Evaluation of the Uncertainty in the Determination of Arsenic in Cosmetics by Inductively Coupled Plasma-mass Spectrometry (ICP-MS)

Abstract: A mathematic model for evaluating the uncertainty of the determination procedure for arsenic in cosmetics by ICP-MS was established. The uncertainty sources for each of the parameters in the model were analysed. The uncertainties of type A (based on the calculation of the statistical distribution of the determination results) was evaluated. According to the international general method, the component uncertainties were synthesized and extended respectively to obtain the uncertainty evaluation. The results showed that the uncertainty of weighing process, the uncertainty of sample digestion solution constant volume, the uncertainty of standard material, the uncertainty of standard curve fitting, and the uncertainty of determination repeatability were main source of the uncertainty. After the evaluation of each uncertainty components, the main component is the uncertainty of the curve fitting introduced by least-square method; the second is the uncertainty of the standard material introduced.

Keywords: uncertainty, ICP-MS, arsenic, cosmetics

1 Introduction

Evaluation of uncertainty of measurement for chemical analysis and laboratory quality control is very important [1–6]. Uncertainty of measurement is composed of multiple components. Some of the component measured column with statistical distribution estimation are available, and characterization and the standard deviation. Other component is available based on experience or other information given probability distribution estimation, also can use the standard deviation.

Analysis of arsenic in cosmetics widely was paid attention. Recently there are some application methods such as atomic fluorescence spectrometry (AFS), inductively coupled plasma emission spectrometry (ICP-OES). Inductively coupled plas-
mass spectrometry (ICP-MS) is a kind of high sensitivity, fast, high speed and efficient detection method, and has been widely used in many fields [7-13]. The results of uncertainty evaluation are particularly important. In this paper the uncertainty of As content in cosmetics by ICP-MS was studied. The results of the study have a certain guide for daily testing work in the laboratory.

2 Materials and Methods

2.1 Instruments, Reagents and Methods

2.1.1 Instruments and Reagents

ICP spectrometer (Agilent7700cx): United States Agilent company; MARSXpress microwave digestion: United States CEM company, with 40 digestion tubes; Electronic analytical balance (resolution 0.0001 g): mettler-toledo instrument (Shanghai) co., LTD.; 5 mL pipette; 100 mL volumetric flask; 65% nitric acid (excellent level pure): Germany MERK company products; Arsenic standard solution (1000 mg/L): provided by the national research centre for certified reference materials; Germanium (Ge) (1000 mg/L) internal standard solution: provided by the national research centre for certified reference materials.

2.1.2 ICP-MS Analysis Parameters

Adjust instruments indicators according to the detection signal in the tuning solution. The indicators of the instrument sensitivity, mass, the resolution, oxide and double charge meet the measurement requirements. Main working parameters are RF power 1250 w, spray chamber temperature 2 °C, pump rate 0.1 r/s, carrier gas (argon) flow 1.0 L/min, Sampling depth 7.2 mm, oxide rate < 1.5 %, double charge rate< 3 %. The internal standard method was used to quantify with 1 mg/L germanium (Ge) as internal standard of arsenic.

2.2 Detection and Method

Weight 0.500 g sample in the digestion tank, add 5 mL nitric acid, stand 30 min, cover relief valve, the digestion tank was put into the microwave digestion system, set up the appropriate program of microwave digestion, catch acid according to relevant steps after complete digestion, remove the digestive solution to 25.0 mL test tube, and constant volume to the scale with the deionized water for determination. Determine $^{75}\text{As}$ concentration in digested solution in $^{72}\text{Ge}$ as online internal standard
using inductively coupled plasma mass spectrometer, quantified after comparing with standard series solution.

3 The Results and Discussion

3.1 The Uncertainty Evaluation Mathematical Model

The mathematical model of arsenic content in the cosmetic as follows:

\[ C_s = \frac{X_0 \times V}{W \times 1000} \]

\( C_s \) is arsenic content in the samples (mg/kg), \( X_0 \) is arsenic concentration in sampling solution (μg/L), \( V \) is the volume of digestion solution (mL), and \( W \) is sample weight (g)

3.2 Uncertainty Source Analysis

According to the detection method and mathematical model, the main sources of uncertainty components are as follows: the uncertainty of weighing process introduction, the uncertainty of sample digestion solution constant volume introduced; the uncertainty of standard material introduced (the uncertainty of arsenic standard solution, the uncertainty of standard series of solution preparation); the uncertainty of standard curve fitting introduction; the uncertainty of determination repeatability introduction.

