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

Ozone

by

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ABSTRACT

The National Institute for Occupational Safety and Health, U.S. Public Health Service, conducted a performance study to determine the reliability of ozone 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 ozone were generated by irradiating a stream of purified air with a very stable low pressure mercury lamp. These concentrations were verified by using an independent chemical method of analysis. Of the two brands of tubes evaluated, neither one met the acceptance standards. The Drager #CH-313 tube was found to be acceptable within an alternate accuracy limit of ±50%.

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

Ozone concentrations of 0.05, 0.10, 0.20, and 0.50 ppm were generated by passing ozone-free air through a quartz tube where it was irradiated with a low pressure mercury lamp as shown in Figure 1. The amount of irradiation was controlled by an adjustable shutter which fit over the lamp. Air was supplied by a compressor and purified before entering the generation system.

The compressed air was first passed through a low pressure regulator and through Drierite* and silica gel filters to remove H_2O. An activated charcoal filter was used to remove hydrocarbons. The flow rate of the air through a calibrated rotameter was controlled by a needle valve before it entered the quartz tube where the ozone was produced. From the quartz tube, the irradiated air stream passed into a sampling manifold.

The manifold was equipped with two sampling ports. These ports were used for testing detector tubes and for taking samples for chemical analysis. Because of the reactive nature of ozone, care was taken to use only glass and teflon tubing from these ports. The ozone concentration was monitored by using a Mast Ozone Meter*, which was calibrated against a neutral KI method[2]. When samples for chemical analysis were taken, a

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vacuum pump was used to draw the ozone from one of the sampling ports through two midget impingers connected in series as shown in Figure 2. The actual flow through the impingers was determined by using a water 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

Known concentrations of ozone were generated by passing purified air through a quartz tube where it was irradiated with ultraviolet rays from a mercury lamp. The flow rate of air was held constant at 5 l/min. The amount of exposure was controlled by an adjustable shutter which fit around the lamp. Ozone concentrations were varied by adjusting the shutter setting. To verify the concentrations, samples of ozone were monitored with a Mast Ozone Meter*. The meter was calibrated against the neutral KI method. Concentrations determined in this manner had to agree within ±10% of the calculated concentrations before the testing of detector tubes could begin. The samples for chemical analysis were taken by drawing ozone 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 10 ml each of a neutral (pH buffered to 6.8) KI solution. The ozone was drawn through a 0.5 l/min. critical orifice and bubbled through the impingers for 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. The amount of color change in the solution was measured with a spectrophotometer and compared to standards to determine the concentration.

The detector tubes were tested by drawing ozone 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. The number of detector tubes tested at each concentration was determined by the size of the batch and MIL-STD-414[3]. Tubes from two manufacturers were tested at four different concentrations. Each tube was read by a panel of three independent readers following the manufacturer's instructions. The readings for each tube were averaged to

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give one reading per tube. The readers were chosen from available personnel and were required to pass a standard color-blindness test. The known concentrations were not revealed to the readers, and they were not allowed to know the readings of the other readers.

EVALUATION

The acceptability of the ozone tubes was determined by using MIL-STD-414. 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 0.05 to 0.50 ppm were evaluated. Of the two ozone tube brands tested, neither one was found to be acceptable at all four concentrations. The Dräger #CH-313 tube was found to be acceptable at two of the four concentrations and the MSA #93865 tube was found to be unacceptable at all four concentrations. The results of these tests and the limits of acceptability are shown in Tables 1-3. These results are representative of one batch only for each brand of tube. There has been no further study made to imply that the same performance may be expected from all batches of the two tube brands.

DISCUSSION OF RESULTS

The Drager #CH-313 tube was found to be acceptable at one and two times the TLV. It was accurate within ±50% at one-half the TLV and within ±45% at five times the TLV. The standard deviations were generally quite low except at one-half the TLV where the standard deviation was very high. Although the color change was quite clear, there was a significant amount of fading at the endpoint of the stain. Also, the stain lengths at the lower concentrations were very short making reading difficult. Channeling was not a significant problem. At all concentrations, the mean readings were somewhat higher than the actual concentrations indicating a possible calibration error.

The MSA #93865 tube was found to be unacceptable at all four concentrations. The best accuracy at any concentration was ±50%. The standard deviations were all low, indicating that a calibration error was a possible cause of failure. At all concentrations, the tubes read considerably higher than the actual concentrations. Also, there was a significant amount of fading at the end of the stain making it extremely difficult to determine the boundary between the stained and unstained reagent.

