Chemical Permeation Test of Commercially Available Gloves Using the ASTM-F1001 Standard
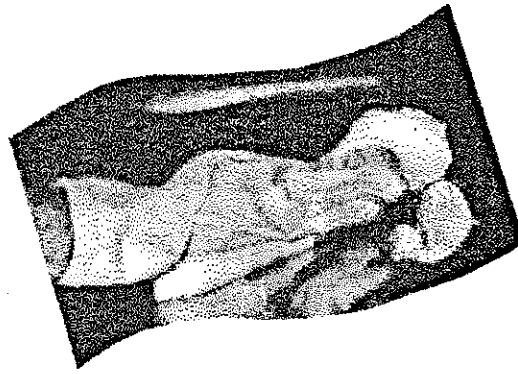
Jaime Lara
Brigitte Roberge
Alberto Velazquez
Hugues Kelisse

ÉTUDES ET RECHERCHES

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REPORT

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Jaime Lara, Brigitte Roberge,
Alberto Velazquez and Hugues Nelisse
Laboratories Division, IRSST

ETUDES ET
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REPORT

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Health problem:
Dermatological problems

Group of workers concerned:
Workers exposed to solvents, detergents, oils, etc.

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1.0 INTRODUCTION

It is well known that direct contact of chemicals with the skin can produce various effects such as serious burning, poisoning by penetration through the skin, and dermatitis. Protective clothing is used to reduce the risk of dermal exposure to chemicals.

Different factors should be considered in the selection of proper protective clothing. These factors include knowledge of what the chemical is, its toxicity, the skin-exposure risk, engineering controls, information on the protective clothing materials (e.g. resistance to chemical by permeation tests), and mechanical resistance (cut, tear and puncture resistance).

This study will deal with the use of chemical permeation values in the selection of protective gloves.

The permeation phenomenon

The barrier effectiveness of the glove material can be determined by permeation testing. Recently, a procedure for performing permeation tests was developed by ASTM COMMITTEE F-23[1]. This method consists of bringing the hazardous chemical into contact with the glove material in a specially-designed permeation cell. This method allows the breakthrough time* and the permeation rate** for each glove material solvent pair to be determined.

The permeation of a chemical through a protective barrier, generally plastic or rubber materials, can be represented by a three-step process[2] as shown in figure 1.

a) Solubilization: The chemical "reacts" with the external layer of the protective material, in some cases dissolving or swelling it.

b) Diffusion: The chemical passes through the material. This process takes place at the molecular level.

c) Desorption: The chemical evaporates on the inside surface of the glove material towards the wearer.

In the selection of protective gloves, it is necessary to take into account both the breakthrough time and the permeation rate. The higher the breakthrough time, the more resistant the glove material to the chemical. The lower the permeation rate, the lower the amount of chemical that passes through the material and that comes into contact with the wearer's skin[3].

* Breakthrough time: elapsed time between contact of the glove material with the chemical and its detection on the inside of the glove.

** Permeation rate: is the amount of a chemical which passes through a glove material per unit time.

The thickness of the glove material and the energy of interaction between glove material and the chemical affect the permeation rate. Thus, the permeation rate decreases as the thickness of the glove material increases. If the interaction energy of the glove material-chemical is high, the permeation rate is also high.

2.0 INTERPRETATION OF PERMEATION DATA

In the selection of protective gloves, users or hygienists must choose one of the following possibilities:

*   Use commercially-available permeation data base systems[4, 5].

*   Use information from manufacturers[6, 8].

*   Test protective glove materials, using permeation method ASTM F-739 in the case where no permeation data exist[1].

