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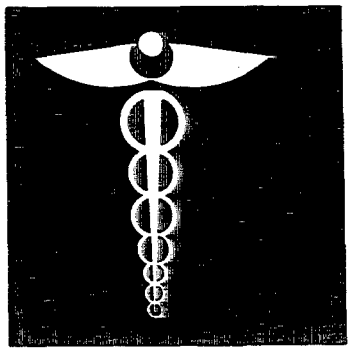

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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by

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ABSTRACT

The U. S. Public Health Service, National Institute for Occupational Safety and Health, conducted a performance study to determine the reliability of trichloroethylene detector tubes. Tubes representing all those available in the United States were tested at concentrations of one-half, one, two, and three times the threshold limit value. Known concentrations of trichloroethylene were generated by means of a dynamic vapor pressure system. These concentrations were verified by using an independent chemical method of analysis. Of the four brands of tubes evaluated, only one was acceptable; the Dräger #CH-244 10/a tube was acceptable within ±25% at the 95% confidence level when tested at one, two, and three 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 measurement of trichloroethylene were tested, if the tubes were intended for use over the range from one-half to three times the threshold limit value (TLV).[1] A description of the test procedures and results is contained within this report.

TESTING EQUIPMENT

Trichloroethylene (C_2 H Cl_3) concentrations of 50, 100, 200, and 300 ppm were dynamically generated by means of a vapor pressure system as shown in Figure 1. Purified nitrogen, the carrier gas, was metered through a heated, double-effect evaporator containing trichloroethylene liquid. Carrier gas leaving the evaporator saturated with trichloroethylene vapor at upwards of 30°C was then passed through a condenser and cooled to 10°C by a constant temperature bath. The nitrogen gas leaving the condenser saturated with trichloroethylene vapor at 10° ±0.02°C formed the final section of the contaminant stream.

The contaminant stream was diluted with 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 an ascarite filter to remove the CO_2. A silica gel filter was used to remove H_2O. Any particulate matter was removed from the air by a membrane capsule filter having a mean pore size of 1.0 micron or less. The air flow was split into two lines in order to control the humidity. One line went

to a H_2O bubbler while the other served as a by-pass. Air flow in the two lines was controlled by two needle valves which were set according to the readings of a temperature-humidity sensor farther down the line. The humidity was held at 50% R.H. The diluting air stream was regulated by a needle valve and measured by a calibrated rotameter. The diluting and contaminant streams were mixed and passed into the sampling bulb.

This bulb was equipped with five sampling ports. Three of these ports were 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. When samples were taken for chemical analysis, a vacuum pump was used to draw the trichloroethylene through a charcoal tube as shown in Figure 2. The actual flow through the charcoal tube 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 PROCEDURE

The generation of trichloroethylene began with the saturation of a metered stream of N_2 in a temperature bath above 30°C. The saturated stream was then cooled to the desired temperature of 10° ±0.02°C by a constant temperature bath using H_2O in a counter current flow condenser to cool the contaminant stream. The concentration of trichloroethylene in the stream is calculated by the following equation:

$$C_M = \frac{P_V}{P_T}$$

In this equation, C_M is the concentration of trichloroethylene in mole fraction, P_V is the vapor pressure of trichloroethylene at the set temperature, and P_T is the total pressure inside the condenser. For this test at 10°C, the vapor pressure of trichloroethylene was taken as 35.4 mm Hg and the total pressure was 745 mm Hg.

To determine the diluting flow rate, the following equation was used:

$$F = \frac{Q \times C_M}{C_D}$$

Where F is the required flow rate of the diluted contaminant stream (total of air plus nitrogen) in lpm, C_M is the mole fraction of trichloroethylene in the contaminant stream, Q is the flow rate of the contaminant stream in µl/min, and C_D is the final desired concentration of trichloroethylene in µl/l (ppm).

To verify the generated concentrations, samples of trichloroethylene were analyzed by chemical methods.[2] A metered volume of the generated mixture was passed through a tube containing activated charcoal, which adsorbed the trichloroethylene. The trichloroethylene was later desorbed in CS_2, and the sample was analyzed with a gas chromatograph equipped with a flame ionization detector. The chemically determined concentrations generally agreed within ±10% of the calculated concentrations before testing of detector tubes began.

The detector tubes were tested by drawing the known concentrations of trichloroethylene 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. Ten detector tubes for each manufacturer or brand 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 three 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 trichloroethylene 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 three times the TLV and within ±35% at one-half times the TLV. They also had to have a lower percentage of defective tubes than allowed by the specifications of MIL-STD-414. The MIL-STD-414 method provides a statistical quality control treatment of the data, and incorporates a 95% confidence level.

