Film Permeability Determination Using Static Permeability Cells

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Introduction

The permeability of a plastic film to a gaseous compound depends on the nature of the film, the property of the chemicals, and environmental conditions. There are several terms that can be used to describe the permeability of a film to a compound, including flux, diffusion coefficient, and mass transfer coefficient (MTC). Flux and diffusion rate depend on the concentration gradient across the film. Mass transfer coefficient, however, is considered to be independent of the concentration gradient and dependent only on the properties of the film and the chemical, in addition to environmental conditions, such as temperature. Mass transfer coefficient is therefore a good parameter to represent the permeability of the film to a specific compound.

The method described here is a static technique used at EPA to determine the MTC. This method is adapted from the technique previously developed by Sharon Papiernik and Scott Yates of Agricultural Research Service (ARS), U.S. Department of Agriculture (USDA) at Riverside, CA (Papiernik et al., 2001, 2002). The testing apparatus consists of an airtight cylinder constructed from two stainless steel caps (chambers) separated by the test film. Test compounds are introduced into the chamber on one side of the film (source chamber) and the concentrations of the test compounds from both sides of the film (source and receiving chambers) are monitored over time by analyzing the vapor in each chamber. The rate of change in the concentrations over time is used to calculate the MTC. A detailed description of the technique and mathematical reasoning relating to the change of concentrations over time and calculation of the MTC can be found in Papiernik et al. (2001, 2002). The MTC is measured at the standard temperature of 25^{o}C in our laboratory unless otherwise specified.

Apparatus

Permeability cell: Stainless steel, ¼ inch thick, 5 inch diameter pipe cut to form 4 cm high cylinders. Each cylinder is welded at one end to a flat steel plate. Two holes

are drilled and threaded on the side of each cylinder (approximately in the middle, opposite to each other) for the installation of 1/16 inch steel (or brass) union connectors. The open end of the pipe is trued and smoothed. A Teflon on/off valve (Applied Separations, Cat. #2406, or equivalent) is screwed on to the union to allow sample introduction or removal (Fig. 1). A stainless steel two-way valve (Swagelok SS-S41GS1, 1/16") may be used as well. The stainless steel valve is screwed directly in the drilled hole. The valves are closed during testing and are used for placing fumigants into the cells and the periodic sampling during the test. Alternatively, a Swagelok cap and a septum can be installed onto the 1/16 inch union in place of the valve. Samples can be collected with a syringe by piercing through the septum.

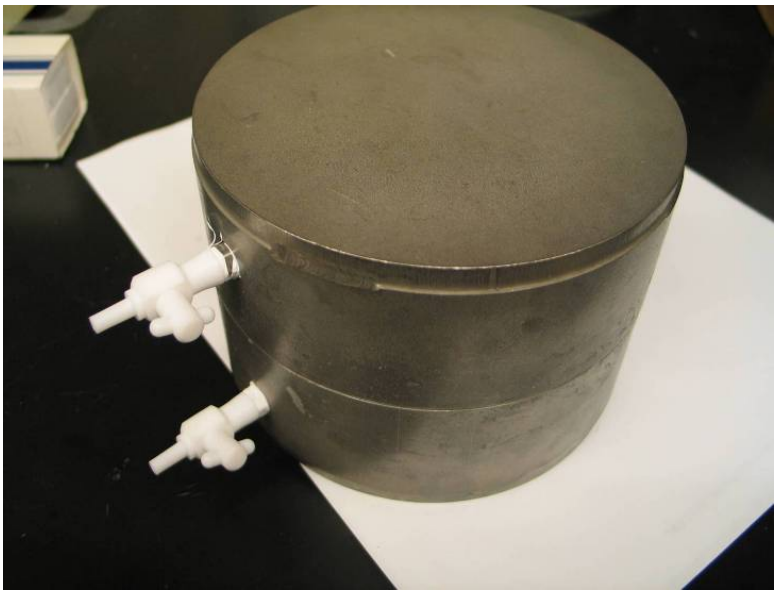

Fig. 1. A picture of the testing apparatus showing the two halves of the permeability cell placed together, and showing placement of the valves. Not shown - valves are also placed on opposite sides of each half.

Fumigant mixing chamber: 1 L glass gas-tight container with valves on both ends and a side sampling port. Other types of gas-tight containers with sampling port may be used. If a clear glass container is used, it is recommended that the glass container be wrapped with aluminum foil to protect the fumigants from light. Some fumigants are photo-degradable.