3.2.1 Uncertainty Introduced In The Weighing Process \( u_{rel}(M) \)

The uncertainty introduced by the sample came mainly from the repeatability of the weighing changes and balance calibration. By balance calibration certificate the allowed error is 0.0001g, uniform probability distribution, take \( K = \sqrt{3} \), and the standard uncertainty is

\[ u(M) = \frac{0.0001}{\sqrt{3}} = 0.000058g \]

Sample average weight \( M \) is 0.5003 g, and the relative uncertainty from the sample weight is
\[ u_{rel}(M) = \frac{u(M)}{M} = \frac{0.000058}{0.5003} = 0.000116 \]

### 3.2.2 Uncertainty of Sample Digestion Solution Constant Volume Introduced \( u_{rel}(V) \)

Transfer sample digestion solution to volumetric flask of 25 mL. The uncertainty mainly includes the following parts: the calibration uncertainty and the uncertainty of temperature effect introduction. The uncertainty of the volumetric flask capacity allowance introduced is \( u_1(V) \). On the basis of JG196-2006 working glass container, the capacity allowance of a level volumetric flask of 25 mL is \( \pm 0.04 \text{ mL} \) at 20 °C, uniform probability distribution, \( K = \sqrt{3} \), and the standard uncertainty of volumetric flask capacity allowance was

\[ u_1(V) = \frac{0.04}{\sqrt{3}} = 0.0231 \text{mL} \]

The uncertainty of temperature introduced is \( u_2(V) \). As we all known, the expansion coefficient of water is \( 2.1 \times 10^{-4} \). The temperature difference is \( \pm 4 \) °C, according to the confidence probability of 95 % (\( k = 1.96 \)) the uncertainty of temperature introduced is

\[ u_2(V) = \frac{25 \times 2.1 \times 10^{-4} \times 4}{1.96} = 0.0107 \text{mL} \]

So the standard uncertainty produced by 25 mL volumetric flask was

\[ u(V) = \sqrt{u_1(V)^2 + u_2(V)^2} = \sqrt{0.0231^2 + 0.0107^2} = 0.02546 \text{mL} \]

Therefore, the relative uncertainty introduced by the constant volume of sample digestion solution was

\[ u_{rel}(V) = \frac{u(V)}{V} = \frac{0.02546}{25} = 0.00102 \]

### 3.2.3 Uncertainty of Standard Material Introduced \( u_{rel}(S) \)

1) Uncertainty of as standard solution \( u_{rel}(\text{As}) \)
According to the standard solution certificate (20 mg/L arsenic standard solution), the relative expanded uncertainty (including 2 factors) is 0.24 %, and the relative uncertainty is:

\[ u_{\text{rel}} (\text{As}) = \frac{0.0024}{2} = 0.0012 \]

2) Uncertainty of standard series of solution preparation

Standard stock solution preparation: precise absorb arsenic (As) element standard solution (20 μg/mL) 1.0 mL into 100 mL volumetric flask, add 2 mL nitric acid, constant volume to the scale with deionized water, shake well, and arsenic (As) standard use solution content is 0.2 μg/mL. According to JJG196–2006 Working Glass Container, the capacity allowance of 1 mL pipette a grade is 0.01 mL. If the probability distribution is uniform, \( k = \sqrt{3} \). The standard uncertainty of the capacity allowance of the pipette was:

\[ u_1(1) = \frac{0.01}{\sqrt{3}} = 0.00577 \text{mL} \]

As we all known, the expansion coefficient of water is \( 2.1 \times 10^{-4} \). The temperature difference is ±4°C, according to the confidence probability of 95% (\( k = 1.96 \)) the uncertainty of temperature introduced is

\[ u_2(1) = \frac{1 \times 2.1 \times 10^{-4} \times 4}{1.96} = 0.000429 \text{mL} \]

