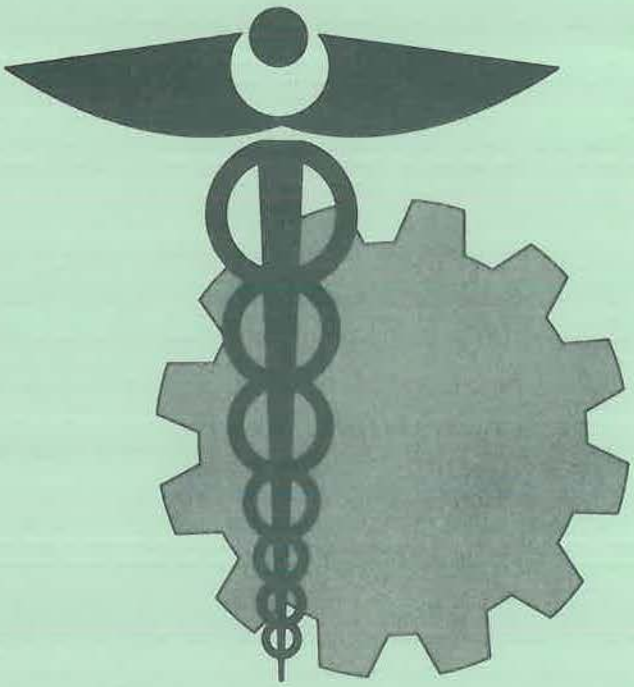
THE EVALUATION OF GAS DETECTOR TUBE SYSTEMS:

HYDROGEN SULFIDE



RR-18

March 1972

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:

Hydrogen Sulfide

by

Bruce A. Johnson

RR-18

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Health Services and Mental Health Administration
National Institute for Occupational Safety and Health
1014 Broadway
Cincinnati, Ohio 45202

March, 1972

THE EVALUATION OF GAS DETECTOR TUBE SYSTEMS:

Hydrogen Sulfide

ABSTRACT

The National Institute for Occupational Safety and Health, U.S. Public Health Service, conducted a performance study to determine the reliability of H_2S 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 H_2S 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 Dräger #CH-298 5/b tube was 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

Hydrogen sulfide (H_2S) concentrations of 5, 10, 20, and 50 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 the gas through a calibrated rotameter and into the condensers. As the nitrogen passed through the condensers, it mixed with the permeating H_2S 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 hydrogen sulfide.

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 the hydrocarbons and to oxidize the 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

---

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

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.

This bulb was equipped with five sampling ports. Three of these ports were fitted with tygon tubing and sealed with clamps. 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 hydrogen sulfide, 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 the H_2S from the fifth port through two midget impingers 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 H_2S began by placing three Dynacal* standard rate permeation tubes inside the two condensers. Two tubes were placed in one condenser and one tube was placed in the other condenser. Each tube was 30 cm long. The temperature inside the condensers was maintained at 30°C. The tubes were weighed on an analytical balance when they were first placed in the condensers and every three or four days thereafter until the tubes 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 30°C, the permeation rate was approximately 457 ng/min-cm.

---

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

The concentration of H_2S 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 H_2S in ppm, k is a conversion constant supplied by the manufacturer of the permeation tubes (0.719 for H_2S at standard conditions), P_t is the permeation rate in ng/min-cm, L is the total length of the permeation tubes 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 H_2S were analyzed by chemical methods. The chemically determined concentrations had to agree within ± 10% of the calculated concentrations before testing of detector tubes could begin. The samples for chemical analysis were taken by drawing H_2S through two 25-ml midget impingers with tapered tips connected in series with glass and teflon tubing as shown in Figure 2. The impingers contained 25 ml each of a suspension of cadmium hydroxide. The H_2S was drawn through a 0.5 l/min critical orifice and bubbled through the impingers for 5-10 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 by the impingers and was multiplied by the sampling time to give the total amount of flow through the impingers. Cadmium sulfide was precipitated out of the solution, and the amount of sulfide was determined by spectrophotometric measurement of the methyl-blue produced by the reaction of the sulfide with a strongly acid solution of N, N-dimethyl-p-phenylenediamine and ferric chloride.[2]

The detector tubes were tested by drawing the H_2S 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 readings for each tube were averaged to give one reading per tube. 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 H_2S 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 MID-STD-414.

