

DEVELOPMENT OF PROCEDURES
TO ASSESS THE PERFORMANCE OF
EXTERNAL LEAK DETECTION DEVICES

VAPOR-PHASE ASTM-FORMATTED METHODS

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INTRODUCTION

From the onset, EPA's development of test methods for characterization of external leak detectors has had several goals. The primary goal has been to provide means by which tank owners and users can select proper detection systems. A secondary goal has been to establish a knowledge base about detector performance upon which regulations could be based.

The first step in test methods development consisted of surveying vendors to get an accurate depiction of the universe of external detectors. The survey demonstrated that there was a great diversity of detectors on the market and that performance data were gathered on widely varying bases or were nonexistent. The survey, however, was very beneficial in providing the foundation for further development of test procedures. The different detector operating principles and critical performance criteria were identified. Also, limited information on performance test procedures developed by vendors and testing agencies was uncovered.

Performance criteria were ranked and grouped where appropriate. Grouping allows multiple performance data to be collected simultaneously; and thus, reduces testing costs. Test methods for the highest ranked criteria were developed based on information gathered during the vendor survey and other knowledge of the field of external leak detection.

The methods were then evaluated with leak detectors available in the market. The purpose of this testing was to demonstrate the "real world" utility of the methods. This evaluation was the first critical step in validating the methods. Operational and theoretical flaws in the original methods were identified and corrected as a result of the evaluation. In addition, results from the evaluation provided EPA with consistent information on typical performance of external leak detectors.

The current plan calls for further validation and clarification so the test methods can be released for general use. EPA hopes that vendors will use the test methods to characterize performance of their detectors so that tank owners are able to select the most appropriate detectors for each underground storage tank site. In addition, EPA hopes that having performance characteristics available on a consistent basis will drive technology toward improved detection capability.

This document includes three draft test methods in ASTM format. These methods are revisions of test procedures developed under Work Assignments 2 and 13. The revisions address use of JP-4 jet fuel and other hydrocarbon liquids as test atmosphere sources. The methods are:

- Standard Test Method for Accuracy and Response Time for Vapor-Phase Out-of-Tank Petroleum Detectors;
- Standard Test Method for Specificity for Vapor-Phase Out-of-Tank Petroleum Detectors; and
- Standard Test Method for Lower Detection Limit for Vapor-Phase Out-of-Tank Petroleum Detectors.

Designation: X 0001

Standard Test Method for
ACCURACY AND RESPONSE TIME FOR VAPOR-PHASE OUT-OF-TANK PETROLEUM DETECTORS

1. Scope

1.1 This test method covers determination of accuracy and response time of vapor-phase out-of-tank petroleum hydrocarbon leak detectors.

1.2 This method is only applicable to components associated with detection of vapor-phase petroleum releases for detection systems utilizing multiple operating principles.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 1 Standard Specification for ASTM Thermometers

E 456 Standard Terminology Relating to Statistics

difference between the average measured value for a series of tests and the true value.

5.4 Response time is the general term that refers to a combination of the more specific terms detection time and fall time. Detection time is the elapsed time from a detector's first contact with a given concentration of petroleum vapors to 95% of its full-scale signal output or to an activated response. Fall time is the elapsed time after the detector is removed from contact with petroleum hydrocarbon vapors until the detector output returns to a stable baseline response.

5.5 Results obtained using this method will permit the most advantageous use of a detector. Weaknesses as well as strengths of the instrument should become apparent. It is not the interest of this method to compare similar detectors of different manufacture, but to enable the user to choose a suitable detector.

6. Interferences

6.1 Conditions that can cause interferences with this method include temperature changes, high temperatures, excessive test apparatus volumes and leaks in the test apparatus. To avoid these conditions, tests should be conducted at constant ($\pm 3^{\circ}\text{C}$), normal laboratory temperatures with a leak-tested test apparatus.

6.2 Cross contamination (e.g., memory effects from residual test atmospheres) may be a major cause of inaccurate data. To minimize this potential problem, avoid using rubber or plastic parts for components of the test apparatus that contact test gases and purge the testing system as described in Section 10.

6.3 Fluctuations of the test chamber internal pressure may significantly affect the detector's response. Maintain a constant internal

chamber pressure (± 0.2 inches of water relative to ambient pressure) while the probe is exposed to the test atmosphere by maintaining a constant inlet and exit test atmosphere flow rate. If the pressure varies outside the acceptance limits, repeat the tests within the accepted pressure fluctuation limits.

7. Apparatus

7.1 *Test apparatus*--The test apparatus, as depicted in Figure 1, shall be constructed from materials that are inert with respect to test gases. The test apparatus consists of a compressed gas cylinder, pressure regulator, tubing, valves, tubing connectors, rotameters, volatilization system, test chamber, thermocouple, and manometer. The volatilization system is depicted in greater detail in Figure 2.

7.1.1 *Compressed gas cylinder*--Ultrahigh-purity air is supplied in standard compressed gas cylinders having Compressed Gas Association (CGA) fittings compatible with regulator fittings.

Note 1--Ultrahigh-purity air may be supplied in compressed gas cylinders having various fittings. Consult specific gas suppliers for details on appropriate fittings.

7.1.2 *Pressure regulator*--A dual stage regulator with a fitting compatible with the test gas cylinder is needed. The regulator shall have a range of at least 0 psi to 15 psi and have a diaphragm made of stainless steel.

7.1.3 *Tubing*--Sufficient tubing to link all test apparatus components is needed. The tubing shall be free from contaminants and have an internal diameter of at least 1/8 inch. The tubing shall be made of a material that is inert with respect to test gases.

7.1.4 *Tubing connectors*--Various compression-type tubing fittings are needed to make test apparatus connections. These fittings shall be free from

contaminants, inert with respect to test gases, and of a material that is compatible with the tubing. These fittings can include, but are not limited to, tees, cross tees, reducers, and elbows. A thermocouple compression fitting is also needed.

7.1.5 *Rotameters*--Two rotameters, each having a flow range bracketing the required flow rates for the detector, are needed to measure test chamber inlet and outlet vapor rates. A third rotameter, capable of delivering 0.2 L/min. of air, is required for continuously flushing the volatilization chamber between tests.

7.1.6 *Valves*--At least one shut-off valve, two flow controlling needle valves, and two three-way ball valves are needed.

Note 2--Gas shut off can be accomplished using a regulator and the integral shut-off valve commonly included with compressed gas cylinders. Many rotameters include an integral flow controlling needle valve.

7.1.7 *Thermocouple*--A thermocouple and temperature readout, or equivalent, that responds from 0°C to 40°C and is accurate to within 1°C over this range is needed.

7.1.8 *Manometer*--A relative pressure manometer is required to monitor the test chamber's internal pressure. The manometer must have a working range of at least 0-10 inches of water (0 to 20 mm Hg) with an accuracy of $\pm 5\%$. The manometer should be scaled using at least 0.2 inches of water (0.4 mm Hg) subdivisions.

7.1.9 *Volatilization chamber*--The volatilization chamber should be gas tight and made from materials that are inert with respect to test gases. Figure 2 schematically depicts the arrangement of the volatilization chamber within the volatilization system. The volatilization chamber should be made from glass to allow for good thermal transfer and visual inspection of the

position of the syringe needle tip. All compression fittings connected to the glass tube should utilize Teflon® ferrules and back ferrules. Nichrome heating wire should be wound around the glass tube with no gaps between each wrap. The volatilization chamber inlet should be fitted with a 1/4-inch, stainless steel tubing tee. The end of the tee directly opposite the entrance to the volatilization chamber should be fitted with a septum to allow insertion of the syringe needle into the heated tubing. The needle should be inserted at a slight angle so that the tip touches the top inner surface of the glass tubing to insure a constant flow of fuel from the needle tip onto the glass surface.

Note 3--If the needle does not touch the glass surface, the test product pumped from the needle will produce droplets rather than a steady stream on the heated surface. This will give rise to fluctuations in vapor-phase test product concentrations.

7.1.10 *Test chamber*--The test chamber should be gas-tight and made from materials that are inert with respect to test gases. Figure 3 depicts a test chamber schematic representation. The test chamber must have fittings to allow connection to the detector probe, a manometer, and a thermocouple. Test chamber volumes should be kept as small as possible without interfering with detector operation. The chamber must also have an inlet and outlet for flow of test atmospheres. Diagrams of suitable test chambers are presented in Appendix A.

7.1.11 *Syringe pump*--A syringe pump that is accurate to $\pm 5\%$ of the desired flow rate is required. The syringe pump must be capable of delivering from 0.05 to 1500 $\mu\text{L/hr}$ over one hour.

7.1.12 *Syringes*--Precision glass syringes with certified $\pm 1\%$ accuracy and repeatability are required. Syringes in 10, 100, 250, 500, and 1000 μL

sizes are recommended.

7.1.13 *Power supply*--An alternating or direct current power supply that is variable from 0 to 50 volts and is capable of delivering at least 2 amperes of current is needed.

7.1.14 *Heating wire*--20 feet of 25-gauge, glass-insulated, Nichrome heating wire with a fixed resistance of 2.1 ohms/ft is required.

7.1.15 *Septum*--An inert septum with a 6 mm diameter is required.

7.2 *Timer*--A timer that is accurate and precise to at least 1 second per 10 minutes is required. Alternatively, a chart recorder or other data acquisition system may be used. If a chart recorder or other data acquisition system is to be used, the timer is not required. If used, the recorder or data acquisition system timing must be accurate and precise to at least one second per 10 minutes.

7.3 *Electronic recorder*--A chart recorder or other electronic data acquisition system may be used if it is compatible with the specific detector that is being evaluated. The output of the data recorder should be accurate and precise to $\pm 2\%$ over the range of output from a quantitative detector. A data recorder used with a qualitative detector must unambiguously identify activated and inactivated states.

7.4 *Thermometer*--ASTM Solvents Distillation Thermometer having a range from -2°C to 52°C and conforming to the requirements for Thermometer 37C as prescribed in Specification E 1.

7.5 *Bubble meter*--Use NBS-traceable soap bubble flow meters to calibrate rotameters. The bubble meters must have a working range that brackets the range of all rotameters.

8. Reagents and Materials

8.1 *Purity of Reagents*--Reagent grade chemicals shall be used in all

tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents for the American Chemical Society where such specifications are available.¹ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of determination.

8.2 *Ultrahigh-Purity Air*--The ultrahigh-purity air standard must have less than 0.5 ppmv total hydrocarbon content. (Caution--Gas under high pressure. See Annex A1.1.)

8.3 *Commercial gasoline*--The commercial gasoline test product shall be unleaded regular or premium gasoline that is purchased at a retail outlet. (Danger--Gasoline is extremely flammable. Vapors are harmful if inhaled. See Annex A1.2. Leaded gasoline should not be used because there are significant additional hazards associated with its handling and disposal).

8.4 *Synthetic Gasoline*--Synthetic gasoline, as used in this method, is an 11-component mixture that is roughly representative of automotive gasoline prepared according to Method X 0004, "Standard Practice for The Preparation of Synthetic Gasoline for Testing Out-of-Tank Petroleum Detectors." (Danger--Synthetic gasoline is extremely flammable. Vapors are harmful if inhaled. See Annex A1.3).

8.5 *JP-4 Jet Fuel*--The JP-4 jet fuel test product shall be purchased from a retail outlet. (Danger--JP-4 jet fuel is flammable. Vapors are harmful if inhaled. See Annex A1.4).

8.6 *Other Test Products*--This test method can also be used with

¹"Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemicals Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., In., New York, NY, and the "United States Pharmacopeia."

other non-viscous, volatile liquids. The method, however, does not directly address use of liquids other than commercial gasoline, the synthetic gasoline described herein, and JP-4 jet fuel. The suitability of this method with regard to other substances should be ascertained before this method is used with those liquids.

8.7 All petroleum hydrocarbon products and hydrocarbon reagents shall be stored in tightly sealed, inert containers away from heat, sparks, and flames. Petroleum fuels shall not be stored for more than 60 days because significant changes in their properties may occur as a result of volatile component losses.

9. Calibration and Standardization

9.1 *Chart Recorder or Other Data Recording System*--If used, a chart recorder or other data recording system should be calibrated along with the detector. The data recording system should be calibrated according to instructions from its manufacturer and the detector manufacturer. Also, any recording device should be compatible with the detector being investigated. Consult specifications from the manufacturers of the recording device and the detector.

9.2 *Detector*--Because of wide design variability among different petroleum detectors, it is impossible to give complete calibration instructions for all possible detector designs. Calibrate all detectors according to manufacturer instructions.

9.3 *Rotameters*--Calibrate each rotameter prior to initiating test procedures, once a year thereafter, and after any internal contamination (e.g., dirt, moisture.) during testing. Instructions accompanying the NBS-traceable bubble meters should be followed. The rotameters are to be calibrated at a minimum of five points ("multipoints") within the working range.

Flow readings should be made from the middle of the ball float. All readings should be made from the upper float on dual-float rotameters until it is off scale. Once the upper float is off scale, readings should be made from the lower float.

9.3.1 *Assembly*--Remove the rotameter from the test system, if assembled, and connect the rotameter in series between a controllable compressed air source and an NBS-traceable bubble meter. Use a bubble meter cylinder that will allow a flow measurement over a period of 15 to 45 seconds.

9.3.2 *First calibration point*--Bring the gas flow rate to the lowest calibration flow for testing. Let the system run at this setting until the rotameter is steady. If the flow rate is not within the first level range, adjust the flow rate until it is within that range and wait for a steady-state value. Record the steady-state flow meter value that is within the first flow rate level. Measure the flow rate with the bubble meter and stopwatch according to the NBS bubble meter instructions. Record each reference flow rate.

9.3.3 *Remaining calibration points*--Record steady-state settings for triplicate runs as described in Section 9.3.2 for at least four more flow rates throughout the rotameter range.

9.4 *Thermocouple*--Perform side-by-side multipoint calibrations for each thermocouple used in the test procedure in a 1-L glass beaker filled with water. The reference thermometer should be an ASTM Solvents Distillation thermometer having a range from -2°C to 52°C and conforming to the requirements for Thermometer 37C as prescribed in Specification E 1. The levels tested are low (room temperature - 10°C), room temperature, and high (room temperature + 10°C).

9.4.1 Insert both the thermocouple and reference thermometer into the beaker of water and add small quantities of ice. Allow the ice to melt and

the temperature to stabilize. Continue adding ice until a steady-state reading ($\pm 0.5^\circ\text{C}$ over two minutes) of room temperature - 10°C ($\pm 2^\circ\text{C}$) occurs.

9.4.2 Repeat this procedure using room temperature water (15°C to 30°C), and water heated to room temperature + 10°C ($\pm 2^\circ\text{C}$). If the temperature difference is more than 1°C , either repeat the test with the same thermocouple or replace the thermocouple and repeat the test until it is acceptable.

9.4.3 Perform thermocouple calibration at the onset of testing and at least once a year.

9.5 *Average Molecular Weight of Commercial Fuels*--Determine the average molecular weight of commercial gasoline and JP-4 jet fuel by cryoscopic osmometry. Average molecular weight values should be $\pm 5\%$ accurate.

Note 4--Synthetic gasoline prepared according to EPA Leak Detector Standard X 0004 has an average molecular weight of 92.83 g/mol.

9.6 *Test Product Density*--The density of test products should be determined by filling a tared 50-mL volumetric flask with test product and weighing the volumetric flask with test product on an analytical balance. Test product density is calculated as follows:

$$\text{Density, g/mL} = (m_t - m_c) \div v \quad (1)$$

Where:

m_t = mass of flask plus test product, g;

m_c = mass of flask, g;

v = flask volume, mL ($v = 50$ mL).

9.7 *Syringe Pump*--Determine the linearity of liquid delivery at each gear setting of the pump at the beginning of testing and at least yearly

thereafter. Calibration should be performed with a 250 μL syringe filled with water. The syringe pump should be set at approximately 50% flow for the gear setting that is being calibrated. Record the initial volume of the syringe. Start the syringe pump and a timer simultaneously. Record the syringe volume after 15, 30, 45, and 60 minutes. The correlation coefficient of delivered volume versus time, as calculated with the following equation, must be 0.995 or better:

$$\text{Correlation coefficient} = \frac{n\sum t_i \Delta V_i - (\sum t_i)(\sum \Delta V_i)}{\sqrt{[n\sum t_i^2 - (\sum t_i)^2][n\sum \Delta V_i^2 - (\sum \Delta V_i)^2]}} \quad (2)$$

Where:

- n = number of calibration points (5);
- t_i = each time increment, minutes; and
- ΔV_i = each corresponding volume change, μL .

9.8 *Syringes*--Calibrate each syringe before initiating testing and yearly thereafter. Syringes should be calibrated at each syringe pump gear setting at a rate corresponding to 50% flow. Calibration should be performed with a syringe filled with water. Record the initial syringe volume, and affix the syringe to the syringe pump. Simultaneously start a timer and the syringe pump. Record the syringe volume after at least 15 minutes (± 1 second). Determine the 100% flow rate for the syringe according to the following equation:

$$100\% \text{ Syringe flow rate, } \mu\text{L/hr} = 6000 \times (V_f - V_i) \div t \div p \quad (3)$$

Where:

- V_f = final syringe volume, μL ;
 V_i = initial syringe volume, μL ;
 t = elapsed time, minutes; and
 p = syringe pump setting, % (50%).

10. Conditioning

10.1 *Before each test*--Purge the test chamber for at least three minutes with ultrahigh-purity air at 0.2 L/min. Turn on the power supply for the volatilization chamber and set the voltage such that a volatilization chamber temperature of $160^\circ\text{C} \pm 15^\circ\text{C}$ is established. Allow the chamber to warm up for five minutes.

10.2 *During each test*--Continuously purge the volatilization chamber with ultrahigh-purity air when it is not in use. The purge-air flow rate should be at least 0.1 L/min.

11. Procedure

11.1 *Test Series*--The detector should be tested a minimum of five times for each combination of test gas and concentration listed in Table 1.

11.1.1 Perform tests in a random order such that variables of test gas and hydrocarbon concentration are isolated.

11.2 *Detector Assembly*--Assemble the detection system as described by the manufacturer. Insert the detector probe into the test chamber. The seal between the probe and the test chamber should be gas tight.

11.2.1 Connect the detector output to a chart recorder or other data acquisition system if one is being used. All connections should be in compliance with specifications from the manufacturers of the detector and the data recording system.

11.3 *Syringe Pump Setup*--Assemble the volatilization system according

to Figure 2. Make sure the syringe needle is inserted into the septum far enough and at a slight angle so that the tip is inside and touching the heating tubing, and not in the tee fitting.

11.4 *Calibration*--Calibrate the detector if necessary. Many detectors do not require any calibration. Perform calibrations, if necessary, according to manufacturer recommendations. Calibration may need to occur before mounting in the test container. If a data recording system is being used, it should be calibrated with the detector. Calibrate the data acquisition system according to manufacturer instructions.

11.5 *Background*--Supply ultrahigh-purity air to the test chamber at a rate that is 0.2 L/min. greater than the detector's aspiration rate.

Note 5--Many detectors are passive and do not aspirate gas samples. Use total test gas flow rates of 0.2 L/min for these detectors. Monitor the detector's response every 15 seconds until a steady-state reading ($\pm 2\%$ change of full scale over one minute) is achieved or 4 minutes has elapsed, whichever is longer. Monitor the temperature inside the test chamber during background testing.

11.6 *Test Atmosphere Response*--Introduce the appropriate test gas to the test chamber by turning on the syringe pump and switching valves so that ultrahigh-purity air flows through the volatilization system and into the test chamber. Monitor the temperature inside the test chamber during testing. The syringe pump injection rate should be determined as follows:

$$\text{Injection rate, } \mu\text{L/hr} = F_g \times \bar{M}_f \times C_g \times 2.6786 \times 10^{-3} \div d_f \quad (4)$$

Where:

F_g = total test gas flow rate, L/min;

\bar{M}_f = test product average molecular weight, g/mol;
 C_g = desired test gas concentration, ppmv; and
 d_f = test product density, g/mL.

