Flavor and Aroma Permeation Concepts and Applications

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Abstract

In this paper, permeation of aromas and flavors through plastic packaging materials is discussed. The importance of understanding aroma and flavor transmission is explained by examples. Aroma and flavor barrier measurement is contrasted with the measurement of O_2, water vapor and CO_2 barriers. Criteria for a measurement system are outlined. Permeation measurement is divided into the actual techniques for accomplishing the permeation and detecting the level of permeation.   The isostatic, quasi-isostatic and sorption / gravimetric permeation methods are compared. Detection methods described and compared are FID, GC/FID, weight, MS, GC/MS, TIR, manometry and PID. Combined detection methods are also discussed.   To effectively meet the criteria, it is concluded that a diffusion cell permeation method with a combined detector is probably the best current option.

Introduction

Permeation of small molecules through packaging materials is a key element of designing packages. Oxygen, water vapor, carbon dioxide, flavors and aromas can all move through polymeric packaging, altering the flavor and quality of foods, beverages and other products. Thus, measurement of the transport of these molecules through packaging materials is an important task within the industry.

Importance of Flavor and Aroma Barrier Testing

Preservation of important sensory qualities of foods is a main focus for designing barrier materials. If the natural flavor and aroma of foods can be preserved longer, then these attributes will not need to be artificially added to make up for their loss during transport and storage. The transition from inert materials such as glass to materials such as plastics has generated much research regarding the interactions of flavors and aromas with polymeric materials.

A good example is when the orange juice industry moved from glass containers to the aseptic drink box. Limonene is the compound responsible for providing citrus juices with their characteristic flavor. However, Manheim et al., (1) reported that limonene was scalped by polyethylene, a common inside layer of aseptic drink boxes. This reduced the shelf life of the juice due to loss of the flavor intensity compared to glass bottles. Besides affecting flavor, limonene sorption into the container wall can also plasticize the LDPE, affecting modulus of elasticity, tensile strength, seal strength and oxygen permeability (2). Therefore, understanding the interaction of this single compound with polymers can lead to a better understanding of how it not only affects the quality of the food but also the physical and chemical properties of the package.

The mechanisms of release of materials, such as antioxidants or aroma compounds, from packages are also important to understand. Miltz et al., (3) studied the diffusion coefficients of BHA and BHT in HDPE for oatmeal cereal and determined that a higher level of antioxidant in the film was necessary due to absorption by the cereal and evaporation of the antioxidants from the package. In another study involving release of aroma compound inclusions held in a beta-cyclodextrin complex, relative humidity (RH) as well as interaction between compounds was found to affect the release of the aroma compounds (4). Specifically, at higher RH (80%), pinene concentration was found to be higher in the GC sample headspace than it was at lower RH (30 and 60%). Also, limonene suppressed release of pinene at 80%RH and limonene release itself was slower than pinene at 80% RH. Overall, the study demonstrated a clear relationship between water equilibrium and release from cyclodextrin. These studies illustrate the complexity of measuring release of compounds from materials.

Foods are not the only products needing flavor and aroma barrier. Household products and health and beauty care products also need protection because of the high cost of many of the aroma compounds used in these products.

How many of you have walked down the soap and detergent aisle and noticed the strong odor emitting from many of the products/packages?

Consumer acceptance isn't the only reason to be concerned about permeation, sorption and migration. Product safety is even more important, particularly as it relates to issues covered by FDA regulations. Solvents from gloss coatings used on labels can migrate through a label, into a bottle and into products intended for ingestion or application to the human body. Benzophenone is a FDA regulated carcinogen that can be found in a variety of lacquer formulations. Littlejohn, (5) found that PET bottle samples did not absorb benzophenone from lacquers while PP absorbed less than HDPE. LDPE bottles absorbed more benzophenone than all of the other bottle samples.

While it is understood that aroma and flavor permeability measurement is important, selection of an appropriate technique to make these measurements that reflects the real-world is difficult.

