Detection Technology Ability of Benzene in Adhesives by Iteration Robust Statistic Technique

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Abstract: In order to analyze and compare the technical level of laboratory detection of benzene in adhesives, the ability test provider PT0031 (CNAS) organized a capability test project for benzene content, in which 146 laboratories participated, uniformity and stability tests, iterative robust statistical techniques and analysis of statistical results, influence of standard solutions, gas chromatography, capillary columns and operating conditions. There were 130 laboratories with qualified test results, accounting for 89.0% of the total feedback.

Keywords: adhesives, benzene, detection ability

1. Introduction

Adhesives are widely used in decoration materials, and occupational diseases caused by adhesive poisoning occur from time to time. Unqualified adhesive products contain harmful substances. The main components are benzene, toluene, xylene, halogenated alkanes and halogenated olefins. These substances can cause skin damage, suffocation, lung disease, gastrointestinal dysfunction, nervous system damage, and hematopoiesis System damage and carcinogenicity, etc. Benzene vapor has an aromatic smell and is highly toxic to humans. It can be poisoned by inhalation and absorption through the skin, causing dizziness, headache, fatigue, and death due to respiratory spasm in severe cases. Benzene has been classified as a carcinogen, and long-term exposure may cause bladder cancer[1-3].

Benzene in substandard adhesives has attracted much attention because of its wide application in adhesives. Benzene in adhesives is routinely tested. National standards GB 18583-2008 "Limit of harmful substances in adhesives for interior decoration materials", GB 30982-2014 "Limit of harmful substances in building adhesives", GB 33372-2020 "Limit of volatile organic compounds in adhesives" clearly require

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benzene content to be less than 5g/kg [4-6]. Since the above detection standards stipulate a wide range of conditions for the determination of benzene content, and the standards have no requirements for accuracy, in order to identify the differences between laboratory test results, domestic laboratories are currently equipped with gas chromatography equipment brands, capillary column models and operating conditions increase the comparability of test results between laboratories[7-9], so it is necessary to compare the determination of benzene in binders between laboratories.

2. Experimental

2.1 Instrumentation and Reagents

Agilent 7890 Gas chromatograph, chromatographic purity benzene, analytical purity ethyl acetate.

2.2 Test Sample

Sample Design: This proficiency testing program uses a total of 2 sets of samples, sample A and B. The two groups of samples have different benzene content. Sample A for the laboratory code 1 to 59, and sample B for the laboratory code 60 to 146.The control experiment process is shown in Figure 1.

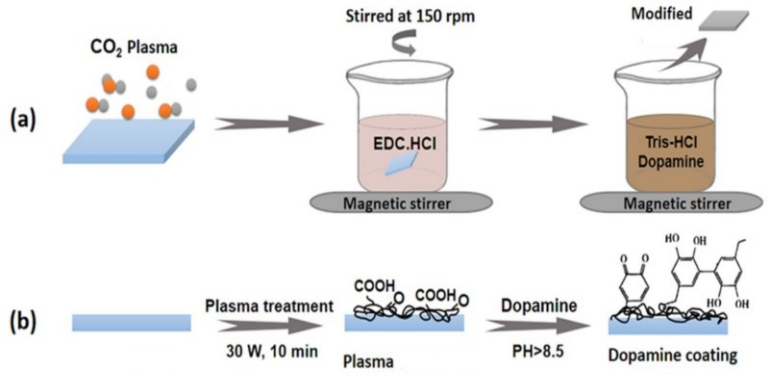

Fig 1. Control trial process for groups A and B

Sample Preparation and Release: This proficiency test uses 2 samples of 9L high polymer quality universal glue, respectively take 2L into a metal bucket, insert a wide-blade agitator and stir for 5 minutes, seal the metal bucket lid and invert the container for 10 minutes, then stand upright and then stand still For 30 minutes, divide into plastic bottles, each container is about 8g, heat-seal the plastic bottles with electromagnetic induction aluminum film, label them, and store them in a cool, dark place.

Samples are sent by courier to every laboratory. "Operating Instructions," "Test Item Receipt Confirmation Form," and "Result Report" were also sent to the participating laboratories. Samples that are received have to be stored at room temperature, sealed.

Uniformity testing: Using the GB 18583-2008 standard, the benzene concentration of ten randomly chosen bottles of prepared samples was determined for uniformity testing. CNAS-GL003:2018 was used to statistically process the data. [10] and the standard deviation of inhomogeneity (Ss) $\leqslant 0.3\ \sigma$ in one-way ANOVA (F-test).

