RR-19

THE EVALUATION OF GAS DETECTOR TUBE SYSTEMS: CHLORINE

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Health Services and Mental Health Administration
National Institute for Occupational Safety and Health

THE EVALUATION OF GAS DETECTOR TUBE SYSTEMS:

Chlorine

by

Bruce A. Johnson

and

C. Paul Roper

RR-19

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Health Services and Mental Health Administration
National Institute for Occupational Safety and Health
Cincinnati, Ohio

June 1972

THE EVALUATION OF GAS DETECTOR TUBE SYSTEMS: Chlorine

ABSTRACT

The National Institute for Occupational Safety and Health, U.S. Public Health Service, conducted a performance study to determine the reliability of Cl_2 detector tubes. Tubes representing all those available in the United States were tested at concentrations of one-half, one, two, and five times the threshold limit value. Known concentrations of Cl_2 were generated by means of a dynamic permeation tube system. These concentrations were verified by using an independent chemical method of analysis. Of the five brands of tubes evaluated, only one was acceptable; the MSA #82399 tube was found to be acceptable within ±25% at the 95% confidence level when tested at one, two, and five times the TLV, and within ±35% at one-half the TLV.

INTRODUCTION

Chemical indicator tubes provide the practicing industrial hygienist with a rapid, inexpensive, and simple method for the determination of gaseous contaminant levels in industrial environments. However, the reliability of these tubes has so often been questioned as to prompt the U. S. Public Health Service, National Institute for Occupational Safety and Health, to undertake a performance study. This study is a continuing research project with the objectives of both informing the industrial hygienist of indicator tube performance and encouraging improved quality control in the manufacturing process of the tubes.

The present detector tube evaluation project is an evaluation program in which tubes representing all those available from all manufacturers marketing indicator tubes in the United States for this contaminant were tested, if they were intended for use over the range from one-half to five times the threshold limit value (TLV).[1] A description of the test procedures and results is contained within this report.

TESTING EQUIPMENT

Chlorine (Cl_2) concentrations of 0.5, 1.0, 2.0, and 5.0 ppm were dynamically generated by means of a permeation tube system as shown in Figure 1. The basic system consisted of two glass condensers, a mixing chamber, and a sampling bulb, all connected in series. Water from a water bath was circulated through the outside of the condensers to keep the temperature inside them constant. The generating system was fed by two gas streams, the contaminant stream and the dilution stream.

The contaminant stream was initially composed of pure nitrogen which was stored in a pressurized cylinder. The nitrogen was passed through tank and pressure regulators and through a needle valve which regulated the flow rate of gas through a calibrated rotameter and into the condensers. As the nitrogen passed through the condensers, it mixed with the permeating Cl_2 and carried it into the mixing chamber. In the mixer, the gas was mixed with various quantities of air from the dilution stream to produce the desired concentrations of chlorine.

The dilution stream consisted of highly purified compressed air. Air from the compressor was first passed through a water and oil filter and into a small electric furnace. The furnace heated the air to 1000°F to burn off hydrocarbons and to oxidize CO to CO_2. The stream then passed through an activated charcoal filter to remove any remaining hydrocarbons

and through a Drierite* drying chamber to remove H_2O. Particulate matter was removed from the air by a membrane capsule filter having a mean pore size of 1.0 micron or less. The flow rate of the air through a calibrated rotameter was controlled by a needle valve before it entered the mixing chamber. From the mixing chamber, the diluted contaminant stream passed into the sampling bulb.

The bulb was equipped with five sampling ports. Three of these ports were sealed with ground glass fittings. A fourth port led to a ventilation outlet located directly above the sampling bulb and the fifth port was used for taking samples for chemical analysis. Because of the highly reactive nature of chlorine, care was taken to use only glass and teflon tubing and fittings from this port. When samples for chemical analysis were taken, a vacuum pump was used to draw Cl_2 from the fifth port through two fritted bubblers connected in series as shown in Figure 2. The actual flow through the impingers was determined by using a mercury manometer to measure the pressure drop below atmospheric pressure created upstream from a critical orifice. The flow rates for different pressure drops were measured with a bubble meter, and a calibration curve was constructed by plotting flow rate against pressure drop.

