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Test Method to Measure Fluid Permeation of Polymeric Materials by Speciation

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1. Scope—This test method described in this document covers a procedure to speciate that is, to determine the amounts of each different fuel constituent that permeates across sheets, films or slabs of plastic materials. One side of the sheet is meant to be in contact with either a liquid test fuel or a saturated test fuel vapor, the other side is meant to be exposed to an environment free of fuel. The test fuel can either be a mixture of a small (usually smaller than ten) number of hydrocarbon, alcohol and ether constituents or it can be a sample of a real automotive fuel, e.g., one that may contain hundreds of different constituents.

Furthermore, Appendix A contains guidelines to speciate evaporative emissions from finished fuel system components such as fuel lines, fuel filler pipes, fuel sender units, connectors and valves.

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2. References

2.1 Applicable Publications—The following publications form a part of this specification to the extent specified herein. Unless otherwise indicated, the latest version of SAE publications shall apply.

2.1.1 SAE PUBLICATIONS—Available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096-0001.

SAE J30—Fuel and Oil Hoses
SAE J1527—Marine Fuel Hoses
SAE J1681—Gasoline and Diesel Surrogates for Materials Testing
SAE J1737—Permeation from Fuel Tubes, Hoses and Fittings
SAE Paper 981360—Fuel Permeation Performance of Polymeric Materials Analyzed by Gas Chromatography and Sorption Technique
SAE Paper 981376—Speciation of Evaporative Emission from Plastic Fuel Tanks
SAE Paper 1999-01-0376—Fuel Permeation Analysis Method Correlation
SAE Paper 1999-01-0377—Vapor and Liquid Composition Differences Resulting from Fuel Evaporation
SAE Paper 1999-01-0380—A Comparison of Vapor and Liquid Fuel Permeation
SAE Paper 2001-01-1999—Fuel Permeation Performance of Polymeric Materials
SAE Paper 2002-01-0635—Comparison of Fuel Hose SHED Test Results and Predicted Values Using Fundamental Material Barrier Properties

2.1.2 ASTM PUBLICATIONS—Available from ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

ASTM Standard: E 96—Test Method for Water Transmission of Materials
ASTM Standard: D 5134—Standard Test Method for Detailed Analysis of Petroleum Naphtas through n-Nonane by Capillary Gas Chromatography

2.1.3 FEDERAL REGULATIONS—Available from the Superintendent of Documents, U. S. Government Printing Office, Mail Stop: SSOP, Washington, DC 20402-9320.

U.S. Code of Federal Regulations, 40 CFR, Chapter 1, Subpart B - §86.101 to 86.157

2.1.4 GENERAL SCIENTIFIC LITERATURE PUBLICATION

J.T. Scanton and D.E. Willis, “Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept”, J.of Chromatographic Science. Volume 23, August, 1985
Jrn of Chromatographic Science P. O. Box 48312, Niles IL 60648

2.2 Related Publication—The following publication is provided for information purposes only and is not a required part of this specification.

2.2.1 SAE PUBLICATION—Available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096-0001.

SAE J2260—Non-Metallic Multilayer Fuel System Tubing

3. Definitions

3.1 Flux—The flux, $F_i(l)$, of a specific fuel constituent i (across a sheet, film or slab of thickness l) is defined as the rate of flow (mass per unit time) of the specified constituent in the direction normal to the face of the sheet, through a unit area of the sheet. An accepted measure of $F_i(l)$ is gm/m^{2}day. The test conditions (test fuel composition, temperature, pressure, etc.) must be stated. Eventually in the course of a permeation test a steady state value, $F_i^{(ss)}(l)$, of the flux, $F_i(l)$, should be reached for each constituent (see 3.3).

3.2 Vapor Transmission Rate—The vapor transmission rate, VTR_i, of a specific fuel constituent (across a sheet, film or slab) is defined as the steady state rate of flow (mass per unit time) of the specified constituent in the direction normal to the face of sheet, through a unit area and for a unit sheet thickness under the conditions of the test. An accepted measure of VTR_i, is gm mm/m^{2}day. The test conditions must be stated. The steady state flux, $F_i^{(ss)}(l)$, and the vapor transmission rate, VTR_i, are related by $VTR_i = l^* F_i^{(ss)}(l)$, where l is the film thickness.

3.3 Measuring Steady State Conditions—When permeation across a plastic film or sheet is measured both the amount of permeate and its composition depend on the time t that has elapsed since the film or sheet was first exposed to the fuel: in other words, each flux $F_i(l)$, is a different function of t. Eventually, a steady state rate of permeation should be attained for each fuel constituent. In other words, for sufficiently long t, each flux $F_i(l)$ should attain a constant (steady state) value, $F_i^{(ss)}(l)$. Of course, this can only be possible if the composition of the test fuel does not change significantly in the course of the experiment. The time required to arrive at steady state is inversely proportional to the square of the film (or sheet) thickness and it varies greatly depending on:

a. The material tested
b. The composition of the test fuel
c. The temperature of the experiment

For the purposes of the present test it is crucial that the steady state permeation rates (as opposed to the transient permeation rates detected prior to the attainment of steady state) be reported.

3.3.1 OPERATIONAL CRITERIA FOR STEADY STATE—An operational definition of steady state permeation may be as follows:

3.3.1.1 In the case of a test fuel constituent i, for which the flux $F_i(l)$ has been determined to be non zero (e.g., above the experimental quantitation limit), $F_i(l)$ will be considered to have attained steady state at time t, provided that (within the precision of the experiment) it has remained constant for an interval of time Δt greater than or equal to t/4.

3.3.1.2 In the case of a test fuel constituent i, for which the flux $F_i(l)$ has remained below the experimental quantitation limit throughout the entire time t over which testing has been conducted, it is not possible to determine the steady state permeation value from the test alone. In this case a null result should be reported together with the time t over which it has been observed. Repeating the experiment with a thinner film of the same material may yield a non null result.