In the interpretation of permeation data, two factors must be taken into account:

a) The difficulty in comparing the breakthrough time and the permeation rate data from different laboratories.

b) The case of gloves having the same generic material.

a) Comparing the permeation data

In the case of permeation tests performed in a laboratory using the same experimental conditions (i.e. analytical system, sensitivity, collecting medium, etc.), the results obtained are comparable. For permeation tests performed in different laboratories or using different analytical methods, data comparisons appear less obvious. For example, the use of a more sensitive detector can result in a shorter breakthrough time for the same protective material. This can in part explain the differences in breakthrough times reported in the literature[4, 5].

b) The case of protective gloves having the same generic material

Important differences in resistance to chemicals can be observed in gloves made of the same generic material but produced by different manufacturers (e.g. neoprene, nitrile, etc.). Differences in manufacturing process and material composition (e.g. additives, stabilizers, cure temperature, etc.) can affect the properties of the glove material.

Because of these differences, it is not possible to conclude from a permeation test on a given glove material/chemical pair that any other protective glove made of the same generic material will behave exactly the same as the tested glove.

For these reasons:

*   Users or hygienists must obtain information on the sensitivity of the reported permeation test in order to compare permeation data from different laboratories.

*   Users or hygienists cannot generalize on glove resistance based on the generic material.

3.0 TESTING GLOVES AT THE IRSST

As mentioned above, one of the major problems in using information from the literature in the selection of protective gloves is in comparing the permeation tests from different laboratories. Furthermore, in the specific case of the Canadian market, there are many protective gloves (imported or Canadian made) for which no information exists on chemical resistance by permeation tests. For these reasons, a program to perform comparative tests on commercially available protective gloves in Canada has been initiated at the IRSST.

In a recent ASTM F-23 subcommittee meeting, the use of neoprene of 0.41 mm thickness from Dupont was proposed as a reference material for performing permeation tests in order to compare analytical methods from different laboratories. This material has been used in the present study.

4.0 DESCRIPTION OF THE ASTM METHOD

ASTM standard 739[1] was developed to evaluate the permeation of a flat surface of a material to a solvent with which it is in contact. This material could be part of the palm or back of a glove, or even any other material used in manufacturing protective clothing (e.g. aprons, boots, coveralls, etc.). This method is applicable regardless of the material exposed to the chemical and serves to quantify the permeation of the protective material to the chemical in the case of continuous exposure. For this evaluation, a glass cell like the one presented in Figure 2 is used.

The permeation cell is made up of two chambers, one for the chemical and the other for the collecting medium, which are separated by the sample under analysis. The components used to attach the various parts of the cell as well as the dimensions are represented in detail in Figure 2.

The two chambers of the permeation cell are made up of a glass tube with an inside diameter of 51 mm. The width of the chemical compartment is 22 mm and that of the collector is 35 mm. The sample is placed between the two chambers and a tight seal is ensured using semi-rigid teflon joints having a diameter of 51 mm.

In the exposure chamber, the solvent can be in gaseous or liquid form. In the case of liquids, the exposure

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chamber has an inlet equipped with a plug to prevent evaporation (this case is presented in Figure 2). For gases, the exposure chamber has two connections (an inlet and an outlet) to allow gas circulation.

In the collection chamber, there are two connections (inlet and outlet) to allow circulation of the collecting medium (gas or liquid). The collecting system is connected to the analytical system. The collecting medium (air, water, etc.) must be inert with respect to the material being analyzed. In certain cases, salty water simulating the perspiration of a person wearing a protective glove can be used as a collecting medium.

During permeation measurements, the breakthrough time and the permeation rate can be determined.

5.0 TEST PROCEDURES

Assembly description

To test the resistance of gloves to solvents, an assembly accomodating up to four permeation cells for simultaneous evaluation has been developed. Figure 3 presents a diagram of the assembly used in this study.

The assembly has the following component parts:

a) ASTM 739-85 permeation cells

b) the valve selector

c) the collecting medium

d) the analytical system

a) *The permeation cells:* The cells used in this study were purchased from Pescelab Company in the United States[1].

b) *The valve selector:* A valve selector allows automatic alternate sampling by each permeation cell every 60 seconds.

c) *The collecting medium:* The collecting medium used in our experiments was purified dry air, the flow being set at 100 mL/min and controlled at the input of each cell by means of gas flowmeters.

d) *The analytical system:* The air from the permeation cells is directed to the analytical system by the valve selector. The analytical system is composed of an AID gas chromatograph equipped with a flame ionization detector (FID). The air volume is injected using a 1.0 mL loop. The analytical system is completed by an HP3390-A signal integrator. The data is subsequently transferred to an IBM-PC computer for processing.