Instructions provided by the syringe pump manufacturer should be followed for proper syringe selection and injection rate setting.

11.6.1 Monitor quantitative detectors until a steady-state ($\pm 2\%$ of full scale over 1 minute) response occurs or for 1 hour, whichever is shorter. Monitor qualitative detectors for a positive response ("activated") for up to 1 hour.

11.7 *Detection Time*--If the detector gives a positive response within 1 hour, the elapsed time between when the test atmosphere was introduced into the chamber and when the detector responded is the detection time. The nature of a response is dependent on whether a detector gives quantitative output or qualitative output.

11.7.1 The period for detection time of quantitative detectors is from introduction of the test atmosphere into the test chamber to the time the detector reaches 95% of its final stable output. Calculate the 95% of final stable output level from the following equation:

$$\text{High level output, ppmv} = \text{BL} + (\text{HL} - \text{BL}) \times 0.95 \quad (5)$$

where:

BL = stable baseline output, ppmv; and

HL = stable high level output, ppmv.

11.7.2 A positive response for qualitative detectors occurs when the detector output goes from an inactivated state to an activated state.

11.7.3 If the detector gives a response within 1 hour, report the elapsed time between when the detector probe was added to the container with test gas and when the detector responded as the detection time.

11.8 *Fall Time*--Simultaneously switch the ultrahigh-purity air flow such that the volatilization chamber is fully bypassed. The air flow rate should be sufficient to produce a 0.2 L/min vent flow rate. Vent and flush the volatilization chamber and turn off the syringe pump. After five minutes, turn off the volatilization air and power supply unless subsequent tests are planned.

Note 6--Fall time is not applicable to some detectors such as qualitative detectors that did not activate in response to addition of gas to the test container.

11.8.1 Start the timer or mark the beginning of the fall time test on the recording system when ultrahigh-purity air is introduced into the test chamber.

11.8.2 Monitor the detector output for fall time response. The nature of a fall time response is dependent on whether a detector gives quantitative or qualitative output. Fall time response for a quantitative detector is when the detector output returns to within 5% of its original stable baseline level. Calculate the 5% stable baseline level according to the following equation:

$$5\% \text{ Stable baseline output, ppmv} = BL + (HL - BL) \times 0.05 \quad (6)$$

where:

BL = stable baseline output, ppmv; and

HL = stable high level output, ppmv.

Fall time response for a qualitative output detector is when the detector output goes from an activated state to an inactivated state.

11.8.3 Continue fall time monitoring for up to 1 hour.

12. Calculations

12.1 *Relative Percent Difference*--Calculate relative percent difference as follows:

$$\text{Relative percent difference, \%} = 200 \times [(V_1 - V_2)/(V_1 + V_2)] \quad (7)$$

where:

V_1 = larger value; and

V_2 = smaller value.

12.2 *Coefficient of Variation*--Calculate the coefficient of variation as follows:

$$\text{Coefficient of variation, \%} = (s/\bar{X}) \times 100 \quad (8)$$

where:

s = standard deviation of n values ($n-1$ degrees of freedom), ppmv; and

\bar{X} = mean of n values, ppmv.

12.3 *Accuracy*--Calculation for accuracy is dependent on the type of output a detector produces.

12.3.1 *Quantitative detectors*--Accuracy for quantitative detectors is a function of systematic error (bias) and random error (precision). Bias and precision calculations are given in Equations 13 and 8, respectively.

Calculate relative accuracy of a set of data as follows:

$$\text{Relative accuracy, \%} = (|\bar{d}| + |cc|) / V_r \times 100 \quad (9)$$

where:

V_r = reference (theoretical) value;

\bar{d} = arithmetic mean of the difference of a data set, Equation 10; and

cc = 2.5% error confidence coefficient (one tailed, Equation 11).

12.3.2 *Mean difference*--Calculate the arithmetic mean of the difference of a data set as follows:

$$\text{Mean difference, ppmv} = 1/n \sum_{i=1}^n d_i \quad (10)$$

where:

d_i = measured response - theoretical response.

12.3.3 *Confidence coefficient*--Calculate the one-tailed 2.5% confidence coefficient (cc) as follows:

$$\text{Confidence coefficient, ppmv} = t_{0.975} \times s/\sqrt{n} \quad (11)$$

where:

s = the standard deviation (n-1) of the data set; and

$t_{0.975}$ = 2.5% t value = from Table 2; and

n = number of tests for a test gas at a particular concentration.

12.3.4 *Qualitative detectors*--Use the following formula to calculate the accuracy of qualitative detectors:

$$\text{Accuracy, \%} = 100 \times (r_p/n) \quad (12)$$

where:

r_p = number of positive responses; and
 n = number of tests for a particular test gas at a particular concentration.

12.4 *Bias*--Bias for quantitative detectors is calculated as follows:

$$\text{Bias, \%} = 100 \times [(\bar{V}_o - V_r)/V_r] \quad (13)$$

where:

V_r = the reference (theoretical) value, ppmv; and

\bar{V}_o = the average observed value, $1/n \sum_{i=1}^n V_i$;

where:

n = the number of tests with a particular test gas at a particular concentration; and

V_i = the individual response to test gas, ppmv;

12.5 *Detection Time*--Calculate detection time according to the following formula:

$$\text{Detection time} = T_2 - T_1 \quad (14)$$

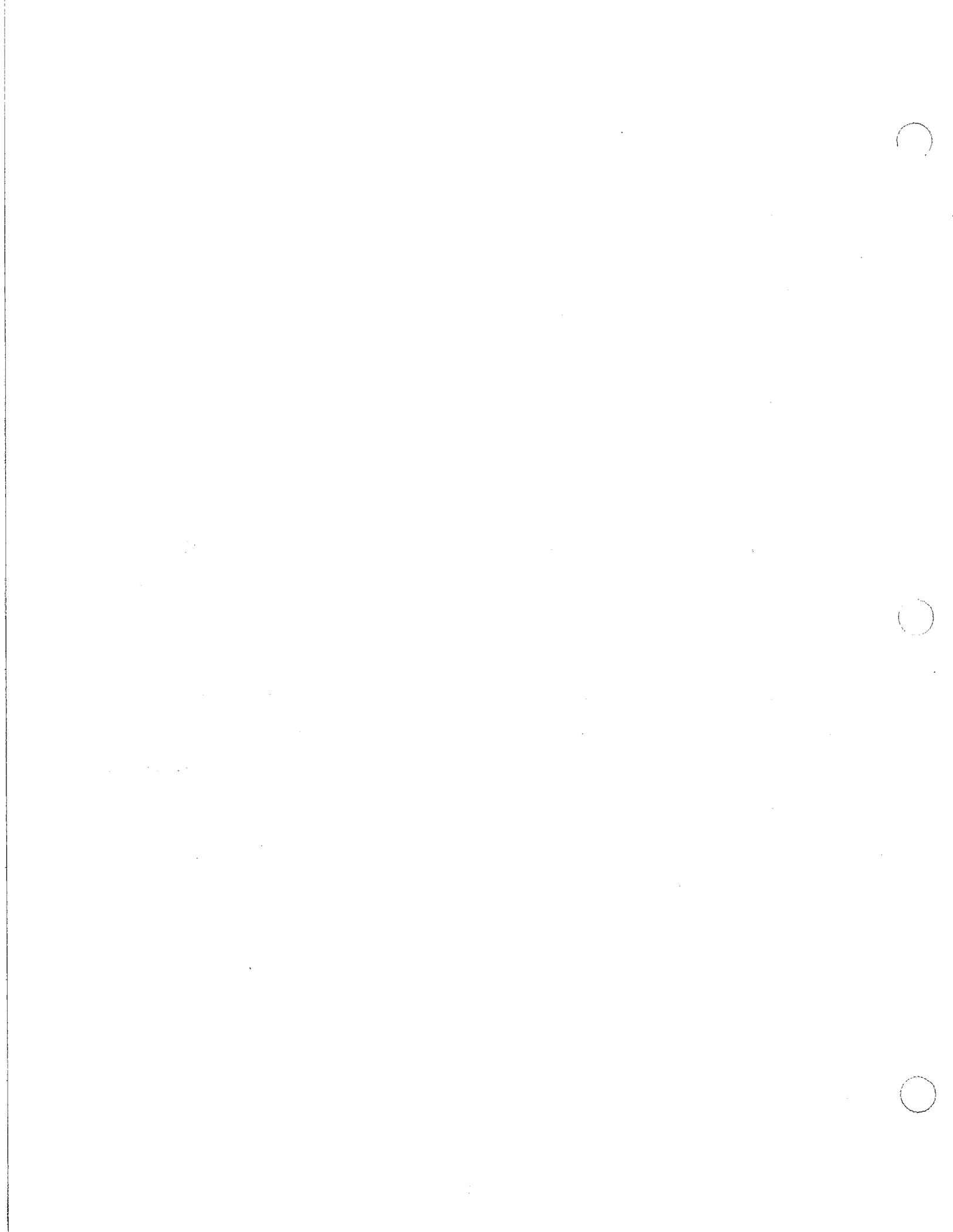
where:

T_1 = clock time when test gas was first added to test chamber; and

T_2 = clock time when detector output went from an inactivated state to an activated state for a qualitative-output detector or from a baseline reading to 95% of stable high level output for a quantitative detector.

12.6 *Fall Time*--Calculate fall time according to the following formula:

$$\text{Fall time} = T_2 - T_1 \quad (15)$$



13.1.5 *Detection Time*--Report detection time in the largest convenient units (seconds, minutes, or hours) for each test gas at every concentration (nominally 50, 500, and 1250 ppmv). If detector response is immediate, report detection time as "<1 second." If the detector does not respond within 1 hour, report detection time as "No response in 1 hour."

13.1.6 *Fall Time*--Report fall time in the largest convenient units (seconds, minutes, or hours) for each test gas at every concentration (nominally 50, 500, and 1250 ppmv). Fall time is not applicable to some detectors such as gas-soluble detectors and qualitative detectors that did not activate in response to addition of test gas to the chamber. For these detectors, report fall time as "NA," not applicable. Also, record the reason(s) why fall time determination was not applicable. If the detector does not respond within 1 hour, report fall time as "No response in 1 hour."

14. Precision and Bias

14.1 *Precision*--The precision of the procedure in Test Method X 0001 for measuring accuracy and response time for vapor-phase out-of-tank petroleum detectors is being determined.

14.2 *Bias*--Since there is no accepted reference material suitable for determining the bias for the procedure in Test Method X 0001 for measuring accuracy and response time for vapor-phase out-of-tank petroleum detectors, no statement on bias is being made.

TABLE 1. Test Atmospheres

Gas Compound	Concentrations (ppmv)
Commercial Gasoline	50 ±5, 500 ±10, 1000 ±50
Synthetic Gasoline	50 ±5, 500 ±10, 1000 ±50
JP-4 Jet Fuel	50 ±5, 500 ±10, 1000 ±50

TABLE 2. 2.5% T Values^A

n-1	t _{0.975}
0	12.706
1	4.303
2	3.182
3	2.776
4	2.571
5	2.447
6	2.365
7	2.306
8	2.262
9	2.228
10	2.201
11	2.179
12	2.160
13	2.145
14	2.131
15	2.120
16	2.110
17	2.101
18	2.093
19	2.086
20	2.080
21	2.074
22	2.069
23	2.064
24	2.060
25	2.056
26	2.052
27	2.048
28	2.045
29	2.042
30	2.021
40	2.000
60	1.980
120	1.960

^ATaken from *CRC Standard Mathematical Tables*, 26th ed. CRC Press, Inc. Boca Raton, FL, 1981.

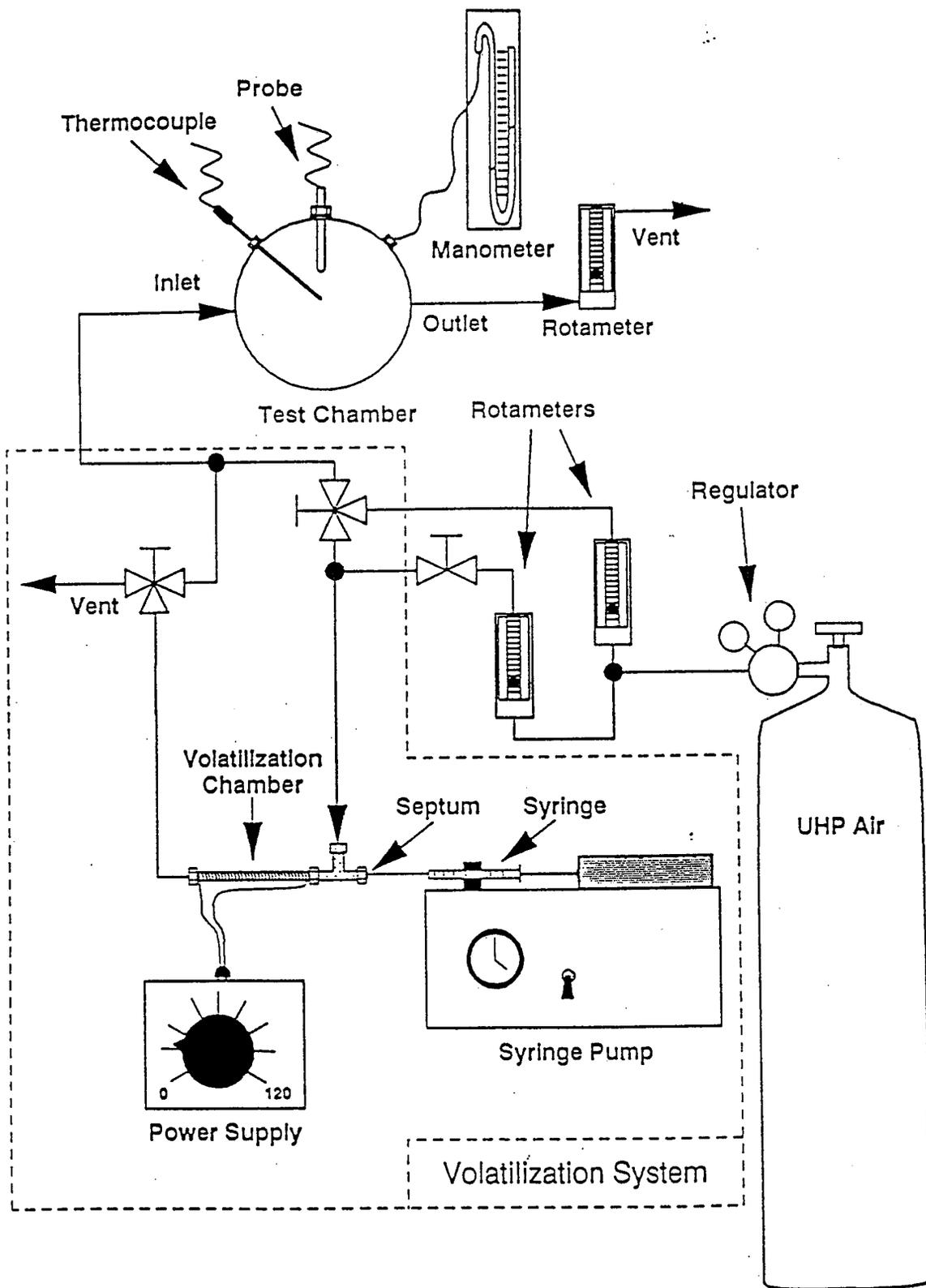
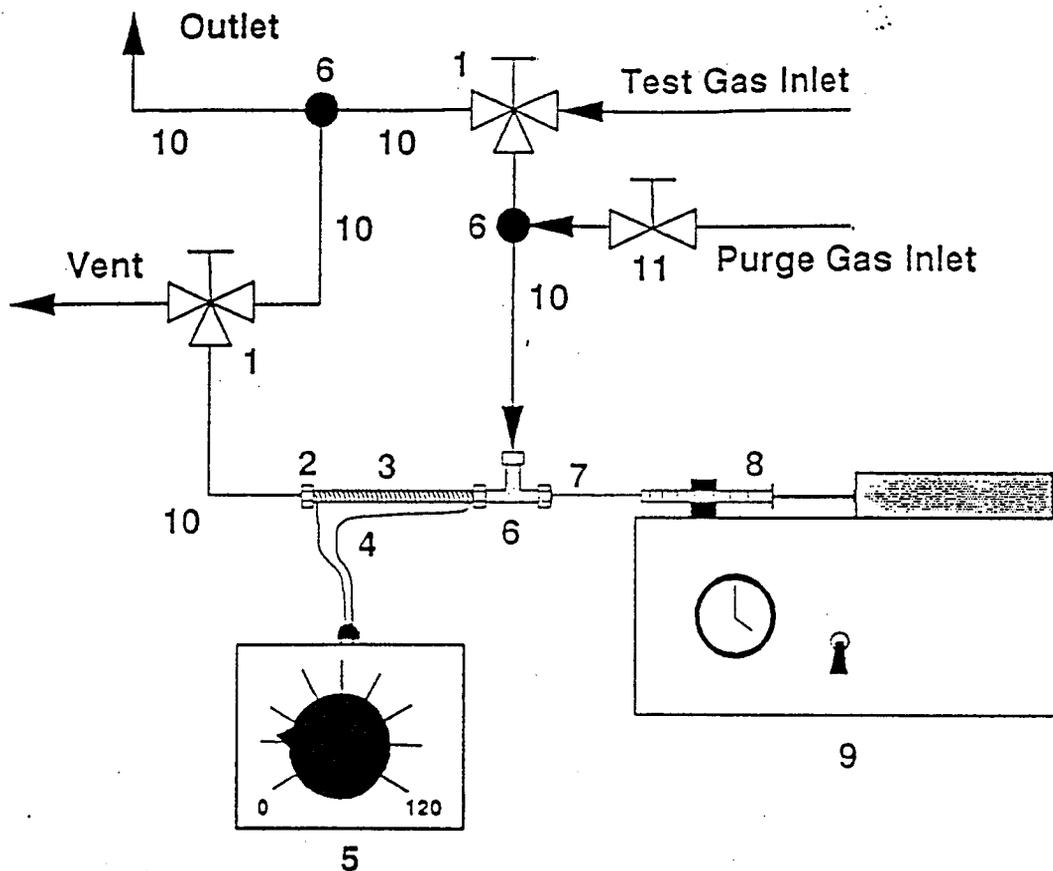


FIG. 1. Test Manifold Schematic Diagram



Description		Specifications
1	3-way valve	stainless steel, 1/4-in. fractional tubing fittings
2	tubing union	stainless steel, 1/4-in. fractional tubing fittings
3	glass tube	1/4-in. O.D., 7-in. long
4	heating wire	Nichrome, 25 gauge, glass insulated, 2.1 Ω /ft
5	power supply	0-50 V, 2 A
6	tee	stainless steel, 1/4-in. fractional tubing fittings
7	septum	6-mm diameter, inert
8	syringe	precision, glass
9	syringe pump	(See text.)
10	tubing	1/4-in. O.D., stainless steel
11	stop valve	stainless steel, 1/4-in. fractional tubing fittings

