Research of Water Vapor Barrier Property Testing Methods for Hollow Containers

Meng Li 1, 1st, Lina Liu 1, 1st, Jinxiu Wang 2, 1st, Shifeng Wang 1, *, Weichang Mao 1, 1st, Xin Chen 3, 1st
1. PLA Naval Medical Center
2. PLA Naval Medical University
3. Jinan Guoke Medical Technology Development Co., Ltd.; Shandong Engineering Research Office, Suzhou Institute of Biomedical Engineering and Technology, Chinese Academy of Sciences
1st: Joint author
*: Corresponding author
156362518@qq.com

Abstract: Barrier property is a characteristic of hollow containers and can be used to meet the need for shelf life of the contents; the hollow container shape is variable, which makes it difficult for overall barrier property testing. Based on this, this paper discusses the common testing methods of water vapor barrier property of hollow containers. Firstly, the advantages and disadvantages of the traditional weighing method and sensor method in testing the water vapor barrier property of containers are compared, typical applications are taken as an example, and finally two new methods, namely electrolytic sensor method and infrared sensor method, which can quickly and accurately test the moisture permeability of hollow containers, are introduced in detail, so as to achieve good and accurate test for various hollow containers, which can provide reference for related industries in selecting testing technologies for container barrier property.

1. Introduction
Hollow containers are mainly plastic containers processed by the hollow molding method, they often exist in the form of bottles, barrels and cans, and can be used to hold various liquid or solid foods, medicines, chemical products and so on. Because the raw materials go through high temperature, cooling, inflation and extension and other technological steps in the container processing process, it is impossible to reflect the final performance of the produced container by testing the related performance of the raw materials [1]. The testing process of barrier property, as an important performance of hollow containers, is difficult due to the irregular shape of the container. In the past, sheets at some positions of the container wall were often cut for barrier estimation test. However, due to the uneven wall thickness of the container, it could not represent the barrier property at the junction at the bottom of the container or the mouth of the container. Therefore, this estimation test method could not accurately characterize the overall barrier property of the container [2]. Taking the water vapor barrier property (i.e. moisture permeability) of the container as an example, the traditional weighing method is often used nowadays to measure the moisture permeability (also called water vapor permeability) of the whole container, but this method has some disadvantages in use. Therefore, the fast and accurate sensor methods, including
electrolytic sensor method and infrared sensor method, are increasingly recommended, especially, the infrared sensor method has the best applicability and repeatability.

2. Test with Weighing Method for Hollow Containers (Traditional Method)

2.1. Test standards and principles of the method
The moisture permeability test method of hollow containers commonly used in the previous period is evolved on the basis of film and sheet moisture permeability test method - weighing method, domestic and foreign standards used for the weighing method test of containers are GB/T 6981-2003 "Test Methods for Moisture Permeability of Rigid Packaging Containers", GB/T 6982-2003 "Test Methods for Moisture Permeability of Flexible Packaging Containers", ASTM D3079-94 (2009) "Standard Test Method for Water Vapor Permeability of Heat-sealed Flexible Packaging for Dry Articles", YBB00092003-2015 "Measurement Methods for Water Vapor Permeability". The above standards can be used for moisture permeability tests of flexible and rigid plastic packaging containers. Although there are differences between various methods, the basic method principle is the same.

In this method, the hollow container sample with desiccant in it is sealed for sample preheating treatment, and then the sample is transferred into the test chamber (room) with constant moisture heat conditions for moisture heat test, according to the moisture permeability of the hollow container sample, the appropriate interval is selected for regular weighing of sample mass, when the amount of moisture permeability is stable, the increase in sample mass and the rate of change of time are used to calculate the amount of moisture permeability of the container.

2.2. Defects of the method
The method is formed on the basis of the more widely used and long-standing film weighing method, it appears to be simple to operate, but it is more difficult to achieve automatic instrument testing, and the test efficiency and accuracy of the results are poor, and there are mainly the following shortcomings:

(1) The test process is time-consuming: according to the weighing interval recommended by relevant standards, for a container with high moisture permeability (low moisture resistance), the recommended minimum weighing interval is at least 3 days; for a container with low moisture permeability (high moisture resistance), the weighing interval of 15 days to 30 days is recommended. Usually the container moisture permeability needs to test at least three points of quality data, so even hollow container samples with high moisture permeability need 7 days to 9 days to complete the test, and testing of samples with low moisture permeability takes several months.