RESULTS

Only tubes manufactured for ranges including 5 to 50 ppm were evaluated. Of the five H_2S tube brands tested, only the Dräger #CH-298 5/b tube was found to be acceptable at all four concentrations. Unico #120b was found to be acceptable at three of the four concentrations, and Bacharach #19-0198, Gastec #8529, and MSA #87414 were found to be acceptable at two of the 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 Dräger #CH-298 tube was the only H_2S tube to meet the specified standards at all four concentrations. The tube produced a very distinct color change, and the standard deviations were generally quite low. However, there was a significant amount of variation in readings among readers due to the fading of the stain at the endpoint and a small amount of channeling. The intensity of the color dropped off enough to make it very difficult to tell where the stain actually ended. At three of the four concentrations, the tubes read slightly higher than the actual concentration.

The Unico#120b was found to be acceptable at all concentrations except at two times the TLV. At this concentration, the tube was accurate to within ± 30%. The Unico tube produced a very clear and sharp stain ending making it a very easy tube to read. Because of the small tube diameter, channeling was not a problem. Readings were consistent in spite of the fact that the stain lengths were very short. The short stain made it very difficult to interpolate between marks on the scale to arrive at tube readings.

The Bacharach #190198 tube was found to be acceptable only at one and five times the TLV. Although the standard deviations were generally small, the mean readings were usually somewhat higher than the actual concentrations. This could have been caused by a calibration error rather than a functional problem with the tube. The color change was quite distinct and easy to see, but the intensity of the color faded at the endpoint of the stain, making it difficult to read. A certain amount of reading error could have resulted from shadows created on the tube by following the manufacturer's suggested method of tube reading. This shadow blended in with the color of the stain and made it difficult to determine where the stain ended. In spite of the fairly large tube diameter, channeling was not observed to be a major problem.

The Gastec #8529 tubes were found to be acceptable at the lower two concentrations. At these concentrations the standard deviations were quite small, but at the upper two concentrations the standard deviations were very high as were the average tube readings. The tubes read high in spite of a distinct color change, probably because of the tailing off of the stain at the endpoint. Other than the poor endpoint, the tubes seem to be easy to read. Channeling does not appear to be a major problem.

The MSA #87414 tubes were found to be acceptable at one and two times the TLV. At 0.5 times the TLV they read very high and were only accurate within ± 70% and at five times the TLV they were accurate within ± 35% because of high readings. The main difficulty in reading these tubes resulted from severe channeling due to the large particle size of the packing. In most cases it was impossible to determine the endpoint of the stain with any degree of accuracy. The color change was fairly distinct but often the staining was uneven. Some particles were stained very dark while others were hardly stained at all. Also, some of the unstained particles were about the same color as the stain, making it difficult to determine the extent of staining.

SUMMARY

Only the Drager #CH-298 H_2S tube was found to be acceptable within ± 25% accuracy at one, two, and five times the TLV and within ± 35% at 0.5 times the TLV. Bacharach #19-0198 and Unico #120b 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 ACGIH for 1971." American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1971.

2. Jacobs, M.B., Braverman, M.M., and Hochleiser, S. "Ultramicrodetermination of Sulfides in Air." Analytical Chemistry, 29:1349, 1957.

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. Dräger - H_2S #CH 298 5/b

Tested: January 5 - 12, 1972

Batch #491811 - Expiration Date, August 1972

	Concentration (ppm)			
	5 (5.55)	10 (11.2)	20 (18.7)	50 (50)
Mean	6.201	12.33	19.6	53.03
S(Std. Dev.)	0.54957	0.7997	1.075	4.531
Qu	2.35	2.085	3.513	2.0899
Q_L	4.7191	4.918	5.188	3.428
% Defective Above Upper Limit	0.163 %	0.78 %	0 %	0.78 %
% Defective Below Lower Limit	0 %	0 %	0 %	0 %
Total % Defective	0.163 %	0.78 %	0 %	0.78 %
Max. Allowable % Defective	15.17 %	15.17 %	15.17%	15.17 %
Acceptable	Yes	Yes	Yes	Yes
Date of Test	1/12/72	1/11/72	1/5/72	1/6/72