So, the standard uncertainty introduced of 1 mL pipette was

\[ u(1) = \sqrt{u_1(1)^2 + u_2(1)^2} = \sqrt{0.00577^2 + 0.000429^2} = 0.005786 \text{mL} \]

Therefore in the preparation of arsenic standard stock solution the relative uncertainty introduced by 1 mL pipette was

\[ u_{\text{rel}}(1) = \frac{u(1)}{1} = \frac{0.005786}{1} = 0.005786 \text{mL} \]

Standard series of solution preparation: from the above 0.2 μg/mL arsenic standard solution respectively absorbs 2 mL, 5 mL, 10 mL, 20 mL into 100 mL volumetric flask and constant volume with 2 % nitric acid solution. According to JJG196–2006 Working Glass Container, the capacity allowance of 10mLA grade pipet is ± 0.025 mL. If
the probability distribution is uniform, \( k \) is \( \sqrt{3} \). The standard uncertainty of the capacity allowance of a grade pipet of 10mL was:

\[
\frac{u_1(10)}{\sqrt{3}} = 0.01443 \text{mL}
\]

As we all known, the expansion coefficient of water is \( 2.1 \times 10^{-4} \). The temperature difference is \( \pm 4 \) °C, according to the confidence probability of 95\% (\( k \) is 1.96) the uncertainty of temperature introduced is

\[
u_2(10) = \frac{10 \times 2.1 \times 10^{-4} \times 4}{1.96} = 0.00429 \text{mL}
\]

So the standard uncertainty introduced of 10 mL pipette was

\[
u(10) = \sqrt{u_1(10)^2 + u_2(10)^2} = \sqrt{0.01443^2 + 0.00429^2} = 0.01505 \text{mL}
\]

Therefore, in the preparation of arsenic standard series solution, the relative uncertainty introduced by 10 mL pipette was

\[
u_{rel}(10) = \frac{\nu(10)}{10} = \frac{0.01505}{10} = 0.001505 \text{mL}
\]

The standard uncertainty of 100 mL volumetric flask was as follows. The uncertainty of capacity allowance of the volumetric flask is \( u_1(V) \). On the basis of JJG196–2006 working glass container, at 20 °C the capacity allowance of 100 mL a level volumetric flask is \( \pm 0.10 \) mL. If the probability distribution is uniform, \( k \) is \( \sqrt{3} \). The standard uncertainty of the capacity allowance of the volumetric flask was

\[
u_1(V) = \frac{0.10}{\sqrt{3}} = 0.0577 \text{mL}
\]

The uncertainty of temperature introduced is \( u_2(V) \). As we all known, the expansion coefficient of water is \( 2.1 \times 10^{-4} \). Temperature difference is \( \pm 4 \) °C, according to 95 \% confidence probability of (\( k \) is 1.96), the standard uncertainty of introduced temperature was

\[
u_2(V) = \frac{100 \times 2.1 \times 10^{-4} \times 4}{1.96} = 0.0428 \text{mL}
\]

So the standard uncertainty generated by the 100 mL volumetric flask was
\[ u(V) = \sqrt{u_1(V)^2 + u_2(V)^2} = \sqrt{0.0577^2 + 0.0428^2} = 0.0718 \text{mL} \]

Therefore, the relative uncertainty of constant volume introduced by sample digestion solution was

\[ u_{rel}(V) = \frac{u(V)}{V} = \frac{0.0718}{100} = 0.000718 \]

To sum up, the uncertainty of standard substances was

\[ u_{rel(\text{standard})} = \sqrt{u_{rel(As)}^2 + u_{rel(1)}^2 + 4u_{rel(10)}^2 + 5u_{rel(100)}^2} = 0.00682 \]

\( u_{rel(As)} \) is 0.0012, \( u_{rel(1)} \) is 0.005786, \( u_{rel(10)} \) is 0.001505, and \( u_{rel(100)} \) is 0.000718.