Adjustable pipette or syringe: 100 µL capacity.

Assortment of gas-tight syringes: from 10 µL to 50 mL in capacity.

Tedlar bag: 0.6 L capacity with sampling port.

Gas chromatograph headspace autosampler vials, caps, crimpers: 10 mL vials or other appropriate gas sample vials.

Two-parts epoxy glue (e.g. Loctite 5 min epoxy glue): To glue the films and the two halves of the permeability cells together.

Aluminum adhesive tape (e.g. Nashua 324A cold weather aluminum tape): To reinforce the sealed joint of the glued permeability cells.

Constant-temperature environmental chamber: To maintain constant temperature for conducting the permeability testing.

Gas chromatograph/mass spectrometer with headspace autosampler (e.g. Agilent 6890 GC/5973 MSD with G1888 headspace sampler): Equipped with 30 m X 0.25 mm DB 624 capillary column, 1.4 μm film thickness. A GC with electron capture detector (ECD) can be used for the analysis of halogenated fumigants, such as methyl bromide, iodomethane, chloropicrin, 1,3-dichloropropene.

Chemicals

Iodomethane, 1,3-dichloropropene (mixture of *cis* and *trans* isomers), dimethyl disulfide, methyl isothiocyanate (transformation product of metam sodium during fumigation) (source: Sigma-Aldrich), chloropicrin (source: Arysta LifeScience), methyl bromide (source: Chemtura Corp) and sulfuryl fluoride (source: Dow Chemical).

Procedures

1. **Permeability cells**

1.1. Cut the films to be tested to approximately 6 X 6 inch pieces.

1.2. Mix a small amount of the two parts (resin and hardener) epoxy glue. Spread a thin layer of the mixed epoxy glue over the rim of the open edge of the permeability cells using a flat stainless steel spatula. Place the cut film to be tested on to one half-cell over the glue. Make sure the film is spread flat and evenly (not stretched and no crevices). Place the other half-cell over the film and the two halves of cells should be aligned and joined together by the glue to form a gas tight seal.

1.3. After the glue is cured (usually overnight), trim the excess film with a razor blade. Apply aluminum tape to the outside of the cells over the seam to provide additional support and sealing of the apparatus. Place the constructed cells inside the temperature-controlled environmental chamber and equilibrate for a minimum of 30 minutes before introducing the fumigants.

2. Fumigant mixture preparation

2.1. Transfer a small amount of the solid fumigant (e.g. methyl isothiocyanate) (about 20-50 mg) into the 1 L glass chamber.

2.2. Transfer about 20-50 μL of each liquid fumigant standard into the 1 L glass mixing chamber using a pipette (e.g. Eppendorf) or syringe.

2.3. For gaseous fumigants (e.g. MeBr and sulfuryl fluoride), transfer a small amount (about 100-500 mL volume) of each gas from the compressed gas cylinder into a Tedlar bag via a small piece of copper tubing. The transferring line is made of short (about 3 inches long) 1/8" copper tubing connected to the tank valve, a valve placed at the end of the copper tubing and a piece of Tygon tubing attached to the valve (Fig. 2). A syringe needle is attached to the end of the Tygon tubing. To transfer the gaseous fumigants from compressed tanks, all the valves are closed first. The tank valve is opened briefly to release some fumigant into the copper tubing. The needle at the end of the Tygon tubing is inserted through the septa into the Tedlar bag. The valve at the end of the copper tubing is then slowly opened to release the fumigant into the Tedlar bag. Do not open the valve fully or quickly.

2.4. Withdraw about 30 mL of the collected gaseous compounds from the Tedlar bag with a gas-tight syringe and place it into the 1 L mixing chamber.

Methyl bromide and sulfuryl fluoride diffuse through the Tedlar bag and degrade over time and therefore cannot be stored in a Tedlar bag for a long time. Some fumigants, such as chloropicrin, 1,3-dichloropropene, methyl isothiocyanate, are photosensitive and degrade quickly when exposed to light. Exposure of the containers containing fumigants to light should be kept at a minimum. The fumigants are left in the mixing chamber for a minimum of 30 minutes to equilibrate before using.

Fig. 2. A picture showing the transfer line (including the fumigant tank, copper tubing, valve, Tygon tubing, and syringe needle). A Tedlar bag and a 1 L glass mixing chamber are also shown in the picture.