6.0 METHOD OF OPERATION

Preparation and conditioning of materials

Each material tested must be made up of either one layer or numerous layers representative of a given protective clothing. In each test, the outside surface of the material is brought into contact with the chemical. The sample must be flat and have a minimum transverse section of 60 mm (a 75 mm diameter circle is an appropriate size).

Before the experiments are carried out, the samples must be maintained at a temperature of 21 ± 3 °C and a relative humidity of 30 to 80 % for a minimum of 24 hours[1].

Permeation measurements

When the sample is placed in the cell (Figure 2), the collecting and analytical systems are started. The air circulating in the collecting chamber is in contact with the inside surface of the sample. When the detector signal has stabilized, the challenge chamber is filled with the chemical which comes into contact with the sample's outside surface. The experiment's starting time (time zero) is considered as being the moment when the cell starts to fill.

A calibration curve has been produced for each solvent. To do this, air samples having chemical concentrations between 0 and 1000 ppm were prepared in Tedlar bags containing a volume of 10 L of air.

Summary of the experimental conditions

Air flow	100 mL/min
Relative humidity	30 - 40 %
Temperature	25 °C
Detector	FID

The gloves evaluated

In this study, different commercially-available gloves from Edmont, Best and Taskall were evaluated. The basic materials were nitrile and neoprene (Table 1). Neoprene having a thickness of 0.41 mm from Dupont was used as a reference material.

The solvents

Thirteen organic solvents recommended in the Standard guide for selection of chemicals to evaluate protective clothing materials (ASTM F1001) were used to evaluate the protective gloves (Table 2)[9].

7.0 RESULTS AND DISCUSSION

Figure 4 shows a typical curve of the data obtained during evaluation of the permeation of protective gloves. This figure represents the solvent vapor concentration crossing the protective membrane as a function of solvent-exposure time. Time zero represents the moment when the solvent is poured into the exposure chamber. The breakthrough time is the time when the first traces of vapor crossing the membrane are detected. Subsequently, the vapor concentration in the collector chamber increases rapidly until it reaches a plateau, which represents the permeation rate in an open loop system. In most of the studies[3, 14], glove permeability is evaluated at an air flow of 500 mL/min. In this study, the flow was set at 100 mL/min in order to increase the sensitivity of the mehtod.

However, this low flow leads to rapid saturation of the FID detector by the chemical's vapors, which in most cases prevented determination of the permeation rate. As a result, only breakthrough times will be reported here.

Tables 3, 4 and 5 present the breakthrough times for the evaluated gloves. Table 3 gives a summary of the breakthrough times for neoprene unsupported gloves. The last column of table 3 represents the breakthrough time for the neoprene reference material. Table 4 gives a summary of breakthrough times for neoprene supported gloves, and Table 5 for nitrile unsupported gloves.

In cases where the breakthrough times for equivalent types of gloves manufactured in the United States are available in the literature, the values are presented in parentheses for comparison purposes. In most cases, the results are observed to be comparable to those found in the literature[4, 7].

In certain cases, a great difference was observed between the breakthrough time reported in the literature and our measurements for the same model of glove. An example is the model 9-922 neoprene glove from Edmont with n-Hexane. According to the literature, this glove has a breakthrough time of 740 minutes, whereas our measurements indicate a breakthrough time of only 63 minutes. Differences such as the composition of the material, its method of manufacture, and the analytical method used for glove evaluation are probable explanations.

Our method's reliability has been checked by repeating the analysis four times for each glove/solvent pair, and in all cases the differences in breakthrough time were found to be less than 5 %.