Contrasting Gas, Water Vapor and Aroma/Flavor Permeability

The techniques for measurement of permeability of oxygen (O_2) and water vapor are well established, and these properties are routinely reported on the data sheets of many commercially available films. Carbon dioxide (CO_2) permeation, which has always been important for carbonated beverages, increased in importance since the mid 1990's with the advent of mass-produced pre-cut salads. Thus, CO_2 permeation is also pretty well understood and established. Permeability data of these permeants are available or readily measurable for most commonly used packaging polymers. While there may be inconsistency regarding the conditions (humidity and temperature) used for the measurement, it is important to note that there is a general industry consensus about the techniques and equipment used to measure permeability of these permeants.

Another important point to consider is that the equipment used to measure permeability of oxygen, water vapor and carbon dioxide is not flexible. One cannot measure oxygen transmission (O_2TR) on a machine designed to measure water vapor transmission, nor can one measure water vapor transmission (WVTR) on a machine designed for oxygen. It is common for companies and universities involved in barrier measurement to have machines for measuring O2TR, machines for measuring WVTR and if needed, a machine or two for measurement of carbon dioxide transmission.

Imagine if we chose to follow this approach for flavor and aroma barrier. Most product flavors are combinations of many compounds. Visualize a large room with a bank of 400 or 500 barrier testing machines, each one designed for a different constituent compound of a complex flavor such as that for coffee. The capital cost would be prohibitive for such a set-up.

This is probably the most significant hurdle we face in measurement of aroma and flavor barrier measurement--finding a system that will analyze permeation for the myriad of flavors and aromas used.

Additionally, there is a very real likelihood of interaction in the "co-diffusion" of the compounds within a flavor. Will one compound affect the sorption and diffusion of another? If so, would it increase or retard diffusion? The possibility of diffusion interactions must at least be considered, so this adds complexity to aroma / flavor transmission measurement.

It is the opinion of the authors that there is not a consensus in the industry regarding the method of measurement of flavor and aroma barrier. This is not unexpected because of the complexity and difficulty of measurement of aroma and flavor barrier. A number of articles regarding this topic have been surveyed as a part of research for a more detailed review article. The good news is that people in industry and academia are working to resolve this issue. In the process of doing this, many attempts have been made, and a lot of data has been generated, especially for common flavors such a limonene.

Criteria for a Measurement System

This paper will look at various measurement systems and comment on their applicability and ease of use. In order to do this, some criteria for the system need to be established. The authors suggest that a good measurement system should:

1. Be reflective of what happens to permeants and permeates in reality, and should be grounded in scientific principles.
2. Allow acquisition of permeation data for individual permeants
3. Allow for the ability to study interactions of multiple permeants
4. Be timely with results
5. Be able to find both the diffusion and solubility coefficients
6. Be reproducible, reliable, reasonably easy to operate and reasonably cost-effective.
7. Be sufficiently precise

Hernandez et al. (6) reported that there are three practical measurement systems for flavor / aroma barrier measurement: iso-static, quasi-isostatic and gravimetric. Miller and Krochta (7) call these methods continuous flow, constant-volume and gravimetric / direct uptake, respectively. Each of these methods has advantages and disadvantages.

Most of the diffusion systems found in this literature search can be fit into one of these three methods. However, this classification really only describes the method used to get the permeant into and through the permeate. Even then, the classification is not really sufficient to describe the techniques, because within each of these is the additional question of whether the system is set up to use adjustable concentrations or if it set up to do saturation vapor pressure permeation.

Another significant, and perhaps more important, difference in the methods found in the literature, and an important difference to the criteria above, is the detection method used to identify the quantity of permeant, and in some cases, to also identify the permeant. The criteria above can only be satisfied with the presence of both a diffusion system and a detection system.