RESULTS

Only tubes manufactured for ranges including 50 to 300 ppm and marketed in the United States were evaluated. Of the four trichloroethylene tubes tested, only the Drager #CH-244 10/a tube was found to be acceptable at all four concentrations. Unico #134 was found to be acceptable at three of the four concentrations, MSA #85833 was acceptable at two of the four concentrations, and MSA #88536 was found acceptable at only one out of the four concentrations. The results of these tests and the limits of acceptability are shown in Tables 1-5. 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 verify that the same performance may be expected from all batches of the other tube brands.

DISCUSSION OF RESULTS

MSA #88536

The MSA #88536 detector tubes were found to be calibrated with acceptable accuracy for trichloroethylene only at one-half the TLV. Although these detector tubes are marketed for the measurement of trichloroethylene (and other substances), the tubes are rather non-specific and will give an indication for almost any halogenated hydrocarbon. In addition, interference can result form hydrogen sulfide, ammonia, halides, halogens, and other hydrocarbons.

The MSA #88536 detector tubes require the simultaneous use of the MSA #87505 pyrolyzer to convert the trichloroethylene to decomposition products which can be detected by the tubes. If trichloroethylene is drawn into the detector tube without using the pyrolyzer, no indication is given. The following difficulties were experienced with the pyrolyzer:

1. It is a bulky extra piece of equipment causing some inconveniences for use in field sampling situations.
2. The batteries are used up quickly (sometimes after ten or less samples) requiring either replacement or overnight recharge before additional samples can be taken.
3. The filaments burn out easily if the required test voltage setting is even slightly exceeded.
4. The use of the pyrolyzer requires an additional connection (pyrolyzer to detector tube) in the sampling system, and thus an additional source of leakage.

5. The manufacturer provides no test which the user can perform to determine if there is leakage in the pyrolyzer or connections, or a test to show if the pyrolyzer is operating properly. No test is provided to ascertain operability, and the manufacturer does not provide a schedule of maintenance. Therfore, there is no way in which the user can determine for himself if the pyrolyzer is working properly.

At all test concentrations above one-half the TLV, the MSA #88536 tube readings were much lower than the actual concentrations. Although the standard deviations were relatively small, the tubes were rather insensitive to concentration differences of 50 ppm. The difference in tube readings for actual concentrations of 50 and 100 ppm amounted to only about 10 ppm, or 2 mm in stain length. The stain was quite faint at 50 ppm, and the end point was very difficult to determine.

MSA #85833

The MSA #85833 detector tubes were found to be calibrated for trichloroethylene with acceptable accuracy at 50 and 200 ppm, but not at 100 and 300 ppm. The tube readings were lower than the actual concentrations at 50 and 100 ppm. Halogenated hydrocarbons other than trichloroethylene interfere with the measurement.

The MSA #85833 detector tubes are temperature sensitive; therefore, correction factors are required. However the manufacturer provides correction factors for only two temperatures. The user is not instructed in what correction factor to apply at temperatures other than the two listed.

The MSA #85833 detector tubes give no indication of trichloroethylene unless used in conjunction with the reactor tubes provided by the manufacturer. The reactor tubes consist of tygon tubing containing sealed glass ampoules of reagents; the ampoules must be broken and the reagents mixed prior to taking a sample. The trichloroethylene vapor must be drawn through the reactor tube where the trichloroethylene is converted into other substances; these substances are then drawn through the detector tube where they produce a stain which can be used to measure the concentration.

The following problems were experienced with the reactor tube:

1. The reagents sometimes did not mix and react properly, producing a brown reagent mixture rather then the normal

green. Much lower readings were obtained in these cases; these readings were not included in the accuracy evaluation.

2. The glass ampoules occasionally pierced through the tygon tubing after being broken, producing leakage and cut fingers.
3. It was difficult to be certain of achieving a tight seal between the reactor tube and the detector tube.
4. The reagents of the reactor tubes were corrosive, staining paper and skin whenever contacted.

Channeling of sample flow (and thus of stain) through the detector tube was a major problem with the MSA #85833 detector tubes. Stains were occasionally 25% longer on one side of the tube than on the other.

At 300 ppm the tube readings varied tremendously, showing a standard deviation of 85 ppm. This standard deviation amounted in magnitude to 25% of the average reading at this concentration. If only a few tubes were used to sample an unknown environment, this large amount of variability could lead to a misleading average reading, causing erroneous interpretations concerning contaminant concentrations.