Stability test: Six samples were chosen at random to verify the stability. The stability of the sample is assessed using the t-test technique in CNAS-GL003, and the data from the uniformity test is compared with the outcomes of each stability test. The cut-off value tα of the degrees of freedom is (n1+n2-2) if the t-value is less than the significant level α (often α=0.05), the sample is stable, and there is no significant difference between the mean values of the stability and uniformity tests.. The process is shown in Figure 2.

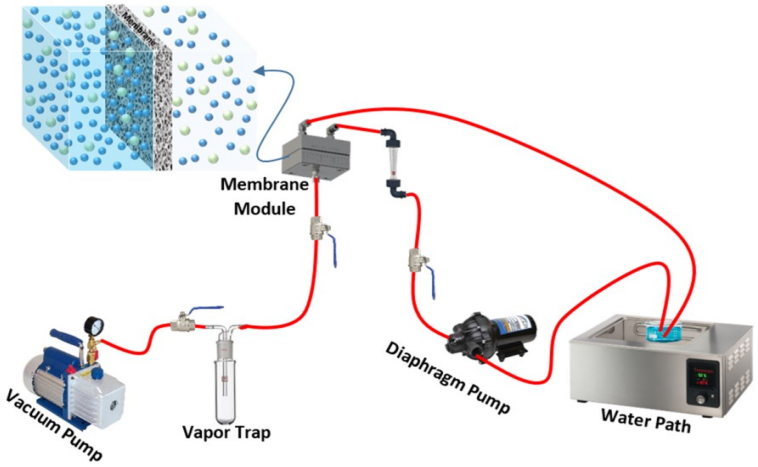

Fig 2. Evaluate the stability of the sample

This proficiency test recommends the use of gas chromatography in the GB 18583-2008 standard to determine the benzene content in samples.

2.3 Statistical Design

The aptitude test x's z-score is computed as follows as:

$$z = (x - X)/\sigma \tag{1}$$

Where

x is the lab test result,

X is the assignment

σ is the standard deviation of the capability assessment.

Validate the capability of the plan according to ISO 13528:2015(E)[11]", the robust averaging algorithm is calculated to estimate the sample population mean, the mean is specified as robust, and the robust standard deviation is used as the standard deviation of the capability assessment. The main process of algorithm A is as follows:

Represents p-item data, in increasing order, as follows: $x_1, x_2, \ldots x_p$

The robust mean and robust standard deviation of these data are calculated as follows. The initial values calculated are as follows (MED represents the median):

$$x^* = \text{med}\, x_i \ (i=1, 2, \ldots \pi) \tag{2}$$

$$s^* = 1.483 \times \text{med}|x_i - x^*| (i=1, 2, \ldots \pi) \tag{3}$$

According to the following steps, update and calculate:

$$\delta = 1.5 s^* \tag{4}$$

For each (i=1, 2, ... p), calculated

$$x_i^* = \begin{cases} x^* - \delta, if\ x_i < x^* - \delta \\ x^* + \delta, if\ x_i < x^* - \delta \\ x_i, other \end{cases} \tag{5}$$

Next, calculate the new valve:

$$x^* = \sum x_i^* / p \tag{6}$$

$$s^* = 1.134 \sqrt{\sum (x_i^* - x^*)^2 / (p-1)} \tag{7}$$

Additionally, the first iteration is finished. The robust mean and robust standard deviation of the data are ultimately acquired. The second iteration type (4) begins at the conclusion of Equation (7) and continues until the new robust mean and the standard deviation of robust convergence to three decimal places stay unchanged. Equation is used to determine the robust mean's standard uncertainty [12,13]:

$$u_x = 1.25 \times \sigma / \sqrt{p} \tag{8}$$

The ability to verify the importance of each statistic and associated calculation method is described in the CNAS-GL002:2018 [12] standard. The traditional explanation of the z-score is as follows. The results given $Z \leqslant 2$ are considered acceptable. The results given $2<Z<3$ are considered to give warning signs. The result given $Z \geqslant 3$ is considered unacceptable.

3. Results And Discussion

3.1 Participate in Lab Assignments

This proficiency test project received test results from 146 laboratories in total, with 57 laboratories in Guangdong, Beijing, and Jiangsu accounting for 39% of the total. 64 national central testing labs, or 44% of all registered laboratories, are among the laboratories taking part in this proficiency exam. The results are shown in Figure 3.