Permeation Methods

Both the isostatic and the quasi-isostatic systems use a diffusion cell. The simplest diffusion cell is typically made of two metal parts with a (usually) small volume between them. The advantage of diffusion cells is that they allow for differential concentration from side to side of the sample being tested. When a flat sheet of packaging material is placed between the two metal parts, there can now be a high-concentration side and a low concentration side.

Isostatic Method

The isostatic method is so named because it uses a constant pressure (7). On the high concentration side of the cell, there can either be liquid permeant for studying permeability at saturation vapor pressure or a system for generating vapor and adjusting the concentration using a carrier gas (usually nitrogen). The inlet to the low concentration side is fed a pure (no permeant) carrier gas stream. The concentration in the low concentration stream is measured over time to find out what the level of permeability is. See Figure 1.

The isostatic method has the advantage of being able to provide a continuous, real-time picture of permeation, as long as it is coupled with a detection system that also works in real-time. This advantage allows for continuous study of unsteady state permeation. The continuously refreshed supply of permeant on one side of the film and the continuously refreshed supply of pure gas on the other maintains a steady chemical potential (driving force) for diffusion. This may not represent all cases, since in a real package, the permeant may be depleted. It is also somewhat more complicated than some of the other systems, with more valves, meters and other controls, but it is manageable.
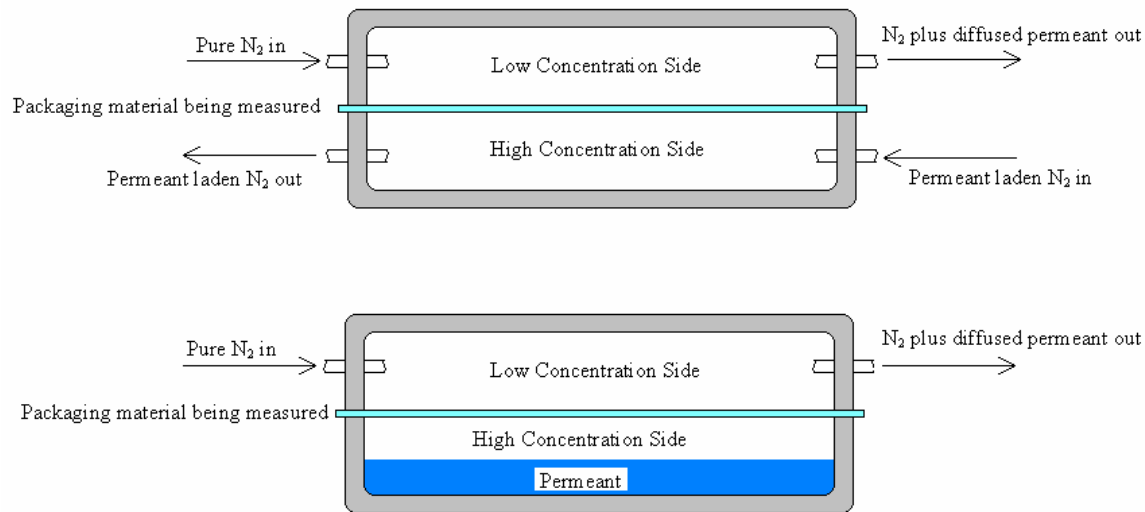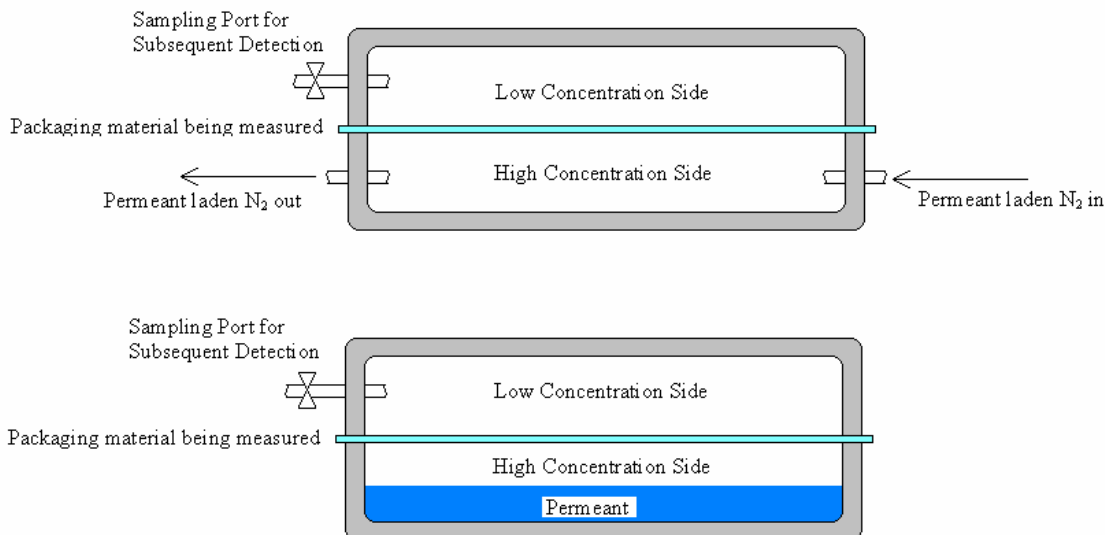
Figure 1. Isostatic Diffusion Cell Schematics

