Labthink Instruments Co., Ltd.
144 Wuyingshan Road, Jinan, P.R.China
Phone: +86 531 85068566
FAX: +86 531 85812140

On Calibrating Oxygen Permeability Testers of Equal-pressure Method

Abstract: this article introduces relevant calibration items of ASTM D 3985. The comparison of empirical tests has proved that test data of different-pressure method vary with that of equal-pressure method. Moreover, working efficiency of oxygen sensor during actual application varies with time. For these reasons, it is necessary to calibrate equal-pressure method instruments.
Key words: calibration, differential-pressure method, equal-pressure method, data comparison

The difference between equal-pressure method and differential-pressure method (the fundamental test method of oxygen permeability testing) in terms of test principle has affected the comparison of their data. In addition, oxygen sensor adopted in equal-pressure method is depleted with time. Therefore, equal-pressure method instruments should be calibrated to evaluate working conditions of oxygen sensor and to correct data system of oxygen permeability test through calibrated factors. However, someone holds that equal-pressure method instruments require no calibration and their original test data can be used directly, which often quotes from ASTM D 3985 for certification. In fact, such quotation cannot hold ground. This article presents detailed analysis to relevant items of ASTM D 3985. It also explores the calibration necessity of oxygen permeability testes of equal-pressure method.

1． Calibration Items in ASTM D 3985

Referential film calibration is one of the most commonly used calibration methods of equal-pressure method. It adopts standard material ‘traceable to the standard value determined by differential-pressure method’ and is carried out in the instrument to be tested. Users can determine whether the instrument works properly or whether the sensor is depleted through comparing tested results with standard value of referential material. However, according to the requirement of ASTM D 3985, such referential material should be SRM 1470 obtained from American National Standards Institute (ANSI).

Those who believed that equal pressure method requires no calibration and the original test data can be used directly often quotes following words of ASTM D 3985 for certification: Limited statistical data on correlations with Test Method D 1434 methods are available; however, the oxygen transmission rate of a standard reference material as determined manometrically by NIST, is in good agreement with the values obtained in the coulometric interlaboratory test using material from the same manufacturing lot. The oxygen sensor used in this test method is a coulometric device that yields a linear output as predicted by Faraday’s Law. In principle, four electrons are produced by the sensor for each molecule of oxygen that passes into it. Considering that the sensor is known to have a basic efficiency of 95 to 98%, it may be considered an “intrinsic” standard that does not require calibration. It should be specifically noted here that coulometric sensor works according to Faraday’s Law, in simple words, one oxygen molecule corresponds four electronics. Since it is impossible to change the corresponding number of electronics to one oxygen molecule, the words that ‘the sensor requires no calibration’ stated in standard really make sense. However, it can by no means be understood as ‘if the sensor requires no calibration, so des the instrument’, which are two different concepts and cannot be mixed. That is why ASTM D3985 adopts referential film to calibrate instrument.

2． Calibration Necessity of Equal-pressure Method

2.1 Sing Data Comparison not persuasive

In ASTM D 3985, test data of SRM 1470 obtained with equal-pressure method and differential-pressure method are compared with good consistency. It is noted in the standard that test data obtained with equal-pressure method is 59.36cm3(STP)/m^2·d·atm with a standard deviation of 1.21cm^3(STP)/m^2·d·atm and standard data provided in NIST obtained with differential-pressure method is 63.8cm^3(STP)/m^2·d·atm with its standard deviation being 0.4cm^3(STP)/m^2·d·atm. However, data comparison here is only of one material, which can be considered as a single data comparison for data systems of equal-pressure method and differential-pressure method. As data systems of several methods may prove to be very close within certain measuring range while tend to vary once outside such measuring range, single data comparison cannot fully represent data relationship of these two methods. Labthink input great efforts in data comparison of differential-pressure method and equal-pressure method. Some of the test results are listed in table 1.

Data comparison of defendable-pressure method and equal-pressure method

number	material	Test data of defendable-pressure method			Test data of equal-pressure method		
		1	2	3	1	2	3
1	Aluminum coated laminated film	0.417	0.402	0.374	0.31	0.36	
2	OPP/VMPET/LLDPE	0.881	0.813	0.882	0.75	0.72	
3	PVDC coated film1 # (20μm)	1.647			1.45	1.43	1.69
4	PE/VMPET/PE(40μm)	2.581	2.63	2.531	2.80	2.79	
5	PET/PVDC	5.30			4.96	4.92	4.98
6	PVDC coated film 2 # (20μm)	7.251	7.811		6.29	6.47	6.56
7	Laminated film1＃	7.98			9.95	10.00	
8	PVDC coated film 3 # (20μm)	28.1			32.66	33.27	33.52
9	CPP(90μm)	31.006			29.41	31.02	30.82
10	PE co-extrusion film (80μm)	61.543	60.899	62.421	61.89	60.75	
11	PE(90μm)	112.532			95.97	91.61	
12	PC(175μm)	383.76	384.32		301.98	297.66	298.53
13	Laminated film 2＃	749.96	752.63	752.84	543.091	557.527	543.683
14	PE milk film	1203.54	1200.31	1208.19	1043.98	1065.55	

Note: data unit of differential-pressure method is cm^3/m^2·24h·0.1MPa; Data unit of equal-pressure method is ml/m^2·day.

Test data of the two methods display good consistency in aspect of increase tendency. However, as far as specific material is concerned, test data of these two methods vary differ. Generally, existing data comparison

has shown the following characteristics: in testing high barrier materials, test data of equal-pressure method tends to be smaller. As to medium barrier materials, test data of the two methods are very close. When low barrier materials are tested, test data of the two methods vary obviously with that of equal-pressure method being smaller. the most close range of test data is between 30～70. It can be seen that single data comparison of SRM 1470 mentioned in ASTM D 3985 is right within this range. But for data comparison in wider range, original test data systems of the two methods will show non-neglectable difference.

2.2 Efficiency of Oxygen Sensor Changes

The efficiency of coulometric oxygen sensor changes during operation, which can also be seen from the efficiency range of 95%～98％ provided in ASTM D3985. Oxygen sensor based on Faraday's law is of consumptive type. In other words, such oxygen sensor has lifespan. During the actual consumption process, what is actually being consumed is rare metal of KOH electrolyte and positive-negative electrode. With the continuously ongoing of chemical reactions, KOH electrolyte and positive-negative electrode are constantly changing in amount. Consequently, working efficiency and react time of oxygen sensor is declining. Once a sensor reaches its time limit, replacement becomes necessary.

2.3 Equal-pressure Method Requires Calibration

According to the above analysis, original test data of equal-pressure method obviously vary with that of differential-pressure method in a wider range. Moreover, the efficiency of oxygen sensor changes with time. Therefore, instruments of equal-pressure method must be calibrated. The use of referential film also testifies this point.

3． Conclusion

Equal-pressure standards mainly adopt referential film calibration. However, in many countries, referential film recognized by national standard institutions is not available. And there is time limit for data stability of referential film. Therefore, the actual application of referential film is somehow hampered. As is analyzed previously, the calibration of equal-pressure method is of great necessary, which makes a widely used calibration method in urgent need. At present, such problem can be better solved using oxygen gas with known concentration which already witnessed similar application in German standard DIN 53380-3. For operation procedures of gas calibration, users can found detailed explanation in follow-up papers.