has been added which states that it refers to calibration gases manufactured according to procedures given in the protocol. The second paragraph has been revised to be more specific to the final version of the protocol.

2.2 CALIBRATION GASES REQUIRED AND SRM AVAILABILITY

The need for including this section was questioned. It is true that inclusion of Sections 2.1 and 2.2 date the protocol, and these sections will become obsolete in time. However, they present comprehensive information on the gases required for continuous source monitoring which are valuable to both manufacturers and users. Periodic updates should be made as necessary, and the date of the update should be indicated for Tables 1 and 2.

2.3 TRACEABILITY PROTOCOL FOR CALIBRATION GASES

Section 3 of the protocol was revised extensively to provide greater clarity, but only two significant changes in the procedure were made. These were the requirement of a monthly multipoint calibration for all instruments using a dilution system and simplified calculations for determining analytical precision.

The question was raised as to what specific instruments or types of instruments should be used in the analytical procedure. This is now covered in the second paragraph, which states that any instrument or method which meets the performance requirements may be used. Since the users will employ the calibration gases for a wide variety of extractive stationary source monitors, it is imperative that the gas concentration be independent of the measurement principle. A review of

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data contained in Scott's Gas Cross Reference Service reports demonstrates that the correct concentration can be obtained by a variety of methods if proper calibration procedures are used. For example, nitric oxide concentrations determined by non-dispersive infrared, chemiluminescence and manual modified Saltzman (colorimetric) techniques were all in the same population. At the September workshop, the problem of variations in hydrocarbon (propane) values from instrument to instrument were mentioned by several people involved in mobile source emissions measurements. This would not be a problem with stationary source measurements at present because there are no requirements for monitoring hydrocarbons, but requirements for stationary source hydrocarbon monitoring may be added in the future. Current problems are related to non-linearity with concentration and the influence of hydrocarbon type and oxygen content of the gas on the response of flame ionization detector (FID) total hydrocarbon analyzers. We believe that the hydrocarbon calibration gas requirements can be specified in new regulations in such a manner as to avoid the need to amend the current protocol.

The suggested statement on impurities in gas mixtures has not been included because it would require analyses for various potential impurities which have no effect on the utility of the gas mixture. The only problem area appears to be the presence of NO_2 in NO mixtures. It is felt to be more appropriate to amend Performance Specification 2 (FR 40, page 46263) to read "NO gas mixtures shall not contain NO_2 in excess of 2% of the NO concentration. An analysis shall be furnished for both NO and NO_2".

2.3.1 Multipoint Calibration

The previous procedure specified calibration curves based on SRM alone. The two to four resulting points were not adequate to define an accurate curve, especially for a non-linear instrument. Since additional SRM to provide more points are not planned, the use of the dilution system involving the highest SRM and zero gas is the best means of achieving an accurate calibration curve. The subsequent check with lower

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SRM will serve to detect flow system errors. Zero gas has been defined.

The use of a flow dilution system for calibration has not been practiced to any extent by gas manufacturers. Thus, they feel uneasy and forsee many problems. In as much as EPA is recommending its use for other analyses such as vinyl chloride, it must be presumed that EPA has sufficient in-house experience to demonstrate the ability to provide accurate mixtures by flow dilution.

One commentator recommended that the higher SRM be diluted with the lower SRM and the useful range be limited to that between the two. This recommendation was rejected because it limits the useful range, uses extra SRM gas and most importantly eliminates the ability to check the flow system accuracy through use of the undiluted lower SRM. Its only advantage would appear to be the elimination of the need for a zero gas. However, gas manufacturers have available zero gases for ambient monitoring instruments which far exceed the requirements for stationary source zero gases.

Because of the additional work involved, the frequency of the multipoint calibration has been extended to a monthly rather than weekly requirement. Any appreciable changes in the calibration curve will be detected by the daily instrument span check.

2.3.2 Instrument Span Check

The purpose of the instrument span check to verify the calibration curve on a daily basis is made clearer. The range of gas concentrations allowable for linear and non-linear instruments has not been changed.

2.3.3 Analysis of Calibration Gases

The need to compare the calibration gases directly to the standards is explained. The responses of most instruments vary throughout the day, especially where ambient conditions are not closely controlled as is the case in most gas analytical laboratories.

A more detailed explanation of the data calculations is provided and an example for a non-linear instrument is given in the Appendix.

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The majority of commentators had difficulty in understanding the previous procedure.