Quasi-isostatic Method

The quasi-isostatic system also uses liquid or a flow of permeant-laden gas on the high concentration side of the film. However, the low concentration side of the cell begins with a pure (no permeant) gas rather than a gas stream. Periodically, the low concentration side is sampled for gas analysis to determine the diffusion. See Figure 2.

As with the isostatic system, an advantage of the quasi-isostatic system is that it allows for differential concentration from side to side of the sample being tested. One disadvantage of the quasi-isostatic system is the fact that the permeant concentration cannot be continuously monitored as it is in the isostatic system. In cases where permeation is fairly slow relative to the time required by the detection system, this is acceptable, but in cases where the permeation is fast, important information can be missed. The second disadvantage is that permeant concentration on the low concentration side can vary due to sampling, thus the rate of diffusion can vary.

Miller and Krochta (7) classify a quasi-isostatic system with liquid permeant as the constant volume method.

Figure 2. Quasi-isostatic Diffusion Cell Schematics

Gravimetric / Sorption Method

In the gravimetric method, the rate of either adsorption or desorption is measured by monitoring the amount of permeant adsorbed or desorbed. The term gravimetric is really a description of the detection method, and is probably a misnomer. Sorption method or uptake method would a better way to describe this permeation method. For adsorption, the polymer sample can be soaked a saturated vapor pressure in a closed vessel or it can be immersed in a carrier gas stream for lower than saturation concentrations. In the case of a carrier gas stream, an electrobalance is often used, combining the diffusion and detection into one method.

Usually, desorption studies involve getting the polymeric material to the saturation point by immersing it in the flavor compound until it stops absorbing , then measuring its rate of permeant loss. This saturation can de done by subjecting it to a gas stream, placing it in a closed vessel with permeant-saturated gas or even immersing it in liquid permeant.

The advantage of the gravimetric / sorption method is that it is fairly simple and easy to understand. The largest disadvantage is that there is not a differential concentration across the film, which is different from the way that packaging barriers are typically used. Also, sorption measurements are often carried out at the saturation vapor pressure, which is sometimes considered a disadvantage because aromas and flavors in foods are often present at much lower partial pressures. There are cases where a saturation pressure is probably appropriate, but the ability to provide permeation at multiple levels is more desirable than saturation only.

None of the three main diffusion methods alone fails any of the criteria mentioned above and yet none are ideal either.

Detection Methods

Many detection methods are used to evaluate the samples or streams coming out of the diffusion systems described above. The most common three methods used are flame ionization detector (FID), gas chromatography with flame ionization (GC/FID) and in the case of gravimetric methods, weight. Mass spectrometry (MS), either alone or in concert with GC is also a commonly used detection method. These and other methods will be described here.

