PRO-TEK™ COLORIMETRIC AIR MONITORING BADGE SYSTEMS
LABORATORY VALIDATION REPORT
SULFUR DIOXIDE BADGE, TYPE C-20

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ABSTRACT

This laboratory validation report for the Du Pont PRO-TEK™ colorimetric air monitoring badge for sulfur dioxide (SO_2) demonstrates that this system, when tested by rigorous and accepted standard laboratory practices, meets the NIOSH accuracy requirements for an analytical sampling method. Adequate storage stability of exposed badges has been shown.

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TABLE OF CONTENTS

PRO-TEK™ Colorimetric Air Monitoring Badge Systems

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SUBSTANCE:	Sulfur Dioxide, SO_2
METHOD:	Du Pont Type C-20 Badge, PT-3 Colorimeter
PROCEDURE:	Colorimetric
DATE ISSUED:	February 16, 1981
DATE REVISED:	-----
SAMPLING RANGE:	10-100 ppm-hours
PRECISION:	MCV = 0.017
OVERALL SYSTEM ACCURACY:	± 12.6 percent

PRINCIPLE OF THE METHOD

The procedure for collection and analysis of air samples of sulfur dioxide using the Du Pont PRO-TEK™ Colorimetric Air Monitoring Badge System (C-20) is described in Attachment A.

This method consists of collection of the sample in a badge that contains absorbing solution and color reagents similar to those described in NIOSH P&CAM, Method No. 160. This method has been tested for validity using similar criteria for validation outlined in Reference 1. Based on these criteria, the absolute total error (sampling and analysis) should be less than 25 percent at the OSHA standard level (equivalent to an eight-hour TWA exposure dose of 40 ppm-hours) 95 percent of the time.

TEST PROTOCOL

The protocol used for testing this method was to:

(A) Analyze 22 samples (two each between 0.325X and 2.5X the OSHA standard) spiked with the appropriate amounts of sodium sulfite to represent exposure dose levels between 0 and 100 ppm-hours of sulfur dioxide.

(B) Analyze 40 samples collected from dynamically generated test atmospheres (10 samples collected at each of 0.825X, 1.1X, 1.675X, and 2.15X the OSHA standard).

(C) Test the storage stability (at 40°F and 77°F) of 11 collected samples.

(D) Assess the overall system accuracy, bias, and precision of the method.

(E) Environmental variables were considered.

(F) Chemicals used for validation were:

Sulfur dioxide in air mixtures from Scott Environmental Technology, Inc., Plumsteadville, Pennsylvania 19849. Accuracy ± 2 percent (traceable to National Bureau of Standards).

ANALYTICAL METHOD

A description of the method of analysis is given in Reference 2. The results of the analytical method linearity tests are in Table 1. The precision of the analytical linearity method shown in Table 1 is MCV = 0.017. (The sensitivity of the method is 10 ppm-hours or 3.2 mg/m^3 for eight hours.)

SAMPLING AND ANALYSIS

The system for generation of test atmospheres of sulfur dioxide is described in Attachment A. An electrochemical Interscan Model 1240SP analyzer was used to measure and verify the sulfur dioxide chamber concentrations. Test atmospheres were generated with certified mixed gas cylinders. Different dose levels (ppm-hours) were generated by varying the sample exposure time. These dose levels represent the measurement of concentrations between 0.825X and 2.15X the OSHA standard levels. The relative humidity in the chamber was less than 5 percent.

Samples were collected as described in Reference 2 with PRO-TEK™ C-20 Colorimetric Badges. Ten samples were collected for each level of exposure for times varying from two to four hours. The results of the analyses of the samples are presented in Table 2.

An additional 22 samples were collected at 1X the OSHA level. These samples were used for the storage stability study.

PRECISION AND ACCURACY

The statistical procedures and a definition of the terms used are described in Reference 2 and summarized in Attachment B.

The precision of the analytical method was assessed with the data in Table 1. The Mean Coefficient of Variation (MCV) for 11 sets of analytical samples was found to be 0.017.

Precision and bias of the total sampling and analytical methods were evaluated using the data in Table 2 and the results obtained from storage stability tests (Tables 5 and 6). The MCV for the four sets of samples collected from test atmospheres is 0.058. The mean value for the concentration found by analysis with the badge at each level was compared with the value for the concentration taken with the sulfur dioxide electrochemical analyzer to obtain a measure of the bias of the method.