Table 1. Example of the amount of fumigants present in the 1 L mixing chamber

Fumigant	Amount of Neat Material in Chamber	Estimated Concentration in Chamber (µg/mL of air)
Sulfuryl fluoride (SF)	30 mL of gas (from Tedlar bag)	129 µg/mL
Methyl bromide (MeBr)	30 mL of gas (from Tedlar bag)	119 µg/mL
Iodomethane (IOM)	20 µL	45.6 µg/mL
Chloropicrin (PIC)	20 µL	33.2 µg/mL
Dimethyl disulfide (DMDS)	20 µL	21.2 µg/mL
Methyl isothiocyanate (MITC)	20 mg*	20 µg/mL*
1,3-Dichloropropene (1,3-D)	40 µL	22 µg/mL (each isomer)

* Concentration of MITC is an example and is adjusted according to the actual weight when making instrument calibration standards.

The estimated concentration of each fumigant, expressed as µg/mL, in the 1 L glass chamber in Table 1 is calculated based on the assumption that the entire amount of each fumigant (20 µL for liquids, 30 mL for gases, and 20 mg for solid) has completely evaporated in the chamber and the resultant gases are well mixed. The mixing chamber may be placed in a warm place (e.g., 40^{o}C oven) to facilitate the vaporization of the

fumigants. With this assumption, the estimated concentration of each fumigant in the vapor phase is calculated based on the amount added (wt) of each compound divided by the chamber volume (1 L). Since complete vaporization and mixing within the chamber cannot be verified, the final chamber concentrations are estimates.

After the linear range of the analytical instrument is established, quantitative transferring of the fumigant vapor to the permeability cells is not required. Excessive amount of the fumigants may be transferred to the mixing chamber to provide a saturated vapor. The amount of each fumigant transferred to the mixing chamber and the subsequent transferring of the fumigant vapor to the permeability testing cells can vary, as long as a sufficient amount was present in the permeability cell for instrument analysis. If ECD is used for halogenated compound analysis, the amount of each fumigant added to the mixing chamber may need to be adjusted to avoid exceeding the detector's signal limit.

3. Introducing and sampling fumigants from permeability cells

3.1 Withdraw approximately 30-40 mL volume of the vapor from the 1 L mixing chamber using a gas tight syringe and inject the vapor into the source side (typically the bottom chamber) of each permeability cell and immediately close the valve (the receiving chamber's valve should also be closed before introducing fumigants). If septum/cap is used in the cell construction, the venting valve should be opened to avoid pressurizing the cells. If an on/off valve is used, the excess air/vapor will escape around the needle and opening of the venting valve is not necessary. The amount of the vapor injected into the permeability cells may be adjusted to obtain sufficient amount of compounds in the cells to be analyzed if instrument sensitivity is a concern. Generally, triplicate permeability cells are constructed for each test film and the MTC is calculated for each replicate and the average of the triplicates is reported.

3.2. At the appropriate sampling interval, withdraw 250 µL gas samples from each receiving and source chamber of the permeability cell using a gas-tight syringe. Follow one of the extraction procedures below:

(a) Inject each collected gas sample into the bottom of a 10-mL headspace autosampler vial. Close the vials immediately using crimped-cap aluminum caps with Teflon-faced butyl rubber septa.

(b) Inject each collected gas sample into the bottom of a GC vial or 10-mL headspace vial filled with approximately 2 mL of hexane. Close the vials immediately using crimped-cap aluminum caps with Teflon-faced butyl rubber septa.

3.3. Periodic sampling begins 5 minutes after placement of the fumigants in the source cells and continues for a period of up to 10 days depending on film type. For high permeability films, a sampling schedule of 5 min, 15 min, 30 min, 1 h, 2 h, 3 h, 4 h, 6 h and 8 h may be used. For low permeability films, longer sampling intervals may be used, for example 5 min, 1 h, 4 h, 8 h, 24 h, 48h, 72h, etc. Low permeability films may require 10 or more days to allow measureable amounts of compounds to permeate through the films and generate enough data points for the mass transfer coefficient calculation. The purpose of frequent sampling is to obtain sufficient data points, particularly at the beginning of the experiment, when the concentration change is the largest, to calculate MTC reliably.

3.4. After testing is complete, move the permeability cells to the fume hood and open the valves to allow fumigants to escape. Disassemble the cells and use a razor blade to scrape the epoxy glue from the cells. A hot-air blower, such as a high heat hair dryer, may be used to heat the epoxy glue to facilitate the removal of epoxy glue from the cells.

