Evaluation of Uncertainty of Trichloromethane Extract

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Abstract—**The overall migration of pulp molding tableware in its food simulants often exceeds the prescribed limit. When that happens, the chloroform extraction experiment should be conducted to determine the residual content. In this paper, the overall migration of pulp molding tableware in the food simulant of 4% (volume fraction) acetic acid and the residual mass of chloroform extraction were tested. The influencing factors of the uncertainty were analyzed, the mathematical model of the uncertainty amount of the total migration amount was established by the experimental method, and the uncertainty components were calculated. The experimental results showed that the expanded uncertainty was 0.278mg/dm^2 (k=2), and the determination result after chloroform extraction was (13.25±0.278) mg/dm^2.**

Index Terms—**trichloromethane, total migration, extracts, uncertainty**

I. Introduction

Plant fiber (e.g., wood powder, wheat straw, bagasse, rice husk, hemp, bamboo fiber, etc.), as an environment-friendly fiber material, has become one of the main material for food contact usage owing to its excellent physical and mechanical properties. At present, plant fibers have been widely used to make food containers and packaging materials. However, under actual conditions of use, such tableware might release fluorescent brighteners, volatile substances, heavy metals and plasticizers that would cause contamination to food, posing hazadous effects to users' health. To solve this problem, experts at home and abroad have done a lot of relative research [1]-[4].

All countries follow different limits for specific substances and overall migration of plant fiber for food contact usage. China stipulates that when the overall migration result in certain food simulant exceeds 10 mg/dm^2, the residue should be extracted by chloroform according to 5.5.2 in GB 31604.8- 2016 [5] and the residue mass after extraction should be used for decision. When reporting the measurement results, a quantitative description of the extraction amount should be specified to determine the reliability of the measurement results and give a correct and credible uncertainty [6]. In this paper, pulp molding tableware was employed to evaluate the uncertainty of measurement of chloroform extract.

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II. Experimental Part

A. Reagents and Instruments

Chloromethane ($CHCl_3$) AR Sinopharm Chemical Reagent Co., Ltd.

Acetic Acid AR Sinopharm Chemical Reagent Co., Ltd

Electronic analytical balance AE-240 Mettler-Toledo Instruments (Shanghai) Co., Ltd.

Thermostatically controlled oven WFO-700W Shanghai Ailang Instrument Co., Ltd.

Electric thermostatic water bath DZKW-S-8 Beijing Ever Bright Medical Treatment Instrument Co., Ltd.

B. Experimental Methods

According to the test method in GB 5009.156-2016, the overall migration of paper pulp molding plates in the food simulant of 4% (volume fraction) acetic acid is 22.6mg/dm^2. For plant fiber food containers, when the overall migration exceeds the prescribed limits (10mg/dm^2), chloroform extracion should be employed to treat the residue. The residue mass after extraction is used to determine the result of overall migration more accurately. The detailed procedures are as follows: Add 50mL of chloroform to the obtained residue. After shaking and filtering with quantitative filter paper, the filtrate is transferred into a thermostatic evaporation dish. The extraction should be repeated three times. The filtrate was evaporated in a water bath until nearly dry. The evaporating dish was transferred into a 105℃ thermostatically controlled oven for drying for 2h. After that, the evaporating dish was taken out and cooled for 0.5h and weighed to get the chloroform extract residue. The mathematical model [7] determined according to the experimental method is as follows:

$$X = \frac{(m_1 - m_2) \times V}{V_1 \times S}$$

where: X -- The overall migration into the simulant, mg/dm^2

m_1 -- The mass of residue from the specimen after chloroform extraction, mg;

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m_2-- The mass of residue from the blank simulant, mg;
V -- Total volume of soaking liquid, mL;
V_1-- Determination of soaking liquid volume, mL;
S -- Contact area between sample and soaking liquid, dm^2.

III. Results and Discussion

A. Sample Test Results

The sample was tested 10 times in parallel according to GB 31604.8-2016, and the results were shown in Table I.

TABLE I. Overall Migration Measurement Results

No.	m_1	m_2	V	V_1	S	X
1	15.8045	0.3253	400	200	2.425	12.77
2	17.3035	0.4657	400	200	2.438	13.81
3	14.2763	0.5128	400	200	2.448	11.24
4	18.8341	0.2637	400	200	2.464	15.07
5	16.5172	0.4035	400	200	2.486	12.96
6	16.8115	0.3852	400	200	2.460	13.35
7	17.3244	0.4255	400	200	2.446	13.82
8	13.3653	0.4317	400	200	2.476	10.45
9	18.7425	0.3835	400	200	2.468	14.88
10	17.6147	0.3714	400	200	2.436	14.16

B. Analysis and Calculation of Factors Causing Uncertainty

The sources of uncertainty mainly comprise the following factors: 1. Weighing of m_1 and m_2. 2. Volume of the soaking liquid. 3. Transferring 200mL of the soaking liquid. 4. Sample's contact area with the soaking liquid. 5. Repeatability of measurement results.