The mean bias for all four levels was found to be - 0.010.

The overall accuracy of the system was found to be $\pm$ 12.6 percent.

ENVIRONMENTAL VARIABLES

Additional badges were tested for exposure temperature effects at 2X TLV. The data in Table 3 show no significant temperature effects.

Both graphical and statistical analyses of the data from a 2^{4-1} factorial designed set of experiments show no significant effects from pressure, humidity, and face velocity on the Du Pont Ammonia Badge, Type C-10. It is assumed that the same would hold true for the sulfur dioxide badge because the physical dimensions of the diffusion controlling member are the same for both badges. (See Reference 2.)

INTERFERENCES

The major known interferences are oxides of nitrogen, ozone, and heavy metal salts. These interferences will not affect the PRO-TEK™ Sulfur Dioxide Colorimetric Badge because they have little or no affinity for the absorbing solution. One blister of the sulfur dioxide badge contains 0.6 percent sulfamic acid, which deactivates absorbed nitrogen dioxide. The effectiveness of sulfamic acid is shown in Table 4.

STORAGE STABILITY

A study was conducted to assess whether sulfur dioxide could be successfully stored as a tetrachlorosulfito mercury complex in exposed badges for one week refrigerated as well as at room temperature. The results of the analyses are presented in Tables 5 and 6.

The criterion for acceptance was that the mean of the samples stored under refrigeration or room temperature for seven days should be within ± 10 percent of the mean of the set analyzed at the beginning of the storage period. The two means of each set compare within 6 percent; thus, the storage stability was deemed adequate.

COLLECTION EFFICIENCY

Collection efficiency tests are necessary for dynamic test methods such as the pump/impinger method. Collection efficiencies for the PRO-TEK™ Colorimetric Air Monitoring Badge are constant throughout the linear range for which the badge is used.

INDEPENDENT METHOD

The independent method used to determine the concentration of sulfur dioxide in the exposure chamber consisted of the continuous collection of samples at a point immediately after the exposure chamber with a calibrated Interscan Model 1240SP sulfur dioxide electrochemical analyzer. Mixed sulfur dioxide/dry air cylinders of approximately 20 ppm (52 mg/m^3) were used. Different dose levels (ppm-hours) were obtained by varying the exposure time. These dose levels represent the measurement of concentrations between 0.8X and 2.2X the OSHA standard level.

Attachment A
Generation of Test Atmospheres

The basic dynamic contaminant generation system used (see Figure 1) was originally developed by Du Pont for the purpose of laboratory validation of sampling methods where an accurate measure of the true contaminant concentration could be determined. The system is constructed of glass and Teflon® FEP-fluorocarbon resin tubing.

Exposure chamber gas contaminant concentrations were established with either certified mixed gas cylinders (Scott Environmental, Plumsteadville, Pennsylvania) or the principle of permeation of an inorganic gas contaminant through a permeation tube.

The generated concentration was verified with calibrated on-line instruments such as an infrared spectrophotometer (Perkin-Elmer Model 299) equipped with dual variable long path cells, a direct reading sulfur dioxide analyzer (Interscan Model 1240SP), a direct reading nitrogen dioxide analyzer (Interscan Model 1154SP), and a direct reading NO, NO_x, and NH_3 analyzer (Thermo Electron Model 10AR). These instruments were calibrated with certified gas cylinders ($\pm$ 2.0 percent) traceable to the National Bureau of Standards.

All chamber exposures were obtained by integrating the concentration generated during the exposure period. Badges were placed in the chamber under zero concentration. Exposure was initiated by introducing the mixed contaminant in air gas into the chamber. On-line instrumentation and a strip-chart recorder were used to monitor the chamber concentration buildup to steady-state conditions. The resulting time-concentration plot was analyzed with Simpson's rule of approximation on a TI-59 electronic calculator that permits calculation of the integrated exposure limit.

Water vapor was added to the system by passing part of the diluent air through a heated gas scrubber that contains water. The actual humidity was determined with an electronic hygrometer (YSI Model 91HC Dew Point Hygrometer with Model 9102 dual probe).