KITAGAWA/UNICO #134

The stains produced in the Kitagawa/Unico #134 were long and easy to read. Readings were consistent and reasonably accurate, as shown in Table 3. No major difficulties were experienced with the Kitagawa tubes. Halogens, halogenated hydrocarbons, and nitrogen dioxide are interferences.

The tubes are temperature sensitive, but the manufacturer provides five temperature correction points from which the user can easily plot a curve to correct his readings for any temperature of use in the range of 0 - 40 degrees C.

The Unico test certification sheet enclosed in each box of tubes seems to be very misleading as to tube accuracy and precision.

The Kitagawa detector tubes must be used in conjunction with the accompanying primer tubes. However, the total system is compact, convenient, and relatively leak-free.

DRÄGER #CH-244 10/a

The Dräger #CH-244 was the only brand which met the specified accuracy standards at all concentrations. The Dräger tube is nicely designed with the oxidation layer conveniently built into the detector tube. The air being sampled first passes through the oxidation layer which contains permanganate which reacts with the trichloroethylene to produce chlorine. The chlorine is then measured in the indicating layer where it reacts with o-tolidine producing an orange reaction product. This tube design configuration provides a very convenient means of oxidation and measurement, and requires no special effort on the part of the user.

The printed scale on the tube itself makes it extremely easy to read. Accuracy and precision are quite good as shown in Table 4. The tube is very sensitive, with concentration differences of 10 ppm easily discernible. Halides, free halogens, and easily cleaned halogenated hydrocarbons are interferences.

SUMMARY

Only the Dräger #CH-244 10/a trichloroethylene detector tube brand was found to be acceptable within ±25% accuracy at one, two, and three times the TLV, and within ±35% accuracy at one-half the TLV. The Kitagawa/Unico #134 brand was found acceptable within an alternate accuracy of ±35% over the entire range of one-half to three times the TLV.

REFERENCES

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

2. White, Lowell D., Taylor, David G., Mouer, Patricia A., and Kupel, Richard E. " A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere." American Industrial Hygiene Association Journal, 31:225, March-April 1970.

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 - TRICHLOR #88536

TESTED: June 17 - August 5, 1971

Batch #89 - Expiration Date, April 1972

MIL-STD-414 STATISTICAL TREATMENT	CONCENTRATION (ppm) 50(46)	100(88)	200(202)	300(280)
Mean ($\bar{x}$)	41.3	53.8	78.6	124.65
Std. Dev. (S)	3.268	4.341	10.865	14.823
Upper Quality Index - Q_u	6.365	12.946	16.006	15.20
Lower Quality Index - Q_L	3.489	-2.810	-6.710	-5.758
% Defective Above Upper Limit	0.0%	0.0%	0.0%	0.0%
% Defective Below Lower Limit	0.0%	100%	100%	100%
Total % Defective	0.0%	100%	100%	100%
Max. Allowable % Defective	15.17%	15.17%	15.17%	15.17%
Acceptable	YES	NO	NO	NO
Date of Test	6/17/71	6/18/71	6/22/71	8/5/71

TABLE 2.

MSA - TRICHLOR #85833

TESTED: June 17 - August 5, 1971

Batch #102 - Expiration Date, June 1972

MIL-STD-414 STATISTICAL TREATMENT	CONCENTRATION (ppm) 50(46)	100(88)	200(202)	300(312)
Mean ($\bar{x}$)	36.5	53.6	189.9	355.1
Std. Dev. (S)	5.543	14.104	22.625	84.623
Upper Quality Index - Q_u	4.619	3.99	2.767	0.412
Lower Quality Index - Q_L	1.191	-0.879	1.697	1.431
% Defective Above Upper Limit	0.0%	0.0%	0.0%	34.57%
% Defective Below Lower Limit	11.46%	80.77%	3.41%	6.94%
Total % Defective	11.46%	80.77%	3.41%	41.51%
Max. Allowable % Defective	15.17%	15.17%	15.17%	15.17%
Acceptable	YES	NO	YES	NO
Date of Test	6/17/71	6/18/71	6/22/71	8/5/71

TABLE 3.

