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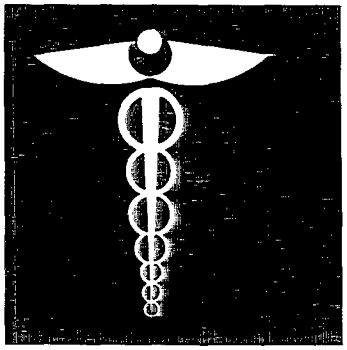
NITROGEN DIOXIDE



U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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THE EVALUATION OF GAS DETECTOR TUBE SYSTEMS:

Nitrogen Dioxide

by

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ABSTRACT

The National Institute for Occupational Safety and Health, U. S. Public Health Service, recently tested nitrogen dioxide gas detector tubes from five manufacturers for reliability. The test gas was generated at concentrations of one-half, one, two, and five times the threshold limit value (TLV) by means of a dynamic permeation tube method. Concentrations were verified analytically using the Saltzman technique for NO_2. The performance requirement of ±25% accuracy at the 95% confidence level at one, two, and five times the TLV and ±35% at one-half the TLV was met by only the Drager CH 30001.5950 detector tube.

INTRODUCTION

Gas detector tubes provide a simple, inexpensive method for determination of the concentration of a given toxic gaseous contaminant in a workplace atmosphere. However, the accuracy of detector tubes has so often been questioned, that the National Institute for Occupational Safety and Health of the U.S. Public Health Service undertook a performance study. The goal of the study is to inform the industrial hygienist of gas detector tube performance and to encourage improved quality control in the manufacturing of the tubes.

TESTING EQUIPMENT

Nitrogen dioxide concentrations of 2.5 ppm, 5.0 ppm, 10.0 ppm, and 25.0 ppm were generated by means of a dynamic permeation tube method (see Figure 1). Liquid nitrogen dioxide, sealed inside a teflon tube and kept at a constant temperature, was placed in condensers where it permeated through the wall of the teflon tube at a known, constant rate. A stream of nitrogen entered the condensers at one end, and this stream together with the permeating nitrogen dioxide was called the contaminant stream. This stream was in turn mixed in the mixing bulb with a known flow rate of purified air, called the dilution air stream, to achieve the desired NO_2 concentration.

The contaminant stream originated from a cylinder of pure nitrogen. The nitrogen was regulated down from cylinder pressure to 10 psig. The stream was then passed through a desiccant, and metered with a needle valve to a constant flow on a rotameter. Next the nitrogen was passed through the two glass* condensers in series which contained the NO_2 permeation tubes. The water in the condenser jackets was kept at constant temperature by an externally circulating constant temperature water bath. The contaminant stream was mixed with the dilution air stream in a glass mixing bulb. The combined stream then flowed to a five-ported glass sampling bulb.

The dilution air stream began as compressed air from the building air system. First the air was passed through an oil and water filter. Next it was regulated down to 20 psig. The air was then heated by an oven to a temperature of 1000°F

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*Because of the reactive nature of nitrogen dioxide, only glass and teflon were used downstream of the permeation tubes.

to burn off hydrocarbons. The heated air was passed through a water cooler to cool it down to ambient temperature. Next the air passed through a bed of activated charcoal, ascarite, and desiccant to remove remaining hydrocarbon impurities - carbon dioxide and water respectively, and then through a particulate filter. Air flow was regulated by a needle valve to a constant flow on a rotameter.

The dilution air stream then mixed with the contaminant stream in the mixing bulb.

Four of the five ports on the glass sampling bulb were used to take detector tube samples or samples for chemical analysis (see Figure 2). The fifth port was used to pass the excess gas generated to a ventilation outlet. When samples were taken for chemical analysis, the gas sample was drawn by a vacuum pump through two fritted glass bubblers connected in series. Flow rate was regulated by a critical orifice calibrated at various pressure drops through the system.