FIG. 2. Volatilization System Schematic Diagram

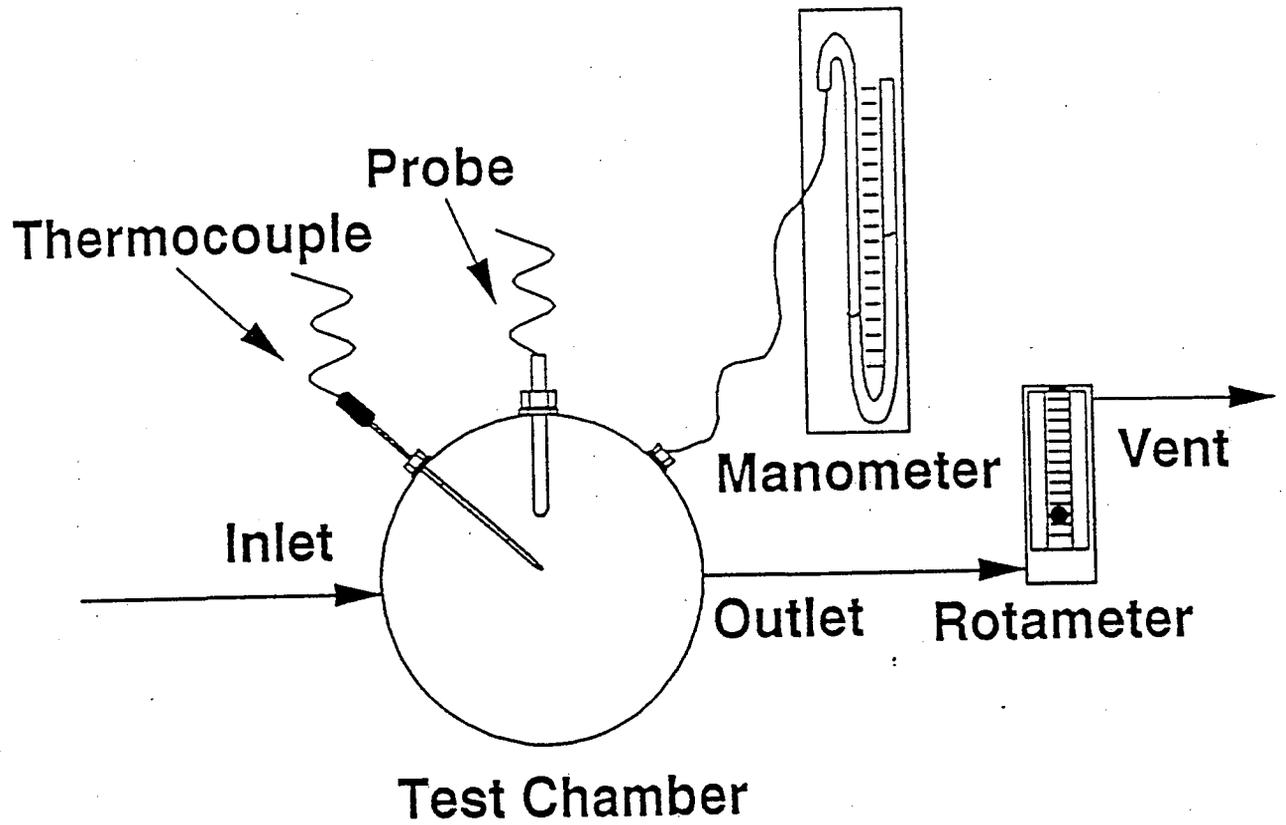


FIG. 3. Test Chamber Schematic Diagram

Detector Name: _____
 Detector Type: _____ Quantitative _____ Qualitative

Test Gas	Concentration, ppmv	Accuracy, %	Precision, %	Bias, %	Detection Time	Fall Time
Commercial Gasoline	50	_____	_____	_____	_____	_____
Commercial Gasoline	500	_____	_____	_____	_____	_____
Commercial Gasoline	1000	_____	_____	_____	_____	_____
Synthetic Gasoline	50	_____	_____	_____	_____	_____
Synthetic Gasoline	500	_____	_____	_____	_____	_____
Synthetic Gasoline	1000	_____	_____	_____	_____	_____
JP-4 Jet Fuel	50	_____	_____	_____	_____	_____
JP-4 Jet Fuel	500	_____	_____	_____	_____	_____
JP-4 Jet Fuel	1000	_____	_____	_____	_____	_____

FIG. 4. Data Recording Form

ANNEX

(Mandatory Information)

A1. PRECAUTIONARY STATEMENTS

A1.1 Compressed Gas. Air.

Caution—Compressed gas under high pressure.

Keep container closed.

Always use a pressure regulator. Release regulator tension before opening cylinder.

Do not transfer to cylinder other than one in which gas is received.

Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is securely supported at all times.

Stand away from cylinder outlet when opening cylinder valve.

Keep cylinder out of sun and away from heat.

Do not use cylinder without label.

Do not use dented or damaged cylinder.

For technical use only.

Do not use for inhalation purposes.

A1.2 Gasoline (including Leaded Gasoline)

Danger—Extremely flammable. Vapors harmful if inhaled.

Vapors may cause flash fire.

Contains toxic lead antiknock components. Harmful if absorbed through skin.

Keep away from heat, sparks, and open flames.

Keep container closed.

Use with adequate ventilation. Avoid buildup of vapors and eliminate all sources of ignition especially nonexplosion-proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist. Avoid prolonged or repeated skin contact.

A1.3 Synthetic Gasoline Mixture

Danger--Extremely flammable. Vapors harmful if inhaled. Vapors may cause flash fire. Contains toxic benzene and other hydrocarbon substances. (See Method X 0000).

Harmful if absorbed through skin.

Keep away from heat, sparks, and open flames.

Keep container closed. Use with adequate ventilation.

Avoid buildup of vapors and eliminate all sources of ignition, especially nonexplosion-proof electric apparatus and heaters.

Avoid prolonged breathing of vapors or spray mist.

Avoid prolonged or repeated skin contact.

A1.4 JP-4 Jet Fuel

Danger--Flammable. Vapors harmful if inhaled.

Vapors may cause flash fire.

Keep away from heat, sparks, and open flames.

Keep container closed.

Use with adequate ventilation, avoid buildup of vapors, and eliminate all sources of ignition, especially nonexplosion-proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist. Avoid prolonged or repeated skin contact.

APPENDIX

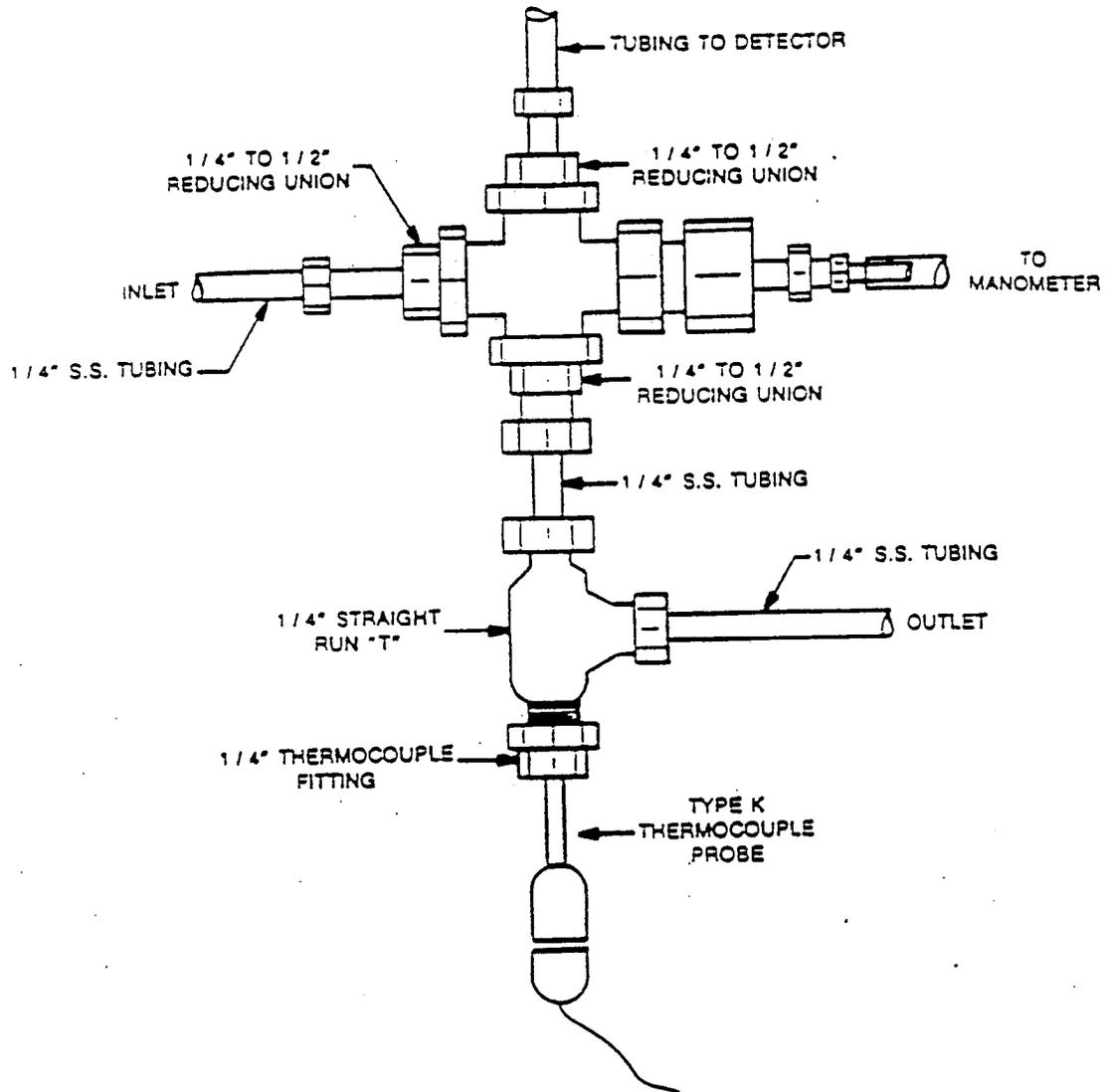
X1. EXAMPLE TEST CHAMBERS

X1.1 It is not reasonable to try to design a single test chamber that accommodates all configurations of detector probes. Instead, it is better to define the general requirements for the chamber and allow specific chambers to be designed to meet requirements for particular probes. Included in this appendix are diagrams of three test chambers that, combined, should be suited to the vast majority of vapor-phase detectors. The included chamber designs may also serve as starting points for alternate chamber designs.

X1.2 *Test Chamber for Tubing Probes*--Figure X1 contains a diagram detailing a test chamber design that should be suitable for almost all vapor-phase detectors that have probes consisting of tubing. These detectors primarily aspirate gas samples through tubing to a sensor located in the control box.

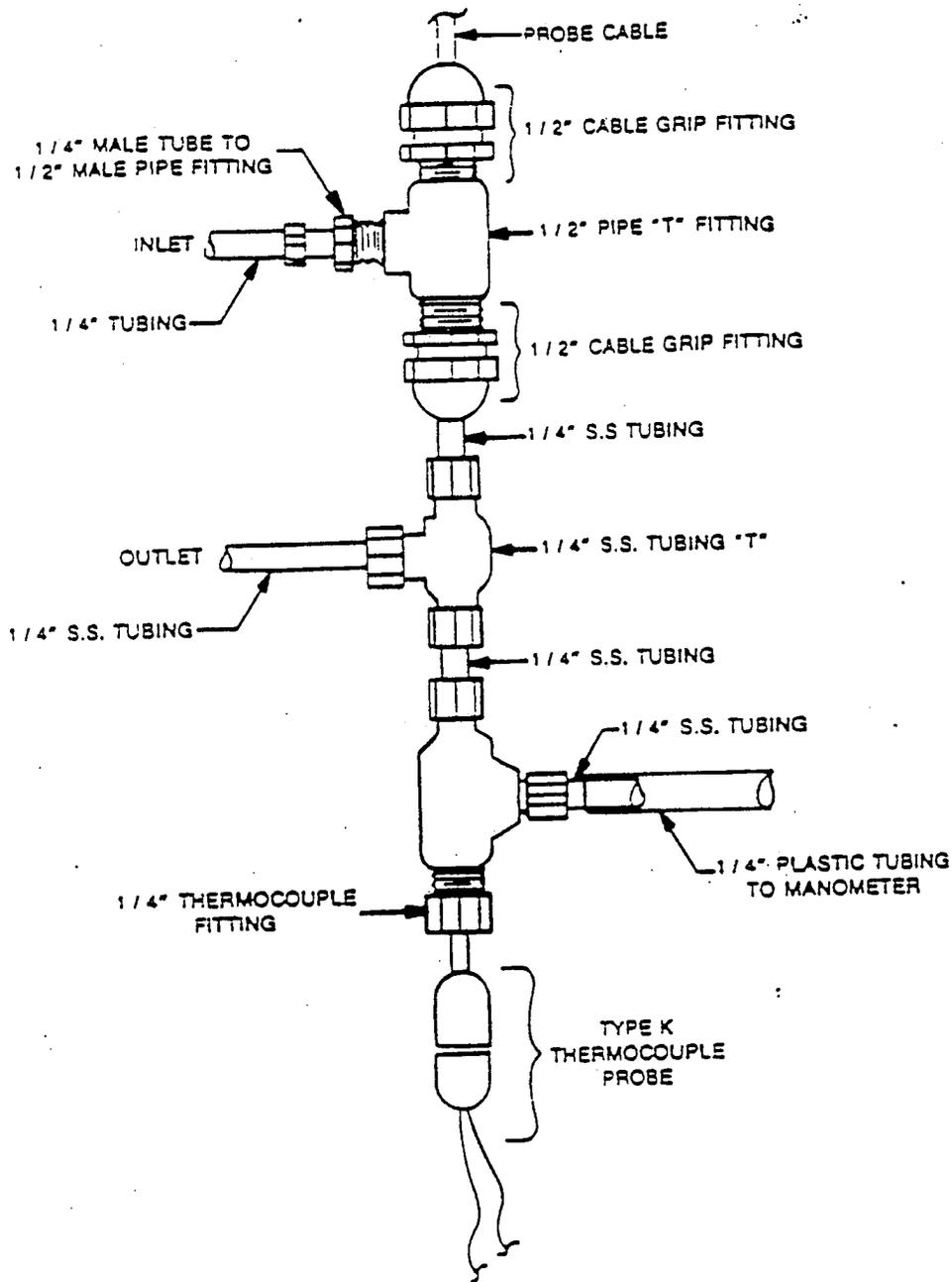
X1.3 *Test Chamber for Probes Up to 3/8-Inch Diameter*--Figure X2 is a diagram of a test chamber design that should be adequate for detector probes with diameters up to 3/8 inch.

X1.4 *Test Chamber for Probes Up to 1-1/4-Inch Diameter*--Figure X3 is a diagram of a test chamber design that should be adequate for detector probes with diameters up to 1-1/4 inches.



287-1292A

FIG. X1. Gas Test Chamber for Tubing Probes



087-1292A

FIG. X2. Gas Test Chamber for Probes with Diameters Up To 3/8 Inch

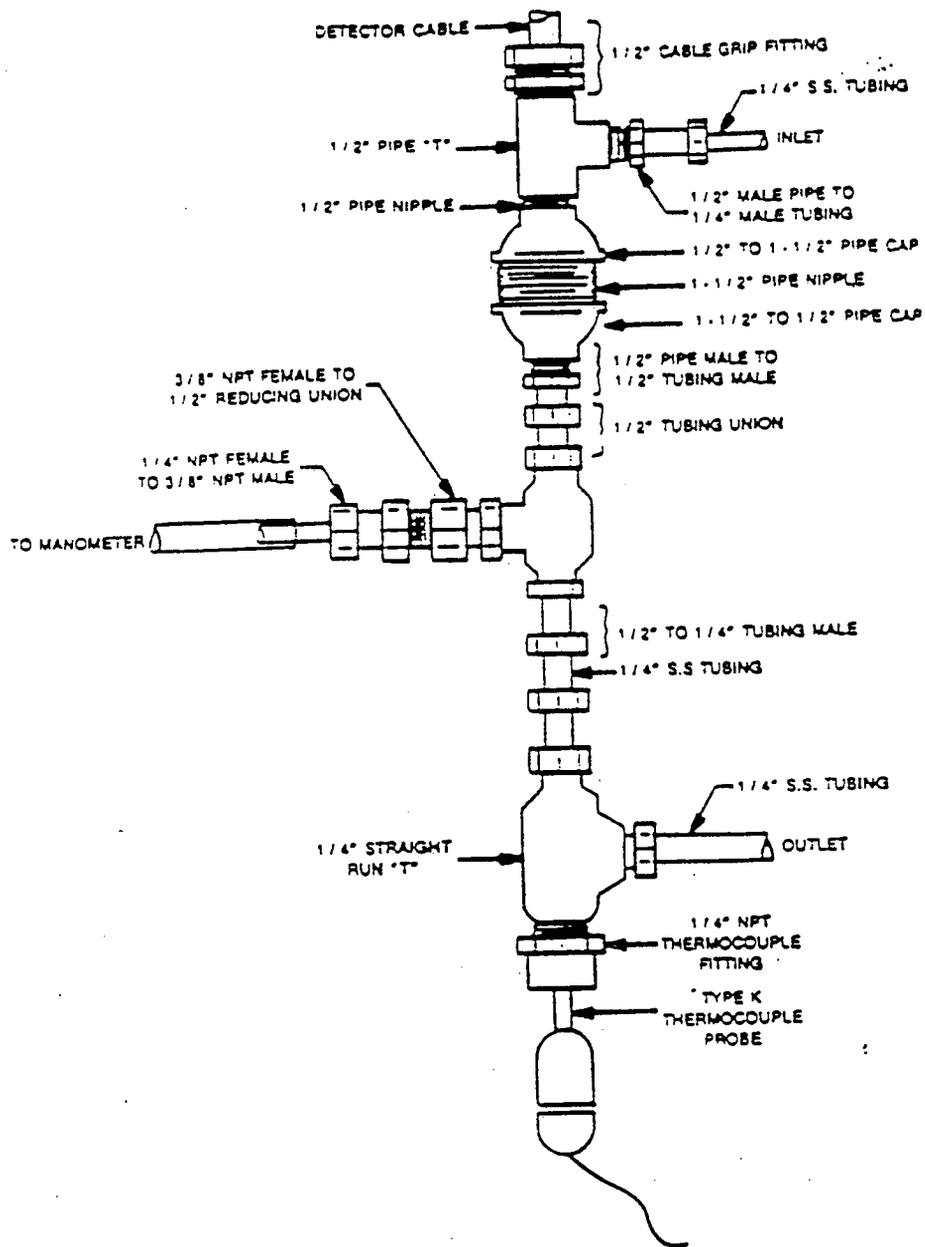


FIG. X3. Gas Test Chamber for Probes with Diameters Up To 1-1/4 Inches

Designation: X 0003

Standard Test Method for
SPECIFICITY FOR VAPOR-PHASE OUT-OF-TANK PETROLEUM DETECTORS

1. Scope

1.1 This test method covers determination of specificity of vapor-phase out-of-tank petroleum hydrocarbon leak detectors.

1.2 This method is only applicable to the components associated with detection of vapor-phase petroleum releases for detection systems utilizing multiple operating principles.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 1 Standard Specification for ASTM Thermometers

E 456 Standard Terminology Relating to Statistics

2.2 *EPA Leak Detector Standards:*

X 0004 Standard Practice for Preparation of Synthetic Gasoline

3. Terminology

3.1 *Definitions* -- For formal definitions of statistical terms, see Terminology E 456.

3.2. Descriptions of Terms Specific to This Method

3.2.1 *activated*--refers to the state of a qualitative detector's response when indicating the presence of hydrocarbon vapors.

3.2.2 *non-activated*--refers to the state of a qualitative detector's response when indicating that no hydrocarbon vapors are detected.

3.2.3 *probe*--component of a detection system that must come into contact with petroleum gas before the gas can be detected.

3.2.4 *qualitative responses*--type of detector response that indicates only the presence or absence of hydrocarbon vapors without determining the specific hydrocarbon concentration.

3.2.5 *quantitative responses*--type of detector response that quantitates the concentration of hydrocarbon vapor present.

3.2.6 *responses*--detector's indication of the presence of petroleum hydrocarbon vapors. Responses can be qualitative or quantitative.

3.2.7 *specificity*--ability of a detector to respond to various substances.

4. Summary of Test Method

4.1 Detector probes are subjected to each of six different test atmospheres inside a sealed test chamber. Test gas concentrations are nominally 500 parts per million by volume (ppmv). Detector response is monitored for up to 1 hour.

5. Significance and Use

5.1 For vapor-phase petroleum hydrocarbon detectors, specificity is a measure of how sensitive a detector is to different test gases.