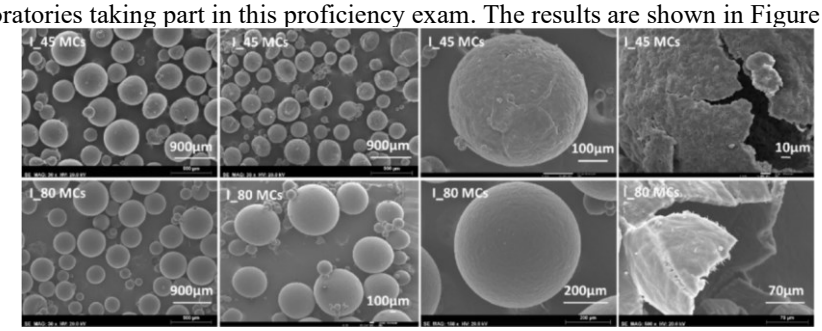

Fig 3. Microscopic and Electron Microscopic Structural Stability of Benzene in Adhesives under Different Magnification Rates

3.2 Uniformity and Stability of the Sample

Measure uniformity twice under the same conditions according to the method in section 1.1.3, calculate the statistical F value and Ss, and calculate the stability according to the method of statistical t value in section 1.1.4.

The accompanying table shows that the F value, Ss value, and T value are all smaller than the critical values t0.05/2(10)=2.23, F0.05(9,10)(3.02), and 0.3σ, respectively. The sample is homogenous and stable at the significance level of 0.05, according to the results.

Table 1. Statistical parameters of homogeneity and stability

Sample	Sample A	Sample B
F Valve	1.23	1.25
Sample standard deviation	0.32	0.11
Standard deviation for proficiency assessment	1.15	0.35
t valve	0.58	0.37

3.3 Mathematical Statistics of Test Scores

The test results of 130 laboratories were found to be good based on the statistical analysis of the aptitude test items, which accounted for 89.0% of the total feedback results; Eight laboratory test findings were unsatisfactory, making up 5.5% of all feedback results, and eight laboratory test results were problem results, making up 5.5% of all feedback results. The results of the competency exam are displayed in the following table, together with the pertinent statistical data. In Figure 4, the flow is displayed.

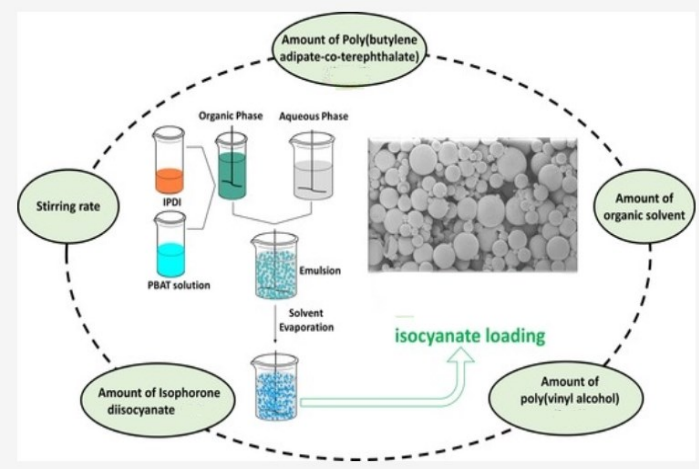

Fig 4. The relevant statistical parameters and proficiency test results

Table 2. Statistical parameters of benzene content

Sample	Sample A	Sample B
Result Number	59	87
Robust mean/(g/kg)	63.14	27.78
Robust standard deviation/(g/kg)	3.84	1.15
Robust coefficient of variation/%	6.08	4.14
Minimum/(g/kg)	44.64	2.216
Maximum/(g/kg)	72.34	38.68
2< | Z | <3	2	6
| Z | ⩾3	2	6

The Z-ratios are sorted by size in Figure 5 to make the outcomes of each laboratory proficiency testing method easy to see. The lab code is written on each column's label. Each lab may quickly determine where its results fall within the plan by comparing them to those of the other participating laboratories using the bar chart.