TESTING PROCEDURE

Nitrogen dioxide was generated using Dynacal* standard rate permeation tubes. Three 30 cm long permeation tubes were placed inside the condensers (see Figure 1). The tubes were kept at 30°C ±0.1°C by the constant temperature water bath. At constant temperature nitrogen dioxide permeated through the wall of the tube at a constant rate. The permeation tubes were weighed prior to insertion into the condensers and at three to four day intervals thereafter. Weight losses due to NO_2 permeation and the corresponding time intervals were recorded. Permeation rates were calculated using the equation:

$$P_T = \frac{\Delta\omega}{(\Delta t)\ (L)}$$

where

P_T = nitrogen dioxide permeation rate at a given temperature (30°C), nanograms/min-cm

$\Delta\omega$ = permeation tube weight loss, nanograms

Δt = time interval between weighings, minutes

L = permeation tube length, cm

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*Mention of commercial products or concerns does not constitute endorsement by the U.S. Public Health Service.

Permeation rates were calculated for each of the three tubes and averaged for subsequent calculations.

The nitrogen dioxide generated by the permeation tubes was swept from the condensers with a constant flow of 138.8 cm^3/min of pure nitrogen. This stream was mixed with dilution air to achieve the desired concentration. The dilution needed was calculated using the following:

$$C = \frac{(K)\ (P_T)\ (L)}{F}$$

or

$$F = \frac{(K)\ (P_T)\ (L)}{C}$$

where

F = total dilution flow needed (includes 138.8 cm^3/min nitrogen flow), cm^3/min

K = conversion factor supplied by the manufacturer for the gas involved (0.532 for nitrogen dioxide) $\frac{\text{ppm } NO_2}{\text{nanogram } NO_2 / cm^3}$

P_T = nitrogen dioxide permeation rate at a given temperature (30°C), nanograms/min-cm

L = permeation tube length, cm

C = desired nitrogen dioxide concentration, ppm

Nitrogen dioxide concentrations were verified chemically by the Saltzman method.[1] The chemically determined concentration and calculated concentration had to agree within 10% before detector tube testing began. Samples were drawn through two Saltzman fritted glass bubblers connected in series (see Figure 2). Flow through the absorbing solution was regulated to approximately 0.5 liter/minute by a critical orifice. Driving force was provided by a vacuum pump. The orifice was calibrated for various upstream pressures indicated by a manometer. Actual nitrogen dioxide concentration was determined spectrophotometrically by the color change in the absorbing solution.

The detector tube samples were taken according to the manufacturer's instructions using the manufacturer's sampling pump. Pumps were checked for leakage and for flow rate specifications according to the manufacturer's instructions. Ten detector tubes from each of the five manufacturers were tested at each of the four nitrogen dioxide concentrations. The detector tubes were read according to manufacturer's instructions by a panel of three independent tube readers. Readings were corrected for density, temperature, and altitude variations according to the manufacturer's instructions. These three readings were then averaged to obtain a single reading for each tube.

EVALUATION

The acceptability of the nitrogen dioxide detector tubes was determined using MIL-STD-414.[2] Standard deviations were calculated using a double specification limit, acceptable quality level of 6.5%, and Inspection Level II. Required accuracy was ±25% at one, two, and five times the TLV, and ±35% at one-half the TLV.[3] Quality indices were obtained and used to determine an estimated per cent defective for each group of detector tubes. To be acceptable, each tube group had to have a per cent defective lower than the maximum allowable in MIL-STD-414.

DISCUSSION OF RESULTS

The results of the NO_2 Detector Tube Test are summarized in Table 1. Of the five detector tube brands tested, only one was found to be acceptable. The Drager CH 30001.5950 tube was acceptable at three test concentrations (Testing at the fourth concentration was not possible, since the range of the tube did not include the highest concentration.). The MSA 83099 detector tube was acceptable at one of the four test concentrations. The Unico 117, Bacharach 19-0154, and Scott-Gastec 8544 detector tubes were unacceptable at all four test concentrations. The performance of each detector tube type will be discussed separately.

Unico 117 (see Table 3)

The Unico 117 detector tubes were found to be generally unsatisfactory. The best accuracy achieved by these tubes at any one test concentration was only ±100%. The tube readings were consistently high, and standard deviations were large (greater than 10% of the mean). However, the tubes showed a good color change with a sharp, easily readable end of stain. Also, channeling was not excessive.