5.2. Results obtained using this method will permit the most advantageous use of a detector. Weaknesses as well as strengths of the instrument should become apparent. It is not the interest of this method to compare similar detectors of different manufacture, but to enable the user to choose a suitable detector.

6. Interferences

6.1 Conditions that can cause interferences with this method include temperature changes, high temperatures, excessive apparatus volumes, and leaks in the test apparatus. To avoid these conditions, tests should be conducted at relatively constant normal laboratory temperatures with a leak-tested test apparatus.

6.2 Cross contamination (i.e., memory effects from residual test atmospheres) may be a major cause of inaccurate data. To minimize this potential problem, avoid using rubber or plastic parts for components of the test apparatus that contact test gases and purge the testing system as described in Section 11.

6.3 Fluctuations of the test chamber internal pressure may significantly affect the detector's response. Maintain a constant internal chamber pressure (± 0.2 inches of water relative to ambient pressure) while the probe is exposed to the test atmosphere by maintaining a constant inlet and exit test atmosphere flow rate. If the pressure varies outside the acceptance limits, repeat the tests within the accepted pressure fluctuation limits.

7. Apparatus

7.1 *Test apparatus*--The test apparatus, as depicted in Figure 1, shall be constructed from materials that are inert with respect to test gases. The test apparatus consists of a compressed gas cylinder, pressure regulator, tubing, valves, tubing connectors, rotameters, volatilization system, test chamber, thermocouple, and manometer. The volatilization system is depicted in greater detail in Figure 2.

7.1.1 *Compressed gas cylinder*--Ultrahigh-purity air is supplied in standard compressed gas cylinders having Compressed Gas Association (CGA) fittings compatible with regulator fittings.

Note 1--Ultrahigh-purity air may be supplied in compressed gas cylinders having various fittings. Consult specific gas suppliers for details on appropriate fittings.

7.1.2 *Pressure regulator*--A dual stage regulator with a fitting compatible with the test gas cylinder is needed. The regulator shall have a range of at least 0 psi to 15 psi and have a diaphragm made of stainless steel.

7.1.3 *Tubing*--Sufficient tubing to link all test apparatus components is needed. The tubing shall be free from contaminants and have an internal diameter of at least 1/8 inch. The tubing shall be made of a material that is inert with respect to test gases.

7.1.4 *Tubing connectors*--Various compression-type tubing fittings are needed to make test apparatus connections. These fittings shall be free from contaminants, inert with respect to test gases, and of a material that is compatible with the tubing. These fittings can include, but are not limited to, tees, cross tees, reducers, and elbows. A thermocouple compression fitting is also needed.

7.1.5 *Rotameters*--Two rotameters, each having a flow range bracketing the required flow rates for the detector, are needed to measure test chamber inlet and outlet vapor rates. A third rotameter, capable of delivering 0.2 L/min of air, is required for continuously flushing the volatilization chamber between tests.

7.1.6 *Valves*--At least one shut-off valve, two flow controlling needle valves, and two three-way ball valves are needed.

Note 2--Gas shut off can be accomplished using a regulator and the integral shut-off valve commonly included with compressed gas cylinders. Many rotameters include an integral flow controlling needle valve.

7.1.7 *Thermocouple*--A thermocouple and temperature readout, or equivalent, that responds from 0°C to 40°C and is accurate to within 1°C over this range is needed.

7.1.8 *Manometer*--A relative pressure manometer is required to monitor the test chamber's internal pressure. The manometer must have a working range of at least 0-10 inches of water (0 to 20 mm Hg) with an accuracy of $\pm 5\%$. The manometer should be scaled using at least 0.2 inches of water (0.4 mm Hg) subdivisions.

7.1.9 *Volatilization chamber*--The volatilization chamber should be gas tight and made from materials that are inert with respect to test gases. Figure 2 schematically depicts the arrangement of the volatilization chamber within the volatilization system. The volatilization chamber should be made from glass to allow for good thermal transfer and visual inspection of the position of the syringe needle tip. All compression fittings connected to the glass tube should utilize Teflon® ferrules and back ferrules. Nichrome heating wire should be wound around the glass tube with no gaps between each wrap. The volatilization chamber inlet should be fitted with a 1/4-inch,

stainless steel tubing tee. The end of the tee directly opposite the entrance to the volatilization chamber should be fitted with a septum to allow insertion of the syringe needle into the heated tubing. The needle should be inserted at a slight angle so that the tip touches the top inner surface of the glass tubing to insure a constant flow of fuel from the needle tip onto the glass surface.

Note 3--If the needle does not touch the glass surface, the test product pumped from the needle will produce droplets rather than a steady stream on the heated surface. This will give rise to fluctuations in vapor-phase test product concentrations.

7.1.10 *Test chamber*--The test chamber should be gas tight and made from materials that are inert with respect to test gases. Figure 3 contains a test chamber schematic representation. The test chamber must have fittings to allow connection to the detector probe, a manometer, and a thermocouple. Test chamber volumes should be kept as small as possible without interfering with detector operation. The chamber must also have an inlet and outlet for flow of test atmospheres. Diagrams of suitable test chambers are presented in Appendix A.

7.1.11 *Syringe pump*--A syringe pump that is accurate to $\pm 5\%$ of the desired flow rate is required. The syringe pump must be capable of delivering from 0.05 to 1500 $\mu\text{L/hr}$ over one hour.

7.1.12 *Syringes*--Precision glass syringes with certified $\pm 1\%$ accuracy and repeatability are required. Syringes from 10 to 1000 μL sizes may be required depending on the detector's gas-flow requirements.

7.1.13 *Power supply*--An alternating or direct current power supply that is variable from 0 to 50 volts and is capable of delivering at least 2 amperes of current is needed.

7.1.14 *Heating wire*--20 feet of 25-gauge, glass-insulated, Nichrome heating wire with a fixed resistance of 2.1 ohms/ft is required.

7.1.15 *Septum*--An inert septum with a 6 mm diameter is required.

7.2 *Timer*--A timer that is accurate and precise to at least one second per 10 minutes is required. Alternatively, a chart recorder or other data acquisition system may be used. If a chart recorder or other data acquisition system is to be used, a timer is not required. If used, the recorder or data acquisition system timing must be accurate and precise to at least one second per 10 minutes.

7.3 *Electronic recorder*--A chart recorder or other electronic data acquisition system may be used if it is compatible with the specific detector that is being evaluated. The output of the data recorder should be accurate to $\pm 2\%$ over the range of output from a quantitative detector. A data recorder used with a qualitative detector must unambiguously identify activated and inactivated states.

7.4 *Thermometer*--ASTM Solvents Distillation Thermometer having a range from -2°C to 52°C and conforming to the requirements for Thermometer 37C as prescribed in Specification E 1.

7.5 *Bubble meter*--Use NBS-traceable soap bubble flow meters to calibrate rotameters. The bubble meters must have a working range that brackets the range of all rotameters.

8. Reagents and Materials

8.1 *Purity of Reagents*--Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents for the American

Chemical Society where such specifications are available.¹ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of determination.

8.2 *Commercial Gasoline*--Commercial gasoline test product shall be unleaded regular or premium gasoline that is purchased at a retail outlet. (The fuel shall contain less than 2% water-miscible substances.

(Danger--Commercial gasoline is extremely flammable. Vapors are harmful if inhaled. Leaded gasoline should not be used because there are significant additional hazards associated with its handling and disposal. See Annex A1.1.)

8.3 *n-Hexane (C₆H₁₂)*--*(Danger--n-Hexane is extremely flammable. Vapors are harmful if inhaled. See Annex A1.2.)*

8.4 *JP-4 Jet Fuel*--JP-4 jet fuel test product shall be purchased at a retail outlet. *(Danger--JP-4 jet fuel is flammable. Vapors are harmful if inhaled. See Annex A1.3.)*

8.5 *Synthetic Gasoline*--Synthetic gasoline, as used in this method, is an 11-component mixture that is roughly representative of automotive gasoline prepared according to Practice X 0004. *(Danger--Synthetic gasoline is extremely flammable. Vapors are harmful if inhaled. See Annex A1.4.)*

8.6 *Toluene (CH₃C₆H₅)*. *(Danger--Toluene is extremely flammable. Vapors are harmful if inhaled. See Annex A1.5.)*

8.7 *Xylene(s) [2(CH₃)C₆H₄]*. *(Danger--Xylene is flammable. Vapors are harmful if inhaled. See Annex A1.6.)*

¹"Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemicals Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., In., New York, NY, and the "United States Pharmacopeia."

8.8 *Other Test Products*--This test method can also be used with other non-viscous volatile liquids. The method, however, does not directly address use of test products other than the liquids described herein, and JP-4 jet fuel. The suitability of this method with regard to other substances should be ascertained before this method is used with those liquids.

8.9 All petroleum hydrocarbon products and hydrocarbon reagents shall be stored in tightly sealed, inert containers away from heat, sparks, and flames. Petroleum fuels shall not be stored for more than 60 days because significant changes in their properties may occur as a result of volatile component losses.

8.10 *Ultrahigh-purity air*--The ultrahigh-purity air standard must have less than 0.5 ppmv total hydrocarbon content. (Caution--Gas under high pressure. See Annex A1.7.)

9. Calibration and Standardization

9.1 *Chart Recorder or Other Data Recording System*--If used, a chart recorder or other data recording system should be calibrated along with the detector. The data recording system should be calibrated according to instructions from its manufacturer and the detector manufacturer. Also, any recording device should be compatible with the detector being investigated. Consult specifications from the manufacturers of the recording device and the detector.

9.2 *Detector*--Because of wide design variability among different petroleum detectors, it is impossible to give complete calibration instructions for all possible detector designs. Calibrate all detectors according to manufacturer instructions.

9.3 *Rotameters*--Calibrate each rotameter prior to initiating test procedures, once a year thereafter, and after any internal contamination

(e.g., dirt, moisture, etc.) during testing. Instructions accompanying the NBS-traceable bubble meters should be followed. The rotameters are to be calibrated at a minimum of five points ("multipoints") within the working range. Flow readings should be made from the middle of the ball float. All readings should be made from the upper float on dual-float rotameters until it is off scale. Once the upper float is off scale, readings should be made from the lower float.

9.3.1 *Assembly*--Remove the rotameter from the test system, if assembled, and connect the rotameter in series between a controllable compressed air source and an NBS-traceable bubble meter. Use a bubble meter cylinder that will allow a flow measurement over a period of 15 to 45 seconds.

9.3.2 *First calibration point*--Bring the gas flow rate to the lowest calibration flow for testing. Let the system run at this setting until the rotameter is steady. If the flow rate is not within the first level range, adjust the flow rate until it is within that range and wait for a steady-state value. Record the steady-state flow meter value that is within the first flow rate level. Measure the flow rate with the bubble meter and stopwatch according to the NBS bubble meter instructions. Record each reference flow rate.

9.3.3 *Remaining calibration points*--Record steady-state settings for triplicate runs as described in Section 9.3.2 for at least four more flow rates throughout the rotameter range.

9.4 *Thermocouple*--Perform side-by-side multipoint calibrations for each thermocouple used in the test procedure in a 1-L glass beaker filled with water. The reference thermometer should be an ASTM Solvents Distillation thermometer having a range from -2°C to 52°C and conforming to the requirements for Thermometer 37C as prescribed in Specification E 1. The

levels tested are low (room temperature - 10°C), room temperature, and high (room temperature + 10°C).

9.4.1 Insert both the thermocouple and reference thermometer into the beaker of water and add small quantities of ice. Allow the ice to melt and the temperature to stabilize. Continue adding ice until a steady-state reading ($\pm 0.5^\circ\text{C}$ over two minutes) of room temperature - 10°C ($\pm 2^\circ\text{C}$) occurs.

9.4.2 Repeat this procedure using room temperature water (15°C to 30°C) and water heated to room temperature + 10°C ($\pm 2^\circ\text{C}$). If the temperature difference is more than 1°C, either repeat the test with the same thermocouple or replace the thermocouple and repeat the test until it is acceptable.

9.4.3 Perform thermocouple calibration at the onset of testing and at least once a year.

9.5 *Average Molecular Weight of Commercial Fuels*--Determine the average molecular weight of commercial gasoline and JP-4 jet fuel by cryoscopic osmometry. Average molecular weight determinations must be $\pm 5\%$ accurate.

Note 4--Synthetic gasoline prepared according to EPA Leak Detector Standard X 0004 has an average molecular weight of 92.83 g/mol.

9.6 *Test Product Density*--The density of test products should be determined by filling a tared 50-mL volumetric flask with test product and weighing the volumetric flask with test product on an analytical balance. Test product density is calculated as follows:

$$\text{Density, g/mL} = (m_t - m_c) \div v \quad (1)$$

Where:

m_t = mass of flask plus test product, g;

m_c = mass of flask, g;

v = flask volume, mL ($v = 50$ mL).

9.7 *Syringe Pump*--Determine the linearity of liquid delivery at each gear setting of the pump at the beginning of testing and at least yearly thereafter. Calibration should be performed with a 250 μ L syringe filled with water. The syringe pump should be set at approximately 50% flow for the gear setting that is being calibrated. Record the initial volume in the syringe. Start the syringe pump and a timer simultaneously. Record the syringe volume after 15, 30, 45, and 60 minutes. The correlation coefficient of delivered volume versus time, as calculated with the following equation, must be 0.995 or better:

$$\text{Correlation Coefficient} = \frac{n \sum t_i \Delta V_i - (\sum t_i)(\sum \Delta V_i)}{\sqrt{[n \sum t_i^2 - (\sum t_i)^2][n \sum \Delta V_i^2 - (\sum \Delta V_i)^2]}} \quad (2)$$

Where:

n = number of calibration points ($n=5$);

t_i = each time increment, minutes; and

ΔV_i = each corresponding volume change, μ L.

9.8 *Syringes*--Calibrate each syringe before initiating testing and yearly thereafter. Syringes should be calibrated at each syringe pump gear setting at a rate corresponding to 50% flow. Calibration should be performed with a syringe filled with water. Record the initial syringe volume, and affix the syringe to the syringe pump. Simultaneously start a timer and the syringe pump. Record the syringe volume after at least 15 minutes (± 1

second). Determine the 100% flow rate for the syringe according to the following equation:

$$100\% \text{ Syringe flow rate, } \mu\text{L/hr} = 6000 \times (V_f - V_i) \div t \div p \quad (3)$$

Where:

V_f = final syringe volume, μL ;

V_i = initial syringe volume, μL ;

t = elapsed time, minutes; and

p = syringe pump setting, % (50%).

10. Conditioning

10.1 *Before Each Test*--Purge the test chamber for at least three minutes with ultrahigh-purity air at 0.2 L/min. Turn on the power supply for the volatilization chamber and set the voltage such that a volatilization chamber temperature of $160^\circ\text{C} \pm 15^\circ\text{C}$ is established. Allow the chamber to warm up for five minutes.

10.2 *During each test*--Continuously purge the volatilization chamber with ultrahigh-purity air when it is not in use. The purge-air flow rate should be at least 0.1 L/min.

11. Procedure

11.1 *Test Series*--The detector should be tested with each test gas. Test gases are commercial gasoline, *n*-hexane, JP-4 jet fuel, synthetic gasoline, toluene, and xylene(s).

11.1.1 Perform tests in a random order.

11.2 *Detector Assembly*--Assemble the detection system as described by the manufacturer. Insert the detector probe into the test chamber. The seal between the probe and the test chamber should be gas tight.

11.3 *Syringe Pump Setup*--Assemble the volatilization system according to Figure 2. Make sure the syringe needle is inserted into the septum far enough and at a slight angle so that the tip is inside and touching the heated tube, and not in the tee fitting.

11.4 *Calibration*--Calibrate the detector if necessary. Many detectors do not require calibration. Perform calibrations, if necessary, according to manufacturer recommendations. Calibration may need to occur before mounting in the test container. If a data recording system is being used, it should be calibrated with the detector. Calibrate the data acquisition system according to manufacturer instructions.

11.5 *Background*--Supply ultrahigh-purity air to the test chamber at a rate that is 0.2 L/min. greater than the detector's aspiration rate.

Note 5: Many detectors are passive and do not aspirate gas samples. Use total test gas flow rates of 0.2 L/min for these detectors.

Monitor the detector's response every 15 seconds until a steady-state reading ($\pm 2\%$ change of full scale over one minute) is achieved or four minutes has elapsed, whichever is longer. Monitor the temperature inside the test chamber during background testing.

11.6 *Test atmosphere response*--Introduce the appropriate test gas to the test chamber at a sufficient rate to produce a 0.2 L/min test system vent flow rate. Monitor the temperature inside the test chamber during testing. The syringe pump injection rate should be determined as follows:

$$\text{Injection rate, } \mu\text{L/hr} = F_g \times \bar{M}_f \times C_g \times 2.6786 \times 10^{-3} \div d_f \quad (4)$$

Where:

F_g = total test gas flow rate, L/min;

\bar{M}_f = test product average molecular weight, g/mol;
 C_g = desired test gas concentration, ppmv; and
 d_f = test product density, g/mL.

Instructions provided by the syringe pump manufacturer should be followed for proper syringe selection and injection rate setting.

11.6.1 Monitor quantitative detectors until a steady-state ($\pm 2\%$ of full scale over 1 minute) response occurs or for 1 hour, whichever is shorter. Monitor qualitative detectors for a positive response ("activated") for up to 1 hour.

12. Calculations

12.1 *Specificity for Quantitative Detectors*--Specificity for quantitative detectors is the ratio of detector output, or measured concentration, to the actual concentration of hydrocarbon test gas expressed as a percentage. The following equation should be used to calculate specificity for quantitative detectors:

$$\text{Specificity, \%} = 100 \times m_d/c \quad (5)$$

Where:

m_d = detector's output reading, ppmv; and

c = hydrocarbon concentration, ppmv ($c = 500$ ppmv).

13. Interpretation of Results

13.1 *Specificity for Qualitative Detectors*--Specificity for qualitative devices should be reported as "activated" if the detector responds within 1 hour. Otherwise, specificity should be reported as "inactivated."

14. Report

14.1 Report detector type (quantitative or qualitative) and specificity results for each test product.

15. Precision and Bias

15.1 *Precision*--The precision of the procedure in Test Method X 0003 for measuring specificity for vapor-phase out-of-tank petroleum detectors is being determined.

15.2 *Bias*--Since there is no accepted reference material suitable for determining the bias for the procedure in Test Method X 0003 for measuring specificity for vapor-phase out-of-tank petroleum detectors, no statement on bias is being made.

