Proficiency Testing for Determination of Water Content in Toluene of Chemical Reagents by iteration robust statistic technique

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Abstract. In order to investigate and improve the level of detection technology of water content in liquid chemical reagents of domestic laboratories, proficiency testing provider PT0031 (CNAS) has organized proficiency testing program of water content in toluene, 48 laboratories from 18 provinces/cities/municipals took part in the PT. This paper introduces the implementation process of proficiency testing for determination of water content in toluene, including sample preparation, homogeneity and stability test, the results of statistics of iteration robust statistic technique and analysis, summarized and analyzed those of the different test standards which are widely used in the laboratories, put forward the technological suggestions for the improvement of the test quality of water content. Satisfactory results were obtained by 43 laboratories, amounting to 89.6% of the total participating laboratories.

1. Introduction

The moisture content is common chemical reagent in the detection of the quality, is an important part of chemical reagent purity determination, influence quality, retention time and stability of chemical reagents, the significance of for the use of chemical reagents next[1]. "GB/T 690-2008", "Chemical reagent benzene", "GB/T 684-1999", "Chemical reagent toluene" and "GB/T 16494-2013" "Chemical reagent xylene" and other specifications and standards have made the requirements of moisture content. The liquid chemical reagents commonly used methods for the determination of water content by Karl Fehu titration [2], related standards are mainly GB/T 606-2003 "Chemical reagent--General method for the determination of water--Karl Fischer method", GB/T 6283-2008"Chemical products—Determination of water Karl·fischer method(general method)". At present the verification activities of the determination of liquid chemical reagent water content is less, and the standard test results of precision requirements, the determination of toluene to verify the ability of moisture content as an example, differences in the recognition of water between the determination results of the laboratory, the inter laboratory increase the comparability of measurement results, improve the detection level laboratory [3]. Through this program, each participating laboratory can not only understand the detection ability of self, can find the gap between the laboratory and similar, but also promote the laboratory to further improve the detection ability and the level of laboratory management, at the same time for CNCA and CNAS in the field of laboratory accreditation supervision.

2. Conceptual design

A. Test Sample
(1) Sample Design: The test sample is a bottle of chemical reagent sealed in brown glass sealed bottle about 30ml of toluene. Each laboratory will receive a sample of toluene, which can be tested directly.

(2) Sample Preparation and Release: Buy 4L bottled commercial chromatography grade chemical reagent toluene from TEDIA company, shake it, and then pack it into 110 bottles of sample. Containers used are brown glass bottles of 35ml, each sample of approximately 30ml. A brown glass bottle with a sample is wrapped in a bubble film and placed in a tin container. It is sealed and delivered to each laboratory by courier. To participate in the laboratory, at the same time receive the "work instructions", "receipt of the items to receive state confirmation form", "results report." The received samples shall be kept in sealed condition at normal temperature.

(3) Homogeneity Test: From the prepared samples, 10 bottles of samples were randomly selected for homogeneity detection. Water content was detected according to GB/T 606-2003, a general method of chemical reagent moisture determination, Carl Fischer method. The CNAS-GL03:2006 "Guidance on Evaluating the Homogeneity and Stability of Samples Used for Proficiency Testing" the provisions of the single factor analysis of variance (F test) and $S_s = 0.3$, criterion for statistical processing of test results.

Stability Test: 6 samples were randomly selected for (4) stability test. According to the CNAS-GL03 t test method for assessing the stability of samples, the results of each test and stability test of homogeneity data were compared, if $t$ is less than the significance level $\alpha$ (usually $\alpha=0.05$) degree of freedom $(n_1+n_2-2)$ the critical value of $T_{\alpha}(n_1+n_2-2)$, the average value between the average and the stability test of homogeneity there was no significant difference, the sample is stable.

B. Test Method
This capability certification is recommended in accordance with GB/T 606-2003 or other technical equivalent or equivalent standards.

C. Statistical Evaluation Method
Check the results of this capacity verification plan laboratory and press the Z value:

$$z = \frac{(X - \bar{X})}{\sigma}$$  \hspace{1cm} (1)

Type: - laboratory test results;
- specified value;
- ability to evaluate standard deviations (variability measures, target standard deviations).