This type of evaluation is presently being carried out in several laboratories in the United States and in Europe. Two commercially-available data banks have been developed[4, 5] from this information. This data, however limited, is at present the best tool for selecting protective gloves. Considering the large variety of materials used in manufacturing protective gloves, as well as the large number of solvents available (it is estimated that there are more than 1,000,000 pure solvents or mixtures), it would be impossible to evaluate each glove with each solvent even with the collaboration of all laboratories carrying out permeation tests. New solutions must therefore be developed.

Solubility parameters

It has already been mentioned that in permeation phenomenon, the most important stage is solubilization. The solvent in contact with the outside surface of the protective glove must react with the polymeric material before passing through it (diffusion).

With pure polymers, the degree of interaction between a polymer and a solvent can be predicted using solubility parameters[10, 12].

The solubility parameter is an intrinsic property of molecules which can be represented by:

$$\delta = \left[\frac{\Delta E}{V}\right]^{1/2} \quad (1)$$

ΔE and V being the cohesion energy and the molar volume of the molecules.

The greater the similarity between the polymer's and the solvent's δ values, the greater the solubility. In other words, the greater the similarity between the material's and the solvent's solubility parameters, the lower the resistance of the glove to the solvent.

Hansen[11] has developed a theory that considers that solubility is the result of the contribution of the dispersion, polar and hydrogen-bonding forces of each molecule. Consequently, the solubility parameter could be represented in the following way:

$$\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \quad (2)$$

δ_t = total solubility
δ_d = solubility due to dispersion forces
δ_p = solubility due to polar forces
δ_h = solubility due to hydrogen bonds

The degree of interaction between the chemical and the polymer material could be evaluated using this theory by the following equation:

$$A = \left[4 (\delta_d^p - \delta_d^s)^2 + (\delta_p^p - \delta_p^s)^2 + (\delta_h^p - \delta_h^s)^2 \right]^{1/2} \quad (3)$$

where indices P and S represent the polymer material and the solvent respectively.

Values of the solubility parameters for solvents[12] and polymer materials[2, 13] are available in the literature.

This approach could be very useful in the selection of protective gloves having the most resistant materials. For applied testing of the theory's validity, Table 6 presents the solubility parameters for the protective glove materials evaluated in this study as well as for the solvents used. In Tables 7 and 8, a comparison is made between our breakthrough time results and the A values calculated using equation 3.

By comparing the experimental values and the A values, we found that in most cases there was very good correlation.

Materials whose solubility parameters are close to those of the solvent are materials least resistant to the solvent. An example is neoprene gloves with dichloromethane (A = 1.1), and tetrachloroethylene (A = 1.0) (Table 7). Permeation measurements confirm that neoprene gloves are not resistant to these solvents, but are more resistant to hexane (A = 5.4) (Table 7).

In other cases, despite the fact that the theory predicts that a material is not resistant to a solvent, permeation measurements show the opposite. For example, the breakthrough times for neoprene gloves obtained with nitrobenzene (Table 3) are higher than the values obtained for the same material with n-hexane, in spite of the fact that the calculated values of A are 1.8 and 5.4 respectively. The probable reason is that the analytical method used to detect nitrobenzene is not adequate because of its high boiling point.

In summary, we can state that the solubility theory could be used to predict the resistance of gloves to solvents. This approach could be used in selecting materials which are theoretically resistant to solvents. However, this potential resistance would have to be confirmed by laboratory tests. This procedure would have the advantage of limiting the number of tests to be carried out. In addition, the solubility theory can be just as useful in researching and developing materials that are more resistant to solvents.