Drager CH 30001.5950 (see Table 4)

The Drager CH 30001.5950 detector tubes were found to be acceptable. They were found to be ±25% accurate at 5 ppm and 10 ppm, and ±35% at 2.5 ppm (one-half the TLV). The tubes were not tested at 25 ppm, since this concentration was beyond the range of the tubes. Color change was good, and the end of stain was very even. The tube readings were generally slightly high but standard deviations were low (less than 10% of the mean). However, according to NIOSH criteria, an acceptable detector tube should cover the entire concentration range from 0.5 to 5 times the TLV. If the Drager CH 30001.5950 tubes were modified to include the 25 ppm concentration, they would have to be re-evaluated since the accuracy of the entire detector tube could be affected.

MSA 83099 (see Table 5)

The MSA 83099 detector tubes performed reasonably well at 2.5 ppm and 10 ppm. They performed poorly at 5 ppm and 25 ppm. At the 2.5 ppm concentration the MSA tubes were ±35% accurate, with a relatively low standard deviation (13% of the mean). At 5 ppm they were only ±100% accurate, with a high standard deviation (30% of the mean). At 10 ppm the MSA tubes were ±50% accurate with a somewhat high standard deviation (18% of the mean). However, they came very close to meeting the ±25% accuracy requirement at 10 ppm. At the 25 ppm concentration the tubes were only ±200% accurate with a high standard deviation (32% of the mean).

It should be noted that 2.5 ppm and 5 ppm were run on the 1 1/2 pump stroke scale, and 10 ppm and 25 ppm were run on the 1/2 pump stroke scale. The MSA detector tubes performed much better at the lower end of each of these scales than at the higher end. The performance of the MSA tubes was also hurt by the fact that the color change was minimal and began fading almost immediately, there was not a very sharp end of stain, and channeling occurred in a number of tubes. They were the most difficult to read of the tubes tested.

Bacharach 19-0154 (see Table 6)

The Bacharach 19-0154 detector tubes were excellent in some respects, but failed to pass the accuracy requirements at any concentration, due to consistently low readings. At 2.5 ppm the Bacharach tubes were ±75% accurate, but with standard deviation at 23% of the mean. At 5 ppm, 10 ppm, and 25 ppm the tubes were ±50% accurate, with low standard deviations (7% to 12% of the mean). The color change was definite and the end of stain was very sharply defined. Also no channeling was experienced with these tubes. This indicates that the main problem with the Bacharach tubes was an inaccurately calibrated scale.

Scott-Gastec 8544 (see Table 7)

The Gastec tube failed at all four concentrations. The cause of failure appeared to be more of a calibration error than a functional error in the tube construction. The standard deviations were low at 5.0 and 10.0 ppm (8% and 10% of the mean, respectively), and somewhat high at 2.5 ppm and 25.0 ppm (17% and 26% of the mean, respectively). Even though the tube failed, it had some good qualities. It gave a distinct yellow stain which was easily read and it gave a well-defined endpoint. Also, channeling does not appear to be a problem. However, the stain tended to fade fairly rapidly.

SUMMARY

Table 1 summarizes the NO_2 detector tube test results. The best accuracy at which each detector tube passed is shown in Table 2.

Only the Drager CH 30001.5950 detector tube was found to be acceptable at ±25% accuracy at one and two times the TLV, and at ±35% accuracy at one-half the TLV. None of the other four brands tested were found to acceptable even at a ±50% accuracy level.

REFERENCES

1. Saltzman, B. E. "Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere." Analytical Chemistry, 29:1949-55, 1954

2. MIL-STD-414. "Military Standard - Sampling Procedures and Tables for Inspection by Variables for Percent Defective." U.S. Department of Defense. June 11, 1957.

3. "Threshold Limit Values of Airborne Contaminants and Physical Agents with Intended Changes Adopted by ACGIH for 1971." American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1971.

TABLE 1.

Summary of NO_2 Detector Tube Test Results

Accuracy ±25% at 5.0, 10.0, and 25.0 ppm and ±35% at 2.5 ppm

Inspection Level II, AQL 6.5%

	TEST LEVEL			
Manufacturer	2.5 ppm	5 ppm	10 ppm	25 ppm
Unico 117	Fail	Fail	Fail	Fail
Drager CH 30001.5950	Pass	Pass	Pass	--
MSA 83099	Pass	Fail	Fail	Fail
Bacharach 19-0154	Fail	Fail	Fail	Fail
Scott Gastec 8544	Fail	Fail	Fail	Fail