TEST PROCEDURES

The generation of Cl_2 began by placing one Dynacal* standard rate permeation tube inside one of the two condensers. The tube was 30 cm long. The temperature inside the condensers was maintained at 10°C. The tubes were weighed on an analytical balance when they were first placed in the condensers and every other day thereafter until the tube reached equilibrium. The weight loss was recorded to five decimal places and the permeation rate in ng/min-cm derived from the following equation.

$$P_t = \frac{\Delta\omega}{\Delta t \times L}$$

In this equation, P_t is the permeation rate, $\Delta\omega$ is the weight loss of the tube in ng, Δt is the time in minutes between weighing, and L is the length of the tube in centimeters. At 10°C, the permeation rate was approximately 430 ng/min-cm.

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

The concentration of Cl_2 was varied by changing the flow rate of air into the mixing chamber. The flow rate of nitrogen was held constant at 35 cm^3/min. The flow rates necessary to produce the desired concentrations were calculated using the following equation.

$$C = \frac{k \times P_t \times L}{F}$$

In this equation, C is the desired concentration of Cl_2 in ppm, k is a conversion constant supplied by the manufacturer of the permeation tubes (0.345 for Cl_2 at standard conditions), P_t is the permeation rate in ng/min-cm, L is the total length of the permeation tube in cm, and F is the flow rate of the diluted contaminant stream (total of air plus nitrogen) in cm^3/min.

To verify the concentrations, samples of Cl_2 were analyzed by chemical methods. The chemically determined concentrations had to agree as closely as possible (preferably within ±10%) with the calculated concentrations before testing of detector tubes could begin. The samples for chemical analysis were taken by drawing Cl_2 through two 100 ml fritted bubblers connected in series with glass fittings as shown in Figure 2. The bubblers contained 50 ml each of a dilute solution of methyl orange. The Cl_2 was bubbled through the bubblers for 10 - 50 minutes. The exact time was measured to the nearest 0.01 minute by using a stop watch. The flow rate was determined from the pressure drop created upstream of a 0.5 lpm critical orifice by the bubblers and was multiplied by the sampling time to give the total amount of flow through the bubblers. The methyl orange was quantitively bleached by free chlorine, and the extent of bleaching was determined by spectrophotometric measurement.[2]

The detector tubes were tested by drawing the Cl_2 through the tubes by means of the manufacturer's pumps and in accordance with his instructions. Pumps were periodically checked against volume and flow rate specifications and changed after each set of 10 tubes. Ten detector tubes for each of five manufacturers were tested at each concentration. Four different concentrations were used. Each tube was read by a panel of three independent readers following the manufacturer's instructions. The readers were chosen from available personnel and were required to pass a standard color-blindness test. The known concentration was not revealed to the readers, and they were not allowed to know the readings of the other readers.

EVALUATION

The acceptability of the Cl_2 tubes was determined by using MIL-STD-414.[3] The standard deviation method was applied to

each set of tubes using a double specification limit, acceptable quality level of 6.5%, and Inspection Level II. By applying this method, quality indices were obtained and estimates of the percentage of the tubes which were defective were made from appropriate tables. To be acceptable, the tubes had to be accurate to within ±25% of the concentration, either chemical or calculated, whichever was closest to the measured concentration, at one, two, and five times the TLV and within ±35% at 0.5 times the TLV. They also had to have a lower percentage of defective tubes than allowed by the specifications of MIL-STD-414.

RESULTS

Only tubes manufactured for ranges including 0.5 to 5.0 ppm were evaluated. Of the five Cl_2 tube brands tested, only the MSA #82399 tube was found to be acceptable at all four concentrations. Bacharach #19-0239 was found to be acceptable at three of the four concentrations and Drager #CH-243 was found to be acceptable at one of the four concentrations. Unico #109 and Gastec #8L(8543) were found to be unacceptable at all four concentrations. The results of these tests and the limits of acceptability are shown in Tables 1 - 6. These results are representative of one batch only for each brand of tube. For the tubes that passed there has been no inspection of manufacturers' quality control programs to ensure the same high quality of tubes for every batch. Likewise, there has been no further study made to imply that the same performance may be expected from all batches of the other tube brands.