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TABLE 1: GLOVES TESTED

NEOPRENE

Unsupported Gloves

Manufacturer	Model	Thickness (mm)
Best	723	0.46
Edmont	29-865	0.48
Taskall	1119	0.49
Taskall	1126	0.73
Reference material from Dupont	-	0.41

Supported Gloves

Best	32	
	6780	
Edmont	9-922	
	8-352	
	19-934	

NITRILE

Unsupported Gloves

Best	730	0.48
Edmont	37-155	0.37
	37-165	0.60

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TABLE 2: CHALLENGE SOLVENTS

		Detection Limit µg/mL
1. Acetone	Fisher certified A.C.S.	0.0024
2. Acetonitrile	Fisher HPLC grade	0.0080
3. Carbon Disulfide	Fisher certified spectroanalyzed	0.0090
4. Dichloromethane	Baker analyzed HPLC	0.0070
5. Diethylamine	Fisher reagent grade	0.029
6. Dimethylformamide	Baker analyzed reagent	0.029
7. Ethyl Acetate	Baker HPLC	0.010
8. n-Hexane	Fisher Reagent grade	0.0018
9. Methanol	Fisher HPLC	0.0070
10. Nitrobenzene	BDH reagent	0.12
11. Tetrachloroethylene	Baker analyzed reagent	0.019
12. Tetrahydrofuran	Fisher certified spectro analyzer	0.012
13. Toluene	Baker analyzed reagent	0.0060

TABLE 3: BREAKTHROUGH TIME (min) FOR NEOPRENE UNSUPPORTED GLOVES

Gloves	Best 723	Edmont 29-865	Taskall 1119	Taskall 1126	Ref. Material from Dupont
Thickness (mm)	0,46	0.48	0.49	0.73	0.41
Solvent					
Acetone	17	17	20	46	14 *
Acetonitrile	23	31	49	101	21
Carbon Disulfide	5 *	3 *	5 *	8 *	4 *
Dichloromethane	5 *	4 *	6 *	8 *	3 *
Diethylamine	9 *	6 *	14 *	26 *	2 *
Dimethylformamide	37	39	66	92	35
Ethyl Acetate	10 *	12 *	21 *	40 *	7 *
n-Hexane	21	44	71	164	14
Methanol	48	85	106	225	36
Nitrobenzene	40 *	35 *	110 *	-	22 *
Tetrachloroethylene	9 *	13 *	19 *	41 *	7 *
Tetrahydrofuran	5 *	7 *	14 *	18 *	4 *
Toluene	8 *	8 *	11 *	12 *	5 *

*Degradation

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TABLE 4: BREAKTHROUGH TIME (min) FOR NEOPRENE SUPPORTED GLOVES

Fabricant	Best		Edmont		
Gloves **Solvent**	32	6780	9 - 922	8 - 352	19 - 934
Acetone	13 *	12 *	12(10) *	3 *	28 *
Acetonitrile	31	46	61(90)	45	121
Carbon Disulfide	5 *	8 *	4 *	4 *	7 *
Dichloromethane	2 *	3 *	2 *	2 *	2 *
Diethylamine	8 *	14 *	6 *	2 *	26 *
Dimethylformamide	29	53	79(60)	47	138
Ethyl Acetate	20 *	16 *	22(20) *	4 *	22 *
n-Hexane	20	24	63(90)	18	88
Methanol	65	93	100(15)	60	182
Tetrachloroethylene	10 *	20 *	14 *	8 *	26 *
Tetrahydrofuran	2 *	6 *	2 *	2 *	10 *
Toluene	8 *	8 *	19 *	12 *	16 *

* Degradation

TABLE 5: BREAKTHROUGH TIME (min) FOR NITRILE UNSUPPORTED GLOVES

Fabricant	Best	Edmont	
Gloves	730	37 - 155	37 - 165
Thickness (mm)	0.48	0.37	0.60
Acetone	9 *	9 *	15 *
Acetonitrile	10 *	13	25
Carbon Disulfide	14	21	36
Dichloromethane	2 *	2 *	2 *
Diethylamine	14	30	65
Dimethylformamide	19	16	33
Ethyl Acetate	10	17	40
n-Hexane	6H	6H	6H
Methanol	34	69	93
Tetrachloroethylene	120	270	360
Tetrahydrofuran	8 *	8 *	9 *
Toluene	11 *	15 *	26 *