SUMMARY

None of the ozone detector tubes tested met the acceptance criterion. The Drager #CH-313 ozone tube was 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. "Reference Method for the Measurement of Photochemical Oxidants Corrected for Interferences Due to Nitrogen Oxides and Sulfur Dioxide." Federal Register, 36:84, ppg. 8195-8199, Washington, D. C., April 30, 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. Drager - Ozone #CH-313

Tested: June 22-27, 1972

Batch #309761 - Expiration Date, May, 1974

	Concentration (ppm) 0.05	0.10	0.20	0.50
Mean	0.0577	0.1072	0.2082	0.6496
S(Std. Dev.)	0.0158	0.0083	0.0239	0.0654
Q_u	0.6105	2.1476	1.7501	-0.3764
Q_L	1.8039	3.8681	2.4367	4.2014
% Defective Above Upper Limit	27.30%	1.14%	3.56%	>50%
% Defective Below Lower Limit	3.13%	0%	0.40%	0%
Total % Defective	30.43%	1.14%	3.96%	>50%
Max. Allowable % Defective	12.99%	12.99%	12.99%	12.99%
Acceptable	No	Yes	Yes	No
Date of Test	6/27/72	6/26/72	6/22/72	6/23/72

Table 2. MSA - Ozone #93865

Tested: Oct. 13-15, 1971

Batch #9

	Concentration (ppm) 0.05(0.055)	0.10(0.10)	0.20(0.23)	0.50(0.54)
Mean	0.073	0.176	0.32	0.86
S(Std. Dev.)	0.006	0.015	0.03	0.08
Qu	.0751	-3.4018	-0.9562	-2.3744
Q_L	5.9569	6.7087	4.4509	5.8379
% Defective Above Upper Limit	27.4%	>50%	>50%	>50%
% Defective Below Lower Limit	0%	0%	0%	0%
Total % Defective	27.4%	>50%	>50%	>50%
Max. Allowable % Defective	13.71%	13.71%	13.71%	13.71%
Acceptable	No	No	No	No
Date of Test	10/15/71	10/14/71	10/14/71	10/13/71

Table 3. Acceptability Limits of Ozone Tubes

Manufacturer	Concentration			
	0.05	0.10	0.20	0.50
Drager #CH-313	±50%	±25%	±25%	±45%
MSA #93865	±50%	±90%	±55%	±75%