4. Sample analysis

4.1. Collected samples are analyzed using a gas chromatograph/mass spectrometer (GC/MSD) with a headspace autosampler. A GC/ECD can also be used in place of GC/MSD for the halogenated compounds. A standard liquid autosampler may be used for sample injection if solvent is used in GC vials (instead of a headspace autosampler, Section 3.1(b)).

The headspace autosampler's initial conditions typically are:
Oven temperature 80^{o}C, loop temperature 90°C, transfer line temperature 100^{o}C, equilibration time 3 min, carrier gas pressure 10 psi, and vial pressure 14 psi.

Suggested GC conditions are:
DB-624 column (30 m X 0.25 mm ID, 1.4 μm film thickness);

Helium carrier gas,	1.2 mL/min.
GC oven temperature	40^{o}C, hold for 3 min.
	50^{o}C, 10^{o}C/min, hold for 10 min.
	110^{o}C, 20^{o}C/min

Mass spectrometer is operated in select ion mode (SIM). The ions monitored are listed in Table 2. Instrument response of the primary ion is used for quantitation, while secondary ions are monitored for analyte confirmation, or in case there is interference with the primary ion.

Table 2. Ions monitored in the GC/MS analysis

Fumigant	Retention time (min)	Primary ion (m/z)	Secondary Ions (m/z)
SF	1.5	102	83, 67
MeBr	2.3	94	96, 79
IOM	3.6	142	127, 141
cis-1,3-D	14.2	75	39, 110
DMDS	14.3	94	79, 45
MITC	16.0	73	45, 72
PIC	16.6	117	119, 82
trans-1,3-D	16.7	75	39, 110

4.2. Fumigant Quantitation.

Linearity of instrument response for each fumigant is demonstrated by injecting fumigant mixtures at varying concentrations into the instrument. The fumigant standard mixtures are prepared by injecting various volumes of the vapor drawn from the 1 L mixing chamber (see "Fumigant mixture preparation" above) into autosampler vials (e.g. 5 µL, 10 µL, 20 µL, 50 µL, 100 µL, 500 µL). The fumigant concentrations in the autosampler vials are estimated using the values in Table 1 and the volume of the standard mixture placed in the vial.

The concentration of fumigant in a cell chamber during a test is calculated by comparing the instrument response found with the instrument calibration curve established with the fumigant standard mixtures. The calculated standard concentrations must be considered as estimates due to the limitations described above ("Fumigant mixture preparation").

5. Data Analysis

The instrument peak area (response) or the estimated concentration of each fumigant, and the sampling time are used to calculate the MTCs using the Film Permeability Calculator (FilmPC v1.0.2), the permeability calculation software developed and provided by Scott Yates of ARS, USDA at Riverside, CA. Because of the data input requirements of the Film Permeability Calculator, the analytical results of each film need to be organized in a precise fashion to efficiently perform the MTC calculation. A Microsoft Excel template was constructed to facilitate the retrieval and organization of the needed instrument-generated data into a format that can be used to input the analytical results into the Film Permeability Calculator. The instrument-generated data from all the

sampling periods for each film for all fumigants are exported to the Excel template and the data retrieval and organization are automatically performed in this template. The organized data are then collectively input into the Film Permeability Calculator in one step. This Excel spreadsheet transformation of the raw data eliminates the need to manually input the individual response (or concentration) values into the Film Permeability Calculator. Detailed description of the Microsoft Excel template and the instruction on how to use the template are available upon request.

The instrument peak response (or estimated concentration) at each sampling interval may also be normalized relative to the amount present at the initial sampling, and these normalized values may be used for the MTC calculation. Normalizing the instrument peak response (or estimated concentration) will display the Y-scale of the graphic output of the Film Permeability Calculator in an easy-to-read format. The percent recovery of each compound at each sampling interval relative to the total amount present at the initial sampling (e.g. 5 min) is used to monitor the integrity of the permeability cell and possible loss of the compounds during sampling and analysis. This information is generated by the template automatically. An example of the recovery of each fumigant from the permeability cell at multiple sampling times is shown in Fig. 3. When low recovery is encountered due to a leak in the cell or loss during sampling and analysis, the calculated MTC is flagged or excluded.