In using the previous operational definition of steady state it is important to keep in mind that, in general, when a plastic material is exposed to a permeant (such as a test fuel), permeant is taken up by that material and the material may undergo significant changes as a result. These changes may include deformations due to swelling, changes in the material elastic properties, plasticization, changes in crystallinity and depletion of additives. All these changes affect how steady state is reached: an understanding of the changes that are likely to occur for the material and the test fuel at hand is important in assessing the test results.

3.4 Test Conditions—In order for the permeation rates measured according to the present procedure to be reproducible–a necessary prerequisite for reliability and ultimate usefulness–the following conditions under which the test procedure takes place must be carefully controlled.

3.4.1 TEMPERATURE—Permeation rates are known to be greatly affected by temperature, therefore test results should state both the test temperature and its standard deviation. Permeation rates usually increase with temperature and a rule of thumb of a 10% increase in permeation per degree centigrade is often quoted. However, the rate of change of permeation with temperature depends on both the material and the test fuel. For example, if the temperature of the experiment is close to the glass transition temperature of the material being tested, a much larger rate of permeation increase with temperature is to be expected.

3.4.2 TEST FUEL COMPOSITION—The value of the flux $F_i(l)$ of a given fuel constituent is a function of the composition of the test fuel. Therefore it is crucial to insure that the composition of the fuel does not change significantly in the course of the experiment. This can be achieved either by using a quantity of fuel much larger than the amount likely to be lost by permeation and evaporation in the course of the test or by periodically replenishing the test fuel. SAE procedure J1681 defines a number of “standard test fluids”.

3.4.3 PRESSURE—External pressure itself has a negligible effect on permeation, since it has a negligible effect on the chemical potential of the permeants. However, pressure differentials between the two sides of the test sheet may cause it to stretch and/or warp and thus influence the results of a permeation test. Furthermore, the saturated vapor pressure of the permeant strongly depends on temperature: this vapor pressure contributes to the total pressure at which the test fuel is held and may also cause deformations (stretching or warping) of the test sheet if the temperature is changed. In order to reduce deformations as much as possible, it is necessary to insure that the total pressure on the two sides of the film is maintained at comparable levels. For example, this can be achieved by venting the test fuel to the outside or by minimizing changes in temperature after the film has been mounted. Clearly, for a given material, the thinner the test film the greater the chances for potentially damaging elastic deformations. Conversely a sufficiently thick test sample will be able to withstand a higher pressure differential between the two sides.

3.4.4 MATERIALS—It is important to keep in mind that both the processing conditions (e.g., cast versus blow molded film) and the additive package may have significant effects on permeation. Thus, it should not be surprising that films of the same polymer obtained from different manufacturers exhibit somewhat different permeation characteristics when exposed to the same test fuel.

3.4.5 LIQUID VERSUS VAPOR EXPOSURE—Standard thermodynamic considerations imply that the permeation rates for films in direct contact with liquid permeant or with its saturated vapor should be the same. While there have been a large number of experimental observations confirming this rule (see SAE papers 981360 and 2001-01-1999), one observation has also been reported where weight loss appears to depend on whether the plastic specimen is exposed to liquid or vapor (see: SAE Paper 1999-01-0380). In this case, it is possible that, the liquid in contact with the plastic material is more effective than its vapor in depleting certain additives from that material, since the presence of the liquid favors convective transport away from the surface of additives leached out of the material. This may hold in particular for additives having relatively high molecular weight that are soluble in the liquid.

Concerning the issue of liquid versus vapor exposure it should be noted that, in the case of liquid exposure, the test film has to support the weight of the fuel. As a result, if the film is very thin, e.g., below 50 microns, it may easily become stretched or warped. This in turn may invalidate the results of the test.

3.4.6 MOISTURE CONTENT AND RELATIVE HUMIDITY—Both the moisture content of the fuel and the relative humidity experienced by the test film (moisture content of the purge gas) may affect permeation rates. Such materials as EVOH and nylons are known to be particularly sensitive to the presence of water; however, for these materials the presence of alcohols in the “test fuels” may overwhelm any effect of this kind. To make consistent comparisons between the results of different tests, the moisture content of the fuel used should either be:

a. Kept to a minimum
b. Controlled to a pre-agreed level
c. Measured and reported

(listed in order of preference).

3.4.7 FILM THICKNESS—Theoretical considerations suggest that the steady state flux, $F_i^{(ss)}(l)$, across a film of thickness l is inversely proportional to the thickness: the definition of vapor transmission rate VTRi is based on this rule. However, this is based on the assumption that the material is uniform through the thickness of the sample. Actual samples may deviate from this assumption. For example, processing conditions are often such that the two surfaces of a film have material properties (crystallinity, local concentration of additives) significantly different from those of the bulk. As a result, for very thin films (typically 50 microns or less) where the surface material accounts for a significant fraction of the overall thickness, the observed values of the steady state flux, $F_i^{(ss)}(l)$, may depart from the rule stated previously.

Furthermore, it should be kept in mind that an absolute variation in thickness (for example, thickness specified to within ±2 microns) represents a much greater uncertainty in percentage terms for a thin film than for a thick one.

3.5 Units of measurements—It has been common practice to use certain engineering units that do not strictly conform to a specific system (such as CGS or MKS). Conversion factors between different commonly used units are as follows:

3.5.1 For the fluxes $F_i(l)$

$$\begin{aligned} 1\ \text{g/m}^2\text{day} &= 6.45\ \ 10^{-2}\text{gm}/(100\text{in}^2)\text{day} \\ &= 1.16\ \ 10^{-9}\text{g}/\text{cm}^2\ \text{sec (CGS unit)} \\ &= 1.16\ \ 10^{-8}\text{kg}/\text{m}^2\ \text{sec (MKS unit)} \end{aligned} \quad \text{(Eq. 1)}$$

3.5.2 For the Vapor Transmission Rate VTR_i

$$\begin{aligned} 1\ \text{g mm/m}^2\text{day} &= 2.54\ \text{g mil}/(100\text{in}^2)\text{day} \\ &= 1.16\ \ 10^{-10}\text{g cm}/\text{cm}^2\ \text{sec (CGS unit)} \\ &= 1.16\ \ 10^{-11}\ \text{g m/m}^2\ \text{sec (MKS units)} \end{aligned} \quad \text{(Eq. 2)}$$

4. Background Information—Governmental Regulatory Agencies are mandating increasingly stringent standards on vehicle evaporative emissions. The tests currently specified by the U.S. Environmental Protection Agency (EPA) and the California Air Resource Board (CARB) are designed to detect and quantify carbon containing species emitted during the tests. For gasoline fueled vehicles the EPA and CARB regulations (see: U.S. Code of Federal Regulations, 40 CFR, Chapter 1, Subpart B - §86.101 to 86.157) do not require speciation of the evaporative emissions: contributions from different carbon containing species are weighted according to their carbon content and independent of their potential environmental threat. For methanol fueled vehicles (that is vehicles using a methanol containing fuel) the EPA and CARB regulations require that a test designed to determine the methanol content of the emissions be performed. The methanol emissions determined in this way are counted towards the total on the basis of the carbon content of methanol.