The statistical calculations of confidence interval have been eliminated. Dr. Ku and Mr. Nelson both pointed out correctly that liberties had been taken with statistical procedures. They both offered statistically valid procedures for determining confidence intervals. Unfortunately, these procedures are so lengthy that their use in gas analysis laboratories would not be cost effective. Instead, a simple calculation of maximum deviation from the mean has been recommended. The 1.5% maximum deviation allowed is in line with the 3% value for 95% confidence previously proposed. It is believed that the proposed procedure, despite its simplicity, will be adequate to detect and remove excessive random errors.

2.3.4 Gas Manufacturers Primary Standards

Gas Manufacturers Primary Standards (GMPS) are defined and their use is extended to all determinations except multipoint calibrations. By combining the required monthly multipoint calibrations with monthly analyses of GMPS it is felt that the use of SRM gas can be minimized. At the same time the accuracy and stability of GMPS will be assured, and acceptable calibration gases will result if the recommended analytical procedures are followed.

2.3.5 Gas Stability

Strong opposition has been voiced by the gas industry to the holding of cylinders of reactive gases until stability is assured. They claim that some manufacturers have the technology to assure stability without holding cylinders for recheck. They claim that holding cylinders will greatly increase the cost and cause delays in making shipments to users.

This part of the protocol still requires stability checks for 60 days as in the draft. The reasoning is that instability is a random occurrence related to interior cylinder wall conditions. Even with aluminum cylinders stability problems can occur if there is a change in

alloy, manufacturing conditions which produce undesirable interior surface conditions and inadequate interior surface treatment. The latter treatments are proprietary and thus difficult for EPA to specify or provide quality assurance without stability checks.

While the holding of a product for future delivery has not been practiced by gas manufacturers, it is not unusual for American industry. We believe that the stability requirement will lead to users placing blanket orders for future delivery of a specified number of cylinders on an as needed basis. This would permit the manufacturers to prepare cylinders in batches without the risk of not being able to ultimately sell them. Of course, the cost of the stability checks and lost cylinder rental would have to be passed on to the user, but this cost would not seem excessive for assuring a stable calibration gas.

As technology improves and stability problems are overcome, the protocol can be revised by transferring certain gas mixtures from the reactive to non-reactive category. We believe that the data generated in the required checks can provide the base for deciding when stability checks are no longer needed. For instance, if the industry shows that over the past six months 98% of all cylinders checked for a particular gas mixture showed less than 1% per month loss and the remaining 2% did not exceed 2% loss per month, sufficient justification would exist to delete the stability requirement for that mixture as long as the same cylinder materials and treatment processes were used.

2.3.6 Submission of Data to Users

At the suggestion of some commentators the information to be attached to the cylinder has been abbreviated by deleting items which might confuse the users' personnel. There is an added requirement for furnishing the user with a detailed cylinder report. This is believed necessary for the user to maintain records showing that he has met the calibration requirements. It also provides him with assurance that the manufacturer is following the protocol.

It was suggested that record-keeping requirements for gas manufacturers be included in the protocol. We agree that this is

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desirable, but we feel that this requirement would best be formulated by EPA based on other EPA record-keeping requirements. We believe that the requirement should be added at the end of Section 5.0.

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3.0 COMMENTS ON OVERALL PROTOCOL

The Specialty Gas Committee of the Compressed Gas Association (CGA) has expressed the opinion that the protocol is restrictive because it addresses specific methodology of preparation and analysis of calibration gases rather than a final product performance standard. They add that this will hinder further development of technology related to production of calibration gases. We strongly disagree with this opinion. First, the protocol does not address or restrict the preparation methods in any manner. Second, the protocol relies primarily on performance requirements to provide quality assurance, and it does not restrict analysis methodology. Rather, it describes how the vendor is to demonstrate that each cylinder meets the performance requirements. The major performance requirements include:

1. The calibration curve for the instrument or method used must be reproducible from day to day (Section 3.2.2).

2. The instrument or method must yield data with high precision (Section 3.3).

3. The calibration gas must have acceptable stability (Section 4.1).

All of the data are referenced to NBS, SRM by monthly calibrations. Our third point of disagreement with the CGA position is that we cannot see how the protocol would hinder the development of technology, and CGA has given no examples to support their contention.

The alternative offered by CGA involves NBS certification of gas manufacturers based on performance. No details as to how the performance is to be assured are given, but we understand that the plan involves periodic analysis of reference mixtures supplied as unknowns by NBS or of NBS analysis of cylinders submitted periodically by the manufacturers. In our opinion, neither of these plans provides adequate quality assurance because they evaluate the capability of the manufacturer in analyzing a few mixtures where special care can be used to achieve high quality results. The plan will not determine whether equally stringent

analytical procedures are used for calibration gases sold to users, and the quality of these gases will not be known. In summary, the CGA plan stresses general performance capability rather than the performance on each cylinder as required by the protocol. We believe that the latter will be much more effective in assuring the overall high quality of calibration gases for stationary source monitors.