(2) Weighing and test environment differences affect the accuracy of the results: the standards require the sample to be removed from the test environment to the weighing environment for weighing, and this environmental difference is easy to destroy the state of osmotic equilibrium of water vapor, affecting the accuracy of the final experimental results. In particular, the shorter the weighing interval, the greater the number of weighing, the more obvious this impact is.

(3) The water vapor pressure difference between the two sides of the sample is difficult to keep stable for a long time: because the desiccant used in the weighing method is limited (existing standards require not more than 100 g), the moisture absorption capacity of the desiccant will gradually decrease as the test proceeds, and even adsorption saturation will occur, and accordingly the water vapor pressure difference between the two sides of the sample will also change. When encountering this problem, desiccant can be replaced to continue the test, but the replacement process will cause quality deviation and further affect the accuracy and repeatability of test results.

(4) Poor repeatability: due to the differences in the sealing preparation and weighing practices of different test operators for container samples, the repeatability of the test results will be affected to a certain extent.

(5) Limited accuracy of the weighing system: since the accuracy of the balance used in the weighing method is closely related to its range, and the amount of moisture permeability of the container is greater
than that of the film test, the accuracy of the test derived from the weighing method in conducting the container test is significantly worse than that in the film test.

3. Test with Sensor Methods for Hollow Containers (New Methods)

3.1. Test standards and principles of the methods

At present, the sensor methods used to test the moisture permeability of hollow containers are mainly electrolytic sensor method and infrared sensor method, the current method of testing containers using electrolytic sensor method is based on GB/T 21529-2008 "Measurement of Water Vapor Transmission Rate of Plastic Films and Sheets - Electrolytic Sensor Method", and test containers in the infrared sensor method and other packaging components have relevant standards that can be implemented. At present, the referable standard is GB/T 31355-2014 "Water Vapor Permeability Test Method for Packaging and Containers - Infrared Sensor Method", and there are no referable foreign standards.

These two sensor methods are basically of the same method principle (as shown in Figure 1), the container sample is used to separate the permeation chamber into two independent airflow systems, a humidity chamber with specified relative humidity is formed at the container said, a flowing dry carrier gas test chamber is formed at the other said. As a result of the water vapor concentration difference at the both sides of the sample, the dry carrier gas carries the water vapor through the wall of the sample to the sensor, the sensor changes the amount of humidity into an electrical signal or current value output, calculates the amount of water vapor through a certain volume of the specimen per unit of time (i.e., water vapor transmission rate). The only difference is that the electrolytic method has a chemical electrolytic tank sensor containing phosphorus pentoxide to test electrolytic current value, while the infrared method uses a sensor that applies the physical principle of water vapor absorption of infrared energy to test electrical signal value.

![Diagram of hollow container testing by sensor method](image_url)

Figure 1: Schematic diagram of hollow container testing by sensor method

1. Test chamber integrated block; 2. Air pipe; 3. Inlet pipe; 4. Container specimen; 5. Outer cover; 6. Outlet pipe; 7. Temperature control device
Usually, the sensor method can realize the moisture permeability test of various shapes of hollow containers, the test accuracy can reach 0.0001g(pkg-d), and the test cycle is greatly shortened (generally only 3 to 4 days), which can ensure a stable, fast and accurate test of container moisture permeability under different temperature and humidity environment conditions.

3.2 Test methods

The electrolytic sensor method and the infrared sensor method are similar in relevant test steps, and different only in the processing data results of the sensor. Taking the infrared sensor method as an example, the specific test methods are as follows:

(1) Sample preparation and connection: moisture permeability testing of the container as a whole usually includes the moisture permeability testing of bottles (barrels, jars) without a cover and those with a cover. When testing the moisture permeability of bottles (barrels, jars), the container needs to be inverted and fixed in the packaging test bracket of the instrument with container mouth down, and then the container and bracket connection is sealed with a good special sealant (such as epoxy resin) (shown in Figure 2). When testing the overall moisture permeability of bottles (barrels, jars) with a cover, a small hole is gently drilled on the container bottom or the container wall to allow the passage of the carrier gas inlet and outlet pipe, the small hole is fixed to the bracket, and then sealant will be sealed at the connection, it is needed to ensure that the recessed part at the container bottom and the pipes are filled with sealant to ensure tightness.