DISCUSSION OF RESULTS

The MSA #82399 tube was the only Cl_2 tube to meet the specified standards at all four concentrations. The tube produced a fairly distinct color change, and the standard deviations were generally quite low. However, there was a considerable amount of rapid fading of the stain at the endpoint making it difficult to determine where the stain actually ended. Although there was a small amount of channeling as a result of uneven packing, channeling was not observed to be a major problem.

The Bacharach #19-0239 tube was found to acceptable at all concentrations except at one-half the TLV. At this concentration the tube was only accurate within ±70%. This inaccuracy was largely a result of extremely short stain lengths and severe channeling. Channeling was also a major problem at the other concentrations. In spite of this, the standard deviations were quite small at the upper three concentrations. The tubes had a very distinct color change which made it easy to read the stain length. Also, there was only a small amount of fading at the endpoint of the stain.

The Drager #CH-243 tube was found to be acceptable only at one-half the TLV. Although the standard deviations were consistently quite small, the mean readings were usually considerably lower than the actual concentrations. This appears to have been caused primarily by a calibration error in the tube. Also, it was very difficult to determine the extent of staining because of the slight color contrast and rapid fading of the stain at the endpoint. There was a small amount of channeling, but not enough to be a major problem.

The Unico #109 tube was found to be unacceptable at all four concentrations. The tubes were found to be accurate within ±40% at one-half the TLV, ±50% at the TLV, and ±30% at two and five times the TLV. The tube had very small standard deviations at all concentrations as a result of a very sharp color change. The primary cause of failure was the extremely short stain lengths making it very difficult to interpolate between marks on the scale to arrive at tube readings. Because of the small tube diameter, channeling was not a problem. The intensity of the color faded quite rapidly.

The Gastec #8L(8543) tube was also found to be unacceptable at all four concentrations. The mean readings were much higher than the actual concentrations, but the standard deviations were generally quite small. The color change was very distinct and the endpoint of the stain was easy to determine. It appears that failure was caused more by a calibration error rather than by a functional problem with the tube. Channeling was not a problem.

SUMMARY

Only the MSA #82399 Cl_2 tube was found to be acceptable within ±25% at one, two, and five times the TLV and within ±35% at one-half the TLV. Bacharach #19-0239 was found to be acceptable at the upper three concentrations, but was only accurate within ±70% at one-half the TLV. Drager #CH-243 and Unico #109 were found to be acceptable within an alternate accuracy limit of ±50%.

REFERENCES

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

2. American Public Health Association. "Tenative Method of Analysis for Free Chlorine Content of the Atmosphere (Methyl Orange Method)." Health Laboratory Science, 8:1, January 1971.

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

Table 1. MSA - Cl_2 #82399

Tested: April 24-May 4, 1972

Batch #154 - Expiration Date, July, 1974

	Concentration (ppm)			
	0.5(0.73)	1.0(1.0)	2.0(2.23)	5.0(5.0)
Mean	0.68	0.92	2.23	4.87
S(Std. Dev.)	0.07	0.09	0.34	0.46
Qu	4.13	3.83	1.63	2.99
Q_L	2.85	1.92	1.63	2.41
% Defective Above Upper Limit	0%	0%	4.18%	0%
% Defective Below Lower Limit	0%	1.62%	4.18%	0.10%
Total % Defective	0%	1.62%	8.36%	0.10%
Max. Allowable % Defective	15.17%	15.17%	15.17%	15.17%
Acceptable	YES	YES	YES	YES
Date of Test	5/4/72	5/2/72	4/25/72	4/28/72