TABLE 2

Summary of NO_2 Detector Tube Test Results

Accuray Level at Which Tubes Passed

Inspection Level II, AQL 6.5%

	TEST LEVEL			
Manufacturer	2.5 ppm	5 ppm	10 ppm	25 ppm
Unico 117	±250%	±125%	±100%	±125%
Drager CH 30001.5950	±35%	±25%	±25%	--
MSA 83099	±35%	±100%	±50%	±200%
Bacharach 19-0154	±75%	±50%	±50%	±50%
Scott-Gastec 8544	±150%	±125%	±100%	±100%

TABLE 3

Unico 117 - NO_2 Tube

Lot 0918110

Expiration Date: Aug. 28, 1973

	Concentration (ppm)			
	2.5	5.0	10.0	25.0
Mean	7.34	10.2	15.36	42.4
Standard Deviation	1.37	1.12	3.89	8.19
Q_u	-2.80	-3.09	-0.74	-1.36
Q_L	4.12	5.50	2.02	2.89
% Defective Above Upper Limit	>50.00	>50.00	>50.00	>50.00
% Defective Below Lower Limit	0.00	0.00	1.07	0.00
Total % Defective	>50.00	>50.00	>51.07	>50.00
Max. Allowable % Defective	15.17	15.17	15.17	15.17
Acceptable	No	No	No	No
Acceptability Limit	±250%	±125%	±100%	±125%
Date of Test	10/12/71	10/8/71	10/7/71	10/6/71

TABLE 4

Drager CH-30001.5950 - NO_2 Tube

Lot 105991

Expiration Date: June, 1972

	Concentration (ppm)			
	2.5	5.0	10.0	25.0
Mean	3.11	6.1	11.3	-
Standard Deviation	.28	0.49	0.91	-
Q_u	1.43	1.34	1.34	-
Q_L	5.07	4.22	4.18	-
% Defective Above Upper Limit	6.94	8.48	8.48	-
% Defective Below Lower Limit	0.00	0.00	0.00	-
Total % Defective	6.94	8.48	8.48	-
Max. Allowable % Defective	15.17	15.17	15.17	-
Acceptable	Yes	Yes	Yes	-
Acceptability Limit	±35%	±25%	±25%	-
Date of Test	10/12/71	10/8/71	10/7/71	-

TABLE 5

MSA 83099 - NO_2 Tube

Lot 99

Expiration Date: May, 1972

	Concentration (ppm)			
	2.5	5.0	10.0	25.0
Mean	2.39	7.52	10.22	52.32
Standard Deviation	.32	2.30	1.88	17.10
Q_u	2.25	-0.55	1.21	-1.23
Q_L	2.78	1.64	1.45	1.96
% Defective Above Upper Limit	0.32	>50.00	11.03	>50.00
% Defective Below Lower Limit	0.00	4.06	6.63	1.38
Total % Defective	0.32	>54.06	17.66	>51.38
Max. Allowable % Defective	15.17	15.17	15.17	15.17
Acceptable	Yes	No	No	No
Acceptability Limit	±35%	±100%	±50%	±200%
Date of Test	10/12/71	10/8/71	10/7/71	10/6/71

TABLE 6

Bacharach 19-0154 - NO_2 Tube

Lot 17

Expiration Date: March, 1972

	Concentration (ppm)			
	2.5	5.0	10.0	25.0
Mean	1.12	3.92	5.4	13.4
Standard Deviation	.26	.48	.59	.98
Q_u	7.65	4.80	10.22	10.62
Q_L	-1.46	.35	-2.45	-0.92
% Defective Above Upper Limit	0.00	0.00	0.00	0.00
% Defective Below Lower Limit	>50.00	36.75	>50.00	>50.00
Total % Defective	>50.00	36.75	>50.00	>50.00
Max. Allowable % Defective	15.17	15.17	15.17	15.17
Acceptable	No	No	No	No
Acceptability Limit	±75%	±50%	±50%	±50%
Date of Test	10/12/71	10/8/71	10/7/71	10/6/71