![Figure 2: Schematic diagram of sample preparation and connection method](image)

(2) Installation of the specimen into the instrument: the sample to be tested is installed in a device with constant known temperature and humidity inside the test instrument, the upper chamber of the test is replaced with a specific outer cover (see Figure 3, the instrument shown is the W3/230 water vapor transmission rate tester), and the sample separates the permeation chamber into a separate airflow system (see the principle of the test method).
Figure 3: Schematic diagram of specimen installation

(3) Carrier gas purging and setting: set the test temperature, humidity and other test parameters, pass the dry carrier gas into the specimen, set the purging time according to the volume of the container specimen, and blow the air inside the specimen at a certain flow rate. After blowing, adjust the carrier gas flow to the set value and keep it stable.

(4) Test and record: the instrument starts the test until the change of voltage output value is within the set ratio, the test reaches a stable state and the test is finished. The instrument automatically records the voltage value and calculates the water vapor transmission rate of the final specimen.

4. Typical Applications of Sensor Methods

When the sensor methods are used to test hollow containers with high moisture resistance (low moisture permeability), the advantages of high test accuracy and fast test efficiency are highlighted, so they have a high utilization rate in food, medicine packaging materials and other industries. Generally, the hollow containers for barrier testing are mainly bottles, barrels, jars and other packages, but special attention shall also be paid to the testing of hollow containers such as soft bags, hoses and bubble caps.

(1) Moisture permeability test of soft bags

When using the weighing method to test infusion bags, doypacks and other soft bags, it is difficult to maintain the space inside the bag, especially when the bag is filled with distilled water or desiccant, making it difficult to realize effective sealing of the bag. Therefore, the use of sensor methods can effectively solve the above-mentioned problems.

When adopting sensor methods for testing, attention shall be paid to the control of the pressure inside and outside the soft bag, ensure that the actual gas through the area is the entire surface area of the soft bag to prevent errors in the experimental results. Therefore, the expansion of the bag can be achieved by passing a certain amount of carrier gas into the bag to maintain sufficient space inside the bag, as shown in Figure 4: Schematic diagram of infusion bag sample preparation.
(2) Moisture permeability test of plastic hoses

It is difficult to realize effective sealing when the weighing method is practiced in moisture permeability test of hoses due to the internal filling of distilled water or desiccant, especially the small size of the hose increases the difficulty of sealing. Therefore, sensor methods are mostly considered in hose test.

In the hose testing process, it is needed to choose the right location for holing, otherwise the sealant cannot seal effectively, usually the middle of the plastic pipe is holed, and it is necessary to ensure that the length of the gas line within the hose can meet adequate blowing without causing hose breakage.

(3) Moisture permeability test of small hollow containers

Bubble caps, capsules and other small hollow containers are small, so the weighing method is used only to test the moisture permeability of their substrates, this method cannot be used to test the moisture permeability of the containers [3], only sensor methods can be used to test those containers, and special custom test brackets and other instrument accessories are needed to complete the sample preparation and connection (such as the schematic diagram of capsule sample preparation shown in Figure 5). In addition, the carrier gas flow rate needs to be strictly controlled throughout the test process to prevent sudden pressure changes due to instantaneous and significant changes in the gas volume inside the bubble cap or capsule, resulting in abnormal sample status and affecting the test results. Therefore, sensor methods have a broader application prospect in the field of testing the moisture permeability of small specimens.
5. Conclusions
The defects of long testing period, poor accuracy of test results and limited applicability of the traditional weighing method, which has been used for many years to test the moisture permeability of hollow containers, have become increasingly prominent, which in turn has led to the rise of the highly accurate, fast and efficient sensor methods in the field of moisture permeability testing of hollow containers. The sensor methods can be used to test the moisture permeability of various types of hollow containers, such as flexible bags, hoses, plastic bottles, drums, etc., providing more rigorous and reliable test data for monitoring the impact of moisture permeability of hollow containers on the shelf life of internal products.

References
[1] Wu Donglei, Zhang Lili, Xu Liang, et al. Oxygen Permeability Testing of PET Barrier Containers and Its Applications in Beer Packaging [J]. Packaging and Food Machinery, 2017, 35(003):62-64.
[2] Zhao Jiang. Development Status of Overall Barrier Property Testing of Hollow Containers [J]. China Packaging, 2018(10):46-47.
[3] Anonymous. Special Discussions on Test Methods of Water Vapor Barrier Property for Hollow Containers and Applications in a QQ Group [J]. Packaging Frontiers 2019(5):4.
[4] Hideo Fukushima, Noboru Takahashi. Hollow Containers and Methods for Manufacturing Hollow Containers.; CN106687280B[P]. 2019.
[5] Yao Xuerong, Liu Lizhi. A Polyethylene Composition with Improved Water Vapor Barrier Properties and Method of Preparation.; CN110713647A[P]. 2020.