FID (Flame Ionization Detector)

The FID is a commonly used device for detection of organics. Essentially, a flame is maintained in the FID unit, which is fed at all times by a mixture of hydrogen (H_2) and nitrogen (N_2). When hydrogen is combusted with air, a relatively ion-free combustion product is created. When an organic (carbon-containing) molecule is introduced, ions are present in the combustion process. The ions impact a collector, which donates electrons to the ions, crating a readable current. The amount of current is proportional to the number of carbon atoms in the mix. (8).

One advantage of the FID is that the current is proportional to the concentration of carbon atoms coming through the flame. This means that it can be calibrated to quantify the amount of carbon atoms, and thus the quantity of material coming through the flame. Additionally, the FID is a continuous device. It will report a response whenever there is an organic compound present in the flame. This makes it a good choice for putting in-line with an isostatic diffusion system. Another advantage is that the FID is the detector of choice for gas chromatographs, and as such, is readily available and fairly well understood.

For aroma / flavor permeation work, the stand-alone FID has a significant disadvantage. While it is capable of "counting" carbon atoms, it is incapable of distinguishing them. This means that one molecule of limonene, $C_{10}H_{16,}$ will produce the same response as 5 molecules of ethyl alcohol, C_2H_5OH. This means that diffusion cells with FID detectors are useful for individual permeants, but are probably not a good choice for studying the interactions of multiple permeants. Another disadvantage of the FID is that it does not detect inorganic compounds.

FID has been used in conjunction with the isostatic diffusion system by commercially available machines (Aromatran® and MAS 2000™).   These machines have been used by a number of researchers. (9, 10, 11, 12, 13, 14)

GC/FID (Gas Chromatograph with FID)

Gas chromatography and FID together are a powerful tool used for many decades in both the food and the packaging industries. The function of chromatography is to separate multiple materials in a mixture. The chromatographic column is either coated with or packed with compounds to which molecules will adhere for a short time. As pure N_2 is fed through the column after a sample is injected, the different molecules will work through the column (elute) at different times. Typically, smaller molecules will flow out more quickly than larger molecules.

When paired with the FID, the GC column solves the FID's most significant shortcoming. It allows different compounds to reach the FID at different, reproducible times. Because of this, the user knows which molecules the FID is detecting by how much time has lapsed since injection into the column, allowing exact calibration.

The advantage of the GC/FID is that separation and quantification can be achieved. This means that interactions between permeants can be studied, as well as individual permeants.   GC/FID systems have been be used with isostatic systems (in conjunction with purge/trap systems to capture the stream) (6, 12, 15), and with quasi-isostatic systems (6, 7, 16, 17, 18). This technique is also used for gravimetric systems, typically in conjunction with a thermal desorption cycle (19, 20).

There are some disadvantages to the GC/FID however. The first is that gas chromatography is a batch process, not a continuous one. This means that the permeation curve is viewed by snapshots rather than by real-time. This is not an issue when the permeation rate is slow, but in cases where permeation rate is high, we may lose valuable information about the unsteady-state. In some cases, this issue can be solved by taking and holding GC samples over time, then running the GC samples out-of-line with the actual diffusion step. An auto-sampling system can also be used to improve the frequency of data points for the quasi-isostatic system (15). However, this process can still only approximate real-time.

Weight Measurement

In adsorption and desorption experiments, weight measurement is the most common detection method, but not the only one used. Often, a sample is suspended in an electrobalance and the permeant stream is flushed through the chamber, thus measuring permeant uptake in real time. Desorption can be measured using the same technique, except that the test begins with a saturated sample and can be flushed with pure N_2.

The advantage of this detection method is that balances are simple and easy to understand. The electrobalance technique offers the added benefit of giving a real-time reading of the adsorbed permeant.