A knowledge of the composition of the permeate that diffuses across a given plastic material is desirable for the following reasons:

a. To arrive at informed decisions as to the environmental impact of the emissions from a construction built of a specific plastic material
b. To optimize the design of multilayer plastic parts used in automotive fuel systems (in these parts each plastic layer acts as a selective filter to certain fuel constituents)
c. To obtain diagnostic information as to the source of the evaporative emissions from a vehicle (see: SAE paper 1999-01-0377 and SAE paper 981376).

5. ***Apparatus and Equipment***—Tests aiming at speciating permeate that diffuses across a film, sheet or slab of plastic material must include the following steps:

a. Capturing the permeate
b. Analyzing the permeate composition
c. Determining the steady state flux $F_i^{(ss)}(l)$ (and the vapor transmission rate VTR_i) from the results of the analysis.

The detailed realization of these steps will differ depending on the type of fuel used in the test, on the type of material being tested, and on the thickness of the film, sheet or slab sample.

In different realizations of this test certain elements of the apparatus and equipment used may be different. However, all realizations must be based on:

a. Permeate collection that uses a purge gas to sweep over the surface of the plastic sample that is not exposed to fuel.
b. Gas Chromatographic (GC) analysis of the permeate composition.

As a result, the pieces of equipment described in items 5.1 to 5.4 are required in all realizations.

Specific realizations may differ:

a. In how and how often permeate is collected from a sample. Typically these items depend on the time required to reach steady state: i.e., ultimately on sample material and sample thickness, since the time required to reach steady state is ordinarily proportional to the square of the thickness.
b. In the way the permeate contained in the purge gas is trapped and eventually injected into the Gas Chromatographic column. This has to be decided on the basis of the permeation level, i.e., ultimately it depends on sample material and sample thickness, since the steady state flux $F_i^{(ss)}(l)$ of permeate constituent i is inversely proportional to the thickness.
c. In the type of Gas Chromatographic column chosen: generally, the type of fuel used in the test guides this choice.

Items 5.5 to 5.6 each describe equipment that is specific to one of two different separate realizations of the test.

5.1 **Permeation Cell**—The permeation cell can be made of stainless steel or anodized aluminum; any other material that is not permeable to fuel and is not otherwise altered (e.g., corroded) in the presence of fuel is acceptable. The cell is divided in two cavities (cups) separated by the test film (see Figure 1). The test fuel mixture is contained in one of the cups (fuel cup); the other cup (permeate collection cup) serves as a collection/sampling unit for the permeate that diffuses across the sample. Depending on whether the test is conducted under liquid or vapor exposure (see 3.4.5) the fuel cup is located above or below the specimen. The plastic film is mounted between the two cavities using two flat gaskets (no more than 0.2 cm thick) made of a suitable low permeation grade of fluorocarbon elastomers such as Viton GFLT or 70% fluorine grade FKM elastomers. The purpose of the gaskets is to prevent leakage of fuel from the fuel cup and loss by leakage of the purge gas/permeate mixture from the permeate collection cup. Any other sealing method that achieves the same purpose (e.g., indium O-rings) is acceptable.

5.1.1 FUEL CUP—The fuel cup may contain an opening to either allow venting of the fuel to the outside or to permit the total pressure within the fuel cup to be regulated by other means: see 3.4.3; it may also contain additional openings to allow replenishing of the fuel during the experiment. If the fuel cup is vented to the outside a long (e.g., longer than 1 meter for 1/16 of an inch diameter) venting tube is required to minimize loss of fuel vapor and hence changes in test fuel composition.

5.1.2 PERMEATE COLLECTION CUP—The permeate collection cup or collection unit contains at least two openings to allow flow of the purge gas in and out of this cup. The shape of the cup and the location of the openings should be such to insure that there are no dead volumes (where permeate may remain trapped) within this cup.

5.2 Purge Gas Source—Inert purge gases such as nitrogen, helium and argon are acceptable; the moisture content of the purge gas should be kept to a minimum, controlled to a pre-agreed level, or be measured and reported: see 3.4.6.

5.3 Temperature Controlled Chamber—An explosion proof temperature controlled (e.g., by air circulation) chamber houses the permeation test cell. The temperature at different locations within the chamber should be uniform to within at least ±1 °C; it should also be stable in time to within less than ±1 °C.