One potential problem emphasized by several gas manufacturers and others is outside of the scope of the present effort, but it is of sufficient importance to discuss briefly. This problem is the potential application of this protocol or a similar protocol to calibration gases for other sources covered in Federal emissions standards, namely mobile source emissions and ambient monitoring. Certainly, it is in the best interest of both suppliers and users that any requirements for calibration gases for mobile source and ambient monitoring be compatible with those promulgated for stationary source monitors. However, there is a notable limitation of SRM to cover the wide range of calibration gas concentrations required for mobile source emissions, and greater accuracy is mandated for mobile source gases than is needed for stationary source monitors. There is no easy solution to this dilemma. It is recommended that the promulgation of the protocol for stationary sources monitors proceed without delay due to concern over gases for other sources. It is further recommended that those responsible for mobile source and ambient monitoring adopt calibration gas protocols which are compatible with the stationary source protocol.

Many of the gas manufacturers believe that the protocol should permit alternatives to the use of NBS, SRM because the current large scale production of NBS, SRM places NBS in direct competition with manufacturers in selling gases to users. It appears true that a substantial portion of SRM are sold to users for checks on purchased gases rather

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than to manufacturers to carry out required traceability procedures. It is our opinion that if manufacturers were permitted to use alternate traceability procedures, users would be more likely to purchase SRM for verification than at present. Thus, the use of alternate procedures would not reduce the NBS share of the market unless the words traceable to NBS, SRM were deleted from the various Federal Register documents.

Some comments questioning the feasibility of issuing a protocol claim that it is better to let each manufacturer use his own procedure and provide a guarantee or certification to the user. This is claimed to be more in the spirit of our free enterprise system. Unfortunately, the words guarantee and certify do little to assure quality which is the objective of the protocol. In fact, no gas manufacturer will guarantee his product beyond the point of offering to replace calibration gas which does not meet specifications. This places the responsibility for analysis accuracy and gas stability squarely on the shoulders of the user, who generally has little capability for performing an independent assessment of gas quality. Out of spec mixtures are usually detected only in the course of audits by regulatory agencies. The user then can get a free replacement cylinder, but usually he is left holding several months of questionable data.

The gas industry should not be expected to provide a guarantee involving greater liability because the potential cost of damages and legal expense would substantially increase the selling price of any cylinder with such a guarantee. Thus, the implementation of this protocol, which requires certain quality assurance procedures for each cylinder, appears to be a far better means of obtaining the required quality of calibration gases.

The section of the draft protocol which dealt with cost was deleted because a number of commentators felt that it was inappropriate to suggest gas selling prices within the protocol. However, some consideration must be given to the added cost of producing gas which meets the protocol requirements. The added cost is best evaluated in terms of the

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total cost for source monitoring incurred by the user and on the impact of poor quality calibration gases on the user's plant operations.

Each monitoring system will usually require from 2 to 4 span gas cylinders per year. The additional cost for gases meeting the protocol will probably range from $50 to $200 per cylinder for gases requiring stability checks. The rough range of added costs would thus be from $100 to $800 per year. The initial costs of the monitoring system, its daily operation and maintenance, data reduction, record keeping, report preparation requirements and miscellaneous costs will almost certainly exceed $10,000 per year and are more likely to be $20,000 to $30,000. The added cost of span gases which meet protocol requirements therefor represent less than ten percent of the total system cost.

The potential cost to the user if the span gas is not stable can be substantial. If the span gas concentration decreases with time, the monitoring system operator will increase the instrument gain to bring the span value back on the calibration curve. This will result in an erroneously high reading for the source being monitored. The source concentration will read too high by about the same percentage that the span gas has decreased. In many cases, this will cause the source pollutant concentration to appear to exceed the emissions standard. In order to remain in compliance, the user may take steps to reduce emissions by decreasing production rates, using a more expensive fuel, adjusting the control device, etc. Each of these unnecessary steps will cost the user considerably more than the added cost of high quality span gas.

Clearly, it is most cost effective that all calibration gases sold to users meet the protocol requirements. The modest cost of assuring quality calibration gases will be a small price to pay for obtaining accurate stationary source monitoring data. We firmly believe that expeditious implementation of the protocol will be of benefit to plant operators, regulatory agencies and the general public.