TABLE 7

Scott-Gastec 8544 - NO_2 Tube

Lot 10501

Expiration Date: Oct. 1972

	Concentration (ppm)			
	2.5	5.0	10.0	25.0
Mean	5.78	11.77	19.17	44.47
Standard Deviation	.99	.88	1.85	11.62
Q_u	-2.44	-5.64	-2.34	-3.75
Q_L	4.21	8.76	5.55	.58
% Defective Above Upper Limit	>50.00	>50.00	>50.00	>50.00
% Defective Below Lower Limit	0.00	0.00	0.00	28.61
Total % Defective	>50.00	>50.00	>50.00	>78.61
Max. Allowable % Defective	15.17	15.17	15.17	15.17
Acceptable	No	No	No	No
Acceptability Limit	±150%	±125%	±100%	±100%
Date of Test	3/10/72	3/6/72	3/1/72	2/29/72

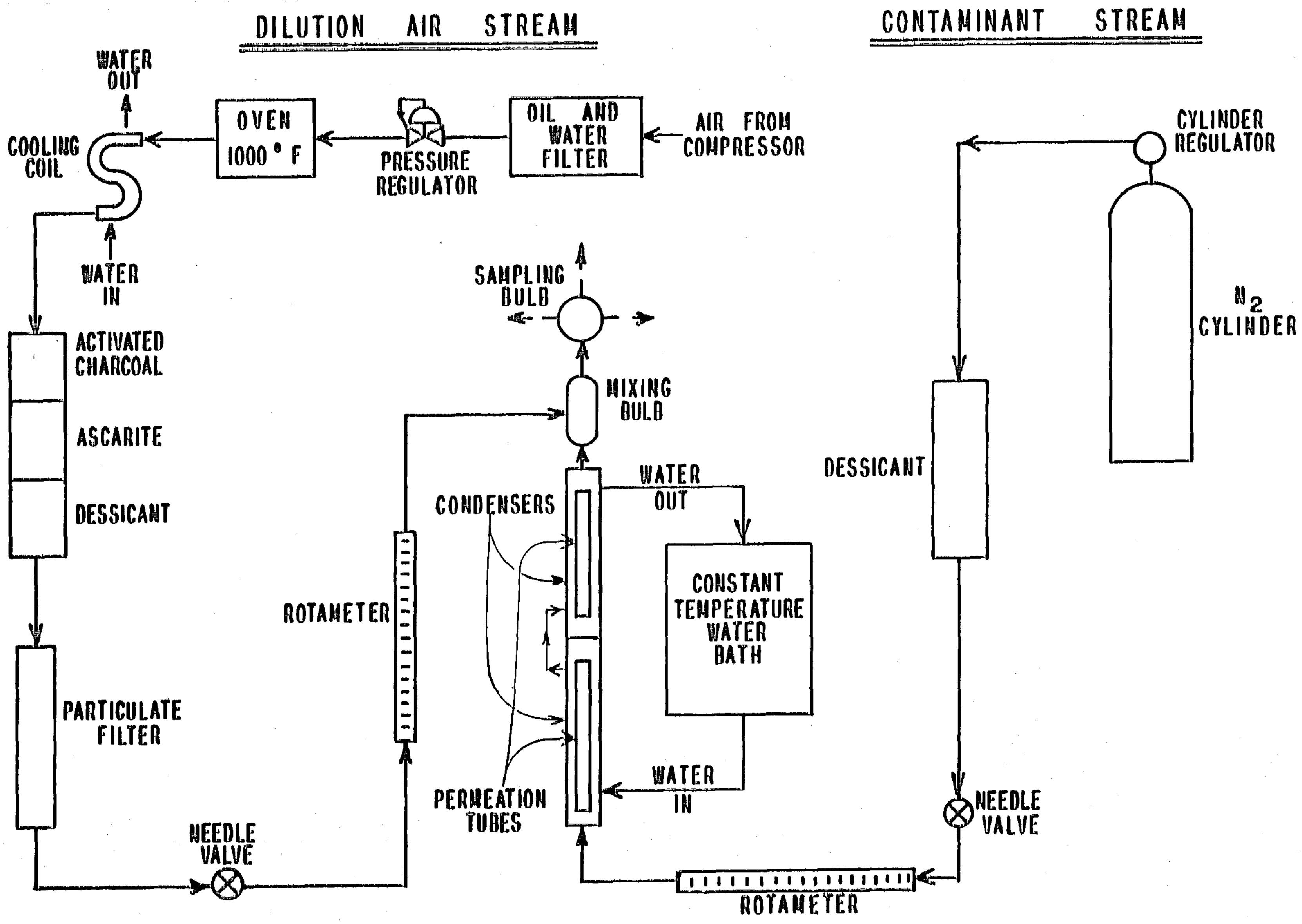

FIGURE I. NO_2 GENERATION SYSTEM

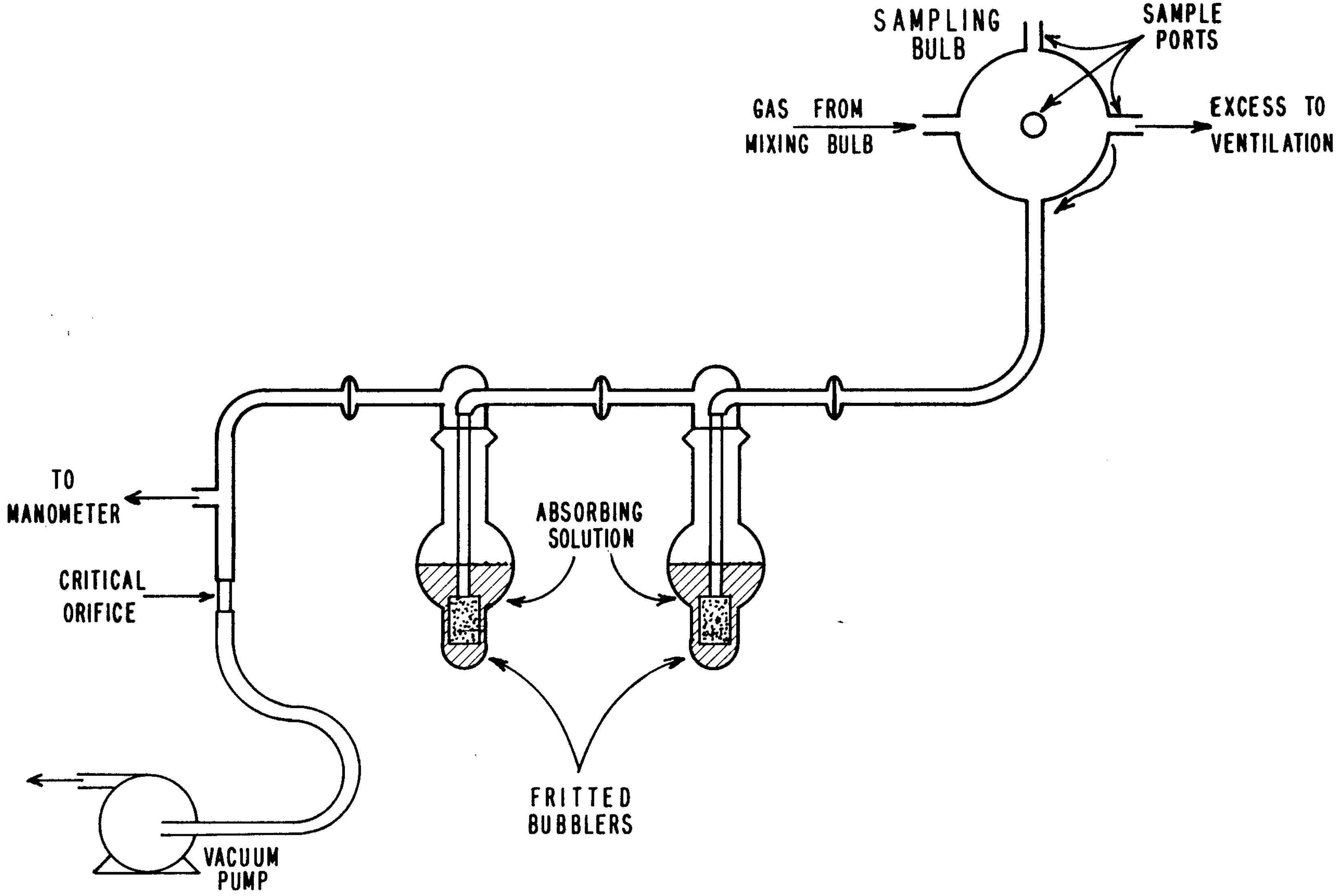

FIGURE 2. CHEMICAL ANALYSIS SAMPLING SYSTEM

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