Uncertainty in Simultaneous Determination of Cr, Ni, As and Pb in Hot-melt Adhesives for Cigarette by Inductively Coupled Plasma Mass Spectrometry

He Aimin

Technology Center, China Tobacco Hebei Industrial Co., Ltd. Weiming South Street No.1, Shijiazhuang, 050051

Keywords: inductively coupled plasma mass spectrometry (ICP-MS); hot-melt adhesive for cigarette; heavy metal element; uncertainty

Abstract: In order to improve the accuracy of measurement results, the uncertainty in simultaneous determination of four heavy metal elements, namely chromium(Cr), nickel(Ni), arsenic(As) and lead(Pb) in hot-melt adhesives for cigarette using inductively coupled plasma mass spectrometry (ICP-MS) with microwave digestion is analyzed on the basis of JJF 1059.1-2012 'Evaluation and Expression of Uncertainty in Measurement', and the uncertainty of the measurement is evaluated based on four aspects, namely the sample preparation, the standard solution preparation, the calibration curve fitting and repeatability examination. The results show that: 1) The calibration curve fitting is the most important factor affecting the combined uncertainty, the second is the standard solution preparation, the third is the repeatability examination, and the last is the sample preparation. 2) As the content of Cr, Ni, As and Pb in hot-melt adhesive for cigarette are 0.3555, 0.0308, 0.0102 and 0.0305μg/g, the expanded uncertainty of measurement results are 0.0321, 0.0102, 0.0057 and 0.0106μg/g (P=0.95, k=2), respectively. It is less likely to get accurate measurement results for the low concentration compared with the high. In order to obtain more close to the true values of the test, it is necessary to improve the accuracy of experimental results in the order of the calibration curve fitting, the standard solution preparation, the repeatability examination and the sample digestion.

1. Introduction

The use of hot melt adhesive is in accordance with the requirements of cigarette processing technology, which can be realized in cigarette processing. Hot melt adhesives that meet the food hygiene standards [1]. YC/T 187-2004 limits the amount of arsenic (As) and lead (Pb) used in hot-melt adhesives for cigarettes [1]. When an analytical method is used to determine whether a material meets the legal limit, the analytic method, the reliability of the results and the results are particularly important [2]. In recent years, uncertainty as an evaluation method to measure the reliability of test results has gained wide attention and has been applied in chemical analysis and measurement. [3-6]. This research uses uncertainty to analyze and evaluate chromium (Cr), nickel (Ni), arsenic (As), and lead (Pb) in hot melt adhesives for cigarettes using microwave digestion pretreatment and ICP-MS. The purpose is tantamount to understand the key factors affecting each measurement link and provide theoretical references for improving the accuracy of test results.

2. Materials and Methods

Experimental methods and procedures were performed according to [7].

3. Results and Discussion

According to the JJF 1059.1-2012[8] assessment of the uncertainty of the measurement process in various aspects of the measurement results, we can see that the uncertainty of Cr, Ni, As and Pb measurement in this experiment mainly comes from the sample preparation, standard working

solution. Formulation, standard work curve fitting and repetitiveness investigation [9], mathematical models can be expressed as:

$$X = \bar{X} \pm \bar{X}\sqrt{u_1^2 + u_2^2 + u_3^2 + u_4^2}$$

Where: X—the content of elements in the sample, μg/g,;—the measured value of the element, μg/g,; u1—the relative standard uncertainty component introduced in the sample preparation; u2—the relative introduction of the standard working solution preparation The standard uncertainty component; u3—The relative standard uncertainty component introduced by the standard work curve fitting; u4—The relative standard uncertainty component introduced by the measurement repeatability.

This part of uncertainty is mainly due to the uncertainty caused by the use of balance weighing samples, namely the legal capacity and the weight of recovery.

Calibration certificate from the balance shows the allowable error A1 = 0.1mg, according to the rectangular distribution, k1 = √3, the second weighing, the sample is weighed in this experiment m_1 = 0.2g, after digestion the volume is made to m2 = 30g, then the uncertainty components produced by the weighing and constant volume are [6]:

$$u_{m,1}=.\frac{\sqrt{2}\times A_1}{k_1\times m_1} = \frac{\sqrt{2}\times 0.1}{\sqrt{3}\times 200}=4.08\times 10^{-4}$$

$$u_{m,2}=.\frac{\sqrt{2}\times A_1}{k_1\times m_2} = \frac{\sqrt{2}\times 0.1}{\sqrt{3}\times 30000}=2.72\times 10^{-6}$$

Uncertainty component introduced by weighing is:

$$u_m = \sqrt{u_{m,1}{}^2 + u_{m,2}{}^2} =4.08\times 10^{-4}$$

During the preparation of the sample, the elements in the sample to be tested may not completely enter the test solution due to incomplete digestion of the sample or element loss, contamination, etc. during the digestion process. This experiment was measured in parallel three times to obtain the recovery rate of Cr, Ni, As, and Pb. According to JJF 1059.1-2012[8], the half width of the interval a=(a_+-a_-)/2(a_+ is the upper limit, a_- is the lower limit), and according to the rectangular distribution, k2=√3, The uncertainty degree of recovery rate is: u_R =a/k_2, and the results are shown in Table 1.