### 3.2.4 Uncertainty of Standard Curve Fitting \( u_{rel}(Y) \)

Standard series solution of five points was determined using online internal standard method, and each point was measured three times. Test results and calculation results were listed in Table 1. According to the data fitting, \( Y = 0.0106C + 0.0036 \), the slope (b) is 0.0106, the correlation coefficient is 0.9995.
### Tab. 1: Test results of standard series solution

<table>
<thead>
<tr>
<th>C standard</th>
<th>Yi</th>
<th>Average</th>
<th>Curve simulation response values Y</th>
<th>(Yi-Y)²</th>
<th>(Cstandard-Cstandard average)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0.0030</td>
<td>0.00315</td>
<td>0.0036</td>
<td>3.6×10⁻⁷</td>
<td>219.4</td>
</tr>
<tr>
<td></td>
<td>0.0037</td>
<td>1.0×10⁻⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0027</td>
<td>8.1×10⁻⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.00</td>
<td>0.0463</td>
<td>0.0464</td>
<td>0.0462</td>
<td>1.0×10⁻⁸</td>
<td>116.64</td>
</tr>
<tr>
<td></td>
<td>0.0460</td>
<td>4.0×10⁻⁸</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0469</td>
<td>4.9×10⁻⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.00</td>
<td>0.1086</td>
<td>0.1091</td>
<td>0.1101</td>
<td>2.25×10⁻⁶</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1089</td>
<td>1.44×10⁻⁶</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1097</td>
<td>1.6×10⁻⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.00</td>
<td>0.2189</td>
<td>0.2188</td>
<td>0.2166</td>
<td>5.29×10⁻⁶</td>
<td>23.04</td>
</tr>
<tr>
<td></td>
<td>0.2194</td>
<td>7.84×10⁻⁶</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2182</td>
<td>2.56×10⁻⁶</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.00</td>
<td>0.4292</td>
<td>0.42877</td>
<td>0.4296</td>
<td>1.6×10⁻⁷</td>
<td>635.04</td>
</tr>
<tr>
<td></td>
<td>0.4277</td>
<td>3.61×10⁻⁶</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4300</td>
<td>1.6×10⁻⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.4×10⁻⁶</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3062.4</td>
<td></td>
</tr>
</tbody>
</table>

Note: 1) Cstandard is each point concentration of standard series solution (μg/L); 2) Yi is the ratio of the corresponding value of the standard series solution for determined elements and the internal standard

\[
\sum(Y_i - Y)^2 = 3062.4
\]

\[
\sum (C_{standard i} - C_{standard})^2
\]

In the type: b is the slope, \(S_Y\) is the residual standard deviation of the regression curve (residual standard deviation), \(p\) is the repeat number of the measurement sample (6 parallel samples, each sample was determined 3 times, \(p=6\times3\)), \(n\) is the points number of the regression curve (n=5), \(C\) is the concentration average of test sample, \(C_0\) is the concentration average of the regression curve at various points, \(C_{oj}\) is the concentration of each standard solution.

The residual standard deviation of curve fitting was
\[ S_Y = \sqrt{\frac{\sum (Y_i - \bar{Y})^2}{p-2}} = \sqrt{8.4 \times 10^{-6}} = 0.0029 \]

\[ C_{\text{standard}} = \frac{0 + 4 + 10 + 20 + 40}{5} = 14.8 \mu\text{g/L} \]

The standard uncertainty of standard curve fitting was

\[ u(Y) = \frac{S_Y}{b} \sqrt{\frac{1}{n} + \frac{1}{p}} + \sum \left( \frac{C_{\text{standard}} - C_{\text{sample}}}{C_{\text{standard}}} \right)^2 \]

\[ = \frac{0.0029}{0.0106} \sqrt{\frac{1}{5} + \frac{1}{18}} + \frac{(14.8 - 4.1484)^2}{3062.4} = 0.0801 \mu\text{g/L} \]

\( S_Y \) is the residual standard deviation of the fitted curve; \( b \) is the slope; \( n \) is the repeated number of the sample (\( n \) is 6); \( p \) is the repeated number of standard solution (5 points, each point was determined 3 times, \( p \) is 15). \( C_{\text{standard}} \) is arsenic concentration of the standard solution at various points; \( C_{\text{sample}} \) is arsenic concentration in digestion solution of the repeat measurement sample.