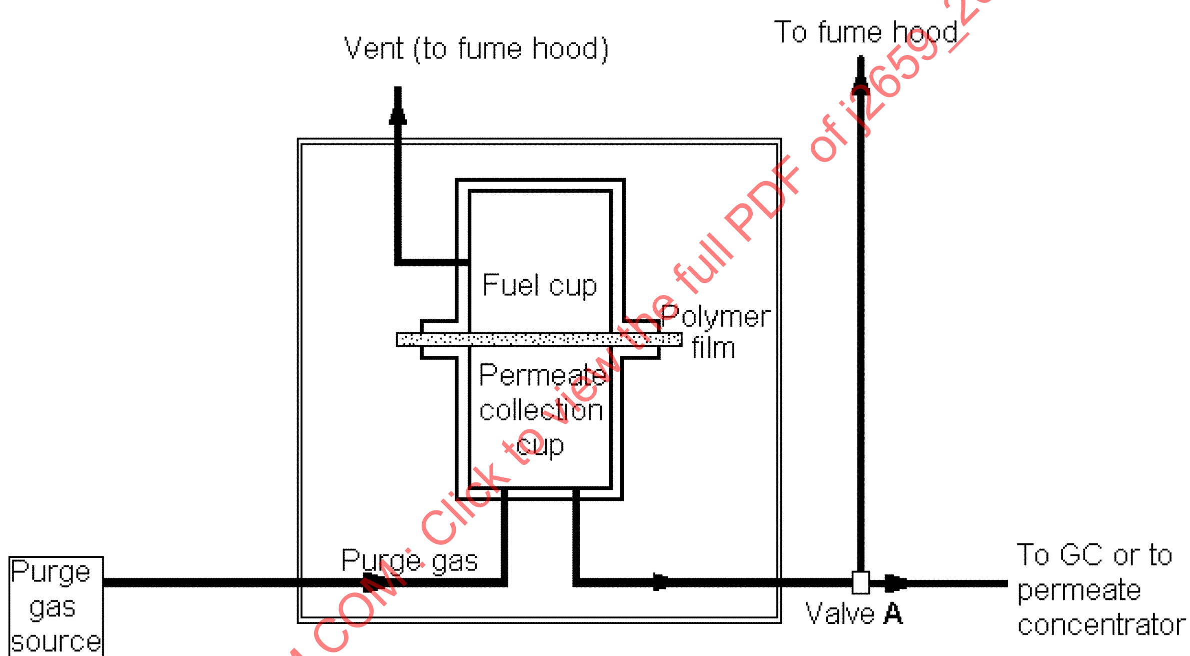

FIGURE 1—SCHEMATIC OF "OPEN LOOP" IMPLEMENTATION OF THE TEST

5.4 Gas Chromatographic Apparatus—A Gas Chromatographic apparatus fitted with one or more chromatographic columns, capable of separating the various constituents of the fuel employed in the test to the required level of precision, and with a Flame Ionization Detector (FID).

5.5 Additional Equipment Needed in an "Open Loop" Realization of the Test—In an "open loop" realization of the test (see Figure 1) purge gas continuously sweeps permeates from the surface of the sample that is not exposed to fuel. The permeates transported by the purge gas are either collected for analysis or diverted into a fume hood (using valve A in Figure 1).

If the concentration of permeates within the purge gas is high enough to provide a sufficiently strong signal, the purge gas can be fed directly to the Gas Chromatograph; otherwise equipment capable of trapping the permeate contained in the purge gas over an appropriate period of time is required. Items 5.5.1 and 5.5.2 are required if the purge gas is fed directly to the Gas Chromatograph; items 5.5.3 and 5.5.4 are required to trap the permeate.

5.5.1 PURGE GAS LINES AND VALVES—Purge gas lines of appropriate diameter (typically 1/8 in) 3.18mm made of a non permeable material such as copper or steel are acceptable. 3-way valves made of a non permeable material such as steel or brass are acceptable.

5.5.2 PURGE GAS FLOW CONTROLLER—A purge gas flow controller that regulates the purge gas flow in the permeate collection cup.

5.5.3 PERMEATE TRAP—A permeate trap, sometimes referred to as permeate concentrator—such as a trap and desorb carbon trap, a cryogenic trap or other such device—capable of completely trapping all the constituents of the test fuel.

5.5.4 DESORBING UNIT—A desorbing unit, capable of completely releasing to the Gas Chromatographic apparatus the permeate captured by the permeate trap.

5.6 Additional Equipment Needed in a "Closed Loop" Realization of the Test—In a "closed loop" realization of the test the permeate collection cup is part of a "closed loop" (see Figure 2) that contains a carrier gas (such as air). The "closed loop" realization is similar in principles of operation to a SHED (Sealed Housing for Evaporative Emissions)—see U.S. Code of Federal Regulations, 40 CFR, Chapter 1, Subpart B - §86.101 to 86.157—and may be thought of as a micro-SHED. In the "closed loop" realization of the test the permeate is allowed to accumulate within the "closed loop" (rather than being continuously swept away as in the "open loop" realization) over the measurement period. Periodically, during the measurement period, the permeate/purge gas mixture present within the closed loop is homogenized, and small samples of this mixture are fed to the Gas Chromatograph. The flux $F_i(l)$ of permeate constituent i is determined from the rate of accumulation of permeate i within the "closed loop". It is important that the vapor pressure of permeates in the closed loop remain well below (less than one hundredth of) the saturated vapor pressure of the same permeates at the temperature of the test, since permeation is driven by the difference in chemical potential (reflected in the difference in vapor pressure) between the two sides of the test sheet. Items are 5.6.1 to 5.6.3 are required in this realization of the test.