R&S166335

The badge exposure chamber used was a miniaturized wind tunnel made of glass rectangular tubing with a water jacket which allowed temperature control. Chamber temperature was controlled by pumping an ethylene glycol-water mixture from a refrigerated circulator (Lauda Model RC-3T) through the chamber glass jacket. Temperatures were measured by thermocouples at the top and bottom of the chamber. The pressure in the chamber was changed by either increasing flow rates with line restriction or using an on-line Du Pont Constant Flow Sampler Pump.

The total flow rate of the system was measured at the end of the apparatus train with an electronic mass flow meter (Hastings Model ALK-5K, calibrated daily with a soap bubble meter). Flow rates could be varied between 0.1 and 2 liters per minute.

PROCEDURES

Solution and Reagent Standardization

Absorbing solutions and color reagents used in the reagent pack generally are similar to those used in NIOSH published impinger methods. Initial badge color development consisted of:

1. Verification of the linear range of the NIOSH impinger test.
2. Reduction of absorbing solution and color reagent volumes to meet reagent pack dimensions.
3. Determination of absorbing solution and color reagent solution storage stability.

All chemicals used were Fisher ACS Grade. All solutions were prepared with distilled water (conductivity, 0.5 μmhos/cm to 2 μmhos/cm). Absorbance maxima of the color forming species were verified on an ultraviolet scanning spectrophotometer (Perkin-Elmer Model 552). The general analytical procedures followed for method development were similar to NIOSH recommended procedures.

Laboratory Exposure Testing and Analysis

The badge exposure chamber can hold up to 12 badges. For PRO-TEK™ badges, most tests involved using four to ten badges at standard conditions of 25°C, 760 mm Hg, less than 5 percent relative humidity, and 10 ft/min face velocity. The chamber design permits easy exposure replication. Sampling times varied from two to eight hours.

R&S166336

Attachment B

Summary of Statistical Terms and Formulae

The statistical analysis employed was similar to NIOSH methods (Reference 4) and is described in Reference 5. Some key terms, statistical formulae, acceptable limits, and statistical tests used in these reports are summarized below.

Mean = Arithmetic mean or average, defined as the sum of all observations divided by the number of observations (n).

Standard Deviation = The positive square root of the variance which is defined as the sum of squares of the deviations of the observations from the mean ($\bar{x}$) divided by one less than the total number of observations (n-1).

$$\text{Std. Dev.} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}}$$

CV = Coefficient of Variation or Relative Standard Deviation, defined as the standard deviation divided by the mean.

$$CV = \frac{\text{Std. Dev.}}{\text{mean}}$$

MCV = Mean (pooled) coefficient of variation; the value is derived from the coefficients of variation obtained from the analysis of 10 samples tested over at least three concentration levels between 0.5X and 2.5X the OSHA standard level. The mathematical equation is expressed as:

$$MCV = \sqrt{\frac{(n_1-1)\ (CV_1)^2 + \ldots\ (n_i-1)\ (CV_i)^2}{\sum_{i=1}^{p} (n_i-1)}}$$

where:

p = number of levels.

(n_i-1) = degrees of freedom, equal to number of observations minus one, at the i^{th} level.

CV_i = coefficient of variation of the observations at the i^{th} level.

R&S166337

b_i = Bias of the ten generated samples at any one concentration. The mathematical equation is expressed as:

$$b_i = \frac{\bar{X}_i, \text{ aver. ppm (badge)} - X_o, \text{ cert. cylinder concn. (ppm)}}{X_o, \text{ cert. cylinder concn. (ppm)}}$$

$\bar{b}$ = Mean (pooled) bias; the value is derived from the individual bias obtained from the analyses of ten samples tested over at least three concentration levels between 0.5X and 2.5X the OSHA standard level. The mathematical equation is expressed as:

$$\bar{b} = \frac{b_1 n_1 + b_2 n_2 + \ldots b_i n_i}{\sum_{i=1}^{p} n_i}$$

where: n = the number of badges exposed at each concentration level.
p = the number of levels.