UNICO - TRICHLOR #134

TESTED: June 17 - August 5, 1971

Batch #1515089 - Expiration Date, Aug. 31, 1971

MIL-STD-414 STATISTICAL TREATMENT	CONCENTRATION (ppm) 50(54)	100(111)	200(208)	300(312)
Mean ($\bar{x}$)	63.4	115.6	250.6	333.7
Std. Dev. (S)	6.769	18.946	24.423	46.7
Upper Quality Index - Q_u	1.403	1.222	0.3849	1.21
Lower Quality Index - Q_L	4.181	1.708	3.873	2.14
% Defective Above Upper Limit	7.44%	10.82%	35.29%	11.03%
% Defective Below Lower Limit	0.0%	3.31%	0.0%	0.61%
Total % Defective	7.44%	14.13%	35.29%	11.64%
Max. Allowable % Defective	15.17%	15.17%	15.17%	15.17%
Acceptable	YES	YES	NO	YES
Date of Test	6/17/71	6/18/71	6/22/71	8/5/71

TABLE 4.

DRAGER - TRICHLOR #CH-244 10/a

TESTED: June 17 - August 5, 1971

Batch #207271 - Expiration Date, September 1972

MIL-STD-414 STATISTICAL TREATMENT	CONCENTRATION (ppm) 50(46)	100(98)	200(208)	300(304)
Mean ($\bar{x}$)	41.1	96.5	222.1	295.2
Std. Dev. (S)	6.244	4.625	7.047	53.59
Upper Quality Index - Q_u	3.363	5.622	5.378	1.582
Lower Quality Index - Q_L	1.794	4.973	9.380	1.254
% Defective Above Upper Limit	0.0%	0.0%	0.0%	4.79%
% Defective Below Lower Limit	2.57%	0.0%	0.0%	10.21%
Total % Defective	2.57%	0.0%	0.0%	15.00%
Max. Allowable % Defective	15.17%	15.17%	15.17%	15.17%
Acceptable	YES	YES	YES	YES
Date of Test	6/17/71	6/18/71	6/22/71	8/5/71

TABLE 5.

ACCEPTABILITY LIMITS - TRICHLOROETHYLENE
Accuracy at Various Concentrations

Manufacturer	Concentration (ppm)			
	50	100	200	300
Dräger #CH-244	±35%	±25%	±25%	±25%
Unico #134	±35%	±25%	±35%	±25%
MSA #85833	±35%	±60%	±25%	±45%
MSA #88536	±35%	±45%	±70%	±65%