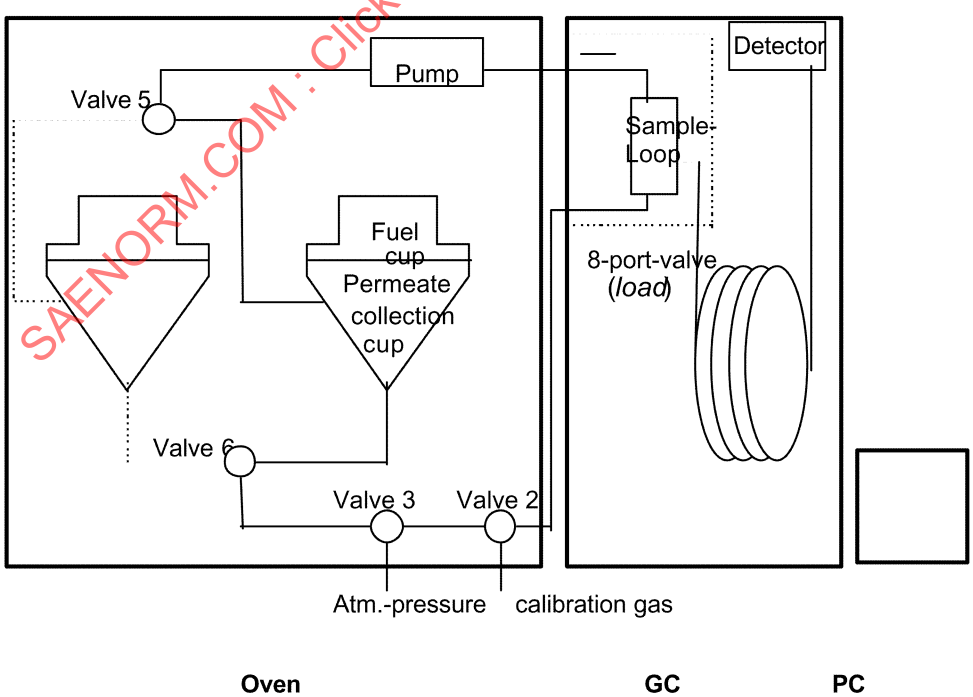

FIGURE 2—SCHEMATIC OF CLOSED LOOP IMPLEMENTATION OF THE TEST

5.6.1 PURGE GAS LINES AND VALVES—Purge gas lines of appropriate diameter (typically 1/8 in) 3.18mm made of a non permeable material such as copper or steel are acceptable. Multi-position valves made of a non permeable material such as steel or brass are acceptable.

5.6.2 MEMBRANE GAS PUMP—The membrane gas pump is designed to homogenize the permeate/purge gas mixture within the “closed loop”. All parts in contact with organic vapors should be made out of a low sorption low permeation material such as ETFE and should be held at the temperature of the test.

5.6.3 VAPORS INJECTION SYSTEM—A vapor injection system capable of sampling a small volume of the permeate/ purge gas mixture and of injecting it to the Gas Chromatograph.

6. Safety Equipment and Facilities—Appropriate safety precautions must be taken when conducting this permeation test because the test fluids are volatile flammable substances. Laboratory staff and management must follow local health and safety laws, regulations and recommended industry guidelines when setting up the apparatus and conducting all parts of the procedure.

7. Test Procedure—The following are the steps to conduct the speciated permeation measurement. The steps described here are meant to be generic in order to accommodate variations in apparatus. Slight modification will be acceptable if the intent of this document is met and the modifications are necessary to properly utilize the specific test apparatus.

7.1 Test Specimen Preparation—Cut a sample of the plastic film appropriate to fit between the two halves of the permeation cell. Measure the thickness of the sample at a number N of points (with $N \geq 4$) at uniformly dispersed locations across the sample. Record the average thickness and its standard deviation. The thickness should be measured as accurately as possible (±0.5% recommended). Also record the area A of the sample enclosed within the inner circumference (or inner perimeter) of the fluoroelastomer gaskets.

7.2 Test Specimen Preconditioning—Appropriate sample preconditioning treatments should be employed if there is a need to remove spurious substances from the sample (e.g., in the case of EVOH and nylon, water that may have been picked up from the environment). However, it is not possible to provide hard and fast rules valid for all samples. Such preconditioning procedures could include:

a. Exposure to a dry nitrogen environment
b. Baking the samples in a vacuum oven held at temperature higher than the temperature of the experiment

However, both the duration and the temperature of the pre-conditioning procedure has to be decided on a sample by sample basis taking into account such factors as sample thickness, glass transition temperature of the material, type of permeant to be used and ultimate goal of the preconditioning procedure.

7.3 Mounting Test Specimen—Place the test specimen between the two metal cups that make up the permeation cell, with one of the flat fluoroelastomer gaskets on each side between the test specimen and the cups. The gaskets must be baked in an oven at 100 °C for 12 hours to outgas hydrocarbons that may have been taken up by the gaskets in previous experiments. Analogous steps should be followed, if a different sealing system (e.g., indium O-rings) is used

The precise sequence of steps to be followed in mounting the specimen depends on the method chosen to control the total pressure on the fuel side of the cell. If the fuel cup is not vented to the outside (or its total pressure is not controlled by other means) it is essential that both the test fuel and the metal cups that make up the cell are heated to the test temperature prior to mounting the film: see 3.4.3.

7.4 Starting Test—Immediately after the sample has been mounted and the two halves of the test cell have been fastened, the cell should be moved into a temperature controlled chamber and the time recorded as the starting time of the experiment.

7.4.1 In an "open loop" realization of the test the inlet and outlet of the permeate collection cup should be connected respectively to the purge gas source and to an outlet tube that is either vented to a fume hood (at times when the permeate is not collected for analysis) or fed to either the Gas Chromatographic apparatus or to the permeate trap. The flow P of the purge gas should be in the 10 to 50 cc/min range (however the range may be higher depending on the equipment used). If the fuel cup is fitted with a venting outlet, the outlet should be connected through the venting tube to a fume hood; if the fuel cup pressure is controlled by an external pressure source, the source should be connected to the fuel cup and the fuel brought to the pressure chosen for the experiment.

7.4.2 In a "closed loop" realization of the test the permeate collection cup is part of the closed loop. If the fuel cup is fitted with a venting outlet, the outlet should be connected through the venting tube to a fume hood; if the fuel cup pressure is controlled by an external pressure source, the source should be connected to the fuel cup and the fuel brought to the pressure chosen for the experiment.

In both the "open" and the "closed loop" realization, if a long time is required for permeation to reach steady state, it is acceptable to store the permeation cell in a separate storage oven at the temperature of the test: in this case steps must be taken to insure that permeate is continuously swept away from the surface of the sheet that is not in contact with the fuel. The cell is moved to the temperature control chamber fitted with the permeate collection equipment when a measurement is required. In transferring the test cell from one oven to another, care should be taken to minimize the time spent at temperatures different from the test temperature.

7.5 Permeate Sample Collection—This step depends on whether an "open" or a "closed loop" realization of the test is implemented.

7.5.1 In an "open loop" realization of the test, at time intervals chosen depending on the test fuel, the sample material, the sample thickness and the temperature of the experiment, the purge gas is diverted either directly to the Gas Chromatograph or to the permeate trap for a time interval Δt that again depends on the factors listed above. In either case the purge gas sample is eventually fed to the Chromatographic column and once separated (speciated) to a Flame Ionization Detector.