Tabale 2. Bacharach - Cl_2 # 19-0239

Tested: April 25-May 4, 1972

Batch #18 - Expiration Date, July 25, 1972

	Concentration (ppm)			
	0.5(.50)	1.0(1.35)	2.0(1.76)	5.0(5.0)
Mean	0.49	1.32	1.88	5.10
S(Std. Dev.)	0.75	0.15	0.27	0.65
Qu	0.75	2.56	1.18	1.77
Q_L	0.66	2.08	2.03	2.08
% Defective Above Upper Limit	23.10%	0.2%	11.68%	2.74%
% Defective Below Lower Limit	25.96%	0.82%	1.03%	0.82%
Total % Defective	49.06%	0.84%	12.71%	3.56%
Max. Allowable % Defective	15.17%	15.17%	15.17%	15.17%
Acceptable	NO	YES	YES	YES
Date of Test	5/4/72	5/2/72	4/25/72	4/28/72

Table 3. Drager - Cl_2 #CH-243

Tested: April 25 - May 4, 1972

Batch #211191 - Expiration Date, Januray, 1974

	Concentration (ppm)			
	0.5(0.5)	1.0(1.0)	2.0(1.76)	5.0(5.0)
Mean	0.49	0.66	1.28	2.86
S(Std. Dev.)	0.03	0.05	0.07	0.21
Q_u	5.38	11.76	13.46	16.14
Q_L	4.63	-1.74	-0.64	-4.25
% Defective Above Upper Limit	0%	0%	0%	0%
% Defective Below Lower Limit	0%	>50%	>50%	>50%
Total % Defective	0%	>50%	>50%	>50%
Max. Allowable % Defective	15.17%	15.17%	15.17%	15.17%
Acceptable	YES	NO	NO	NO
Date of Test	5/4/72	5/2/72	4/25/72	4/28/72

Table 4. Unico - Cl_2 #109

Tested: April 25,- May 4, 1972

Batch #1118051 - Expiration Date, June 23, 1972

	Concentration (ppm)			
	0.5(0.73)	1.0 (1.35)	2.0(2.23	5.0(5.45)
Mean	0.80	1.38	2.29	6.20
S(Std. Dev.)	0.18	0.44	0.46	0.61
Qu	1.02	0.69	1.07	1.00
Q_L	1.81	0.84	1.33	3.44
% Defective Above Upper Limit	15.46%	24.99%	14.22%	15.97%
% Defective Below Lower Limit	2.40%	20.39%	8.66%	0%
Total % Defective	17.86%	45.38%	22.88%	15.97%
Max. Allowable % Defective	15.17%	15.17%	15.17%	15.17%
Acceptable	NO	NO	NO	NO
Date of Test	5/4/72	5/2/72	4/25/72	4/28/72

Table 5. Gastec - Cl_2 #8L(8543)

Tested: April 25 - May 4, 1972

Batch #10602 - Expiration Date, October, 1972

	Concentration (ppm)			
	0.5(0.73)	1.0(1.53)	2.0(2.23)	5.0 (5.45)
Mean	1.24	1.88	3.78	8.93
S(Std. Dev.)	0.24	0.21	0.28	1.27
Qu	-1.05	0.14	-3.61	-1.67
Q_L	3.15	3.50	7.64	3.80
% Defective Above Upper Limit	>50%	42.35%	>50%	>50%
% Defective Below Lower Limit	0%	0%	0%	0%
Total % Defective	>50%	42.35%	>50%	>50%
Max. Allowable % Defective	15.17%	15.17%	15.17%	15.17%
Acceptable	NO	NO	NO	NO
Date of Test	5/4/72	5/2/72	4/25/72	4/28/72

Tabale 6. Acceptability Limits Cl_2

Manufacturer	Concentration			
	0.5	1.0	2.0	5.0
Bacharach #19-0239	±70%	±25%	±25%	±25%
Drager #CH-243	±35%	±40%	±35%	±50%
Unico-Kitagawa #109	±40%	±50%	±30%	±30%
MSA #82399	±35%	±25%	±25%	±25%
Scott-Gastec #8L(8543)	±105%	±40%	±85%	±90%