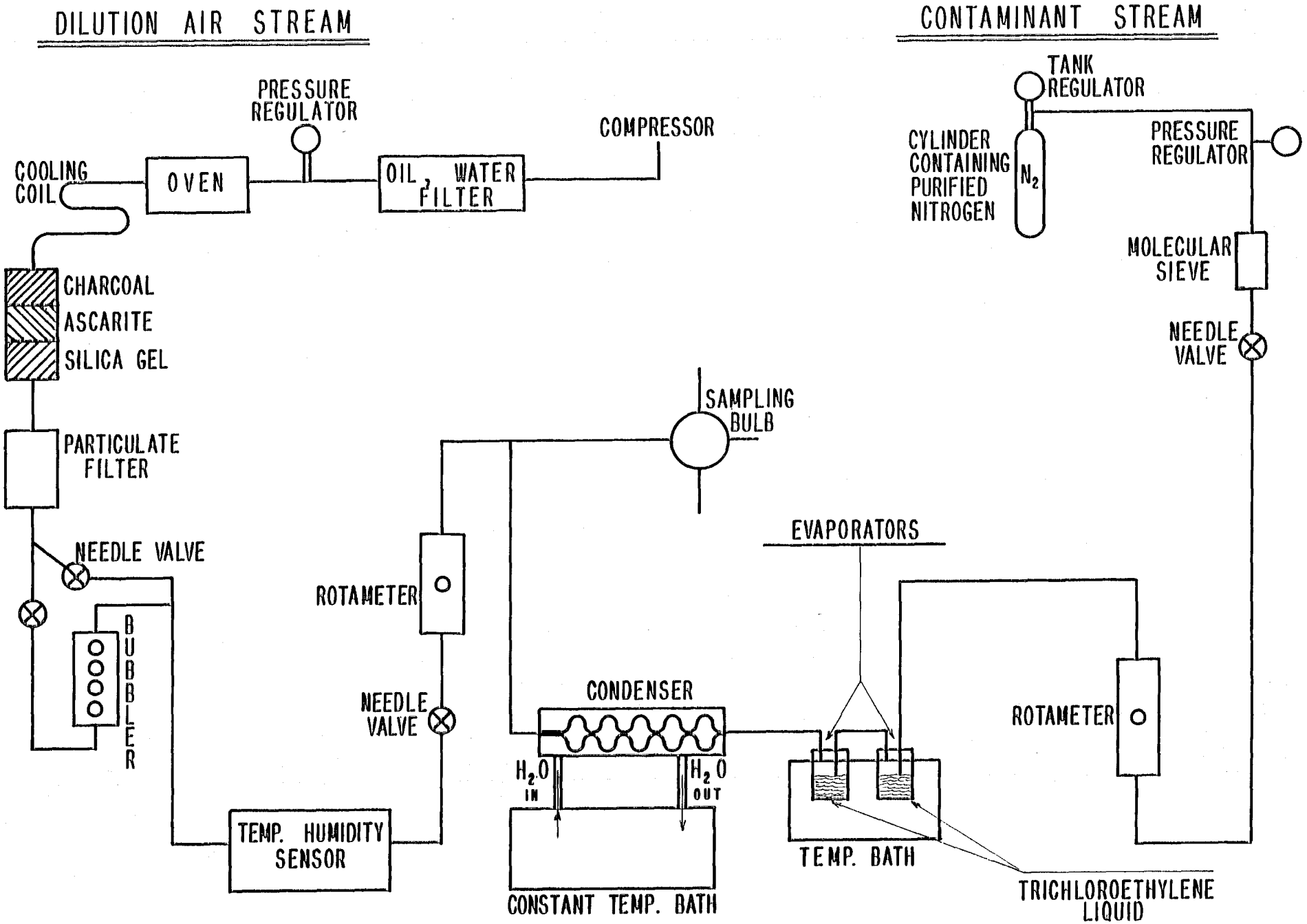

FIGURE 1. VAPOR PRESSURE GENERATION SYSTEM

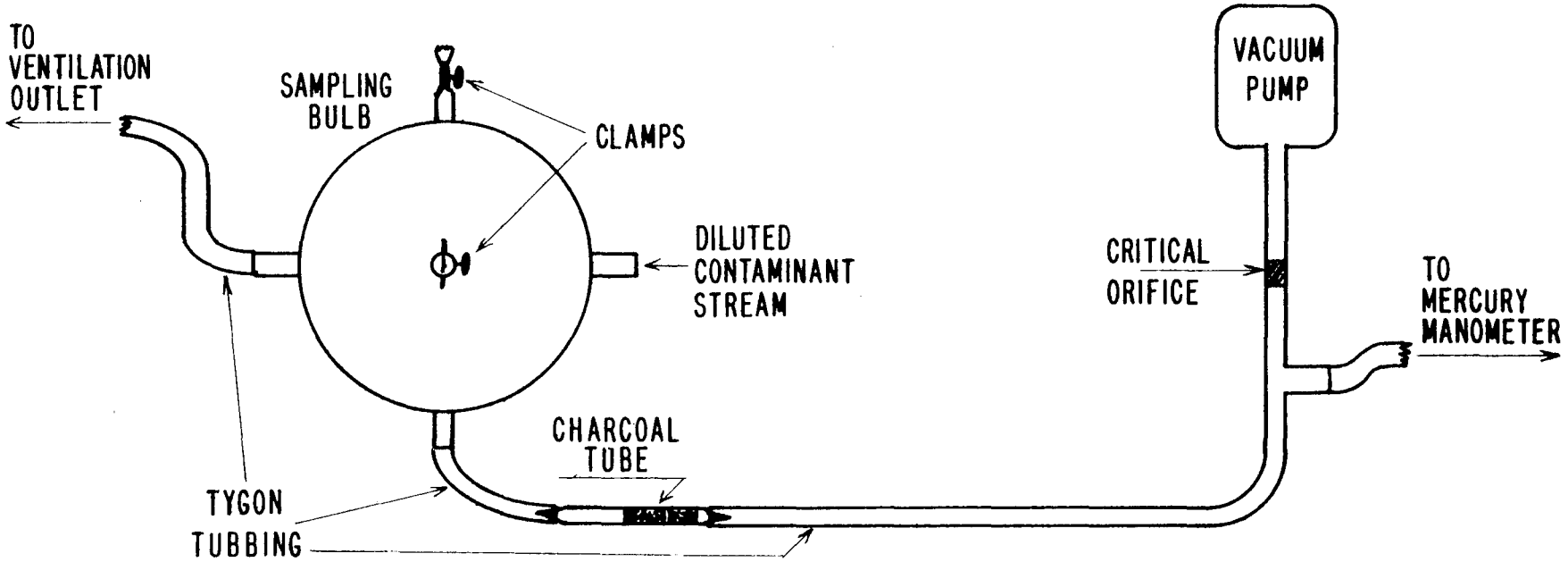

FIGURE 2. SAMPLING APPARATUS — CHARCOAL TUBE

☆ U.S. GOVERNMENT PRINTING OFFICE: 1972—759-573/1362