7.5.2 In a "closed loop" realization of the test, a small sample of the permeate/purge gas mixture within the closed loop is periodically (at time intervals chosen depending on the test fuel, the sample material, the sample thickness and the temperature of the experiment) homogenized; a small sample of the homogenized permeate/purge gas mixture is then injected to the Gas Chromatograph.

7.6 Calibration of the Gas Chromatograph—This step depends on the type of test fuel used.

7.6.1 If the test fuel is a mixture of a small number of hydrocarbon, alcohol and ether constituents, the Gas Chromatograph should be calibrated by introducing in the Chromatograph a mixture of known composition and similar in nature to the expected permeate mixture in order to produce a standard curve. For each constituent (or group of constituents) the area under each peak can than be translated into a mass amount M_i of the constituent (or group of constituents) in question.

7.6.2 If the test fuel is a real automotive fuel, e.g., one that may contain hundreds of different constituents, the FID of the Gas Chromatograph should be calibrated against various known propane/air mixtures. This calibration step results in the calibration factor ($C_{propane}$) of mg propane injected and the area counts under the propane peak of the chromatogram.

The position and identification of the test gasoline constituents peaks has to be done once for every new test fuel. Peak identification of complex gasolines should be carried out with the aid of the chromatogram results from ASTM D 5134 (Modified; a DHAX analyses). After positive identification of a constituent, the relative retention time is calculated with toluene as reference peak. This reference constituent was chosen because a) it is present in almost every test fuel, b) there is no interference with other hydrocarbons and c) the peak is midway in the GC temperature program. The flame factor (f_i) of every known individual constituent in the chromatogram is calculated against propane, using the ECN method (see: J.T. Scanton and D.E. Willis, J. of Chromatographic Science. Volume 23, August 1985).

For each constituent (or group of constituents) the area under each peak in combination with flame response factors and propane calibration can than be translated into a mass amount M_i of the constituent (or group of constituents) in question.

7.7 Shutting Down the Test Apparatus

7.7.1 Turn off sources of heat (allow system to cool down before the other steps are followed).

7.7.2 Turn off source of pressure (if any) for the test fuel.

7.7.3 Disconnect pressure controller or vent.

7.7.4 Disconnect the permeation cell from the permeate collection loop (“open” or “closed”).

7.7.5 Move test cell out of the temperature controlled chamber

7.7.6 Open the test cell and record the status of the film (any unusual warping or crinkling)

7.7.7 Retain the remaining test fuel for analysis.

8. Calculations and Report

8.1 Calculate the Flux of Each Constituent and the Total Flux at Each Collection Time—This calculation depends on whether an “open” or a “closed loop” realization of the test is implemented.

8.1.1 In an “open loop” implementation the flux $F_i(l)$ of each constituent (through a film of thickness l) at each measurement time is obtained by dividing M_i (the measured mass amount of constituent “i”) by the collection time Δt and by the area A of the sample enclosed within the inner diameter (or perimeter) of the gaskets:

$$F_i(l) = M_i/(A \cdot (\Delta t/1440)) \quad \text{(Eq. 3)}$$

where

$F_i(l)$ = flux of constituent i in $g/(m^2 \cdot day)$
A = area in m^2
Δt = collection time in minutes

8.1.2 In a “closed loop” implementation, assuming that sampling of the permeate/purge gas mixture within the loop occurs at times t_1, t_2, .., t_N, the flux $F_i(l)$ of each constituent (through a film of thickness l) can be obtained from the slope $S_i = (M_i(t_{k+1})-M_i(t_k))/(t_{k+1}-t_k)$; here $M_i(t_k)$ is the mass of species i contained in the permeate sample collected at time t_k. If V_f is the ratio between the volume of the “closed loop” and the volume of the permeate sample injected in the GC and A is the area of the sample enclosed within the inner diameter (or perimeter) of the gaskets:

$$F_i(l) = (S_i \cdot V_f \cdot 1440)/A \qquad \text{(Eq. 4)}$$

where

$F_i(l)$ = flux of constituent i in g/(m^2 · day)
S_i = slope of the mass, M_i, of permeate constituent i in the sample versus time, in gm/min
A = area in m^2
V_f = ratio between the volume of the closed loop and the volume of the permeate sample injected in the GC

8.1.3 The total flux permeating across the sheet is obtained by summing the contributions $F_i(l)$ from all the different fuel constituents. For the relation between this result and the total flux obtained with other measurement techniques see 9.1.

8.2 Obtain the Steady State Flux and the Steady Sate Vapor Transmission Rate of Each Constituent—The steady state flux, $F_i^{(ss)}(l)$, of each constituent is obtained from a set of successive measurements of the fluxes $F_i(l)$ using the guidelines outlined in 3.3. The vapor transmission rate, VTR_i, is obtained by multiplying the thickness, l, of the film with the steady state flux:

$$VTR_i(\text{in}(g \cdot mm)/(m^2 \cdot day)) = l(\text{in } mm) * F_i^{(ss)}(\text{in } g/(m^2 \cdot day)) \qquad \text{(Eq. 5)}$$

8.3 Reporting Results—At a minimum for each film sample the following data should be reported:

8.3.1 Material description (manufacturer and trade name)

8.3.2 Brief description of pre-conditioning procedure (if any)

8.3.3 Thickness l of the film and standard deviation of the thickness

8.3.4 Temperature of the experiment

8.3.5 Pressure in the fuel cup (if different from ambient)

8.3.6 Steady state flux , $F_i^{(ss)}$, and vapor transmission rate, VTR_i, of each constituent (any of the units described in 3.5 is acceptable) and total steady state flux.

8.3.7 Optionally a more complete report should include the entire time development of the flux $F_i(l)$ (e.g., $F_i(l)$ versus t) and a report on the composition of the residual test fuel.

9. *Additional Information*

9.1 Relations with other Measurement Techniques—Unspeciated measurements of the transmission rate of fuel across plastic films or sheets conducted thus far fall in two broad classes:

a. Weight loss measurements (these include adaptations to fuel of ASTM standard E 96 as well as various adaptations of SAE J30, SAE J1527, and SAE J1737.
b. Measurements where the plastic film to be tested is mounted on a cell similar to the one shown in Figure 1, but the purge gas from the cell is fed directly to a flame ionization detector calibrated to some specific hydrocarbon standard (e.g., propane).

