Evaluation of Uncertainty in Determination of the Migration of Antimony in Pet Samples by Inductively Coupled Plasma Mass Spectrometry

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Keywords: Polyethylene terephthalate (pet), The migration of antimony, Uncertainty, Inductively coupled plasma mass spectrometer (icp-ms)

Abstract: This experiment was based on "Determination of arsenic, cadmium, chromium, lead and the migration of arsenic, cadmium, chromium, nickel, lead, antimony, zinc in food contact materials and products"(GB/T 31604.49-2016), using inductively coupled plasma mass spectrometry Analyzer (ICP-MS) for analysis and detection of antimony migration in food packaging polyethylene terephthalate (PET) samples. The main sources of uncertainty in the test process was analyzed, and it was evaluated the values of standard uncertainty, synthetic uncertainty, and extended uncertainty. And then it was evaluated the applicability of the method by analyzing the results of the uncertainty.

1. Introduction

In recent years, the production of polyethylene terephthalate (PET) was developed rapidly. However, due to the complexity of the raw materials and processes for industrial production of PET, the processed PET was contained some small molecule chemicals. These small molecule chemicals would migrate and enter food during the food was contacted PET, which was potentially harmful to human health. Especially the wide application of recycled PET materials brings greater challenges to food safety[1].

2. Experimental Section

2.1 Experimental Basis

This experiment was mainly based on the standard method of "Determination of arsenic, cadmium, chromium, lead and the migration of arsenic, cadmium, chromium, nickel, lead, antimony and zinc" (GB/T 31604.49-2016) in food contact materials and products to measure the migration of antimony.

2.2 Equipment and Reagents

Reference material: Antimony in water (1000mg/L), Beijing Tanmo Quality Inspection Technology Co., Ltd.;

Equipments: (1) Electro- thermostatic draught drying cabinet (101-3AB); (2) Inductively coupled plasma mass spectrometer (PerkinElmer NexION 350X);

2.3 Experimental Procedure

Add 4% acetic acid solution to the samples and make sure that the distance between the liquid surface and the upper edge of the product does not exceed 1 cm. Soaking it in the oven at 60℃ for 10 days. The soaking solution makes them thoroughly mixed[3~4]. Then, take a part of the immersion to do analysis of ICP-MS. At the same time, do blank analysis[5].

3. Establishment of Mathematical Model

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a) Identify sources of uncertainty

Main sources of uncertainty in antimony migration: (1) Uncertainty due to preprocessing and repeated measurements; (2) The relative uncertainty of the calibration of the standard solution brought by the uncertainty of the working curve and the standard solution; (3) Uncertainty coming from instrument calibration.

b) According to the standard, the migration of antimony in the sample can be expressed by the following formula:

$$X = \frac{(A - A_0) \times F}{1000\rho}$$

Where: X – the migration of antimony (mg/kg);

ρ – Density of simulant (kg/L);

F – Dilution factor

A – Concentration of sample antimony (μg/L);

A_0 – Blank concentration (μg/L);

(ρ =1kg/L,F=1,A_0=0μg/L)

4. Uncertainty Evaluation

4.1 Uncertainty Due to Preprocessing and Repeated Measurements

The measurement repeatability of the sample mainly includes the repeatability of taking 4% acetic acid volume and the repeatability of the sample solution concentration measurement. The uncertainty caused by the above process was complicated and then considered.

The effects of sample pretreatment and measurement repeatability were evaluated with a type A uncertainty. The same sample was tested 9 times under the same conditions in parallel, and the measurement results were presented in table 1.