OSA = Overall System Accuracy; defined as the percent difference between a measured concentration and the true concentration of a sample. The mathematical equation is expressed as:

$$OSA = \pm \left[\begin{matrix} \text{Absolute} \\ \text{Mean Bias} \end{matrix} + 2\ (MCV) \right] \times 100$$

Test for Rejection of an Observation

The Q test (2) was used to identify an outlier observation. The spread between the questionable observation and its nearest neighbor is divided by the spread separating the highest and lowest result in a set. This quotient (Q) is compared with the appropriate Q value in the table. The questionable observation may be rejected with 90 percent confidence if the calculated Q value exceeds that in the table below:

Number of Observations	Q
2	--
3	0.94
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

R&S166338

REFERENCES

1. D. G. Taylor, R. E. Kupel, J. M. Bryant, Documentation of NIOSH Validation Tests, Publication No. 77-185.

2. E. V. Kring, Ph.D.; W. J. Lautenberger, Ph.D.; W. B. Baker; J. J. Douglas; and R. A. Hoffman, "A New Colorimetric Air Monitoring Badge System for Ammonia, Sulfur Dioxide and Nitrogen Dioxide," submitted for publication to AIHA.

3. D. G. Taylor, R. E. Kupel, J. M. Bryant, Documentation of NIOSH Validation Tests, Back-Up Data Report No. S 308.

4. NIOSH Manual of Analytical Methods, 2nd Ed. Part 1-5 DHEW (NIOSH) Pub. No. 77-157A.

5. R. B. Dean and W. J. Dixon, Anal. Chem. 23:636 (1951).

Table 1

Sulfur Dioxide Analysis

Level[a]	$\mu g\ SO_3^{=}$ Taken[b]	$\mu g\ SO_2$ Taken	Absorbance at 548 nM
0	0	0	0
	0	0	0
			n = 2
			m = 0
			Std. Dev. = 0
			CV_1 = 0
0.325X	2.13	1.7	0.12
	2.13	1.7	0.13
			n = 2
			m = 0.125
			Std. Dev. = 0.00707
			CV_2 = 0.0566
0.675X	4.13	3.3	0.24
	4.13	3.3	0.24
			n = 2
			m = 0.24
			Std. Dev. = 0.00
			CV_3 = 0.00
0.975X	6.25	5.0	0.35
	6.25	5.0	0.34
			n = 2
			m = 0.345
			Std. Dev. = 0.00707
			CV_4 = 0.0205
1.375X	8.25	6.6	0.48
	8.25	6.6	0.46
			n = 2
			m = 0.470
			Std. Dev. = 0.0141
			CV_5 = 0.03009
1.575X	10.38	8.3	0.56
	10.38	8.3	0.57
			n = 2
			m = 0.565
			Std. Dev. = 0.00707
			CV_6 = 0.01252

[a]Equivalent to an eight-hour Time Weighted Average (TWA) concentration for Permissible Exposure Limit (PEL) of 5 ppm (13 mg/m^3).

[b]Standardized solutions of sodium sulfite were used to prepare the spiked samples.

Table 1

Sulfur Dioxide Analysis (Continued)

Level[a]	μg $SO_3^=$ Taken[b]	μg SO_2 Taken	Absorbance at 548 nM
1.85X	12.50	10.0	0.66
	12.50	10.0	0.66
			n = 2
			m = 0.66
			Std. Dev. = 0.00
			CV_7 = 0.00
2.025X	13.50	10.8	0.70
	13.50	10.8	0.69
			n = 2
			m = 0.695
			Std. Dev. = 0.00707
			CV_8 = 0.01017
2.05X	14.5	11.6	0.73
	14.5	11.6	0.72
			n = 2
			m = 0.725
			Std. Dev. = 0.00707
			CV_9 = 0.00975
2.30X	15.6	12.5	0.82
	15.6	12.5	0.85
			n = 2
			m = 0.835
			Std. Dev. = 0.0212
			CV_{10} = 0.0254
2.50X	16.6	13.3	0.89
	16.6	13.3	0.88
			n = 2
			m = 0.885
			Std. Dev. = 0.00707
			CV_{11} = 0.00799

MCV = 0.017

[a]Equivalent to an eight-hour Time Weighted Average (TWA) concentration for Permissible Exposure Limit (PEL) of 5 ppm (13 mg/m^3).