The main disadvantage of measurements belonging to class (a) is the possibility that leakage (see SAE paper 1999-01-0376) will take place and lead to an overestimate of the total flux. Under the assumption that leakage is not a problem the total flux obtained from measurements of class (a) should be equal (all other test conditions being equal) to the sum of the fluxes $F_i^{(ss)}$ obtained from the present test.

Measurements belonging to class (b) do not suffer from the leakage problem, but are more difficult to compare to the results of the present test since the total flux found from measurements of class (b) is a weighted average of the fluxes F_i obtained from the present test, but the weights are different for each constituent and depend on the type of FID used. Specifically, if m_i is the molecular weight per carbon of species i, m is the molecular weight per carbon of the hydrocarbon standard used to calibrate the FID, and R_i is the relative response factor for species i, then the total hydrocarbon flux F_T obtained from measurements of class (b) is related to the fluxes F_i obtained from the present test by:

$$F_T = \sum_i F_i(m_i/(m \cdot R_i)) \qquad \text{(Eq. 6)}$$

where the sum runs over every constituent i of the test fuel. Note that to compare the results of class (a) tests for the total flux to the total flux F_T of the equation 6 one needs to know the separate fluxes F_i.

9.2 Accelerating the Test in Order to Cut the Time Needed to Achieve Steady State—Often results for the steady state fluxes $F_i^{(ss)}$ are required at a given temperature T_1; however, if the entire test is performed at this temperature the time required to attain steady state may be prohibitively long. In these instances an upper estimate of the fluxes $F_i^{(ss)}$ at the temperature T_1 may be obtained by performing the test at an higher temperature T_2 and, once steady state has been achieved, by lowering the temperature to T_1 and waiting for $F_i^{(ss)}$ to attain a (lower) constant value. The acceleration achieved in this way can be substantial: for example, if the permeation increases by 10% per degree C, a difference $(T_2 - T_1)$ equal to 10 °C may result in a reduction as large as a factor 0.386 in the time required to reach steady state at T_2 compared to T_1. However, once the temperature is lowered to T_1, the apparent near constant value of the flux may hide a very slow (hard to detect) decrease corresponding to the fact that the concentration of fuel within the sheet is decreasing very slowly to the level corresponding to the temperature T_1. For this reason the results for $F_i^{(ss)}$ at T_1 obtained from the accelerated test should be regarded as an upper limit to the actual value of $F_i^{(ss)}$ at T_1.

PREPARED BY THE SAE PERMEATION STANDARDS COMMITTEE

APPENDIX A

GUIDELINES FOR SPECIATION OF FUEL LOSSES FROM FINISHED FUEL SYSTEM COMPONENTS

A.1 Background—The permeation cell arrangement discussed in Section 5 ensures that only fuel permeating through the test sheet, film, or slab reaches the permeate collection cup. In other words the way in which the test sheet is fixtured guarantees that, unless the sheet specimen is damaged, there is no leak path through which the film can flow from the fuel cup to the permeate collection cup. For finished fuel system components, because of the great number of possible component shapes and geometries, the type of fixture used for speciated permeation testing has to be designed on a case by case basis and often there is no simple way to guarantee that the results are not affected by extraordinary leakage. Note that some micro-leakage may be a normal part of the component behavior in the actual vehicle environment. What is of concern is leakage beyond that which might be considered “normal.” Furthermore, it should be noted that the component being tested may have to be fixtured during the test in ways that are different from the way in which the component is mounted in a vehicle. Therefore care must be exercised to ensure that the test results are representative of actual field performance.

Once a satisfactory solution to the fixturing problem has been found (see Figures A1 and A2 for possible solutions) the collection of the permeate and the Gas Chromatographic analysis can be performed in the way described in Section 7: in other words the test becomes a straightforward extension of the test for sheet specimens. For this reason the present Appendix focuses on how to address the fixturing issue for finished fuel system components in a number of common geometries. With regard to the leakage problem, it should be noted that the same issue and similar solutions are discussed in the Proposed SAE Procedure for Fuel Permeation Testing using Gravimetric Methods.

A.2 Fuel Lines and Hoses—Since total permeation is proportional to the area through which permeation can take place, one way to assess the contribution of leakage is to test specimens of different areas and to check that the proportionality law is obeyed. This is relatively straightforward in the case of fuel lines and fuel hoses: the basic idea is to have liquid fuel or saturated fuel vapor inside different lengths of the line (or hose) that is being tested, seal both ends of the line (or hose), put the line or hose sealed in this way in a capture volume that plays the role of the permeate collection cup in the test for material sheets and then collect and analyze fluid losses from the line (or hose) in the way described in Section 7: the measured fluxes $F_i(l)$ due to permeation should be proportional to the length of the line (or hose) being tested. Any systematic offset from this proportionality could be attributed to leakage. Specific guidelines are as follows:

A.2.1 Seal one end of hose/tube with a stainless barbed fitting. Fitting should be tight and appear to be leak-proof. Then fill the hose/tube with test fuel: the amount of fuel should be as close to 100% of the volume as practically possible. At this point seal the other end with same type of fitting—again the fitting should be tight and appear to be leak-proof. Since in this configuration the fuel line (or hose) is sealed, the vapor pressure (and hence the total pressure within the line will change if the temperature of the test is different from the temperature at which the fixture is prepared. Alternatively one end of the line (or hose) can be attached to a stainless steel or anodized aluminum fuel container while the other end is sealed: in this second configuration it is possible to vent the fuel container to the outside and to minimize pressure differences (see Figure A1).

A.2.2 Place the sealed hose/tube into a capture volume. This fixture should have an input and an output for the carrier gas, and it should be leak tight. The shape of this fixture should be such that there are no dead volumes, where permeate can remain trapped. Capture volumes that are not much larger than the sample are preferable.