One disadvantage is that, by detecting weight alone, the interaction of multiple permeants cannot be gauged.

Weight has been typically used only in sorption techniques (6, 12, 17, 20, 21, 22)

MS (Mass Spectrometry)

Like FID, mass spectrometry can be attached to the exit of a diffusion cell to analyze the permeant. In an MS unit, the permeants that enter the device are impinged by an electron beam. Some of the permeant molecules are ionized. These ions are accelerated, using an opposite charge of voltage, through the device. The ions are then subjected to a magnetic or an electric field which changes how the ions flow depending on their mass to charge ratio. This field deflects some ions off of their linear path, depending on the nature of the field and the mass of the ion. By manipulating the fields, ranges of ions can be separated. When the ions collide with the metal ion detector, it donates electrons. This can be measured as an amperage, which is then amplified. (23, 24)

Advantages of MS are that it gives both quantitative and qualitative information, as opposed to the FID that provides only quantitative information. This benefits researchers who wish to study the interactions of multiple permeants.

Some researchers have suggested that using MS as a detection system is complex and difficult to operate (15). Another disadvantage of MS is that it must be run in vacuum and can accept only small amounts of permeant. In some cases, this is addressed by placing vacuum on the low concentration-side of the diffusion cell. This adds a pressure differential to the diffusion that could have an effect on the permeation rate (26). In other cases, the MS is isolated from the permeation cell by a sampling port system. However, this will, of course, mean the loss of real-time detection. Caldecourt & Tou (29) attempted an atmospheric pressure ionization mass spectrometer to overcome the disadvantage of the vacuum in conventional MS. This was placed at the outlet of an isostatic diffusion cell. The system was found to have very good sensitivity. However, the authors reported that it was complex in operation and expensive. Tou et al (26) addressed this problem by utilizing hollow fibers to "tap" into the polymer stream. The technique developed by Tou et al has resulted in several papers (25, 26, 27, 28).

Currently, a commercial machine is being marketed with MS as the detector (30).

GC/MS (Gas Chromatograph with Mass Spectrometer)

The GC/MS system of detection improves further on the GC/FID system by analyzing the GC elution stream and identifying the compounds as they exit the chromatography column.

GC/MS can be used for any diffusion system, as long as steps are taken for sampling.
This technique could prove especially useful for looking at interactions of multiple permeants with similar molecular size, since such compounds may elute from the column at similar times. GC/MS systems can be used for isostatic, quasi-isostatic and sorption systems. The most significant disadvantage of this powerful system is that, like the GC/FID system, this system is also not a real-time measurement.

GC/MS has been reported in the literature in conjunction with sorption (31, 32).

TIR (Transmission Infrared Spectrophotometry)

A modified "gravimetric" system developed by Cava et al (22) showed that transmission IR can be used to develop permeability data during desorption.

The advantage of this detection system is that it is easy to use. The disadvantage is that the permeants must have some peak that is different from the polymer being studied, and from co-permeants in a multiple-permeant system.

Additionally, a transmission IR system is probably not suitable for low presence of permeant, or for thick films, opaque films and materials containing metal.

Manometric Detector

Devices are being marketed currently (30, 33) which use a manometer to detect partial pressure of permeant as it moves through the diffusion cell. This system relies on a vacuum on the low-concentration side of the diffusion cell and measures the pressure changes across the polymer as diffusion occurs.

The advantage of this system is that the use of a manometer is simple and pretty well understood. One disadvantage is that manometry is probably not capable of the measurement of interactions between multiple permeants. If two permeants travel through the package, partial pressure will change, but such a detector will not know which one. Additionally, the use of a vacuum on one side of the chamber may affect the permeation rate.