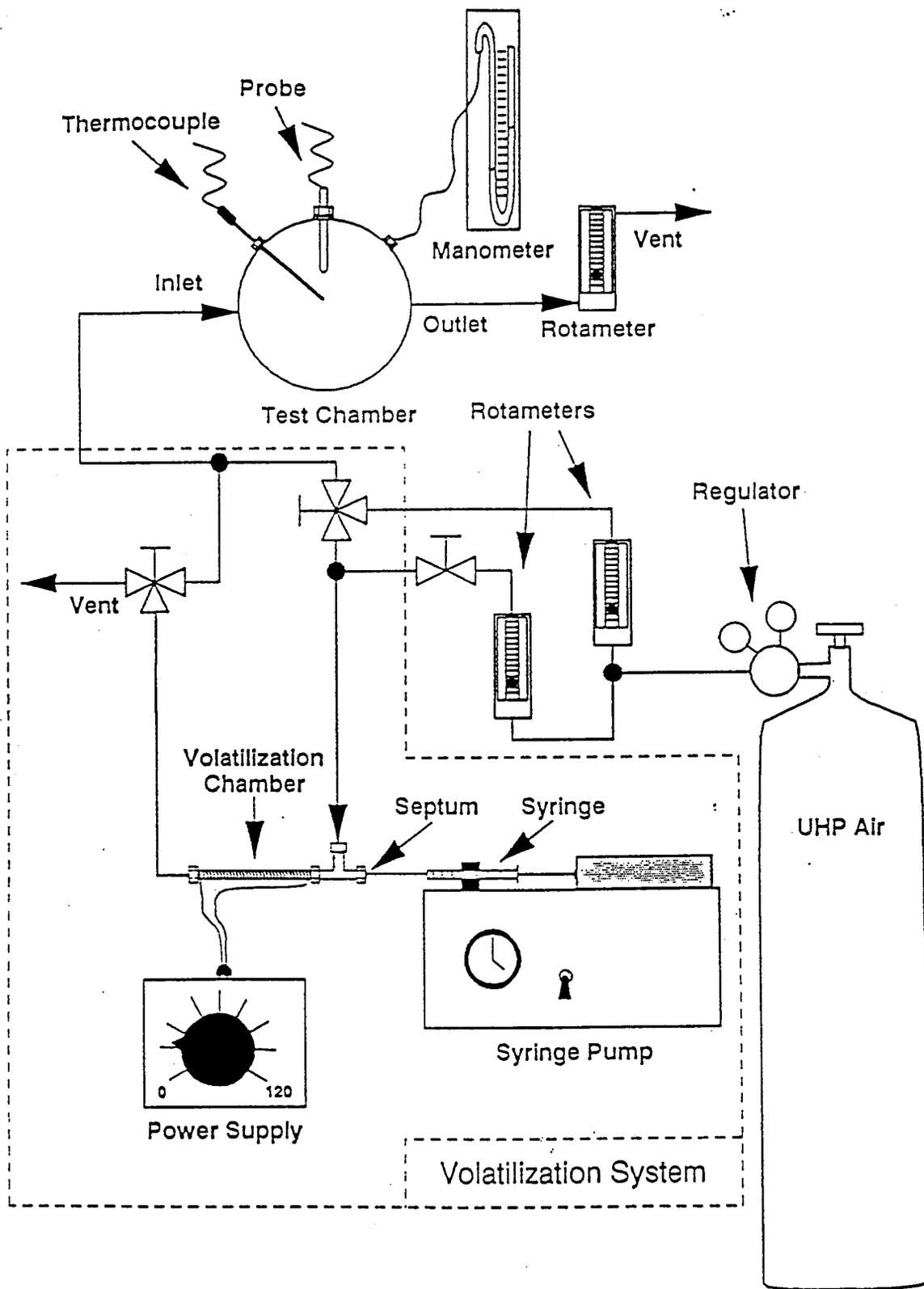
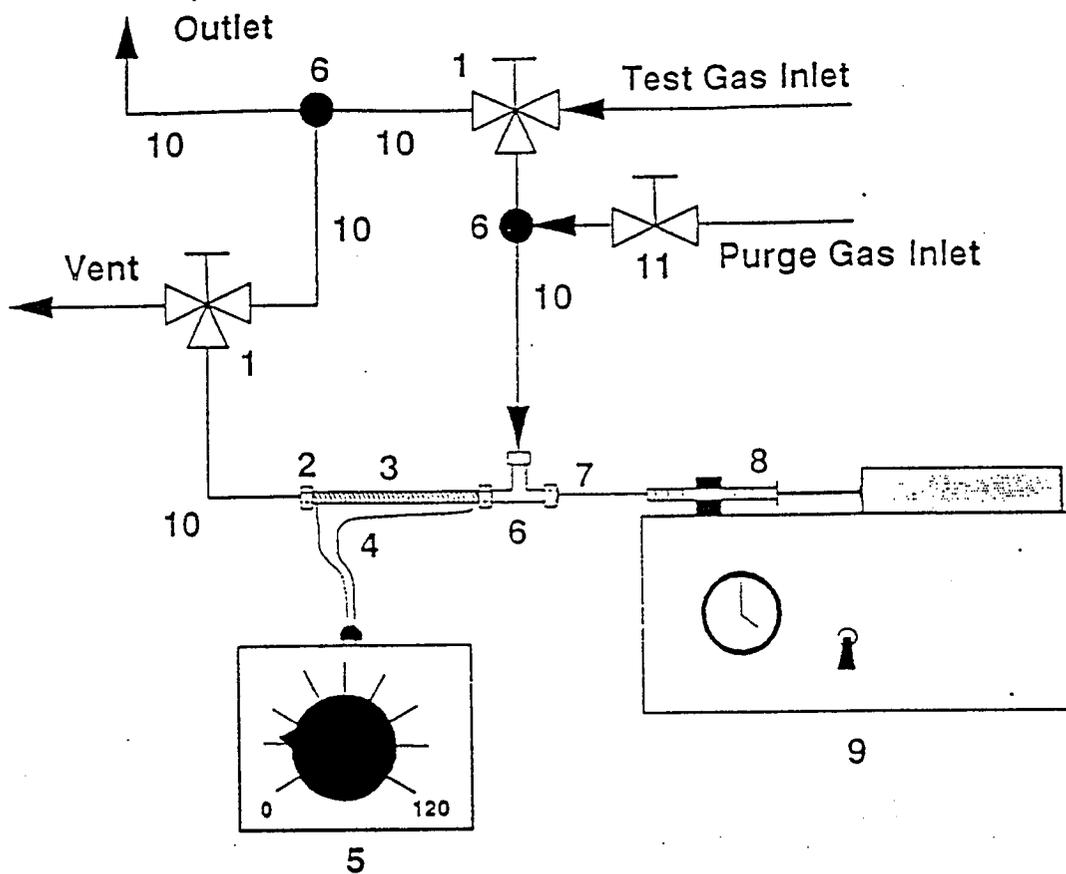


FIG. 1. Test Manifold Schematic Diagram



Description		Specifications
1	3-way valve	stainless steel, 1/4-in. fractional tubing fittings
2	tubing union	stainless steel, 1/4-in. fractional tubing fittings
3	glass tube	1/4-in. O.D., 7-in. long
4	heating wire	Nichrome, 25 gauge, glass insulated, 2.1 Ω /ft
5	power supply	0-50 V, 2 A
6	tee	stainless steel, 1/4-in. fractional tubing fittings
7	septum	6-mm diameter, inert
8	syringe	precision, glass
9	syringe pump	(See text.)
10	tubing	1/4-in. O.D., stainless steel
11	stop valve	stainless steel, 1/4-in. fractional tubing fittings

FIG. 2. Volatilization System Schematic Diagram

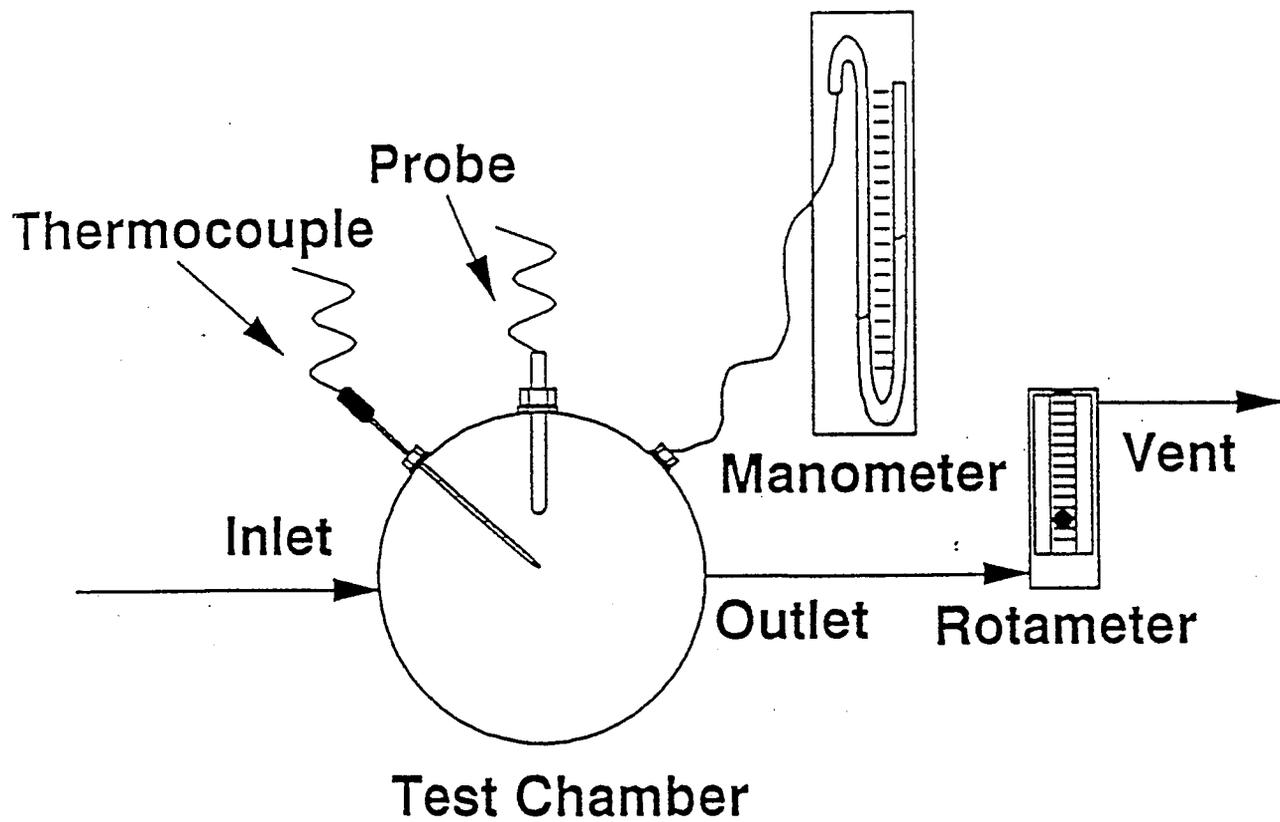


FIG. 3. Test Chamber Schematic Diagram

ANNEX

(Mandatory Information)

A1. PRECAUTIONARY STATEMENTS

A1.1 Gasoline (including Leaded Gasoline)

Danger--Extremely flammable. Vapors harmful if inhaled.

Vapors may cause flash fire.

Contains toxic lead antiknock components. Harmful if absorbed through skin.

Keep away from heat, sparks, and open flames.

Keep container closed.

Use with adequate ventilation. Avoid buildup of vapors and eliminate all sources of ignition especially nonexplosion-proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist. Avoid prolonged or repeated skin contact.

A1.2 n-Hexane

Danger--Extremely flammable. Vapors harmful if inhaled.

Vapors may cause flash fire.

Keep away from heat, sparks, and open flames.

Keep container closed.

Use with adequate ventilation. Avoid buildup of vapors and eliminate all sources of ignition especially nonexplosion-proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist. Avoid prolonged or repeated skin contact.

A1.3 Jet Fuel (JP-4)

Danger--Flammable. Vapors harmful if inhaled.

Vapors may cause flash fire.

Keep away from heat, sparks, and open flames.

Keep container closed.

Use with adequate ventilation. Avoid buildup of vapors and eliminate all sources of ignition especially nonexplosion-proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist. Avoid prolonged or repeated skin contact.

A1.4 Synthetic Gasoline Mixture

Danger--Extremely flammable. Vapors harmful if inhaled. Vapors may cause flash fire. Contains toxic benzene and other hydrocarbon substances (See Method X 0004).

Harmful if absorbed through skin.

Keep away from heat, sparks, and open flames.

Keep container closed. Use with adequate ventilation.

Avoid buildup of vapors and eliminate all sources of ignition, especially nonexplosion-proof electric apparatus and heaters.

Avoid prolonged breathing of vapors or spray mist.

Avoid prolonged or repeated skin contact.

A1.5 Toluene

Danger--Extremely flammable. Vapors harmful if inhaled.

Vapors may cause flash fire.

Keep away from heat, sparks, and open flames.

Keep container closed.

Use with adequate ventilation. Avoid buildup of vapors and eliminate all sources of ignition especially nonexplosion-proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist. Avoid prolonged or repeated skin contact.

A1.6 Compressed Gas. Air.

Caution--Compressed gas under high pressure.

Keep container closed.

Always use a pressure regulator. Release regulator tension before opening cylinder.

Do not transfer to cylinder other than one in which gas is received.

Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is supported at all times.

Stand away from cylinder outlet when opening cylinder valve.

Keep cylinder out of sun and away from heat.

Do not use cylinder without label.

Do not use dented or damaged cylinder.

For technical use only. Do not use for inhalation purposes.

APPENDIX

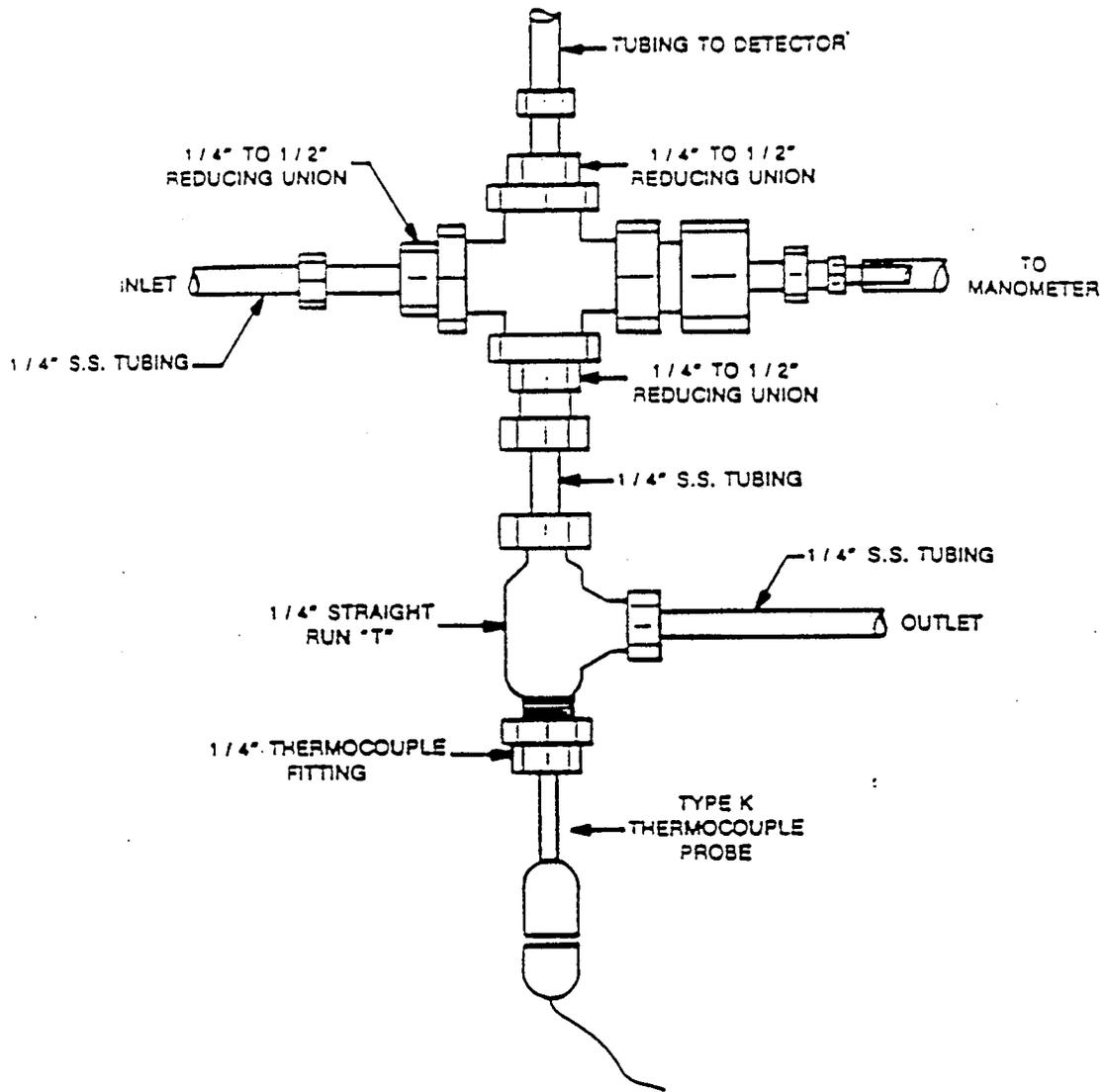
X1. EXAMPLE TEST CHAMBERS

X1.1 It is not reasonable to try to design a single test chamber that accommodates all configurations of detector probes. Instead, it is better to define the general requirements for the chamber and allow specific chambers to be designed to meet requirements for particular probes. Included in this appendix are diagrams of three test chambers that, combined, should be suited to the vast majority of vapor-phase detectors. The included chamber designs may also serve as starting points for alternate chamber designs.

X1.2 *Test Chamber for Tubing Probes*--Figure X1 contains a diagram detailing a test chamber design that should be suitable for almost all vapor-phase detectors that have probes consisting of tubing. These detectors primarily aspirate gas samples through tubing to a sensor located in the control box.

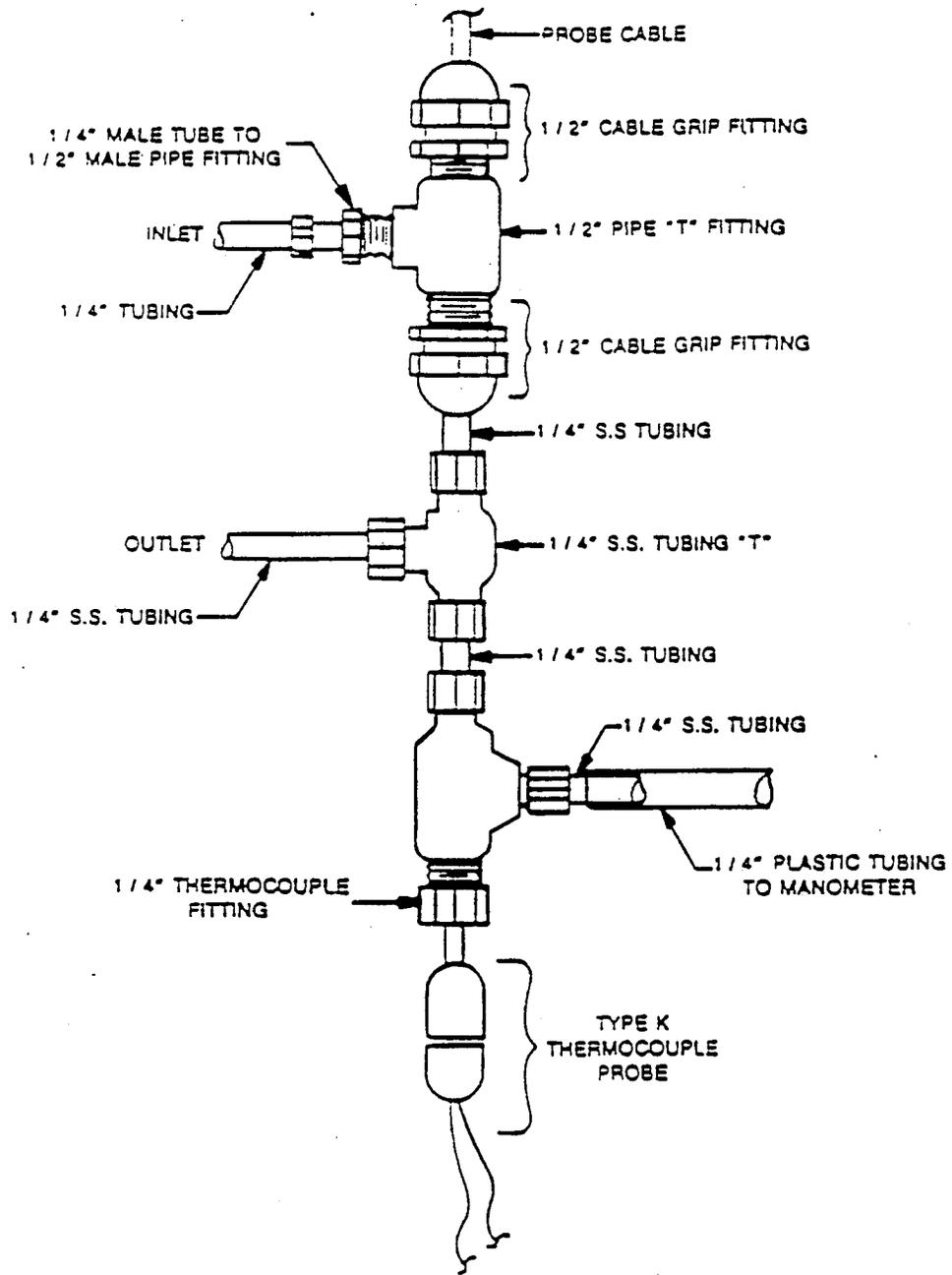
X1.3 *Test Chamber for Probes Up to 3/8-Inch Diameter*--Figure X2 is a diagram of a test chamber design that should be adequate for detector probes with diameters up to 3/8 inch.