[b]Standardized solutions of sodium sulfite were used to prepare the spiked samples.

R&S166341

Table 2

Sulfur Dioxide Sampling and Analysis

Test Level	Found (C-20 Badge) (ppm-hrs)	ppm	mg/m^3	Taken (SO_2 Analyzer) (ppm-hrs)	ppm	mg/m^3
0.84X	34	4.25	11.1	33.4	4.2	10.9
	34	4.25	11.1			
	33	4.13	10.7			
	33	4.13	10.7			
	35	4.38	11.4			
	33	4.13	10.7			
	31	3.88	10.1			
	34	4.25	11.1			
	34	4.25	11.1			
	29	3.63	9.4			
1.11X	49	6.13	15.9	45.4	5.6	14.4
	45	5.63	14.6			
	40	5.00	13.0			
	44	5.50	14.3			
	52	6.50	16.9			
	41	5.13	13.3			
	44	5.50	14.3			
	44	5.50	14.3			
	50	6.25	16.3			
	46	5.75	15.0			

$n = 10$
Std. Dev. $= 1.764$
$CV_1 = 0.0534$
$Bias_1 = -0.015$

$n = 10$
Std. Dev. $= 3.837$
$CV_2 = 0.084$
$Bias_2 = +0.0247$

R&SI66342

Table 2

Sulfur Dioxide Sampling and Analysis (Continued)

Test Level (OSHA std.)	Found (ppm-hrs)	Found ppm	Found mg/m^3	Taken (ppm-hrs)	Taken ppm	Taken mg/m^3
1.68X	66	8.25	21.5	67.2	8.4	21.8
	65	8.13	21.1			
	62	7.75	20.2			
	69	8.63	22.4			
	67	8.38	21.8			
	69	8.63	22.4			
	64	8.00	20.8			
	67	8.38	21.8			
	66	8.25	21.5			
	67	8.38	21.8			

n = 10
Std. Dev. = 2.150
CV_3 = 0.0325
$Bias_3$ = -0.0149

2.17X	80	10.0	26.0	82.8	10.4	26.9
	87	10.9	28.3			
	81	10.1	26.3			
	88	11.0	28.6			
	90	11.3	29.3			
	97	12.1	31.5			
	85	10.6	27.6			
	81	10.1	26.3			
	82	10.3	26.7			
	86	10.8	28.0			

n = 10
Std. Dev. = 5.208
CV_4 = 0.0608
$Bias_4$ = -0.0350

MCV = 0.058
Mean Bias = -0.010

Overall System Accuracy = $\pm$ [Absolute Mean Bias + 2 (MCV)] x 100

OSA = $\pm$ [.01 + 2 (0.058)] x 100

OSA = $\pm$ 12.6%

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Table 3

Temperature Effect Study at
10.4 ppm (27 mg/m^3) TWA for Eight Hours

Temp. °C	Temp. °K	No. of Badges Tested	Average Absorbance
10.1	283.1	8	0.73
25	298	34	0.77
41.3	314	11	0.75

Table 4

Effect of NO_2 (Common Interference) on Analytical Method

μg SO_2 Added	μl NO_2 Added	μg SO_2 Found	
		With Sulfamic Acid	Without Sulfamic Acid
38.4	0	41.2	41.2
38.4	4	41.2	42.0
38.4	8	41.3	40.2
38.4	12	41.0	22.4
38.4	16	41.0	20.2
38.4	20	41.0	22.4
38.4	24	41.0	16.0
38.4	28	41.2	15.6
38.4	32	40.4	14.0
38.4	40	41.2	11.6

Table 5

Storage Stability Study
(Refrigerated)

Samples Analyzed Immediately (mg/m^3)	Samples Analyzed After One Week (mg/m^3)
14.3	15.5
14.9	14.9
16.4	14.4
14.2	15.9
14.3	13.8
14.0	14.0
15.6	15.0
Mean = 14.8	Mean = 14.8
Std. Dev. = 0.886	Std. Dev. = 0.769
CV = 0.060	CV = 0.052

Table 6

Storage Stability Study
(Room Temperature)