1) Uncertainty of electronic balance weighing

The uncertainty introduced in the process of weighing m1 and m2 mainly originates from the uncertainty of the electronic balance. When handling the electronic balance, the operation procedures must be strictly followed, including cleaning the weighing plate, preventing contamination while taking away and putting on weighing vessels [8]. The uncertainty of the electronic balance comes from the following three factors: the standard uncertainty caused by standard weights, the standard uncertainty caused by measurement repeatability, and the uncertainty caused by the accuracy of the electronic balance.3.2.1.1 Standard uncertainty caused by standard weights.

According to the verification regulation in JJG99-2006 Weights, the extended uncertainty limit of E2 grade 200g weights is 0.10mg, k=3, normal distribution, then the standard uncertainty is:

$$\frac{0.10}{3} = 0.033mg$$

a) Standard uncertainty caused by measurement repeatability

This factor is A-class standard. The electronic balance is measured for 10 consecutive times with 200g standard weights, and the measurement results are obtained as follows: 200.0001g, 200.0002g, 200.0000g, 200.0001g, 200.0001g, 200.0000g, 200.0001g, 200.0000g, 200.0002g, and 200.0000g.

The arithmetic mean of the measurement results is:

$$\overline{X} = \frac{1}{n}\sum_{i=1}^{n} X_i = \frac{1}{10}\sum_{i=1}^{10} X_i = 200.0001g$$

According to Bessel's formula [9], the standard deviation of the measurement results is:

$$S = \sqrt{\frac{\sum_{i=1}^{n}\left(X_i - \overline{X}\right)^2}{n-1}} = \sqrt{\frac{\sum_{i=1}^{10}\left(X_i - \overline{X}\right)^2}{10-1}} \approx 0.079mg$$

In the actual experiment, each measurement is repeated for 6 times, and the standard uncertainty can be obtained as:

$$\frac{0.079}{\sqrt{6}} = 0.032mg$$

b) Uncertainty caused by the accuracy of the electronic balance

The verification certificate of the electronic balance indicates that its accuracy is ± 0.1mg. Suppose it's uniform distribution, B-class standard, the uncertainty can be obtained as:

$$\frac{0.1/2}{\sqrt{3}} = 0.029mg$$

c) Uncertainty of electronic balance weighing

The standard uncertainty [10] of weighing is obtained from the combination of the above three factors:

$$U(m) = 2\sqrt{0.033^2 + 0.032^2 + 0.029^2} = 0.1087mg$$

The mean value of (m_1-m_2) calculated from Table I is 16.22mg.

The relative standard uncertainty is:

$$U_r(\Delta m) = \frac{0.1087}{16.22} = 0.0067$$

2) Uncertainty of soaking liquid volume

The uncertainty of soaking liquid volume mainly arises from three factors: volume deviation of the measuring cylinder, experimental temperature, and reading.

a) Standard uncertainty caused by volume deviation of the measuring cylinder

According to the manufacturer's technical specifications, the volume deviation of 500 mL measuring cylinder is ±2.5mL. Without the confidence and distribution information, the standard uncertainty is calculated according to the triangular distribution:

$$\frac{2.5}{\sqrt{6}} = 1.021\text{mL}$$

b) Standard uncertainty caused by experimental temperature

For chloroform, the experimental temperature must be at (23 ±2)℃. Compared with the container, the soaking liquid has a larger volume expansion (the expansion coefficient of water is 2.1×10^{-4}℃$^{-1}$). The temperature range will lead to uncertainty in the volume measurement. Suppose the temperature follows rectangular distribution, the standard uncertainty of the volume of 400 mL is:

$$\frac{2.1\times10^{-4}\times400\times2}{\sqrt{3}}=0.0973\text{mL}$$

c) Standard uncertainty caused by reading

When recording the volume of the soaking liquid, the required accuracy for reading the soak volume is 2%. However, in practice, an uncertainty of about 1% is allowed while using the measuring cylinder. Suppose it's a triangular distribution, and the standard uncertainty is:

$$\frac{0.01\times400}{\sqrt{6}}=1.633\text{mL}$$

d) Uncertainty of soaking liquid volume

In this paper, the volume of the soaking liquid was 400 mL, and the standard uncertainty of the immersion liquid volume was obtained by the combination of the above three factors:

$$U(v)=\sqrt{1.021^2+0.0973^2+1.633^2}=1.928\text{mL}$$

The relative standard uncertainty is:

$$U_r(\Delta v)=\frac{1.928}{400}=0.0048$$

3) Uncertainty introduced by the transferring 200mL of the soaking liquid

According to the calculation steps in 2.2.2:

$$U(200)=\sqrt{(\frac{2.5}{\sqrt{6}})^2+\left(\frac{2.1\times10^{-4}\times200\times2}{\sqrt{3}}\right)^2+\left(\frac{0.01\times200}{\sqrt{6}}\right)^2}=1.308\text{mL}$$

The relative standard uncertainty is:

$$U_r(200)=\frac{1.308}{200}=0.0065$$

4) Uncertainty introduced by sample's surface area

The ratio of surface area to volume in this test is S/V= 6dm^2/1000mL; therefore, for 400 mL soaking liquid, the corresponding sampling area was 2.4dm^2. At 95% confidence interval, the measurement deviation is estimated to be 0.5mm, and the measurement uncertainty of its estimated size is 0.255mm (the value at 95% confidence interval divided by 1.96) [11]. Since the sample has a intact geometric shape, the uncertainty of area calculation is negligible. The standard uncertainty of measured sample area is:

$$U(s)=\sqrt{0.0255^2+0.0255^2}=0.036\text{dm}^2$$

The relative standard uncertainty is:

$$U_r(\Delta s)=\frac{0.036}{400}=0.00009$$

5) Uncertainty introduced by repeatability of measurement results

According to the data listed in Table I, the overall migration of the measured sample can be calculated as: 12.77, 13.81, 11.24, 15.07, 12.96, 13.35, 13.82, 10.45, 14.88, 14.16mg/dm^2, with an average value of 13.25 mg/dm^2.

The standard deviation is calculated by:

$$S=\sqrt{\frac{\sum_{i=1}^{n}\left(X_i-\overline{X}\right)^2}{n-1}}=0.882\quad(n=10)$$

The standard uncertainty of measurement repeatability is:

$$U(n)=\frac{0.882}{\sqrt{10}}=0.279$$

The relative standard uncertainty is:

$$U_r(n)=\frac{0.279}{13.25}=0.021$$

C. Combined Relative Standard Uncertainty

The combined relative standard uncertainty of the measurement obtained from the above calculation results is:

$$U_r(X)=\sqrt{U_r(\Delta m)+U_r(\Delta v)+U_r(200)+U_r(\Delta s)+U_r(n)}=$$
$$\sqrt{0.0067^2+0.0048^2+0.0065^2+0.00009^2+0.021^2}$$
$$=0.0105$$

$$U(X)=0.0105\times13.25=0.139\,\text{mg}/\text{dm}^2$$

D. Expanded Uncertainty

Take the coverage factor k=2, $U=2\times0.139=0.278\,\text{mg}/\text{dm}^2$.

E. Reporting the Result

According to the calculation results, the overall migration after chloroform extraction is (13.25±0.278) mg/dm^2, k=2 (95% confidence interval).

IV. Conclusion

The overall migration of pulp molding tableware in the food simulant 4% (volume fraction) acetic acid often exceeds the limit quantity prescribed in the standard, posing potential health risk to users. The result demonstrated that this product is not suitable for holding acidic food. Therefore, the conditions of utilization should be specified in the product label, in case improper use of

the product could contaminate food and threaten people's health.

From the above analysis and calculation, it can be concluded that the uncertainty in measuring the overall migration of nonvolatile mainly originates from electronic balance weighing and parallel measurement of the sample. Therefore, the accuracy of measurement can be improved by choosing electronic balance with high accuracy and increasing the times of parallel measurements.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Feng Guo and Wanru Zhou conducted literature review, experimental design, data analysis and data collation. Chengjun Shen has completed the proofreading and translation of the paper, and all authors have approved the final version.

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Quality and Safety Evaluation Technology of Food Plastic Packaging Materials under Specific Conditions of Use.
Paper Title: Discussion of the Performance on Impact Resistance of Six Plastic Films.
Paper Title: Demonstration of the Physical and Mechanical Properties of a New Polyester Film.