X1.4 *Test Chamber for Probes Up to 1-1/4-Inch Diameter*--Figure X3 is a diagram of a test chamber design that should be adequate for detector probes with diameters up to 1-1/4 inches.



C87-1292A

FIG. X1. Gas Test Chamber for Tubing Probes



D87-1292A

FIG. X2. Gas Test Chamber for Probes with Diameters Up To 3/8 Inch

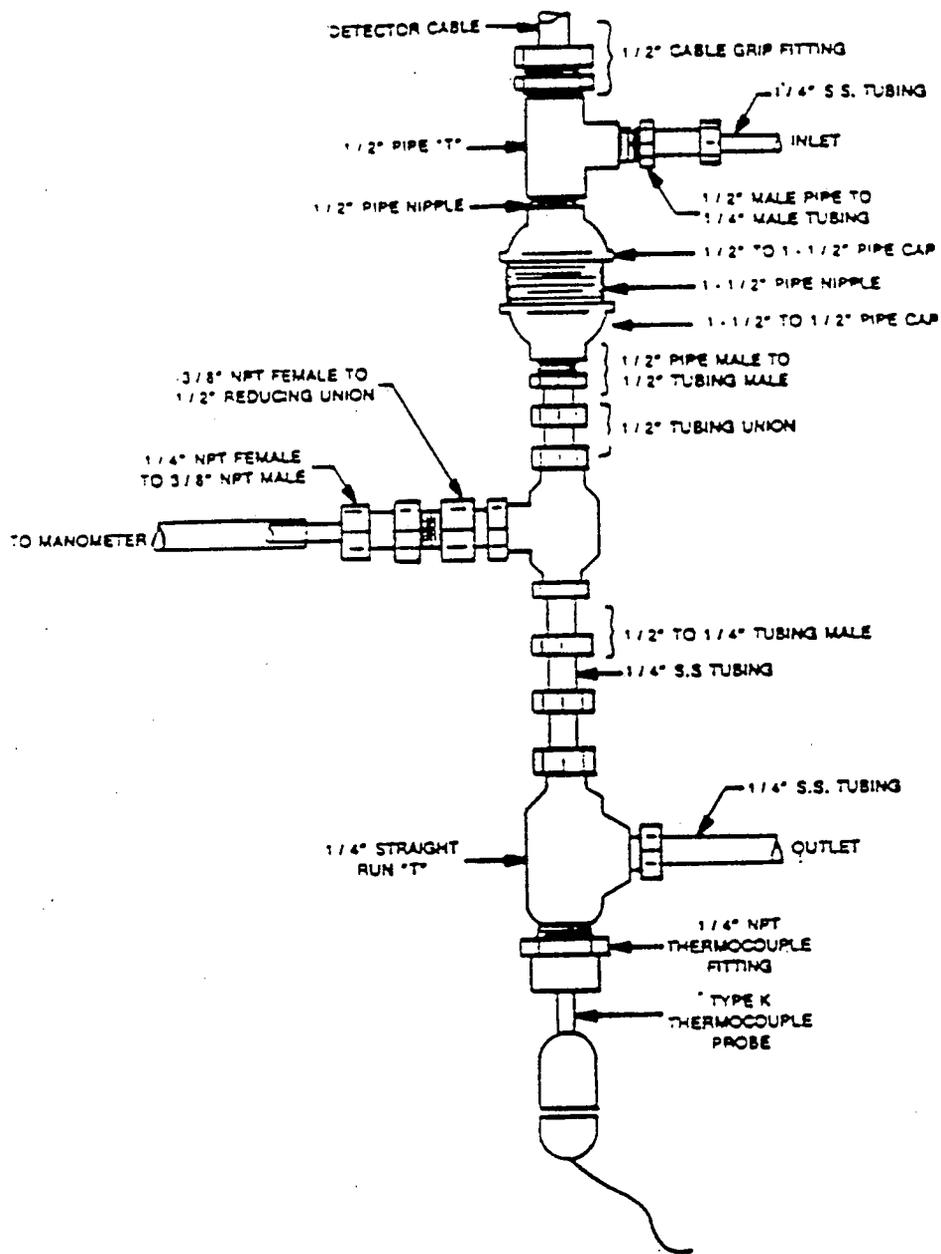


FIG. X3. Gas Test Chamber for Probes with Diameters Up To 1-1/4 Inches

Designation: X 0006

Standard Test Method for
LOWER DETECTION LIMIT FOR VAPOR-PHASE OUT-OF-TANK PETROLEUM DETECTORS

1. Scope

1.1 This test method covers determination of the lower detection limit of vapor-phase out-of-tank petroleum hydrocarbon leak detectors.

1.2 This method is only applicable to the components associated with detection of vapor-phase petroleum releases for detection systems utilizing multiple operating principles.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 1 Standard Specification for ASTM Thermometers

E 456 Standard Terminology Relating to Statistics

2.2 *EPA Leak Detector Standards:*

X 0004 Standard Practice for Preparation of Synthetic Gasoline

3. Terminology

3.1 *Definitions*--For formal definitions of statistical terms, see Terminology E 456.

3.2. Descriptions of Terms Specific to This Method

3.2.1 *activated*--refers to the state of a qualitative detector's response when indicating the presence of hydrocarbon vapors.

3.2.2 *critical level*--point at which a detector's response becomes significantly different from a blank response.

3.2.3 *lower detection limit*--minimum concentration of hydrocarbon test vapor that has only a 5 percent chance of not being detected at a 95 percent confidence level.

3.2.4 *non-activated*--refers to the state of a qualitative detector's response when indicating that no hydrocarbon vapors are detected.

3.2.5 *probe*--component of a detection system that must come into contact with hydrocarbon vapor before the vapor can be detected.

3.2.6 *qualitative responses*--type of detector response that indicates only the presence or absence of hydrocarbon vapors without determining the specific concentration.

3.2.7 *quantitative responses*--type of detector response that quantitates the concentration of hydrocarbon vapor present.

3.2.8 *responses*--detector's indication of the presence of petroleum hydrocarbon vapors. Responses can be qualitative or quantitative.

4. Summary of Test Method

4.1 Detector probes are subjected to test atmospheres of either commercial gasoline, a synthetic gasoline mixture, or JP-4 jet fuel inside a

sealed test chamber. Test atmospheres are made by accurately delivering liquid fuel into a heated volatilization chamber through which ultrahigh-purity air is fed at a controlled rate. Detectors are screened at several different test product concentrations to determine the lowest concentration to which the detectors will respond reliably. Test product concentrations are 10 parts per million by volume (ppmv), 50 ppmv, 100 ppmv, 500 ppmv, and 1000 ppmv.

4.2 The concentration at which a detector is tested is referred to as the lower detection limit, or "LDL." For qualitative detectors, the next lowest concentration is referred to as "LDL-." Quantitative detectors require seven tests for each test gas at the LDL concentration. Qualitative detectors require a total of twelve tests for each gas, six tests at both the LDL and LDL- concentrations. If a qualitative detector fails to respond positively to one or more of the six LDL tests, then the LDL concentration is increased and six more tests are performed at the new LDL concentration. Similarly, if a detector responds positively six times to the LDL concentration and one or more times to the LDL- concentration, the LDL- concentration is decreased and six more tests are performed at the new LDL- concentration.

5. Significance and Use

5.1 For vapor-phase petroleum hydrocarbon detectors, the lower detection limit, or "LDL," is the minimum hydrocarbon concentration to which a detector will respond positively. This method uses hydrocarbon gas concentrations from 10 ppmv to 1000 ppmv. Commercial gasoline, a synthetic gasoline mixture, and JP-4 jet fuel are the hydrocarbon test products used in this method.

5.2 The lower limits of a detector's ability to detect hydrocarbon vapors may be described in terms of two types of detection errors that are

possible. One type of error involves concluding that hydrocarbon product is present when there actually is not any product. This is the classic "false alarm," which is referred to as a false positive or Type I error. The risk of making a Type I error is usually denoted as α (alpha). The second type of error that can be made is referred to as a false negative or Type II error. This is the error of not detecting the presence of hydrocarbon product, and the risk associated with making this type of error is denoted as β (beta). Limits of detectors described below are based on the risks associated with these two types of error to prescribed hydrocarbon vapor concentrations.

5.3 Data obtained from repeated testing of quantitative detectors will be used to define two characteristics associated with the detector capabilities. These two characteristics, corresponding to the two possible types of detection errors described above, will be referred to as the critical level and the detection limit. The critical level is the decision-point test-vapor concentration, above which hydrocarbons are "detected" and below which they are "not detected." For quantitative detectors, the critical point will be established at a concentration corresponding to a 5 percent risk of false positive error. The detection limit will be defined as a second, higher test-vapor concentration, at which the risk of false negative error is no more than 5 percent. The estimated magnitude of α and β risk assume a normal error distribution.

5.3.1 Figure 1 shows the critical level, the lower detection limit, and the α and β risks applicable to quantitative detectors. The critical level is the point at which detector response becomes significantly different from a blank response. The two bell-shaped curves represent probability density functions (PDF). The curve on the left represents the PDF for possible detector responses for a test vapor having a true hydrocarbon

concentration of zero. The critical level (L_c) is located on the right tail of the curve. The critical level will be established using a one-sided tolerance limit for normal distribution. Using the tolerance limit approach, it may be stated with 95 percent confidence that a false positive error will be made no more than five percent of the time.

5.3.2 The curve to the right in Figure 1 represents the PDF for possible detector responses for a test vapor having a true hydrocarbon concentration equal to the detection limit (L_D). The detection limit will be established by letting the false negative error coincide with the false positive error at the critical level and then applying the tolerance limit equation. Using the tolerance limit, it can be stated with 95 percent confidence that the lower detection limit concentration is the lowest concentration that has only a five percent chance of not being detected.

5.4 Qualitative detectors require a different test strategy because the data collected are attribute measurements. The critical level and the detection limit may still be used to characterize detector performance, and the risk of detection error may still be expressed in terms of α and β . However, different levels of α and β will be used for these detectors. Figure 2 illustrates the probability of detection versus concentration for qualitative detectors. The false positive risk α is dependent on the detector and represents the probability that the detector will go to an activated state at zero concentration. For these detectors, the critical level is defined as the test vapor concentration at which the detector has a fifty percent probability of detection. The lower detection limit is the test vapor concentration at which the detector has a probability of not activating that is equal to the false negative risk β .

5.4.1 The critical level and lower detection limit will be established with 95 percent confidence to be within a range bounded by a lower test vapor concentration (LDL-) and an upper test vapor concentration (LDL). LDL and LDL- will be established by measuring the detector response six times at the LDL concentration and six times at the LDL- concentration. If the detector responds six times at the higher concentration and does not respond to the lower concentration, it will be concluded with 95 percent confidence that the critical level and lower detection limit are between the LDL- and LDL concentrations. If, however, the detector fails to respond to one or more of the six tests, then the LDL concentration will be increased and six more tests will be performed at the new LDL concentration. Similarly, if the detector responds six times to the LDL concentration and one or more times to the LDL- concentration, then the LDL- concentration will be decreased and six more tests will be performed at the new LDL- concentration.

5.4.2 A risk of 50 percent will be set for false negative error (β) and false positive error (α). This risk level requires six tests at the LDL and LDL- test vapor concentrations. By establishing these risk levels, it can be stated with 95 percent confidence that the detector will respond to a minimum of 50 percent to the LDL concentration and a maximum of 50 percent to the LDL- concentration. The number of experiments is based on a binomial distribution and is directly related to false positive risk and false negative risk.

5.5 Results obtained using this method will permit the most advantageous use of a detector. Weaknesses as well as strengths of the instrument should become apparent. It is not the interest of this method to compare similar detectors of different manufacture, but to enable the user to choose a suitable detector.

6. Interferences

6.1 Conditions that can cause interferences with this method include temperature changes, high temperatures, excessive test apparatus volumes, and leaks in the test apparatus. To avoid these conditions, tests should be conducted at constant normal laboratory temperatures with a leak-tested test apparatus.

6.2 Cross contamination (e.g., memory effects from residual test atmospheres) may be a major cause of inaccurate data. To minimize this potential problem, avoid using rubber or plastic parts for components of the test apparatus that contact test gases and purge the testing system as described in Section 10.

6.3 Fluctuations of the test chamber internal pressure may significantly affect the detector's response. Maintain a constant internal chamber pressure (± 0.2 inches of water relative to ambient pressure) while the probe is exposed to the test atmosphere by maintaining a constant inlet and exit test atmosphere flow rate. If the pressure varies outside the acceptance limits, repeat the tests within the accepted pressure fluctuation limits.

7. Apparatus

7.1 *Test apparatus*--The test apparatus, as depicted in Figure 3, shall be constructed from materials that are inert with respect to test gases. The test apparatus consists of a compressed gas cylinder, pressure regulator, tubing, valves, tubing connectors, rotameters, volatilization system, test chamber, thermocouple, and manometer. The volatilization system is depicted in greater detail in Figure 4.

7.1.1 *Compressed gas cylinder*--Ultrahigh-purity air is supplied in standard compressed gas cylinders having Compressed Gas Association (CGA) fittings compatible with regulator fittings.

Note 1--Ultrahigh-purity air may be supplied in compressed gas cylinders having various fittings. Consult specific gas suppliers on details on appropriate fittings.

7.1.2 *Pressure regulator*--At least one dual stage regulator with a fitting compatible with the test gas cylinders is needed. The regulator shall have a range of at least 0 psi to 15 psi and have a diaphragm made of stainless steel.

7.1.3 *Tubing*--Sufficient tubing to link all test apparatus components is needed. The tubing shall be free from contaminants and have an internal diameter of at least 1/8 inch. The tubing shall be made of a material that is inert with respect to test gases.

7.1.4 *Tubing connectors*--Various compression-type tubing fittings are needed to make test apparatus connections. These fittings shall be free from contaminants, inert with respect to test gases, and of a material that is compatible with the tubing. These fittings can include, but are not limited to, tees, cross tees, reducers, and elbows. A thermocouple compression fitting is also needed.

7.1.5 *Rotameters*--Two rotameters, each having a flow range bracketing the required flow rates for the detector, are needed to measure test chamber inlet and outlet flow rates. Another rotameter, capable of delivering 0.2 L/min of air, is required for continuously flushing the volatilization chambers between tests.

7.1.6 *Valves*--A shut-off valve and a flow controlling needle valve are needed.

Note 2--Gas shut off can be accomplished using a regulator and the integral shut-off valve commonly included with compressed gas cylinders. Many rotameters include an integral flow controlling needle valve.

7.1.7 *Thermocouple*--A thermocouple and temperature readout, or equivalent, that responds from 0°C to 40°C and is accurate to within 1°C over this range is needed.

7.1.8 *Manometer*--A relative pressure manometer is required to monitor the test chamber's internal pressure. The manometer must have a working range of at least 0-10 inches of water (0 to 20 mm Hg) with an accuracy of $\pm 5\%$. The manometer should be scaled using at least 0.2 inches of water (0.4 mm Hg) subdivisions.

7.1.9 *Volatilization chamber*--The volatilization chamber should be gas tight and made from materials that are inert with respect to test gases. Figure 4 schematically depicts the arrangement of the volatilization chamber within the volatilization system. The volatilization chamber should be made from glass to allow for good thermal transfer and visual inspection of the position of the syringe needle tip. All compression fittings connected to the glass tube should utilize Teflon® ferrules and back ferrules. Nichrome heating wire should be wound around the glass tube with no gaps between each wrap. The volatilization chamber inlet should be fitted with a 1/4-inch, stainless steel tubing tee. The end of the tee directly opposite the entrance to the volatilization chamber should be fitted with a septum to allow insertion of the syringe needle into the heated tubing. The needle should be inserted at a slight angle so that the tip touches the inner surface of the glass tubing to insure a constant flow of fuel from the needle tip onto the glass surface.

Note 3--If the needle does not touch the glass surface, the test product pumped from the needle will produce droplets rather than a steady stream on the heated surface. This will give rise to fluctuations in vapor-phase test product concentrations.

7.1.10 *Test chamber*--The test chamber should be gas tight and made from materials that are inert with respect to test gases. Figure 5 contains a test chamber schematic representation. The test chamber must have fittings to allow connection to the detector probe, a manometer, and a thermocouple. The chamber must also have an inlet and outlet for flow of test atmospheres. Test chamber volumes should be kept as small as possible without interfering with detector operation. Diagrams of suitable test chambers are presented in Appendix A.

7.1.11 *Syringe pump*--A syringe pump that is accurate to $\pm 5\%$ of the desired flow rate is required. The syringe pump must be capable of delivering from 0.05 to 1500 $\mu\text{L/hr}$ over one hour.

7.1.12 *Syringes*--Precision glass syringes with certified $\pm 1\%$ accuracy and repeatability are required. Syringes in 10, 100, 250, 500, and 1000 μL sizes are recommended.

7.1.13 *Power Supply*--An alternating or direct current power supply that is variable from 0 to 50 volts and is capable of delivering at least 2 amperes of current is needed.

7.1.14 *Heating wire*--20 feet of 25-gauge, glass-insulated, Nichrome heating wire with a fixed resistance of 2.1 ohms/ft is required.

7.1.15 *Septum*--An inert septum with a 6 mm diameter is required.

7.2 *Timer*--A timer that is accurate and precise to at least one second per 10 minutes is required. Alternatively, a chart recorder or other data acquisition system may be used. If a chart recorder or other data acquisition system is to be used, the timer is not required. If used, the recorder or data acquisition system timing must be accurate and precise to at least one second per 10 minutes.

7.3 *Electronic recorder*--A chart recorder or other electronic data

acquisition system may be used if it is compatible with the specific detector that is being evaluated. The output of the data recorder should be accurate and precise to $\pm 2\%$ over the range of output from a quantitative detector. A data recorder used with a qualitative detector must unambiguously identify activated and inactivated states.

7.4 *Thermometer*--ASTM Solvents Distillation Thermometer having a range from -2°C to 52°C and conforming to the requirements for Thermometer 37C as prescribed in Specification E 1.

7.5 *Bubble meter*--Use NBS-traceable soap bubble flow meters to calibrate rotameters. The bubble meters must have a working range that brackets the range of all rotameters.

8. Reagents and Materials

8.1 *Purity of Reagents*--Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents for the American Chemical Society where such specifications are available.¹ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of determination.

8.2 *Ultrahigh-Purity Air*--The ultrahigh-purity air standard must have less than 0.5 ppmv total hydrocarbon content. (Caution--Gas under high pressure. See Annex A1.1.)

8.3 *Commercial gasoline*--Commercial gasoline test product shall be unleaded regular or premium gasoline that is purchased at a retail outlet.

¹"Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemicals Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., In., New York, NY, and the "United States Pharmacopeia."

(Danger--Gasoline is extremely flammable. Vapors are harmful if inhaled. See Annex A1.2. Leaded gasoline should not be used because there are significant additional hazards associated with its handling and disposal).

8.4 *Synthetic Gasoline*--Synthetic gasoline, as used in this method, is an 11-component mixture that is roughly representative of automotive gasoline prepared according to Method X 0004, "Standard Practice for The Preparation of Synthetic Gasoline for Testing Out-of-Tank Petroleum Detectors."

(Danger--Synthetic gasoline is extremely flammable. Vapors are harmful if inhaled. See Annex A1.3).