Samples Analyzed Immediately (mg/m^3)	Samples Analyzed After Seven Days at Room Temperature (mg/m^3)
14.6	13.4
14.6	12.3
13.0	13.3
13.8	13.8
Mean = 14.0	Mean = 13.2
Std. Dev. = 0.766	Std. Dev. = 0.637
CV = 0.055	CV = 0.048

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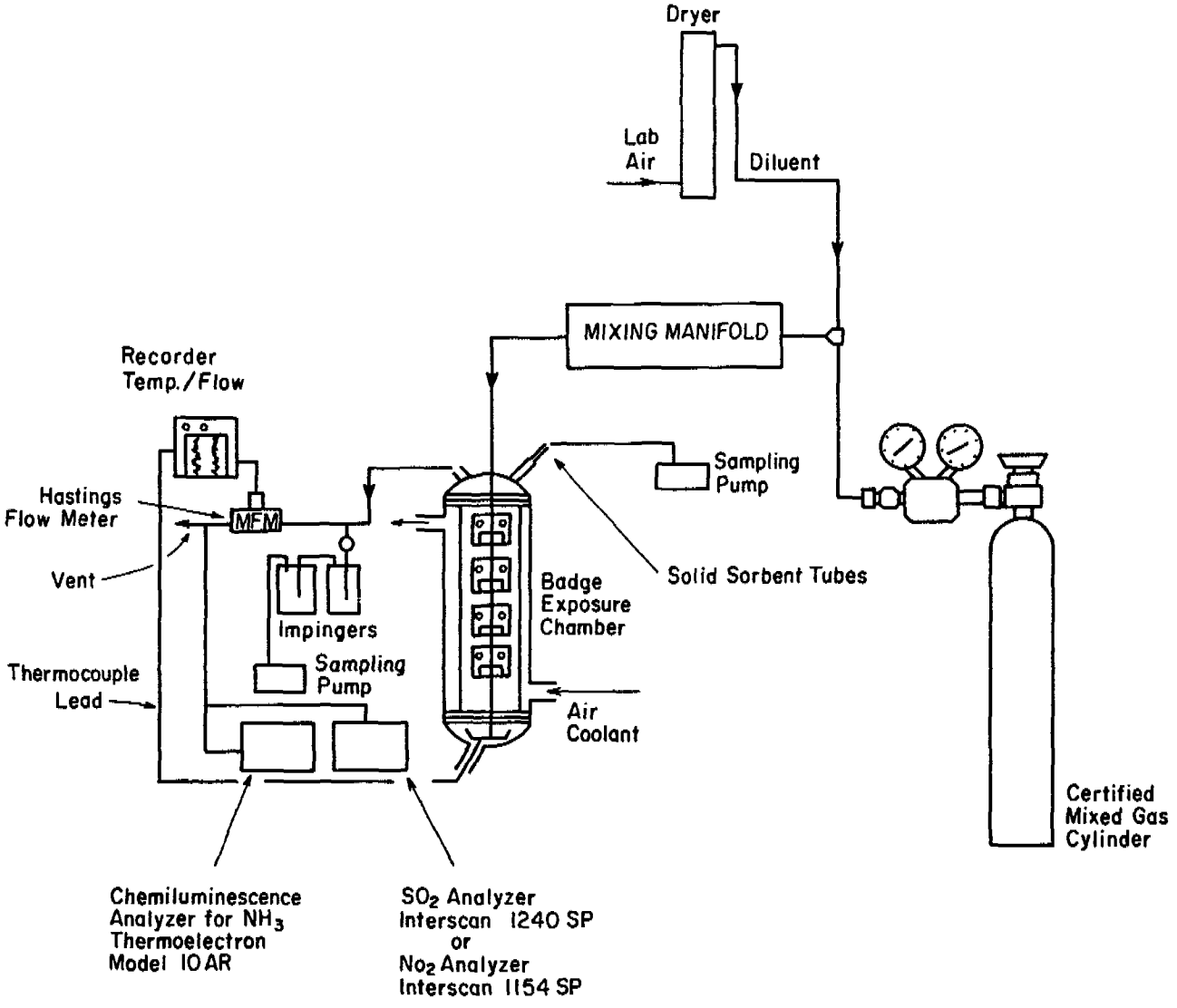
FIGURE 1

LIQUID SORBENT LABORATORY VALIDATION APPARATUS



R&S166347