Table 2. Unico - H_2S #120b

Tested: January 5-14, 1972

Batch #207370 - Expiration Date, Feb. 1972

	Concentration (ppm) 5 (5.9)	 10 (10)	 20 (18.7)	 50 (47.4)
Mean	4.68	8.90	15.366	45.432
S (Std. Dev.)	0.267	0.546	1.869	3.216
Qu	12.29	6.59	4.283	4.297
Q_L	3.17	2.565	0.7173	3.073
% Defective Above Upper Limit	0 %	0 %	0 %	0 %
% Defective Below Lower Limit	0 %	0.017%	24.03 %	0 %
Total % Defective	0 %	0.017%	24.03 %	0 %
Max. Allowable % Defective	15.17%	15.17 %	15.17 %	15.17 %
Acceptable	Yes	Yes	No	Yes
Date of Test	1/14/72	1/11/72	1/5/72	1/6/72

Table 3. Gastec - H_2S #8529

Tested: Feb. 28 - Mar. 3, 1972

Batch #10404 - Expiration Date, Oct. 1974

	Concentration (ppm)			
	5 (5)	10 (10.57)	20 (20.6)	50 (50)
Mean	4.70	10.33	26.56	75.17
S (Std. Dev.)	0.644	1.08	4.33	9.24
Qu	4.27	2.67	- 0.188	- 1.37
Q_L	1.73	2.23	2.56	4.08
% Defective Above Upper Limit	0 %	0.003 %	> 50 %	> 50 %
% Defective Below Upper Limit	3.11%	0.366 %	0.02%	0 %
Total % Defective	3.11%	0.369 %	> 50 %	> 50 %
Max. Allowable % Defective	15.17%	15.17 %	15.17%	15.17%
Acceptable	Yes	Yes	No	No
Date of Test	2/28/72	2/29/72	3/2/72	3/3/72

Table 4. Bacharach - H_2S #19-0198

Tested: January 5 - 14, 1972

Batch #32 - Expiration Date, None Given

	Concentration (ppm)			
	5 (5.9)	10 (10)	20 (20)	50 (47.4)
Mean	7.516	10.868	24.868	48.90
S (Std. Dev.)	0.485	0.707	2.051	2.266
Qu	0.927	4.430	0.0644	4.567
Q_L	7.597	3.491	4.8113	5,891
% Defective Above Upper Limit	17.84 %	0 %	50 %	0 %
% Defective Below Lower Limit	0 %	0 %	0 %	0 %
Total % Defective	17.84 %	0 %	50 %	0 %
Max. Allowable % Defective	15,17 %	15.17%	15.17 %	15.17 %
Acceptable	No	Yes	No	Yes
Date of Test	1/14/72	1/11/72	1/5/72	1/6/72

Table 5. MSA - H_2S #87414

Tested: January 5 - 12, 1972

Batch #147 - Expiration Date, Mar. 1972

	Concentration (ppm)			
	5 (5.55)	10 (11.2)	20 (20)	50 (50)
Mean	8.358	10.90	19.2	55.00
S (Std. Dev.)	0.862	1.723	2.852	9.921
Qu	- 1.004	1.799	1.464	0.756
Q_L	5.51	1.451	1.815	1.764
% Defective Above Upper Limit	>50 %	2.49 %	6.47 %	22.79%
% Defective Below Lower Limit	0 %	6.63 %	2.40 %	2.83%
Total % Defective	>50 %	9.12 %	8.87 %	25.62%
Max. Allowable % Defective	15.17%	15.17 %	15.17 %	15.17%
Acceptable	No	Yes	Yes	No
Date of Test	1/12/72	1/11/72	1/5/72	1/6/72

Table 6. Acceptability Limits H_2S

Manufacturer	Concentration			
	5	10	20	50
Bacharach #19-0198	± 40%	± 25%	± 35%	± 25%
Draeger #CH-2985/b	± 35%	± 25%	± 25%	± 25%
Unico-Kitagawa #120b	± 35%	± 25%	± 30%	± 25%
MSA #87414	± 70%	± 25%	± 25%	± 35%
Scott-Gastec #8529	± 35%	± 25%	± 55%	± 70%