* Degradation

TABLE 6: SOLUBILITY PARAMETERS FOR SOLVENTS AND POLYMER MATERIALS

Solvent	δ_d	δ_p	δ_h
Acetone	7.6	5.1	3.4
Acetonitrile	7.5	8.8	3.0
Carbon Disulfide	10.0	0.0	0.3
Dichloromethane	9.0	3.1	2.7
Diethylamine	7.3	1.1	3.0
Dimethylformamide	8.5	6.7	5.5
Ethyl Acetate	7.7	2.6	3.5
n-Hexane	7.3	0.0	0.0
Methanol	7.4	6.0	10.9
Nitrobenzene	9.8	4.2	2.0
Tetrachloroethylene	9.3	3.2	1.4
Tetrahydrofuran	8.2	2.8	3.9
Toluene	8.8	0.7	1.0

Polymer			
Neoprene	9.4	2.6	2.2
Nitrile	9.4	5.2	3.1

TABLE 7: COMPARISON BETWEEN BREAKTHROUGH TIMES OF A NEOPRENE MATERIAL (FROM DUPONT) AND A VALUES

| Breakthrough time (min.)		A values (eq. 3)	
Methanol	36	Methanol	10.2
Dimethylformamide	35	Acetronitrile	7.3
Acetonitrile	21	Dimethylformamide	5.6
n-Hexane	14	n-Hexane	5.4
Acetone	14	Acetone	4.5
Ethyl Acetate	7 *	Diethylamine	4.5
Tetrachloroethylene	7 *	Ethyl Acetate	4.5
Diethylamine	2 *	Carbon Disulfide	3.4
Tetrahydrofuran	4 *	Tetrahydrofuran	2.9
Toluene	5 *	Toluene	2.5
Dichloromethane	3 *	Nitrobenzene	1.8
Carbon Disulfide	4 *	Dichloromethane	1.1
Nitrobenzene*	22 *	Tetrachloroethylene	1.0

* Degradation

I R S S T

**TABLE 8: COMPARISON BETWEEN BREAKTHROUGH TIMES OF A NITRILE GLOVE MATERIAL (EDMONT 37-155) AND A VALUES**

Breakthrough time (min.)		A values (eq. 3)	
n-Hexane	360	Methanol	8.8
Tetrachloroethylene	270	n-Hexane	7.4
Methanol	69	Carbon Disulfide	6.0
Diethylamine	30	Diethylamine	5.9
Carbon Disulfide	21	Acetonitrile	5.2
Dimethylformamide	16	Toluene	5.1
Ethyl Acetate	17	Ethyl Acetate	4.3
Acetone	9	Acetone	3.6
Tetrahydrofuran	8	Tetrahydrofuran	3.5
Dichloromethane	2	Dimethylformamide	3.4
Toluene	15	Tetrachloroethylene	2.6
Acetonitrile	13	Dichloromethane	2.3
Nitrobenzene (NT)	-	Nitrobenzene	1.7