8.5 *JP-4 Jet Fuel*--The JP-4 jet fuel test product shall be purchased from a retail outlet. (Danger--JP-4 jet fuel is flammable. Vapors are harmful if inhaled. See Annex A1.4).

8.6 *Other Test Products*--This test method can also be used with other non-viscous, volatile liquids. The method, however, does not directly address use of liquids other than commercial gasoline, the synthetic gasoline described herein, and JP-4 jet fuel. The suitability of this method with regard to other substances should be ascertained before this method is used with those liquids.

8.7 All petroleum hydrocarbon products and hydrocarbon reagents shall be stored in tightly sealed, inert containers away from heat, sparks, and flames. Petroleum fuels shall not be stored for more than 60 days because significant changes in their properties may occur as a result of volatile component losses.

9. Calibration and Standardization

9.1 *Chart Recorder or Other Data Recording System*--If used, a chart recorder or other data recording system should be calibrated along with the detector. The data recording system should be calibrated according to

instructions from its manufacturer and the detector manufacturer. Also, any recording device should be compatible with the detector being investigated. Consult specifications from the manufacturers of the recording device and the detector.

9.2 *Detector*--Because of wide design variability among different petroleum detectors, it is impossible to give complete calibration instructions for all possible detector designs. Calibrate all detectors according to manufacturer instructions.

9.3 *Rotameters*--Calibrate each rotameter prior to initiating test procedures, once a year thereafter, and after any internal contamination (e.g., dirt or moisture) during testing. Instructions accompanying the NBS-traceable bubble meters should be followed. The rotameters are to be calibrated at a minimum of five points ("multipoints") within the working range. Flow readings should be made from the middle of the ball float. All readings should be made from the upper float on dual-float rotameters until it is off scale. Once the upper float is off scale, readings should be made from the lower float.

9.3.1 *Assembly*--Remove the rotameter from the test system, if assembled, and connect the rotameter in series between a controllable compressed air source and an NBS-traceable bubble meter. Use a bubble meter cylinder that will allow a flow measurement over a period of 15 to 45 seconds.

9.3.2 *First calibration point*--Bring the gas flow rate to the lowest calibration flow for testing. Let the system run at this setting until the rotameter is steady. If the flow rate is not within the first level range, adjust the flow rate until it is within that range and wait for a steady-state value. Record the steady-state flow meter value that is within the first flow rate level. Measure the flow rate with the bubble meter and stopwatch

according to the NBS bubble meter instructions. Record each reference flow rate.

9.3.3 *Remaining calibration points*--Record steady-state settings for triplicate runs as described in Section 10.3.2 for at least four more flow rates throughout the rotameter range.

9.4 *Thermocouple*--Perform side-by-side multipoint calibrations for each thermocouple used in the test procedure in a 1-L glass beaker filled with water. The reference thermometer should be an ASTM Solvents Distillation thermometer having a range from -2°C to 52°C and conforming to the requirements for Thermometer 37C as prescribed in Specification E 1. The levels tested are low (room temperature - 10°C), room temperature, and high (room temperature + 10°C).

9.4.1 Insert both the thermocouple and reference thermometer into the beaker of water and add small quantities of ice. Allow the ice to melt and the temperature to stabilize. Continue adding ice until a steady-state reading ($\pm 0.5^{\circ}\text{C}$ over two minutes) of room temperature - 10°C ($\pm 2^{\circ}\text{C}$) occurs.

9.4.2 Repeat this procedure using room temperature water (15°C to 30°C), and room temperature + 10°C ($\pm 2^{\circ}\text{C}$) water. If the temperature difference is more than 1°C , either repeat the test with the same thermocouple or replace the thermocouple and repeat the test until it is acceptable.

9.4.3 Perform thermocouple calibration at the onset of testing and at least once a year.

9.5 *Average Molecular Weight of Commercial Fuels*--Determine the average molecular weight of commercial gasoline and JP-4 jet fuel by cryoscopic osmometry. Average molecular weight values should be $\pm 5\%$ accurate.

Note 4--Synthetic gasoline prepared according to EPA Leak Detector Standard X 0004 has an average molecular weight of 92.83 g/mol .

9.6 *Test Product Density*--The density of test products should be determined by filling a tared 50-mL volumetric flask with test product and weighing the volumetric flask with test product on an analytical balance. Test product density is calculated as follows:

$$\text{Density, g/mL} = (m_t - m_c) \div v \quad (1)$$

Where:

m_t = mass of flask plus test product, g;

m_c = mass of flask, g;

v = flask volume, mL ($v = 50$ mL).

9.7 *Syringe Pump*--Determine the linearity of liquid delivery at each gear setting of the pump at the beginning of testing and at least yearly thereafter. Calibration should be performed with a 250 μ L syringe filled with water. The syringe pump should be set at approximately 50% flow for the gear setting that is being calibrated. Record the initial volume in the syringe. Start the syringe pump and a timer simultaneously. Record the syringe volume after 15, 30, 45, and 60 minutes. The correlation coefficient of delivered volume versus time, as calculated with the following equation, must be 0.995 or better:

$$\text{Correlation coefficient} = \frac{n\sum t_i \Delta V_i - (\sum t_i)(\sum \Delta V_i)}{\sqrt{[n\sum t_i^2 - (\sum t_i)^2][n\sum \Delta V_i^2 - (\sum \Delta V_i)^2]}} \quad (2)$$

Where:

n = number of calibration points (5);

t_i = each time increment, minutes; and
 ΔV_i = each corresponding volume change, μL .

9.8 *Syringes*--Calibrate each syringe before initiating testing and yearly thereafter. Syringes should be calibrated at each syringe pump gear setting at a rate corresponding to 50% flow. Calibration should be performed with a syringe filled with water. Record the initial syringe volume, and affix the syringe to the syringe pump. Simultaneously start a timer and the syringe pump. Record the syringe volume after at least 15 minutes (± 1 second). Determine the 100% flow rate for the syringe according to the following equation:

$$\text{100\% Syringe flow rate, } \mu\text{L/hr} = 6000 \times (V_f - V_i) \div t \div p \quad (3)$$

Where:

V_f = final syringe volume, μL ;
 V_i = initial syringe volume, μL ;
 t = elapsed time, minutes; and
 p = syringe pump setting, % (50%).

10. Conditioning

10.1 *Before Each Test*--Purge the test chamber for at least three minutes with ultrahigh-purity air at 0.2 L/min. Turn on the power supply for the volatilization chamber and set the voltage such that a volatilization chamber temperature of $160^\circ\text{C} \pm 15^\circ\text{C}$ is established. Allow the chamber to warm up for five minutes.

10.2 *During each test*--Continuously purge the volatilization chamber with ultrahigh-purity air when it is not in use. The purge-air flow rate should be at least 0.1 L/min.

11. Procedure

11.1 *Test Series*--Quantitative detectors shall be tested seven times for each test product. Qualitative detectors shall be tested a total of twelve tests for each test gas, six tests at both the LDL and LDL- concentrations. If a qualitative detector fails to respond positively to one or more of the six LDL tests, then the LDL concentration shall be increased and six more tests shall be performed at the new LDL concentration. Similarly, if a detector responds positively six times to the LDL concentration and one or more times to the LDL- concentration, the LDL- concentration shall be decreased and six more tests shall be performed at the new LDL- concentration.

11.1.1 Perform tests in a random order such that variables of test gas and hydrocarbon concentration are isolated.

11.2 *Detector Assembly*--Assemble the detection system as described by the manufacturer. Insert the detector probe into the test chamber. The seal between the probe and the test chamber should be gas tight.

11.2.1 Connect the detector output to a chart recorder or other data acquisition system if one is being used. All connections should be in compliance with specifications from the manufacturers of the detector and the data recording system.

11.3 *Syringe Pump Setup*--Assemble the volatilization system according to Figure 4. Make sure the syringe needle is inserted into the septum far enough and at a slight angle so that the tip is inside and touching the top of the heating tubing, and not in the tee fitting.

11.4 *Calibration*--Calibrate the detector if necessary. Many detectors do not require calibration. Perform calibrations, if necessary, according to manufacturer recommendations. Calibration may need to occur

before mounting in the test container. If a data recording system is being used, it should be calibrated with the detector. Calibrate the data acquisition system according to manufacturer instructions.

11.5 *Background*--Supply ultrahigh-purity air to the test chamber at a rate that is 0.2 L/min. greater than the detector's aspiration rate.

Note 5--Many detectors are passive and do not aspirate gas samples. Use total test gas flow rates of 0.2 L/min for these detectors.

Monitor the detector's response every 15 seconds until a steady-state reading ($\pm 2\%$ change of full scale over one minute) is achieved or four minutes has elapsed, whichever is longer. Monitor the temperature inside the test chamber during background testing.

11.6 *Identify LDL Concentration*--Based on previous testing or vendor information, identify the lowest hydrocarbon concentration to which the detector is known to respond. This test gas concentration is referred to as the lower detection limit, or "LDL." The LDL may be different for each test product.

11.6.1 If the LDL test gas concentration is unknown, begin with the 1000 parts per million by volume (ppmv) concentration and then test at successively lower standard concentrations until the detector does not respond. The standard test gas concentrations are 10 ppmv, 50 ppmv, 100 ppmv, 500 ppmv, and 1000 ppmv. The highest test gas concentration for JP-4 jet fuel should be 500 ppmv.

11.7 *Test Atmosphere Response*--Introduce the appropriate test gas to the test chamber by turning on the syringe pump and switching valves so that ultrahigh-purity air flows through the volatilization system and into the test chamber. Monitor the temperature inside the test chamber during testing. The

syringe pump injection rate should be determined as follows:

$$\text{Injection rate, } \mu\text{L/hr} = F_g \times \bar{M}_f \times C_g \times 2.6786 \times 10^{-3} \div d_f \quad (4)$$

Where:

F_g = total test gas flow rate, L/min;

\bar{M}_f = test product average molecular weight, g/mol;

C_g = desired test gas concentration, ppmv; and

d_f = test product density, g/mL.

Instructions provided by the syringe pump manufacturer should be followed for proper syringe selection and injection rate setting.

11.7.1 Monitor quantitative detectors until a steady-state ($\pm 2\%$ of full scale over 1 minute) response occurs or for 1 hour, whichever is shorter.

Monitor qualitative detectors for a positive response ("activated") for up to 1 hour.

12. Calculation

12.1 *Critical Level for Quantitative Detectors*--Calculate the critical level for quantitative detectors as follows:

$$\text{Critical level, ppmv} = K \times s + B \quad (5)$$

Where:

K = tolerance limit statistic from Table 1;

s = standard deviation ($n-1$ degrees of freedom) of the data set, ppmv; and

B = absolute bias = $|V_o - V_r|$, ppmv;

Where:

quantitative detectors. For qualitative detectors, report the LDL and LDL-concentrations.

15. Precision and Bias

15.1 *Precision*--The precision of the procedure in Test Method X 0006 for measuring lower detection limit for vapor-phase out-of-tank petroleum detectors is being determined.

15.2 *Bias*--Since there is no accepted reference material suitable for determining the bias for the procedure in Test Method X 0006 for measuring lower detection limit for vapor-phase out-of-tank petroleum detectors, no statement on bias is being made.

Table 1. One-Sided Tolerance Limit Factors for a Five-Percent Beta Error
at a Ninety-Five-Percent Confidence Level^A

Number of Tests (n)	Tolerance Limit Factor (K)
3	7.655
4	5.145
5	4.202
6	3.707
7	3.399
8	3.188
9	3.031
10	2.911
11	2.815
12	2.736
13	2.670
14	2.614
15	2.566
16	2.523
17	2.486
18	2.453
19	2.423
20	2.396
21	2.371
22	2.350
23	2.329
24	2.309
25	2.292
30	2.220
35	2.166
40	2.126
45	2.092
50	2.065

^ATaken from Natrella, M.G., Experimental Statistics. National Bureau of Standards Handbook 91. United States Department of Standards. Stock Number 003-003-00135-0. August, 1963. Reprinted October, 1966.

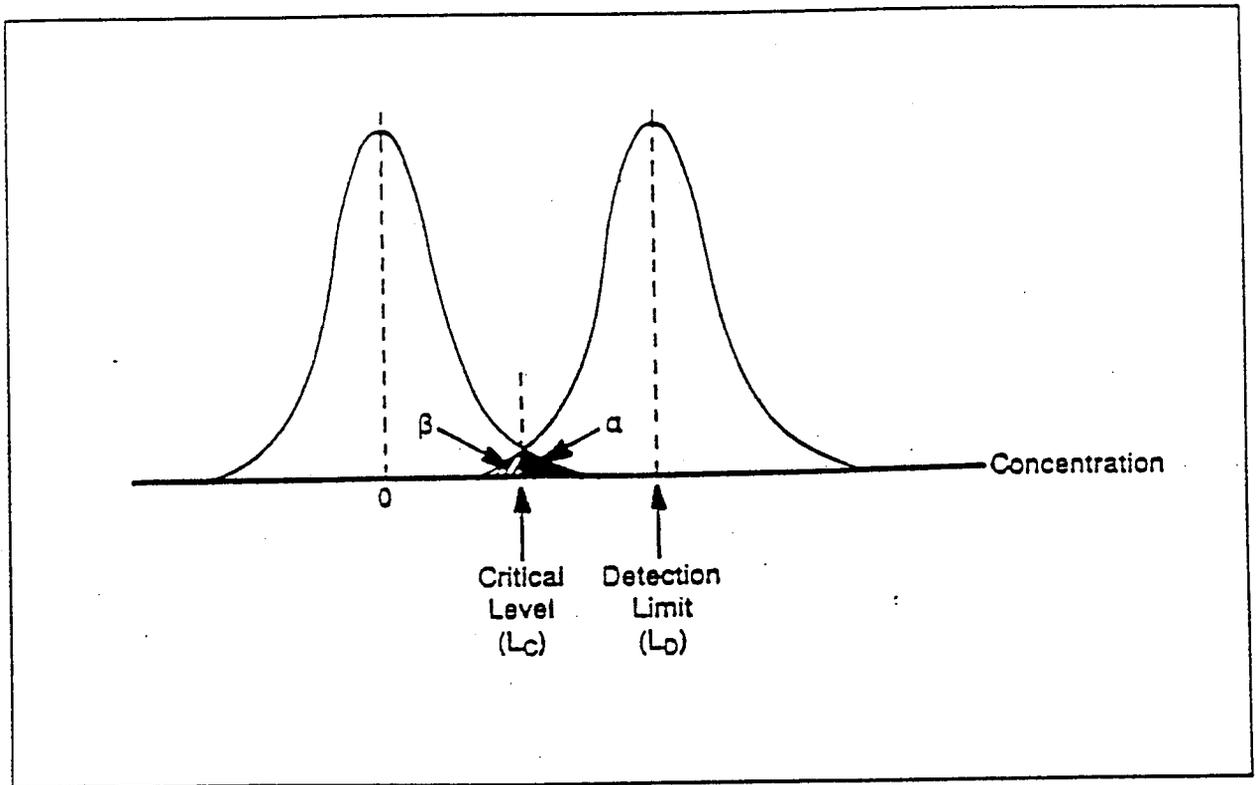
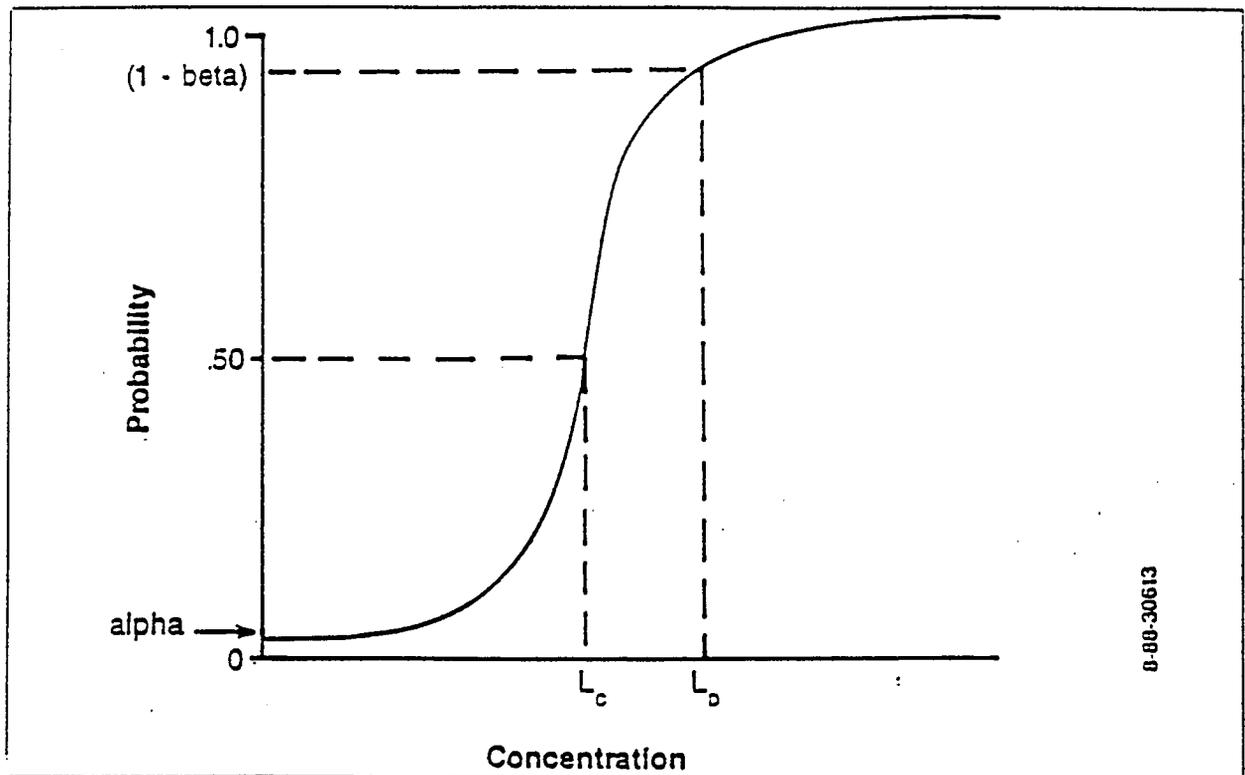


FIG. 1. Graphical Representation of Detection Limit and Critical Level



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FIG. 2. Probability of Detection Versus Concentration

