The testing method of proficiency testing sample's homogeneity and stability

Abstract: As a Cooperation unit，Labthink participated the plastic packaging material permeability proficiency testing project which was orginzed by Certification and Accreditation Administration of P.R.C, and accomplished the test specimen's homogeneity and stability splendidly. This paper introduced specifically for the sample choice and the significance with method of sample homogeneity, stability testing in this proficiency testing project.
Key Words: OTR, WVTR, proficiency testing, homogeneity, stability.

Certification and Accreditation Administration of P.R.C organized the laboratory proficiency testing of "the plastic packaging material permeability test - - the test of OTR and WVTR" in nationwide on 2007. And the sample's homogeneity and stability comparison accomplished all by the Labthink.

The homogeneity of sample's comparison is very significant. We utilized it fully in the laboratory comparison and then developed the laboratory proficiency testing project. When carry out proficiency testing project, the organizer must guarantee that the unsatisfactory result in proficiency testing will not impute to the sample and sample's changeability. Therefore, the quantity of test characteristic of proficiency testing must carry on the homogeneity testing and the stability testing. This paper will introduce that in detail between the plastic packaging material permeability test proficiency testing project sample and the test condition of the homogeneity and stability.

1. **The sample's preparation**

This proficiency testing use "Split-level" sample design, the sample is the polyester film, which divided into two groups of A and B. They have the close thickness and the same basic material. Whereas, there is still exist a slight difference in two groups samples and result in a slight difference between experimental results. This kind of sample design could inspect the difference between different laboratories and the same laboratory simultaneously.

2．**The testing of homogeneity and stability**

2.1 The testing of homogeneity

For the preparation of batch sample's proficiency testing plan, the homogeneity test is essential. According to the stipulation of CNAS-GL03 "Guidance on Evaluating the Homogeneity and Stability of Samples Used for Proficiency Testing", the sample's homogeneity tests procedure are as follows.

1. To extract samples at random from A and B groups for the homogeneity testing.

2. To extract each sample and reiterate testing 2 times under the same experimental condition at least.

3. The homogeneity test use VAC-V1 Gas Permeability Tester and TSY-T3 Water Vapor Permeability Tester. Its test principle is consistent with this proficiency testing's recommend method.

4. For the unusual value in the test, it could not be rejected at will before the reason was verified.

5. Using the single factor ANOVA method to count the test result and carry on the homogeneity analysis.

The single factor ANOVA method is the most commonly method to appraise material's homogeneity. The basic method is extracts i samples (i=1, 2 ... m), and each sample tests j times (j=1, 2 ... n) under the same experimental condition. According to the following formula to count statistics F:

$$\overline{x_i} = \sum_{j=1}^{n} x_{ij} / n_i \qquad \overline{\overline{x}} = \sum_{i=1}^{m} \overline{x_i} / m$$

Sum of squares $\qquad SS_1 = \sum_{i=1}^{m} n_i \left(\overline{x_i} - \overline{\overline{x}} \right)^2 \qquad SS_2 = \sum_{i=1}^{m} \sum_{j=1}^{n_i} \left(x_{ij} - \overline{x_i} \right)^2$

Mean square $\qquad MS_1 = \dfrac{SS_1}{f_1} = \dfrac{SS_1}{m-1} \qquad MS_2 = \dfrac{SS_2}{f_2} = \dfrac{SS_2}{\sum_{i=1}^{m} n_i - m}$

Statistics $\quad F = \dfrac{MS_1}{MS_2}$

If $F < F_{\alpha(f1, f2)}$ (usually takes significance level $\alpha=0.05$), then it indicated no special difference among samples and the same sample, therefore, the sample is homogeny.

2.2 Stability test

In proficiency testing, the sample need to transmit to each participates laboratory, and it might affect the stablility of testing samples'OTR and WVTR. Therefore it must be test the stability. The test method carries out CNAS-GL03 "Guidance on Evaluating the Homogeneity and Stability of Samples Used for Proficiency Testing".

1. Extracting samples at random from A and B groups for stability test, the sample numbers should have enough representation.

2. Using two kind of environment--38℃/50％RH and 48℃/90％RH--to process the samples. It simulates summer's temperature and humidity environment of most districts in our country.

3. The stability test is also use VAC-V1 Gas Permeability Tester and TSY-T3 Water Vapor Permeability Tester

4. Using the T testing method to count the test result and to carry on the stability analysis

T testing method includes two count methods, one is the comparison between series of survey mean values and normal/reference values, the other is the consistence between two mean values.

For the first method $t = \dfrac{|\bar{x} - \mu|\sqrt{n}}{S}$

For the second method $t = \dfrac{|\bar{x_2} - \bar{x_1}|}{\sqrt{\dfrac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2} \times \dfrac{n_1 + n_2}{n_1 \times n_2}}}$

And, $\bar{x}$ is the mean value which measured n times, n is the measurement time, S is the standard deviation of measured result. In the first method μ is the normal value or the reference value, and in the second method the subscript expressed separately of parameter which belongs to the first testing or the second testing. In order to ensure accuracy of mean value and standard deviation's, the survey times should not less than 6 times.

Using T value which obtains by the computation to appraisal sample's stability, for the first method, the crucial value of t is tα (n-1) (usually takes significance level α=0.05), for the second method, the marginal value of t is tα (n1+n2-2) (usually takes significance level α=0.05). If t< the crucial value of t, then it indicated no special difference between two mean values, the sample is stable.

2.3 The sample test data of this proficiency testing

Through the single factor ANOVA method and the t testing method, Labthink obtained 108 homogeneity tentative data with 44 stability test data. These test data gained expert's consistent approval to the comparison sample and the material's selection conform to the requirement completely. Therefore it could use in this proficiency testing project. Because the data is numerous, here has only enumerated the testing WVTR data of B group test specimen.

Table1. The WVTR data of sample's stability testing from B group （g/m^2·24h）

Testing time（j） Sample Number(i)	1	2	3	Mean value
1	15.107	16.751	15.655	15.838
2	15.848	15.429	15.397	15.558
3	14.398	15.203	15.622	15.074
4	16.042	15.300	15.558	15.633
5	15.848	16.138	15.461	15.816
6	15.945	15.461	16.751	16.052
7	14.462	15.365	15.945	15.257
8	15.526	16.138	15.558	15.741
9	15.526	15.912	15.945	15.794
Total mean value	15.640			

Table2: the data of single factor ANOVA analysis

The source of ANOVA	degree of freedom		Sum of squares		Mean square		F
between samples	f_1	8	SS_1	2.243	MS_1	0.280	0.984
Of sample itself	f_2	18	SS_2	5.129	MS_2	0.285	

F marginal value is $F_{0.05} (8, 18) = 2.51$, the computation obtains the F value is 0.984. This value is smaller than the F marginal value, this indicate that the significance level at 0.05, the sample's WVTR is very homogeneous.

3．The significance of sample testing

Through volume test data, Labthink proved the sample's homogeneity and stability in "the plastic packaging material permeability test - - the test of OTR and WVTR" proficiency testing . They are satisfy the request of CNAS-GL03 "Guidance on Evaluating the Homogeneity and Stability of Samples Used for Proficiency Testing" completely. Therefore, this proficiency testing can avoid the sample's changeability between them and themselves. It could reflect the whole level of current domestic permeability testing accurately.