(NT) = Not tested

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FIGURE 1: SCHEMATIC REPRESENTATION OF THE PERMEATION PHENOMENON IN A POLYMERIC MATERIAL
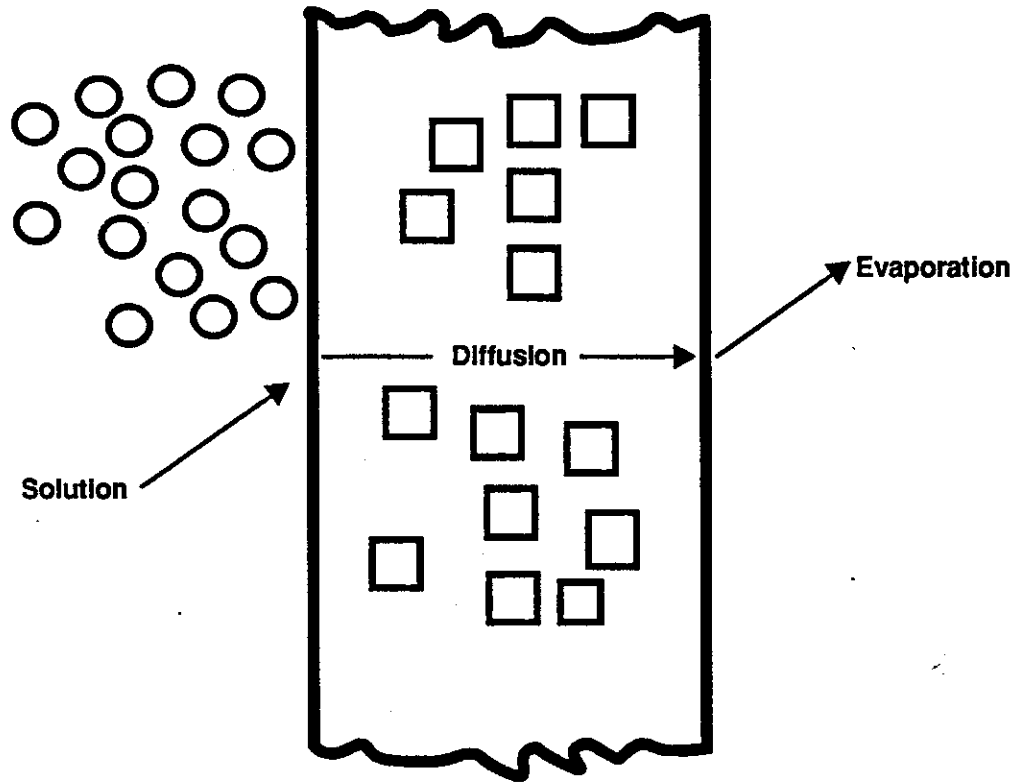
FIGURE 2: STANDARD ASTM 739 PERMEATION CELL
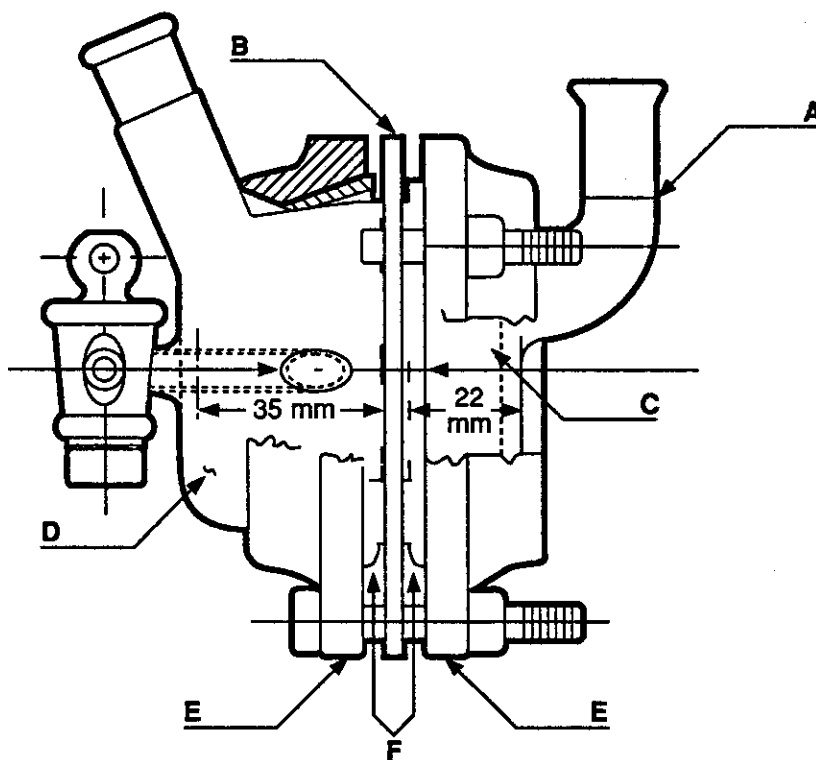