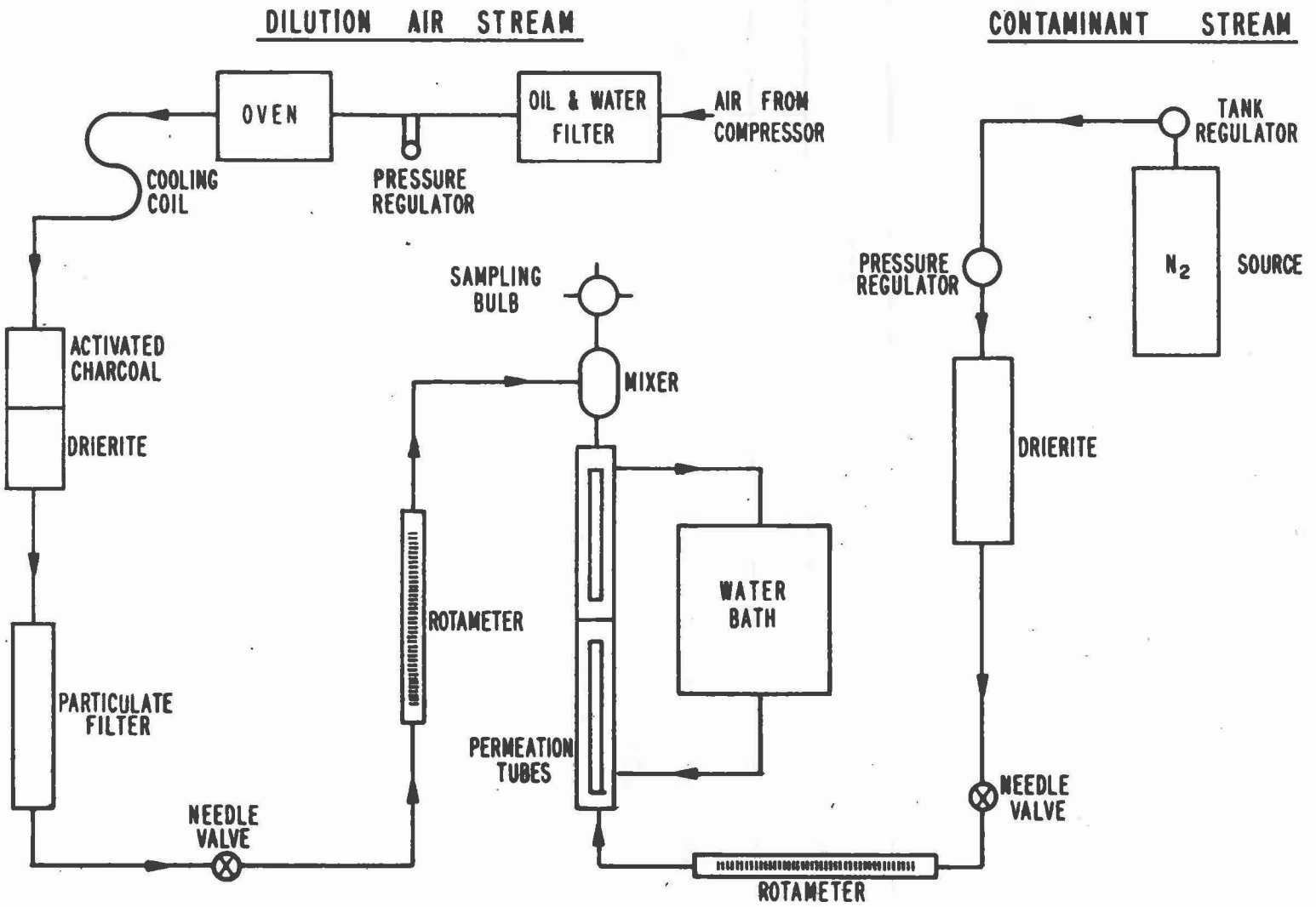

FIGURE 1. PERMEATION TUBE GENERATION SYSTEM

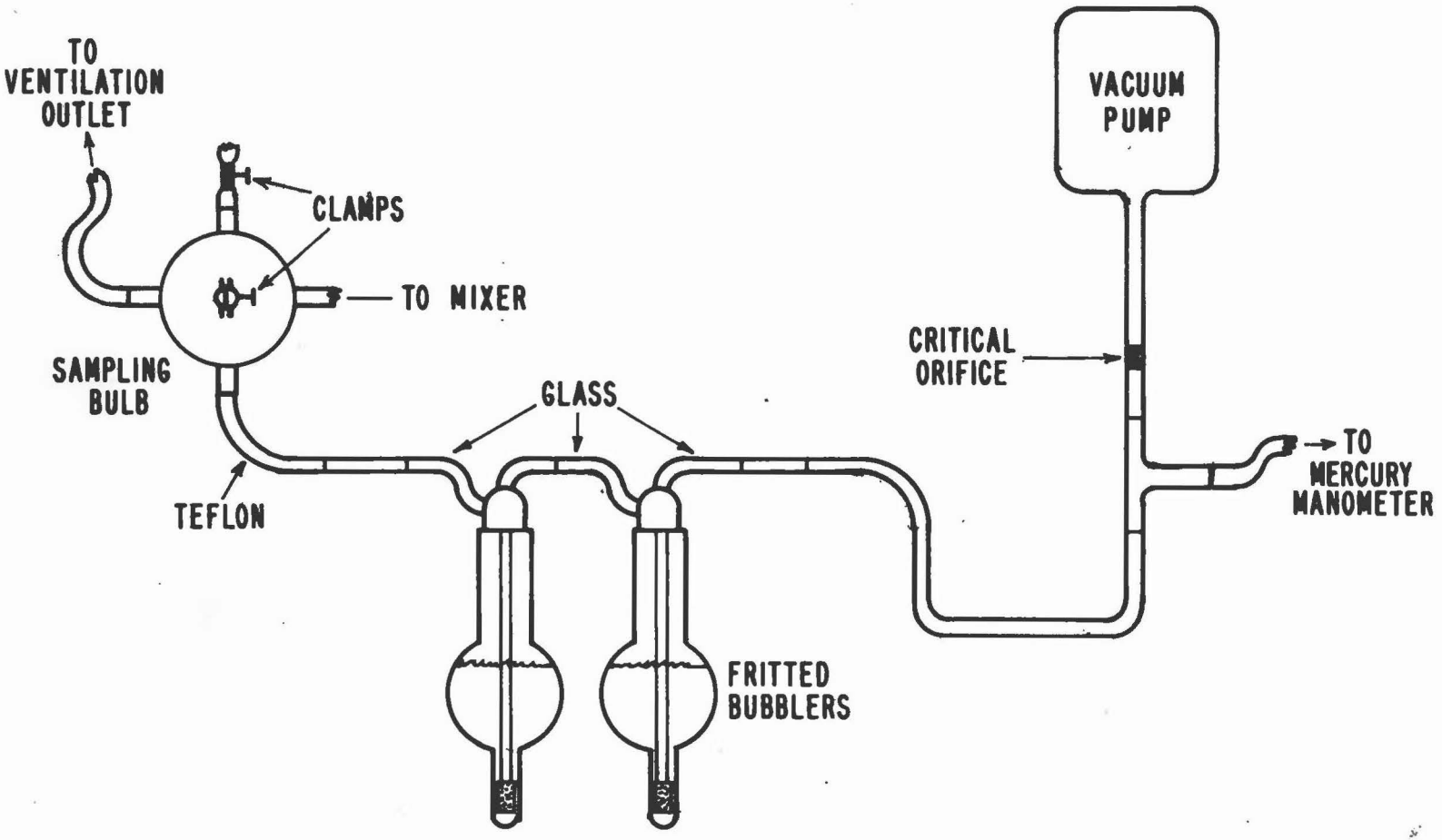

FIGURE 2. SAMPLING APPARATUS - FRITTED BUBBLERS

☆ U.S. GOVERNMENT PRINTING OFFICE: 1972—759-570/1316