The ability to verify the plan in accordance with the ISO 13528:2015 (E) "Statistical methods for use in proficiency testing by interlaboratory comparison", according to ISO 13528:2015 (E) C appendix A computing robust average algorithm to estimate the sample population mean, the average value is specified as a robust, robust standard errors as evaluation standard poor. The main process of the algorithm A is as follows. The P lab data is sorted first in ascending order:

The robust mean values and robust standard deviations for these data are calculated as. The initial value of the calculation is as follows (MED means median value):

$$\bar{x}^* = \text{med} x_i \quad (i=1,2,\ldots,p)$$  \hspace{1cm} (2)

$$s^* = 1.483 \times \text{med} |x_i - \bar{x}^*| \quad (i=1,2,\ldots,p)$$  \hspace{1cm} (3)

According to the following steps, update and value and calculate:

$$\delta = 1.5s^*$$  \hspace{1cm} (4)

For each $(i=1,2,\ldots,P)$, calculate

$$x_i^* = \begin{cases} x^* - \delta, & \text{if } x_i < x^* - \delta \\ x^* + \delta, & \text{if } x_i < x^* - \delta \\ x_i, & \text{other} \end{cases}$$  \hspace{1cm} (5)

Next, the new sum is calculated:

$$x^* = \frac{\sum x_i^*}{p}$$  \hspace{1cm} (6)
\[ s^* = 1.134 \sqrt{\sum (x_i^* - x^* )^2 / (p - 1)} \]  

(7)

So far, the first iteration was completed. The second iteration type (4) from beginning to end the formula (7), in turn, until the new robust average and robust convergence to the standard deviation of third decimal digits remained unchanged, and finally get the data robust average and robust standard deviation [4]. The standard uncertainty of the robust mean is calculated by the press:

\[ u_s = 1.25 \times s^* / \sqrt{p} \]  

(8)

Ability to validate the significance of each statistic and related computational methods see CNAS-GL02:2014," Guidance on Statistic Treatment of Proficiency Testing Results and Performance Evaluation ", and ISO 13528:2015(E) standards. The laboratory evaluation results in Z, the score is less than 2, the result is normal, indicating the detection ability of laboratory at the present situation is still satisfactory; 2<Z<3, the suspicious value description of laboratory current detection capability of the Z; more than 3, the outlier the current value that laboratory detection ability not satisfied with the situation.

3. Results and discussion

A. Participation in Laboratory Distribution

The ability to verify a total of 48 laboratories participated in, including production enterprises, quality supervision departments, inspection and quarantine system, social detection mechanism and a small amount of Research Institute, Petro China and other units, all submitted test results. To report the results of the laboratory are distributed in 18 provinces, autonomous regions and municipalities directly under the central government; in the laboratory the number and distribution of wide coverage, to a certain extent can reflect the ability of determination of moisture content of liquid chemical reagents in our laboratory, and provides a basis for determining and monitoring of our laboratory the detection ability.

B. Uniformity and Stability of the Sample

According to the method of uniformity in the 2.3 section in the same conditions for 2 times were calculated between mean square and mean square in the sample were 50.24, 41.27, F-measure computing statistics for 1.21, less than the critical value F(0.05 (9,10) (3.02); the calculation of statistics value is 2.12, less than the critical value of 0.3 sigma (10.7). It is showed that the sample was homogeneous at 0.05 significance levels.

Stability is calculated by 2.4 in section S before =6.97, S after =8.09, and the calculated statistic =1.64 is less than the critical value t(0.05/2 (10) =2.23. It showed that the sample was stable at 0.05 significance level.

C. Test Results and Mathematical Statistics

(1) Test Result: Test results were presented in 48 laboratories, and the results were shown in table 1.

| No. | Result No. | No. | Result No. | No. | Result No. | Result |
|-----|-----------|-----|-----------|-----|-----------|--------|
| 1   | 364.0     | 11  | 455.6     | 21  | 357.0     | 31     | 409.0   | 41     | 408.7   |
| 2   | 365.0     | 12  | 394.6     | 22  | 353.4     | 32     | 310.6   | 42     | 429.5   |
| 3   | 390.8     | 13  | 337.4     | 23  | 391.7     | 33     | 395.0   | 43     | 449.5   |
| 4   | 366.2     | 14  | 398.0     | 24  | 370.1     | 34     | 432.1   | 44     | 454.4   |
| 5   | 374.2     | 15  | 428.4     | 25  | 533.4     | 35     | 400.0   | 45     | 717.0   |
| 6   | 409.6     | 16  | 400.0     | 26  | 412.2     | 36     | 368.0   | 46     | 402.2   |
| 7   | 391.1     | 17  | 405.2     | 27  | 371.2     | 37     | 350.0   | 47     | 411.0   |
| 8   | 404.8     | 18  | 469.5     | 28  | 344.5     | 38     | 401.3   | 48     | 357.0   |
| 9   | 404.3     | 19  | 402.4     | 29  | 375.6     | 39     | 300.5   |        |        |
| 10  | 397.0     | 20  | 399.6     | 30  | 415.1     | 40     | 407.3   |        |        |
Statistics the frequency of all laboratory results, grouped according to the content, and frequency histograms, as shown in figure 1.