A = Fill level
B = Sample material
C = Challenge chamber
D = Collecting medium chamber
E = Aluminum flanges
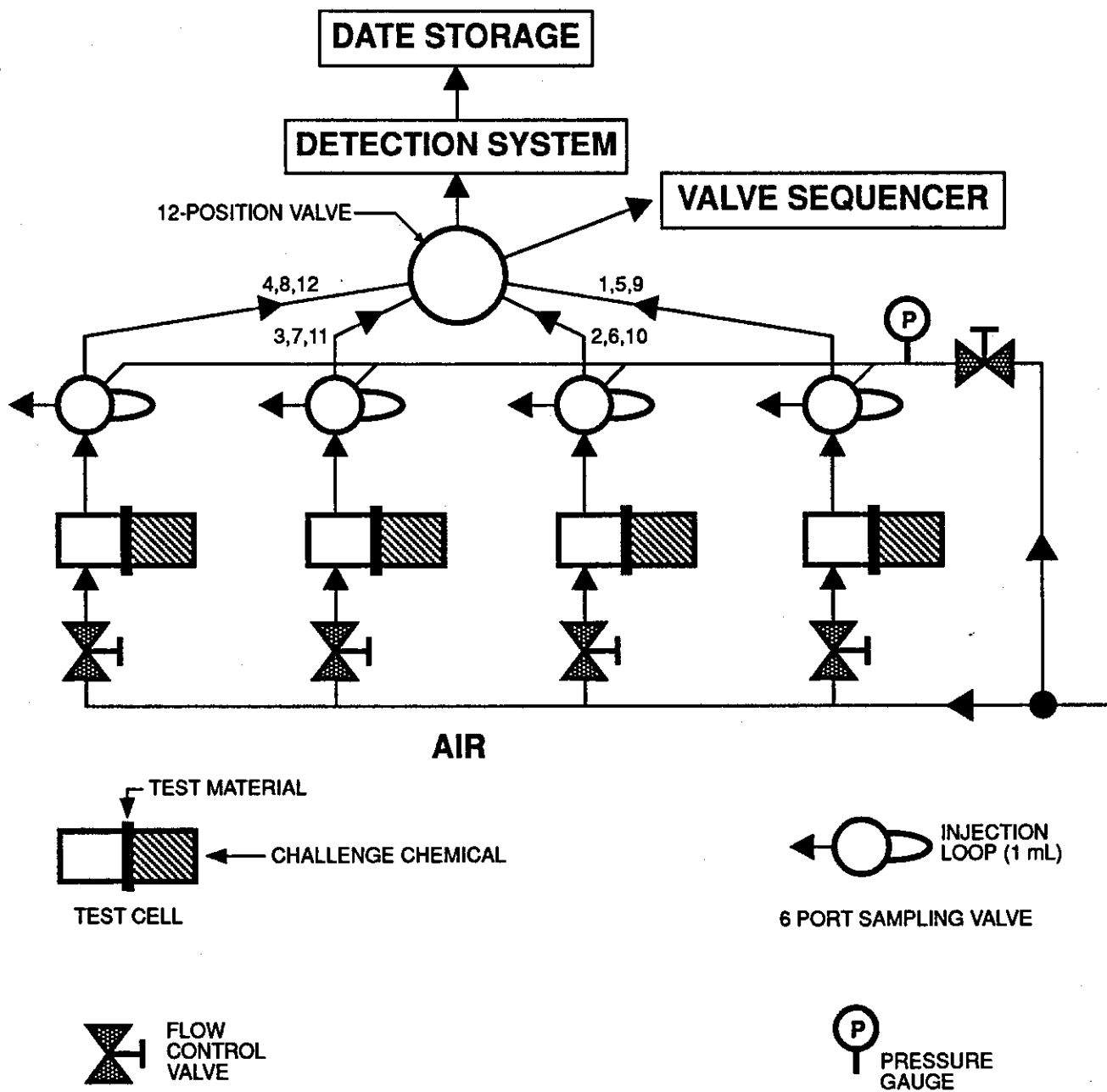F = Material specimen holder (in Teflon)

FIGURE 3: AUTOMATED OPEN-LOOP PERMEATION SYSTEM

FIGURE 4: TYPICAL PERMEATION CURVE IN A OPEN LOOP SYSTEM