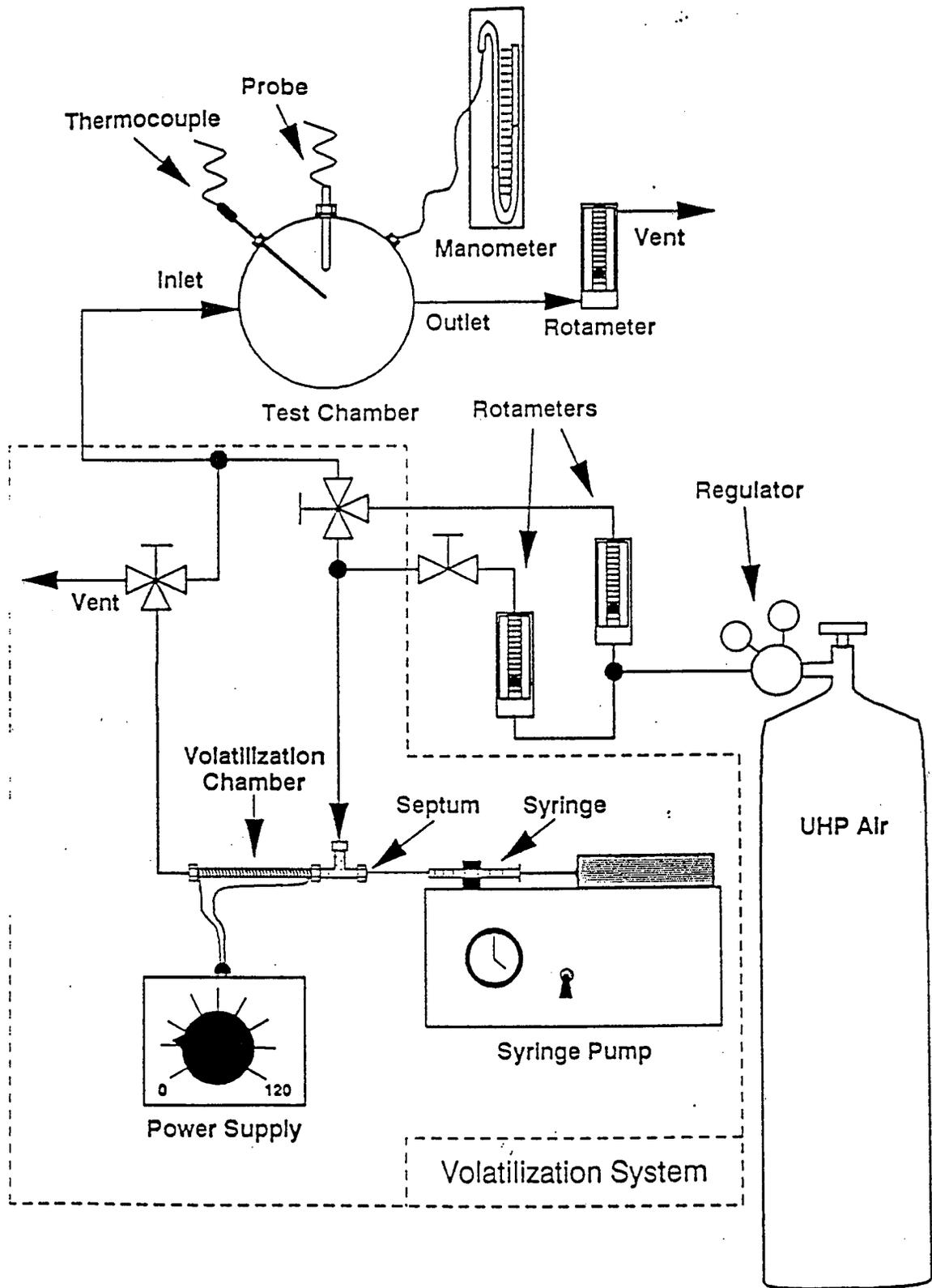
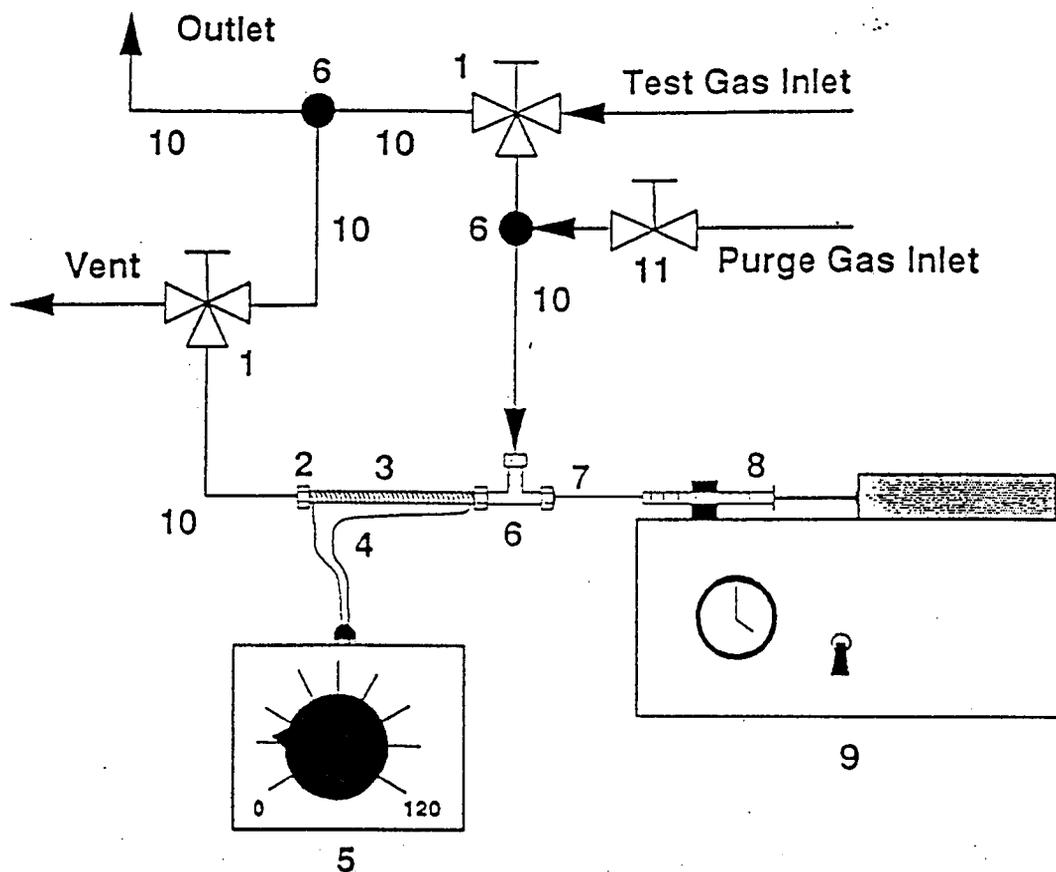


FIG. 3. Test Manifold Schematic Diagram



Description		Specifications
1	3-way valve	stainless steel, 1/4-in. fractional tubing fittings
2	tubing union	stainless steel, 1/4-in. fractional tubing fittings
3	glass tube	1/4-in. O.D., 7-in. long
4	heating wire	Nichrome, 25 gauge, glass insulated, 2.1 Ω /ft
5	power supply	0-50 V, 2 A
6	tee	stainless steel, 1/4-in. fractional tubing fittings
7	septum	6-mm diameter, inert
8	syringe	precision, glass
9	syringe pump	(See text.)
10	tubing	1/4-in. O.D., stainless steel
11	stop valve	stainless steel, 1/4-in. fractional tubing fittings

FIG. 4. Volatilization System Schematic Diagram

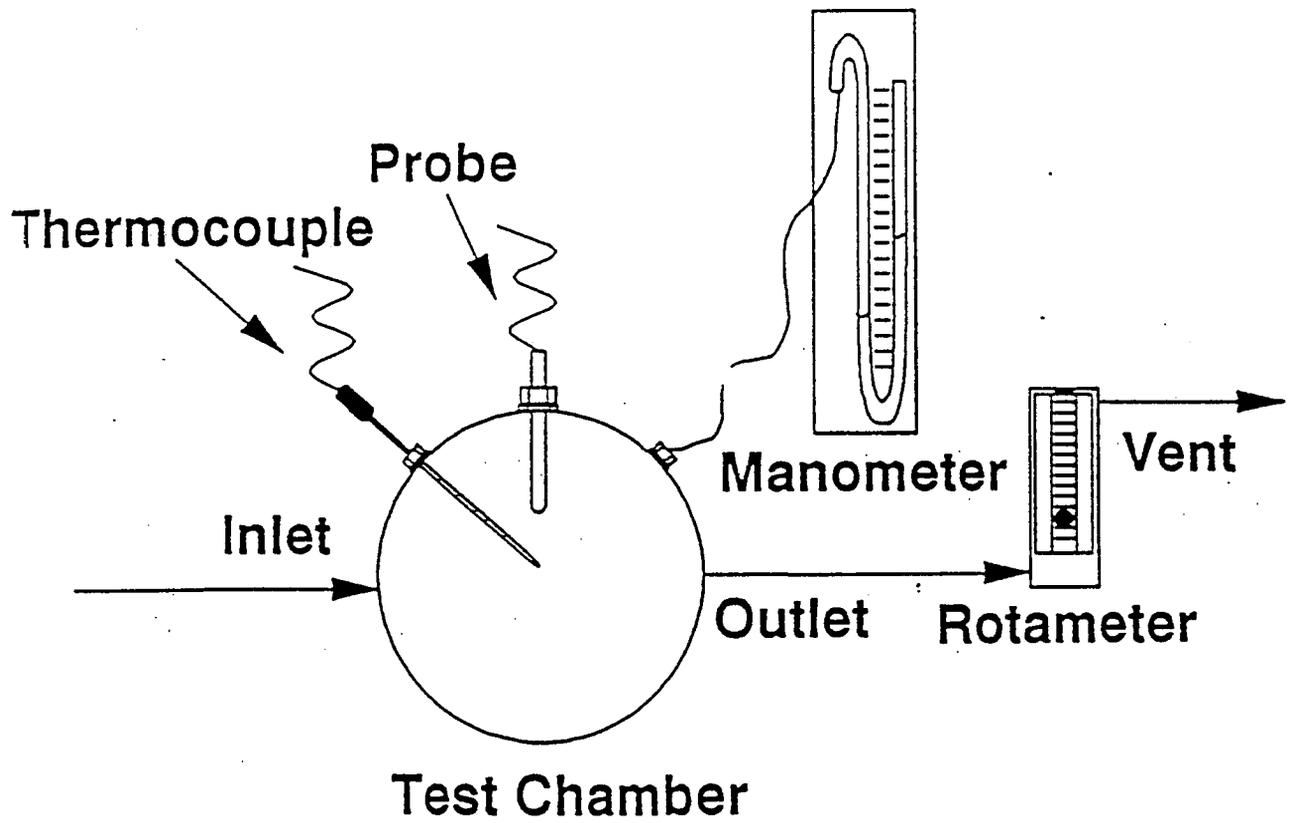


FIG. 5. Test Chamber Schematic Diagram

ANNEX

(Mandatory Information)

A1. PRECAUTIONARY STATEMENTS

A1.1 Compressed Gas. Air.

Caution—Compressed gas under high pressure.

Keep container closed.

Always use a pressure regulator. Release regulator tension before opening cylinder.

Do not transfer to cylinder other than one in which gas is received.

Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is securely supported at all times.

Stand away from cylinder outlet when opening cylinder valve.

Keep cylinder out of sun and away from heat.

Do not use cylinder without label.

Do not use dented or damaged cylinder.

For technical use only.

Do not use for inhalation purposes.

A1.2 Gasoline (including Leaded Gasoline)

Danger—Extremely flammable. Vapors harmful if inhaled.

Vapors may cause flash fire.

Contains toxic lead antiknock components. Harmful if absorbed through skin.

Keep away from heat, sparks, and open flames.

Keep container closed.

Use with adequate ventilation. Avoid buildup of vapors and eliminate all sources of ignition especially nonexplosion-proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist. Avoid prolonged or repeated skin contact.

A1.3 Synthetic Gasoline Mixture

Danger--Extremely flammable. Vapors harmful if inhaled. Vapors may cause flash fire. Contains toxic benzene and other hydrocarbon substances. (See Method X 0000).

Harmful if absorbed through skin.

Keep away from heat, sparks, and open flames.

Keep container closed. Use with adequate ventilation.

Avoid buildup of vapors and eliminate all sources of ignition, especially nonexplosion-proof electric apparatus and heaters.

Avoid prolonged breathing of vapors or spray mist.

Avoid prolonged or repeated skin contact.

A1.4 JP-4 Jet Fuel

Danger--Flammable. Vapors harmful if inhaled.

Vapors may cause flash fire.

Keep away from heat, sparks, and open flames.

Keep container closed.

Use with adequate ventilation, avoid buildup of vapors, and eliminate all sources of ignition, especially nonexplosion-proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist. Avoid prolonged or repeated skin contact.

APPENDIX

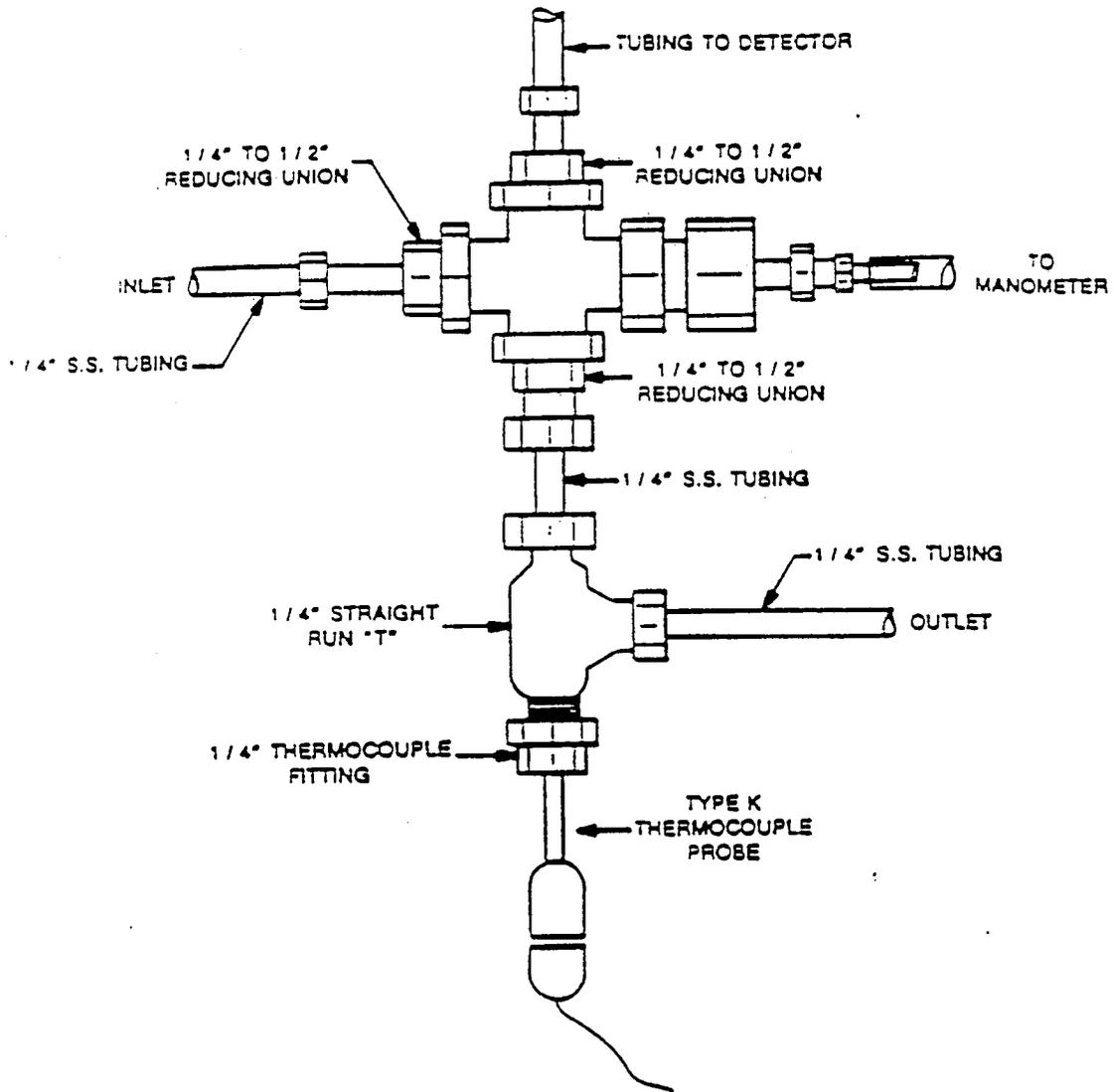
X1. EXAMPLE TEST CHAMBERS

X1.1 It is not reasonable to try to design a single test chamber that accommodates all configurations of detector probes. Instead, it is better to define the general requirements for the chamber and allow specific chambers to be designed to meet requirements for particular probes. Included in this appendix are diagrams of three test chambers that, combined, should be suited to the vast majority of vapor-phase detectors. The included chamber designs may also serve as starting points for alternate chamber designs.

X1.2 *Test Chamber for Tubing Probes*--Figure X1 contains a diagram detailing a test chamber design that should be suitable for almost all vapor-phase detectors that have probes consisting of tubing. These detectors primarily aspirate gas samples through tubing to a sensor located in the control box.

X1.3 *Test Chamber for Probes Up to 3/8-Inch Diameter*--Figure X2 is a diagram of a test chamber design that should be adequate for detector probes with diameters up to 3/8 inch.

X1.4 *Test Chamber for Probes Up to 1-1/4-Inch Diameter*--Figure X3 is a diagram of a test chamber design that should be adequate for detector probes with diameters up to 1-1/4 inches.



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FIG. X1. Gas Test Chamber for Tubing Probes

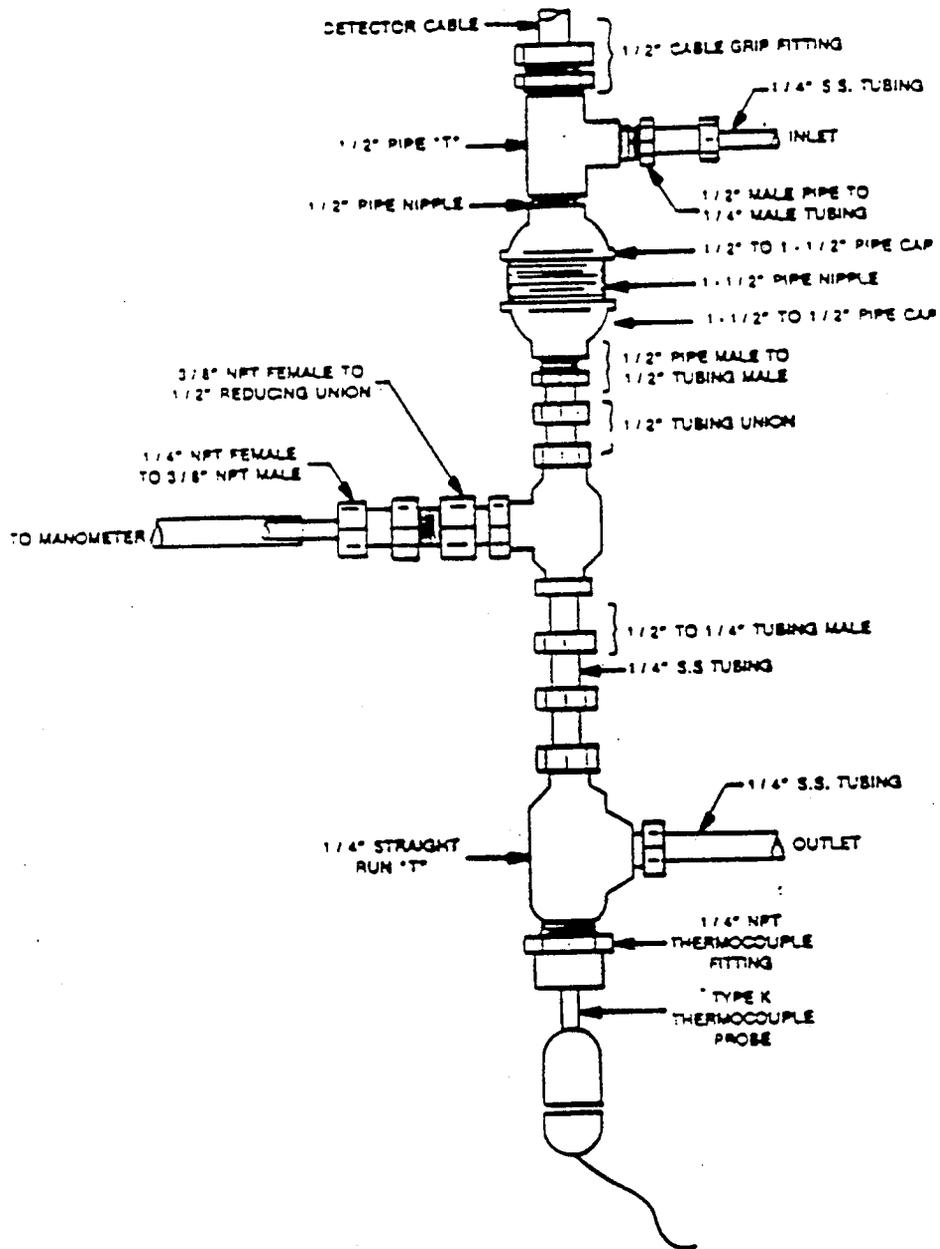


FIG. X3. Gas Test Chamber for Probes with Diameters Up to 1-1/4 Inches