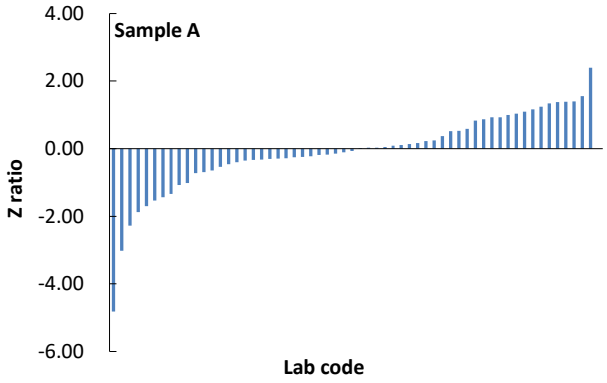

Fig 5. Z ratio of the content of benzene of sample A

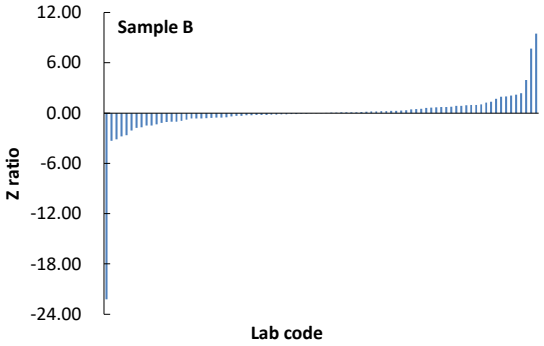

Fig 6. Z ratio of the content of benzene of sample B

4. Conclusion

All laboratories participating in this ability test are tested according to Annex B of GB 18583-2008 "Limit of Hazardous Substances for Adhesives for Interior Decoration Materials". 11% of labs had problems or were dissatisfied with the results. According to the feedback information of the testing equipment and operating conditions of each laboratory, the determination of benzene content in the adhesive should pay attention to the following points.

1) The purity of the standard solution benzene has a certain influence on the test results. The GB 18583-2008 standard stipulates that chromatographic grade benzene should be used to prepare the standard solution. Ensure that the prepared standard solution is accurate and meets the standard requirements. The diluent ethyl acetate should also choose analytical reagents produced by regular manufacturers, and blank. During the sample preparation process, ensure that the test sample adhesive is fully dissolved in ethyl acetate. The standard solutions used in the laboratories of this proficiency testing program mainly include brands such as Dr, Beijing Tanmo Quality Inspection Technology Co., Ltd., Chinese Academy of Metrology, and Standard Sample Research Institute of the Ministry of Environmental Protection.

2) For the preparation of standard solutions and sample solutions, high-precision electronic balances and calibrated volumetric flasks should be used. The organic reagents and samples used in the experiment are volatile. When weighing, add an appropriate amount of diluting solvent to the volumetric flask, and then add the sample. The weighing process should be rapid and the stopper should be closed in time to minimize the risk of component volatilization. Influence. When configuring the solution, consider the influence of ambient temperature on the volume of the volumetric flask. The laboratory with conditions can be carried out at 20°C. The volumetric flask and reagents need to be kept at a constant temperature to 20°C in advance. When the laboratory does not have the conditions, the volume is fixed at other temperatures. The volume of the volumetric flask should be corrected for temperature based on the glass expansion coefficient.

3) According to the requirements of GB 18583-2008, a capillary

chromatography column with dimethyl polysiloxane as the stationary liquid should be selected. The chromatographic columns used in the laboratories of this proficiency testing program mainly include DB-1/HP-1 (17 companies), DB-5/HP-5 (11 companies), DB-624/DB-1301 (6% cyanopropyl-phenyl 94% methyl polysiloxane , Medium polarity chromatography column) (14 companies), DB-WAX/HP-INNOWAX[16] (polyethylene glycol, polar chromatography column) (27 companies), DB-FFAP (acid-modified polyethylene glycol, Polar chromatographic column) (4 companies). 63.9% of laboratories used 30m length chromatographic columns, and some laboratories used 50m and 60m chromatographic columns. The selection of the chromatographic column should ensure the separation between the components [15], avoid the front and tail of the chromatographic peak, try to obtain sharp and symmetrical chromatographic peaks, and ensure the accuracy of quantitative calculations.

4) The appropriate linear range of the standard curve should be selected so that the test values fall within the standard curve. When testing low-content samples, the highest point of the standard curve can be appropriately lowered to improve the accuracy. For the gas chromatographic detection of benzene content, 88.4% of the laboratories used the aliquoting mode in this ability test, and the dispensing ratio was generally concentrated between 5~50, of which 20 were the most common. Split injection is suitable for most volatile samples and prevents column contamination.

5) All instruments used in the experiment should be within the verification or calibration period. It is necessary to check the instruments before the experiment to ensure that the technical indicators of the instruments can meet the relevant requirements. The instruments used in the laboratories of the proficiency testing program mainly include imported brands such as Agilent, Shimadzu, PE, Thermo, and BRUKER, and domestic instrument brands such as Beifen Ruili, Beijing Dongxi Analysis, and Tianmei, but the proportion of domestic instruments is relatively low.

Acknowledgment

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