The relative uncertainty introduced by standard curve fitting was

\[ u_{\text{rel}}(Y) = \frac{u(Y)}{C_{\text{sample}}} = \frac{0.0801}{4.1484} = 0.0193 \]

### 3.2.5 Uncertainty of Determination Repeatability Introduction \( u_{\text{rel}}(X) \)

Sample 6 times measurement process and the results were shown in Table 2.

Weight 0.500g sample in digestion jar, add 5 mL nitric acid, put for 30 min, cover the relief valve, put the digestion tank into the microwave digestion system, set up the appropriate microwave digestion parameters according to relevant steps, after digestion completely catch the acid, remove the digestive solution to 25.0 mL test tube, scale with the deionized water for determination.

From Table 2, it showed that the sample standard deviation of the determination results were as follows:

\[ s = \sqrt{\frac{\sum (X_i - \bar{X})^2}{n-1}} = 0.00663 \text{mg/kg} \]
C for solution concentration of the continuous measurement in six copies sample solution, each sample measured three times, C is 4.1484 μg/L, so the uncertainty standard of the average 6 determination replicates was as follow:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample weight(M/g)</th>
<th>As concentration in digestion solution C_{standard} /(μg/L)</th>
<th>Arsenic content in the samples X/(mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5002</td>
<td>4.2212</td>
<td>0.2110</td>
</tr>
<tr>
<td>2</td>
<td>0.5003</td>
<td>4.1626</td>
<td>0.2080</td>
</tr>
<tr>
<td>3</td>
<td>0.5005</td>
<td>4.2658</td>
<td>0.2131</td>
</tr>
<tr>
<td>4</td>
<td>0.5004</td>
<td>4.0497</td>
<td>0.2023</td>
</tr>
<tr>
<td>5</td>
<td>0.5003</td>
<td>4.1656</td>
<td>0.2082</td>
</tr>
<tr>
<td>6</td>
<td>0.5002</td>
<td>4.0252</td>
<td>0.2012</td>
</tr>
<tr>
<td>Average M</td>
<td>0.5003</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Average X</td>
<td>-</td>
<td>0.2073</td>
<td>-</td>
</tr>
</tbody>
</table>

### 3.3 Final Relative Synthesis Uncertainty of Standard Uncertainty

\[
\begin{align*}
\text{u}_{rel} &= \sqrt{u_{rel}(M)^2 + u_{rel}(V)^2 + u_{rel}(s\text{tandard})^2 + u_{rel}(Y)^2 + u_{rel}(X)^2} = 0.0205 \\
\text{u}_{rel}(M) &= 0.000116, \text{u}_{rel}(V) &= 0.00102, \text{u}_{rel}(s\text{tandard}) &= 0.00682, \text{u}_{rel}(Y) &= 0.0193, \text{and} \text{u}_{rel}(X) &= 0.000461.
\end{align*}
\]

The average of arsenic content in the sample 6 replicates X is 0.2073 mg/kg, synthetic standard uncertainty is:

\[
u = 0.2073 \times 0.0205 = 0.00425 \text{ mg/kg}.
\]

If extension factor k is 2, the expanded uncertainty U is that 0.00425 plus 2, the result is 0.008 mg/kg.
3.4 Results Expression

According to the above results of the uncertainty evaluation, the uncertainty evaluation result of determination on arsenic content by microwave digestion - inductively coupled plasma mass spectrometry in cosmetics should be represented as:

\[ X = (0.207 \pm 0.008) \text{ mg/kg (k=2)} \]

4 Conclusions

From our studies, mainly sources of the uncertainty for the determination on As content in cosmetics by ICP-MS was: the uncertainty of weighing process introduction, the uncertainty of sample digestion solution constant volume introduced, the uncertainty of standard material introduced (the uncertainty of arsenic standard solution, the uncertainty of standard series of solution preparation), the uncertainty of standard curve fitting introduction, the uncertainty of determination repeatability introduction. The uncertainty of the weighing process introduction is the least compared of the uncertainty caused by other factors, and the uncertainty of standard curve fitting introduction is the largest.

Acknowledgement: This research is financially supported by the National Quality Infrastructure of National Major Scientific Research Issues 2016YFF0201904-02 and the project of General Administration of Quality Supervision, Inspection and quarantine 2011QK144.

References