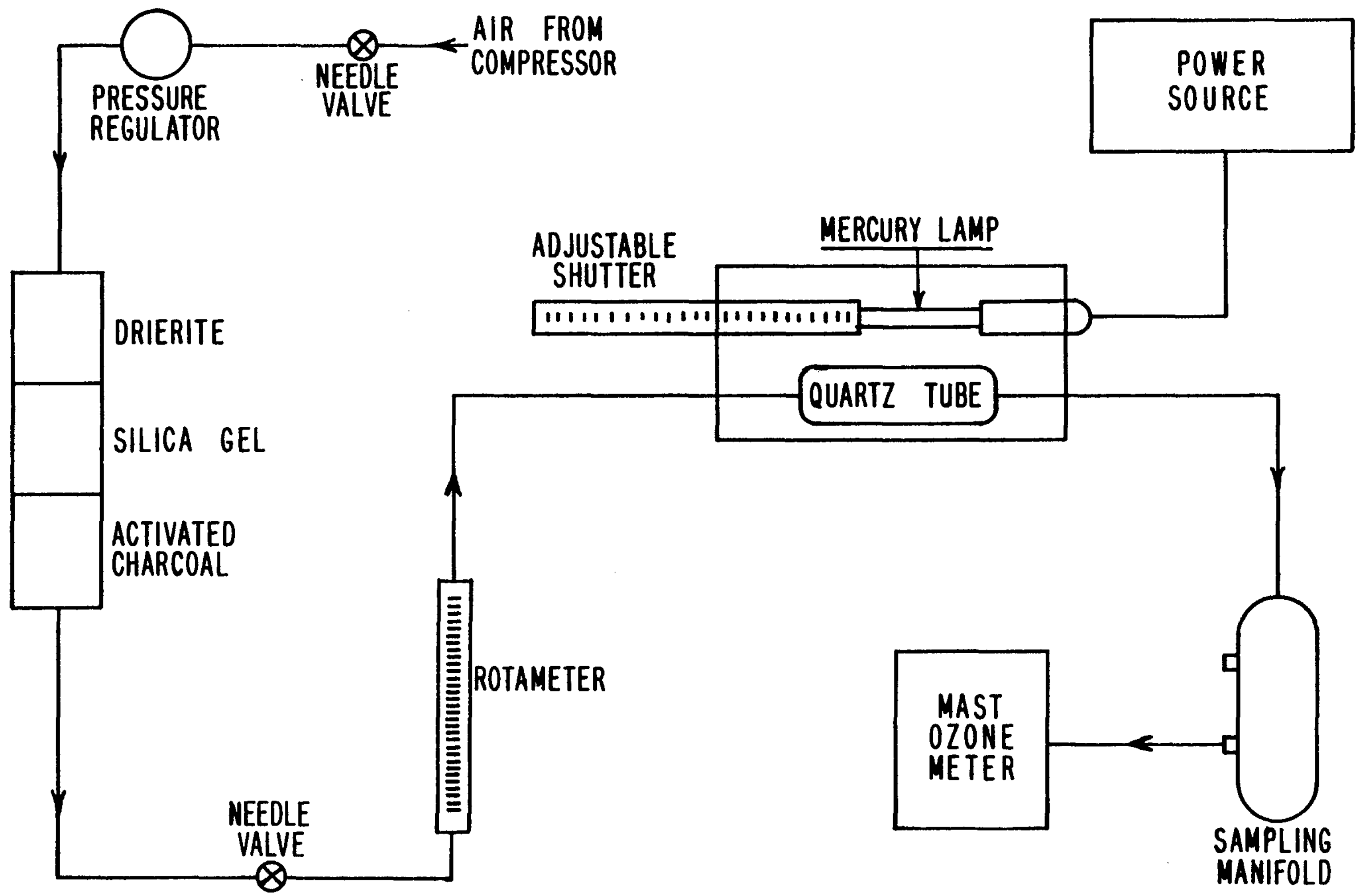

FIGURE 1. OZONE GENERATION SYSTEM

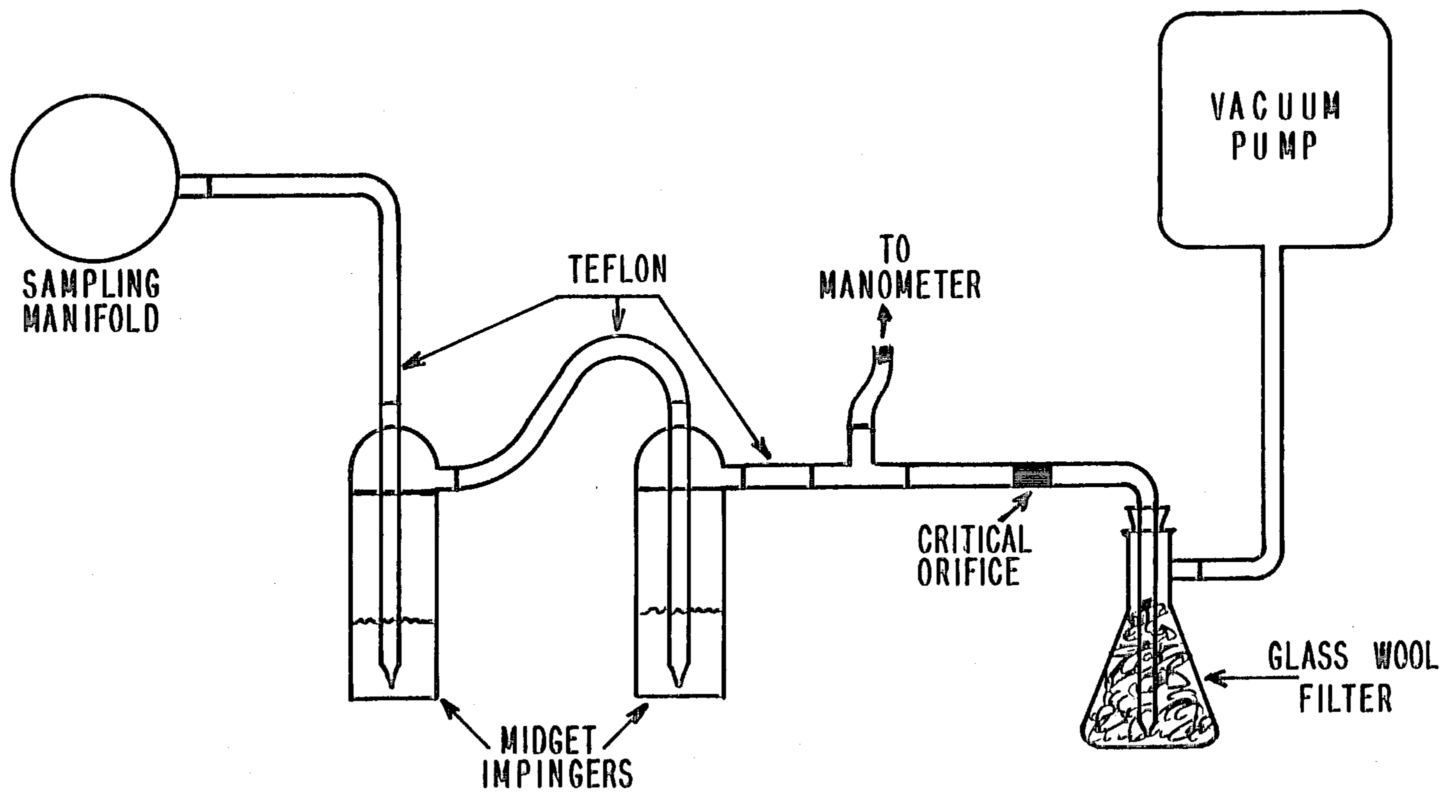

FIGURE 2. MIDGET IMPINGER SAMPLING APPARATUS

☆ U.S. GOVERNMENT PRINTING OFFICE: 1972— 759-573/1361