Table 1 Nine Measurements Of the Same Sample

Times	1	2	3	4	5	6	7	8	9
Sb (μg/L)	24.43	24.36	24.37	24.40	24.43	24.42	24.35	24.39	24.38
Sb (mg/kg)	0.02443	0.02436	0.02437	0.02440	0.02443	0.02442	0.02435	0.02439	0.02438

The average value of 9 measurements: $\overline{X}$ =24.39μg/L=0.02439 mg/kg

Standard uncertainty *u(X)* can be calculated by the following formula[6]:

$u(X) = \sqrt{\frac{\sum_{i=1}^{n}(Xi-\bar{X})^2}{n(n-1)}}$=0.01μg/L=0.00001 mg/kg

Thus, relative uncertainty $u_{rel}(X)$ was:

$u_{rel}(X) = \frac{u(X)}{\bar{X}}$=0.00041

4.2 Uncertainty Introduced by Standard Curve Measurement

a)Uncertainty of standard solution concentration

The standard solution was 1000mg / L, produced by Beijing Tanmo Quality Inspection Technology Co., Ltd. According to the relative expanded uncertainty given by the standard substance certificate, 1%, k = 2, so the uncertainty introduced by the standard solution was:

$u_{rel}(S) = \frac{1\%}{2} = 0.005$ (DOF: $\propto$)

b)Uncertainty due to standard curve fitting

Uses 5 concentration levels of antimony standard solutions, and the results were presented by table 2.

Table 2 Antimony Standard Curve Concentration and Correlation Coefficient

Concentration of Sb (μg/L)	0.573	1.462	10.126	47.914	101.025	$\overline{\square_{\square}}$ =32.22
cps	0.001	0.012	0.122	0.599	1.270	$\overline{\square_{\square}}$ =0.4008
Standard curve	$y = ax - b = 0.013x - 0.006$					
Correlation coefficient	r=0.9996					

The sample solution was measured 9 times. The average concentration ($\bar{x}$) obtained from the linear regression equation of the standard working curve obtained by cps was 24.39 μg/L. The standard uncertainty was introduced by the least square method to fit the standard curve. It could be calculated by the following formula[7]: $u(c) = \frac{s(y)}{a}\sqrt{\frac{1}{p}+\frac{1}{n}+\frac{(\bar{x}-\overline{c_x})^2}{\sum_{i=1}^{n}(c_x-\overline{c_x})^2}}$

among which, a=0.013;b=-0.006,twice tests P=9, n=5:

$\sum_{i=1}^{5}(c_x-\overline{c_x})^2$=7416.162

$s(y) = \sqrt{\frac{\sum_{i=1}^{5}[c_y-(b+ac_x)]^2}{n-2}}$=0.0296μg/L

$u(c) = \frac{0.102}{0.013}\sqrt{\frac{1}{9}+\frac{1}{5}+\frac{(24.39-32.22)^2}{7416.162}}$=0.319μg/L

Thus, the relative uncertainty $u_{rel}(c)$ was:

$u_{rel}(c) = \frac{u(C)}{\bar{X}}$ =0.0131

Thus, the relative uncertainty introduced by standard curve $u_{rel}(C)$ was:

$u_{rel}(C) = \sqrt{u_{rel}^2(S)+u_{rel}^2(c)}$ =0.000197 (DOF: $\propto$)

4.3 Uncertainty of Instrument Calibration

The detection limit of Sb was 0.03 μg / L, and the uncertainty given by the ICP-MS calibration certificate was u (k) = 0.6 μg / L, k = 2. So the standard uncertainty of the calibration result was[8]:

$u(K) = \frac{u(k)}{k}$=0.3μg/L

The relative uncertainty was:

$u_{rel}(K) = \frac{u(K)}{\bar{X}}$=0.012

Thus, the relative uncertainty of the antimony migration of the sample was as following:

$U_{rel} = \sqrt{u_{rel}^2(X)+u_{rel}^2(C)+u_{rel}^2(K)}$=0.012

At the 95% confidence level, when k=2, the relative expanded uncertainty of the determination of antimony migration in the sample was as following:

$U = 2 \times U_{rel} \times 0.02439$=0.00058536 mg/kg (DOF: $\propto$)

The migration amount of the sample antimony:

X= (0.02439±0.00058536) mg/kg

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