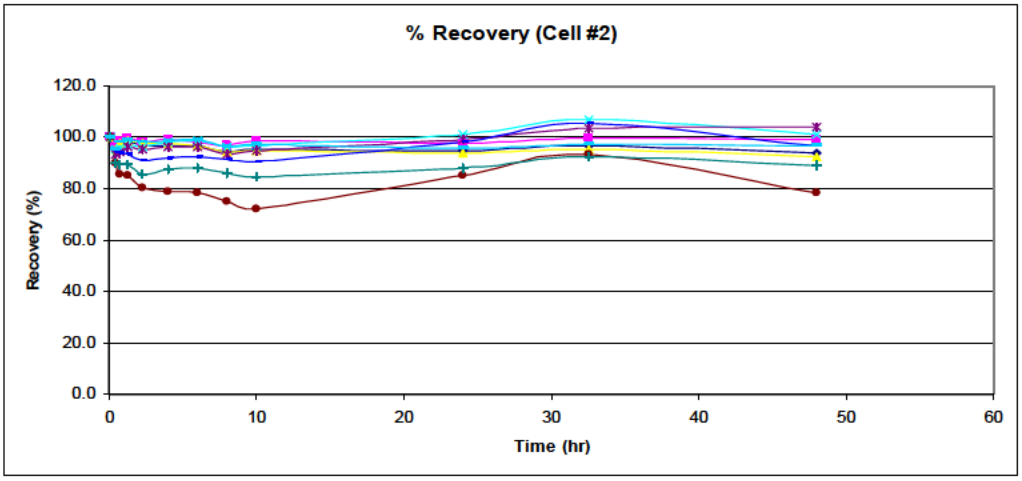

Fig 3. An example of the recoveries of various fumigants from the permeability cell monitored over time. The recoveries represent total amount present in both chambers relative to the amount present at the initial 5 min sampling.

The Film Permeability Calculator will calculate MTC based on the required data input of 1) sampling time (in hours), 2) amount of fumigant in the source chamber, and 3) amount of fumigant in the receiving chamber of the permeability cell. The default of the Film Permeability Calculator is to exclude α and k_p values. However, these two

parameters may be included if the curve fitting is not symmetrical and data points do not follow expected trend. The MTC calculation may be re-run with different values of these terms. The output of the film Permeability Calculator includes the MTC (*h*, cm/hr), the 95% confidence limits of the calculated MTC, and associated statistical parameters. An example of the graphic output of an MTC calculation is shown in Fig. 4 with the measured data points and fitted curves shown.

References

(1) S.K. Papiernik, S.R. Yates, and J. Gan (2001) An approach for estimating the permeability of agricultural films. *Environ. Sci. Technol*., 35, 1240-1246.

(2) S.K. Papiernik, F.F. Ernst, and S.R. Yates (2002) An apparatus for measuring the gas permeability of films. *J. Environ. Qual*., 31, 358-361.

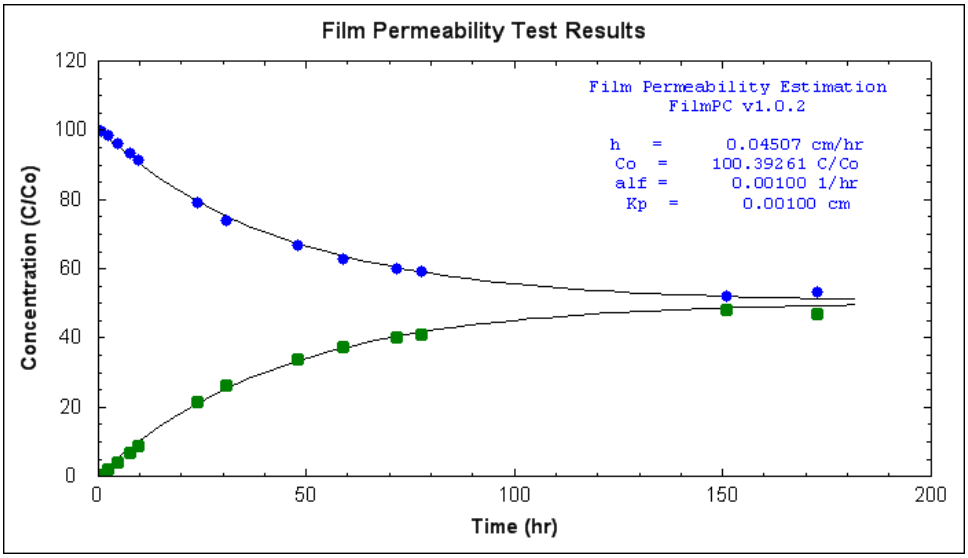

Fig. 4. An example of the Film Permeability Calculator graphic output.