Photoionization detector (PID)

Photoionization detectors use a UV lamp of a given energy to bombard compounds, thus splitting off electrons and creating ions. The ions are then drawn toward the detector using a voltage potential. The ions in a PID system are detected by a means similar to FID and MS, i.e. by current. PID's have very good sensitivity for quantities. (34) However, like FID and manometry, PID alone is not a good tool for study of permeant interaction. It detects quantity but does not distinguish between compounds. Also, depending on the lamp energy and the ionization potential of the compound, some compounds are not detected by the PID. Caldecourt & Tou (29) studied the use of this detector in-line with an isostatic system.

Combined Detection Systems

All of the detection systems outlined above have one or more shortcomings. Typically, methods that perform well at discerning between permeants are not real-time or affect the test in some way. Real-time methods (e.g. FID or electrobalance weight) that do not require vacuum are not effective to discern between permeants.

Some researchers, such as Zhou et al (15) have utilized automation and technology to reduce the sampling/analysis time of methods such as GC/FID.

Other researchers have combined detection methods to overcome this. Laoharavee and Giacin (10) combined a purge and trap GC/FID system with a MAS 2000 machine (isostatic/FID) to study multi-permeant interactions. Nielsen and Giacin (20) conducted sorption of a multi-permeant blend using an electrobalance, then used GC\FID (after thermal desorption) to determine the steady-state concentrations of the individual permeants. Paik (32) combined weighing and GC/MS to study permeation of components of a commercial orange flavored commercial powdered drink into various films. Perhaps the most elaborate solution was reported by Stevens (35) that uses a GC with MS, FID, PID and an olfactory "sniff" port.

<u>**Conclusions**</u>

Aroma and flavor barrier systems consist of permeation systems and detection systems. Permeation systems are isostatic, quasi-isostatic and sorption (gravimetric). All of these systems have advantages and disadvantages. Detection systems are FID, GC/FID, weight, MS, GC/MS, TIR, manometric and PID, and all of these also have strong points and weaknesses.

There is no perfect solution to aroma and flavor barrier measurement. The diffusion cell techniques probably offer a more "real-world" measurement tactic due to the differential concentration across the packaging material. Of these, the isostatic method has a better opportunity to detect fast, unsteady state diffusion. This benefit is only of use if a detection method is selected that can measure real-time. Most of the detection techniques require some sort of a trade-off: real-time vs. multi-permeant ability vs. ease of operation. Currently, the best we can do to meet all of the needed criteria at a reasonable cost is to combine multiple detection systems with one of the permeation methods.

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Need to Understand Aroma / Flavor Permeation

Transition from Glass & Metal to Plastics

- Lower cost, lighter, more versatile, etc.
- Less inert than glass & metal

Need to Understand Aroma / Flavor Permeation

Package/Product Interactions of Concern

- Example- Limonene & LDPE
  - Loss of citrus flavor in orange juice
  - Loss of mechanical properties in LDPE

Need to Understand Aroma / Flavor Permeation

Mechanisms to Be Discovered

- **Example: Aroma release from cyclodextrin carrier (active packaging)**
  - **Complex relationships between Limonene, pinene and relative humidity**

Need to Understand Aroma / Flavor Permeation

Regulatory Considerations

- **Example: Benzophenone in label coatings for pharmaceutical coatings**
  - **Permeability different for different bottles**

Problems with Measuring Aroma / Flavor Permeation

- **More compounds than O_2, water vapor**
- **More complicated also**
  - **Molecule size**
  - **Interactions**
- **Not completely understood**
- **No real consensus as to test method**

Analysis of Current Measurement Methods

- Divided in two areas
  - Permeation method
  - Detection method

Permeation Methods

- Isostatic
  - Diffusion cell
  - Flow on low concentration side
  - Saturated vapor or adjustable on high concentration side
  - Can be sampled continuously