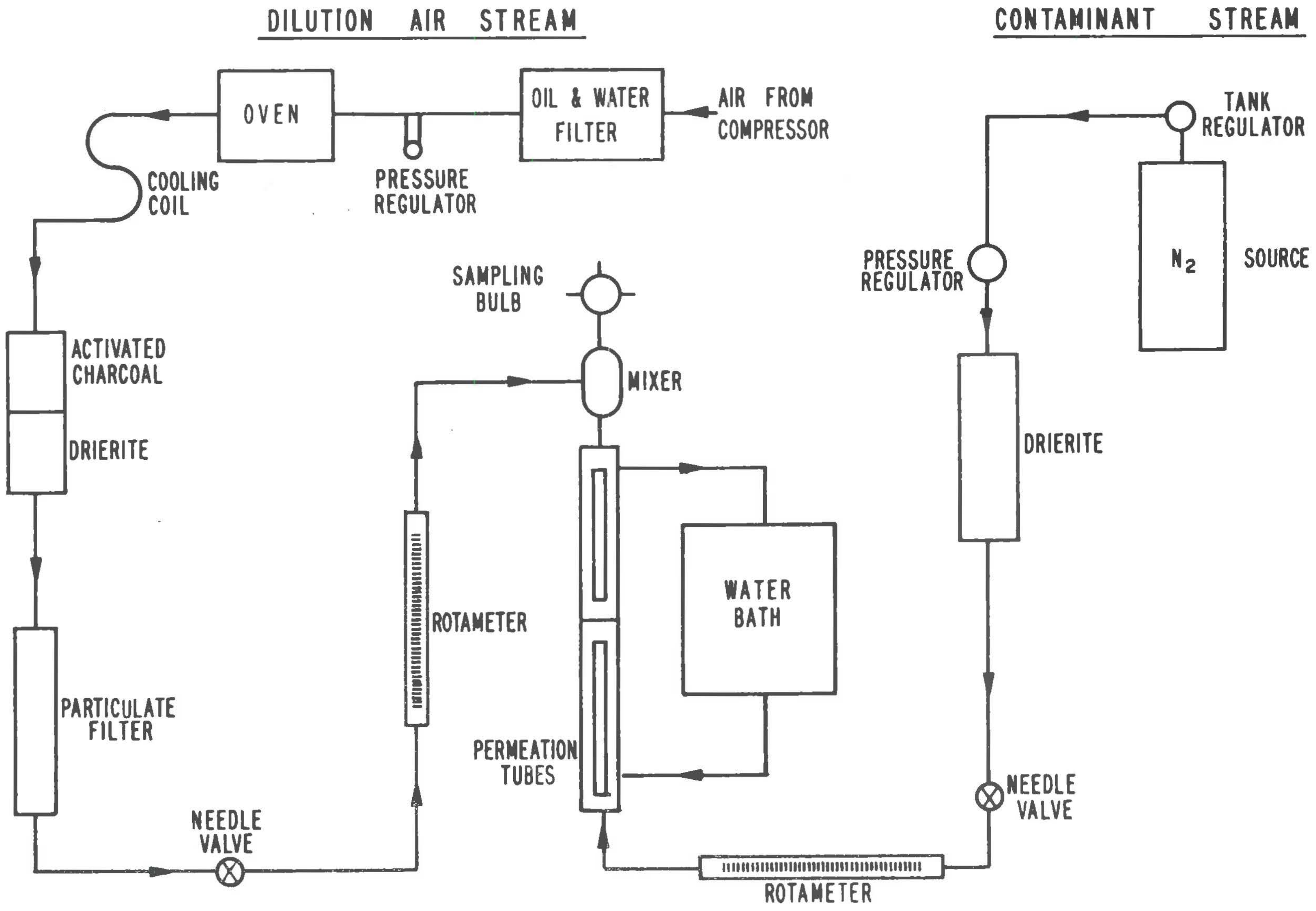


FIGURE 1. PERMEATION TUBE GENERATION SYSTEM