A.2.3 The sample collection and Gas Chromatographic analysis should be performed according to the directions specified in Section 7: the measurements should produce the mass m_i per unit time of fuel constituent i emitted from the fixture. Eventually, m_i should reach a steady state value $m_i^{(ss)}$.

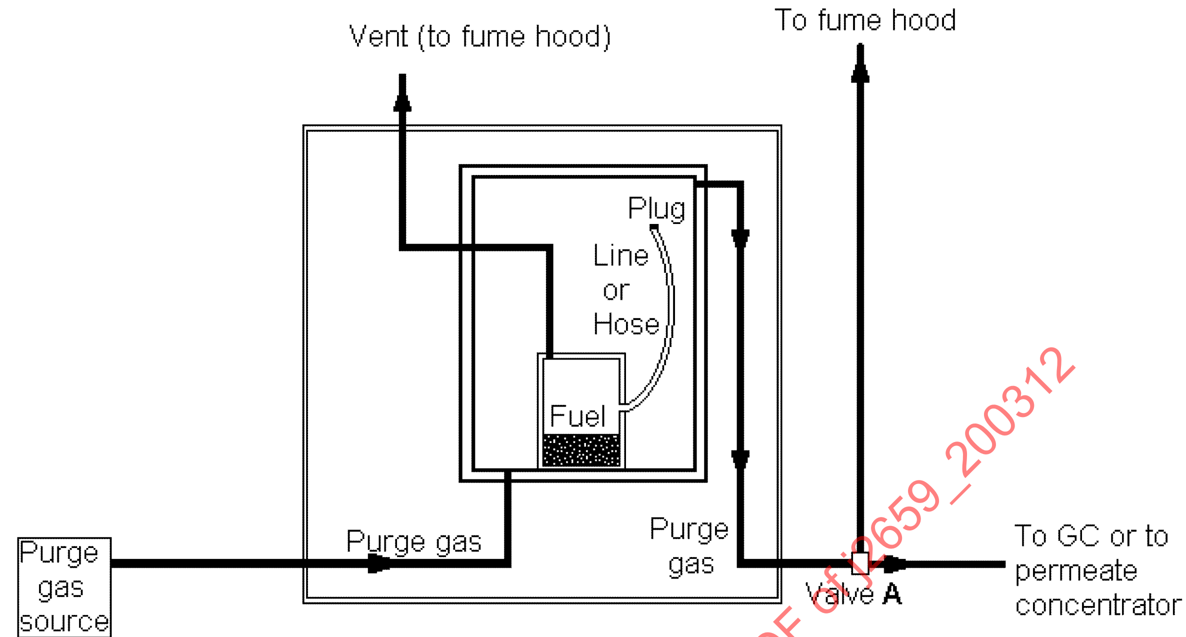

FIGURE A1—SCHEMATIC OF A POSSIBLE OPEN LOOP IMPLEMENTATION OF THE FUEL LINE TEST: ONE END OF THE LINE IS ATTACHED TO A METAL FUEL CONTAINER, THE OTHER END IS SEALED. BOTH THE FUEL CONTAINER AND THE LINE BEING TESTED ARE ENCLOSED IN THE CAPTURE VOLUME THAT IS BEING SWEPT BY THE PURGE GAS.

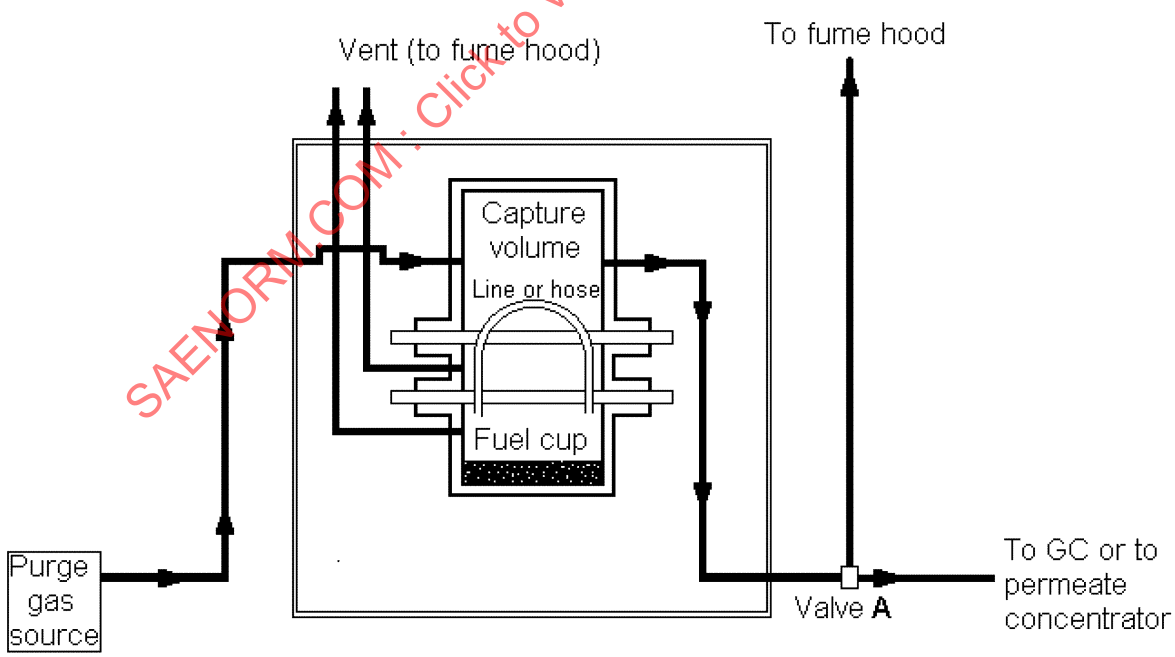

FIGURE A2—SCHEMATIC OF A POSSIBLE OPEN LOOP IMPLEMENTATION OF THE FUEL LINE TEST: IN THIS CASE BOTH ENDS OF THE LINE ARE ATTACHED TO A METAL FUEL CONTAINER AND THE CAPTURE VOLUME DOES NOT CONTAIN THE CONNECTORS, SO THAT THE RESULTS SHOULD NOT BE AFFECTED BY SPURIOUS LEAKAGE.