Permeation Methods
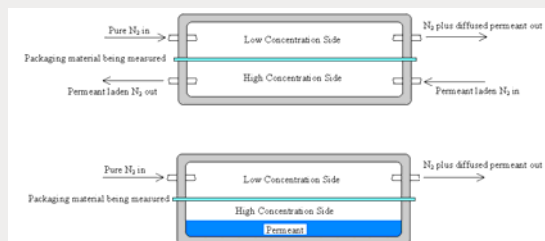
- Isostatic

Permeation Methods

•**Quasi-Isostatic**

  •**Diffusion cell**

  •**No flow on low concentration side**

  •**Saturated vapor or adjustable on high concentration side**

  •**Low permeability side sampled periodically**

Permeation Methods

•**Quasi-Isostatic**
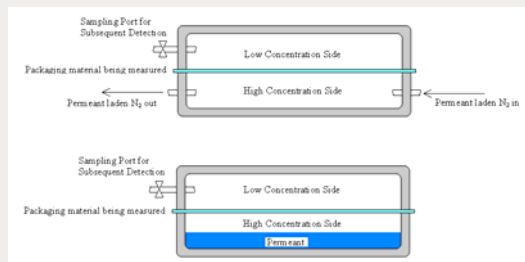
Permeation Methods

•**Sorption (aka Gravimetric)**

  •**No diffusion cell (no differential across package)**

  •**Saturated vapor or adjustable or soak in liquid permeant**

  •**Measured during sorption or during desorption**

Permeation Methods

•**Sorption (aka Gravimetric)**
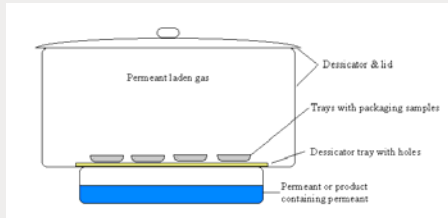
Permeation Methods

•**All satisfactory**

•**Diffusion cells more "real-world"**

•**Isostatic offers real-time read IF detection allows**

Detection Methods

•**Schematic of Electrobalance**
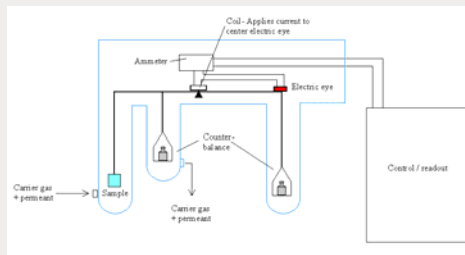
Adapted from: Ultra Micro Weight Determination in Controlled Environments. ed. Wolsky & Zdanuk. Wiley. 1969

Detection Methods

•FID Schematic

Adapted from Modern Practice of Gas Chromatography Ed. R. Grob, Wiley 1995

Detection Methods

•GC/FID Schematic

Detection Methods

•MS Schematic

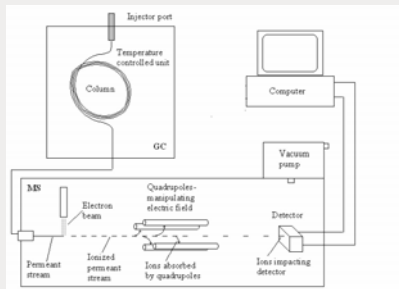Adapted from Detectors for Capillary Chromatography. Ed. Hill and McMinn Wiley 1992

Detection Methods

•**GC/MS Schematic**

Adapted from Detectors for Capillary Chromatography. Ed. Hill and McMinn Wiley 1992

Detection Methods

•**Other methods**

  •**Manometer**

  •**PID**

  •**TIR**

Detection Methods

•**Combined methods**

  •**FID and GC/FID**

  •**Gravimetric and GC/FID**

  •**Gravimetric and GC/MS**

  •**FID, PID, GC/MS, Olfactory**

Detection Methods

- None meets all needs

- MS method comes close, but deemed "complex" by some researchers

- Combined methods probably best option given current technology

Thank You

PRESENTED BY
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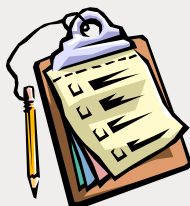**Professor**

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Please remember to turn in your evaluation sheet...