![Histogram showing of frequency distribution of testing results.](image1)

**Figure 1.** Histogram showing of frequency distribution of testing results.

Frequency distribution diagram shows that although there are individual extreme values, the overall data of this capability verification result appear to be in the middle and less at both ends. Mathematical Statistics of Test Results: The results show that the ability of statistical validation plan, there are 43 laboratories for the detection results with satisfactory results, accounting for 89.6% of the total number of detection results; 3 laboratories results for the problem, accounting for 6.2% of the total number of detection results; 2 laboratories were not satisfied with the results, accounting for 4.2% of the total number of feedback results. For statistical parameters, see table 2.

| Test item                      | Water content |
|--------------------------------|---------------|
| Result number                  | 48            |
| Robust mean (mg/kg)            | 395.3         |
| Robust standard deviation (mg/kg) | 35.7         |
| Standard uncertainty (mg/kg)   | 6.4           |
| Robust coefficient of variation (%) | 9.0           |
| Minimum (mg/kg)                | 300.5         |
| Maximum (mg/kg)                | 717.0         |
| Range (mg/kg)                  | 416.5         |

In order to clearly indicate the results of each laboratory's ability validation program, the Z radio are arranged in order of size (Fig. 2). Each column is marked with the code of the laboratory. From the bar chart, it is easy for each laboratory to compare its results with the results of other participating laboratories to find out where the results are in the plan.
In the laboratory the ability to verify the determination of water content standards, including GB/T 606-2003 "Chemical reagent--General method for the determination of water--Karl Fischer method", GB/T 1600-2001"Testing method of water in pesticides"," GB/T 2288-2008 "Coking products - Determination of moisture content", GB/T 6283-2008"Chemical products—Determination of water Karl-fischer method(general method )", SH/T 0246-1992 "Light petroleum products - Determination of moisture content (power law) " and ASTM D1364-02 (2012) " Standard Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method )", ASTM D6304-16e1 " Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration" , ASTM E203-16 " Standard Test Method for Water Using Volumetric Karl Fischer Titration", and ASTM E1064-16 "Standard Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration", determination of the above criteria are based on the principle of Carle Fischer method, there are 70.8% laboratories using GB/T 606-2003 and GB/T 6283-2008 two test standard; 71.4% laboratories using the moisture meter of Metrohm and METTLER TOLEDO companies. For the determination of water content of chemical reagent, there are many factors that influence the result of determination. The following points should be paid attention to in every laboratory:

1) the state of the instrument is the key factor for the result to be accurate, to ensure the tightness of the instrument line, to isolate the reaction system from the outside, and to avoid the pollution of the platinum electrode.

2) it should be minimized the water content of the Carle Fischer Reagent itself and the instrument system[5].

3) the sampling volume is correct or not is the key, the minimum amount of sampling to ensure its moisture content should be greater than the resolution of the instrument, sampling the maximum amount guarantee water capacity of the water does not exceed the system, such as the Kulun general Carle Fischer method, sample volume control in the absolute amount of water can get accurate results in 100μg -1000μg, and Carle Fischer method considering Carle Fischer Reagent Titration, besides, used to determine whether the balance after verification[6].

4) the automatic instrument parameters should be adjusted to a more suitable state, such as drift should be less than a certain value, otherwise it will bring greater uncertainty.

5) recommend using Merck, kGaA, apura, water-standard, Hydranal[7].

4. Conclusions
This work explores the use of toluene samples to carry out the ability to detect chemical reagent liquid water content verification, 48 laboratories in 18 provinces, autonomous regions and municipalities directly under the central government to participate in the verification activities this ability, through the statistical A algorithm based on robust technology, the test results of the satisfaction rate is 89.6%, that robust coefficient of variation was 9%. Most of the domestic testing laboratory has ability to detect liquid chemical reagent water, and objectively reflect the level of detection in the laboratory,
laboratory technology and promote the level of laboratory management and other aspects of the improvement, in particular are not satisfied with the results of detection in the validation plan ability of the laboratory, should actively look for reasons daily, to take steps to ensure the accuracy of test results.

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6. References
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