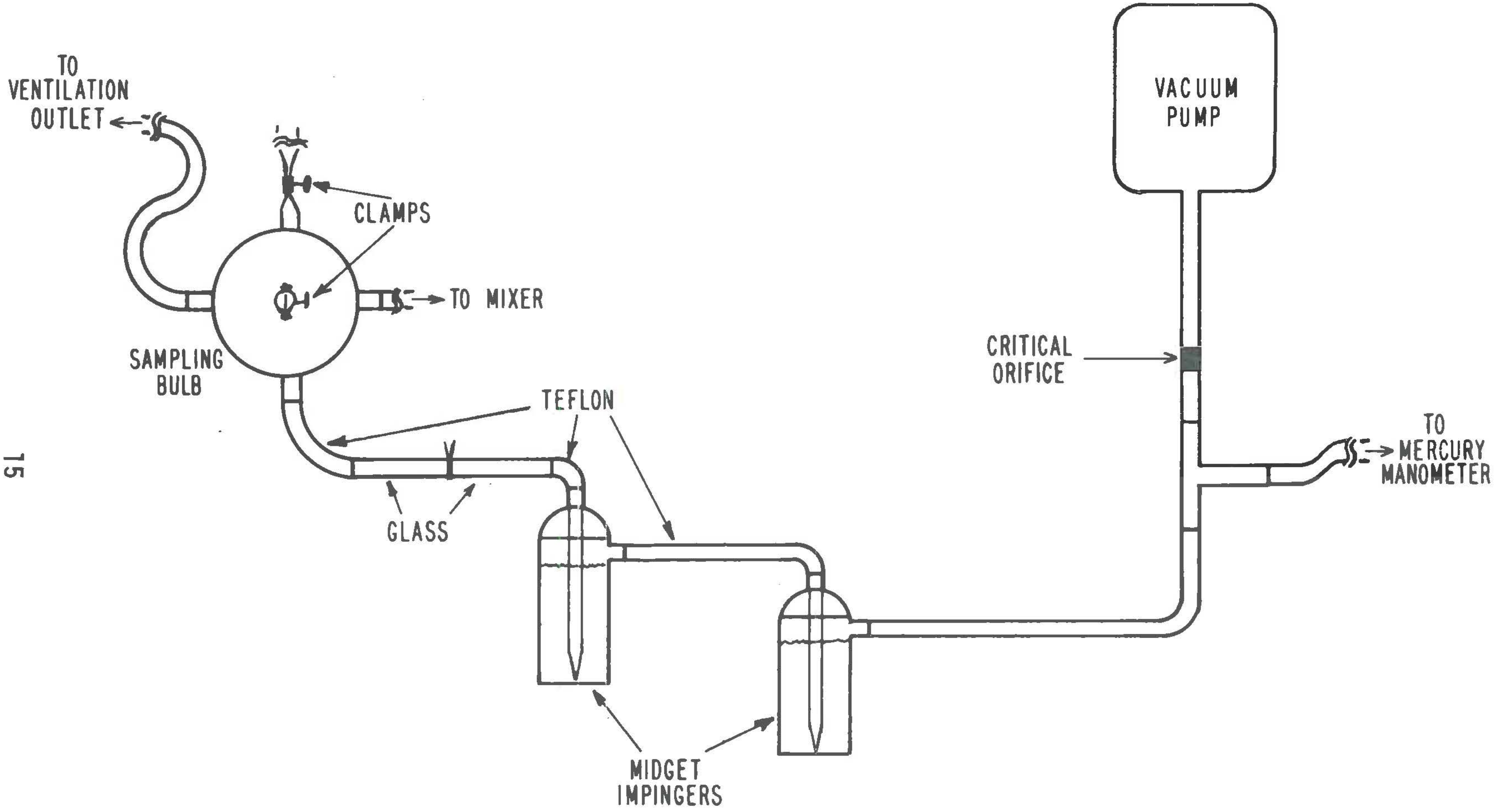


FIGURE 2. SAMPLING APPARATUS - MIDGET IMPINGERS