Table 1 Uncertainty caused by the recovery rate

Element	Recovery rate/%	a	u_R
53Cr	93.1～97.3	0.021	1.21×10^{-2}
60Ni	101.5～105.2	0.018	1.07×10^{-2}
75As	106.0～110.6	0.023	1.33×10^{-2}
208Pb	116.9～119.6	0.014	7.79×10^{-3}

2.1.3 Uncertainty component caused by sample preparation

$$u_{1(Cr)} = \sqrt{u_m{}^2 + u_{R(Cr)}{}^2} =1.21\times 10^{-2}$$

$$u_{1(Ni)} = \sqrt{u_m{}^2 + u_{R(Ni)}{}^2} =1.07\times 10^{-2}$$

$$u_{1(As)} = \sqrt{u_m{}^2 + u_{R(As)}{}^2} =1.33\times 10^{-2}$$

$$u_{1(Pb)} = \sqrt{u_m{}^2 + u_{R(Pb)}{}^2} =7.80\times 10^{-3}$$

Uncertainty in this part comes from the standard substance solution itself, the pipefitting and

constant volume during the preparation of the working standard solution.

According to the certificate, the uncertainty of the standard substance solution (ρ=10mg/L) used in this experiment is H=±0.5%. According to the uniform distribution, k3=√3, the relative standard uncertainty component introduced by the standard substance solution is:

$$u_b = \frac{H}{k_3} = \frac{0.005}{\sqrt{3}} = 2.89\times 10^{-3}$$

This uncertainty includes the uncertainty introduced by pipettes and volumetric flasks. The principal sources are two types: 1. The uncertainty brought by the calibration; 2. The uncertainty brought by the temperature effect.

In the standard solution dilution process of this experiment, 0.1, 0.2, 0.5, 1, 2, 5, and 10 ml pipettes and 50 ml volumetric flasks were accustomed. Take a 0.5 ml pipettes as an example. The uncertainty is evaluated as follows:

Uncertainty components of pipetting introduced

1) The uncertainty component of calibration introduced: The allowable error of a 0.5 ml blow-out pipette by JJG196-2006[10] is B=±0.005 ml, distributed in a triangle, k4=√6, then the uncertainty component calibrated introduced by the 0.5 ml blow-out shift tube is:

$$u_{tp(0.5,1)} = \frac{B}{k_4 \times V_1} = \frac{0.005}{\sqrt{6}\times 0.5} = 4.08 \times 10^{-3}$$

In the formula: V1—the volume removed by the pipette, ml.

2) The uncertainty component introduced by the temperature effect: the temperature change during the experiment is D=±3°C, according to the rectangular distribution, k5=√3, the water expansion coefficient α=2.1×10-4, then the uncertainty component of the 0.5 ml pipette introduced by temperature effect is:

$$u_{tp(0.5,2)} = \frac{V_1 \times D \times \alpha}{V_1 \times k_5} = \frac{0.5\times 3\times 2.1\times 10^{-4}}{0.5\times\sqrt{3}} = 3.64\times 10^{-4}$$

The relative standard uncertainty component introduced by the 0.5 ml pipette is:

$$u_{tp(0.5)} = \sqrt{u^2_{tp(0.5,1)} + u^2_{tp(0.5,2)}} = 4.10\times 10^{-3}$$

The uncertainties introduced by the calibration of 0.1, 0.2, 1, 2, 5, and 10 ml pipettes, the uncertainty introduced by the temperature effect, the results of the composite relative calibration uncertainty are shown in Table 2.

(2) Constant volume introduced uncertainty component

The uncertainty introduced by the calibration of the 50ml volumetric flask u_(f(50,1)), the uncertainty introduced by the temperature effect u_(f(50,2)), the relative standard uncertainty u_(f(50)), the calculation method is the same as in 2.2.2(1). The results are shown in Table 2

Tab.2 Uncertainty of the pipette and volumetric flask

Number	Size/ml	Calibration tolerance/ml	Uncertainty			Type	Times
			Calibration	Temperature	Combined		
$tp_{(0.1)}$	0.1	0.002	8.16×10^{-3}	3.64×10^{-4}	8.17×10^{-3}	A, blow out type	1
$tp_{(0.2)}$	0.2	0.003	6.12×10^{-3}	3.64×10^{-4}	6.13×10^{-3}	A, blow out type	1
$tp_{(0.5)}$	0.5	0.005	4.08×10^{-3}	3.64×10^{-4}	4.10×10^{-3}	A, blow out type	2
$tp_{(1)}$	1	0.008	3.27×10^{-3}	3.64×10^{-4}	3.29×10^{-3}	A	1
$tp_{(2)}$	2	0.012	2.45×10^{-3}	3.64×10^{-4}	2.48×10^{-3}	A	1
$tp_{(5)}$	5	0.025	2.04×10^{-3}	3.64×10^{-4}	2.07×10^{-3}	A	1
$tp_{(10)}$	10	0.050	2.04×10^{-3}	3.64×10^{-4}	2.07×10^{-3}	A	1
$f_{(50)}$	50	0.050	4.08×10^{-4}	3.64×10^{-4}	5.47×10^{-4}	A	9

In this experiment, 0.1, 0.2, 0.5, 1, 2, 5, and 10 mL volumetric pipettes and 50 mL volumetric flasks were used during the preparation of the standard solution. Among them, 0.5 mL pipettes were used twice and the remaining volume was used once. The 50 mL volumetric flasks were used nine times. The composite standard uncertainty components introduced by pipettes and volumetric flasks were:

$$u_{tp} = \sqrt{u_{tp(0.1)}^2 + u_{tp(0.2)}^2 + 2u_{tp(0.5)}^2 + u_{tp(1)}^2 + u_{tp(2)}^2 + u_{tp(5)}^2 + u_{tp(10)}^2} = 1.28\times 10^{-2}$$

$$u_f = \sqrt{9 \times u_{f(50)}^2} = 1.64\times 10\text{-}3$$

$$u_s = \sqrt{u_{tp(0.1,1)}^2 + u_{tp(0.1,2)}^2 + u_{tp(0.2,1)}^2 + u_{tp(0.2,2)}^2 + 2u_{tp(0.5,1)}^2 + 2u_{tp(0.5,2)}^2 + u_{tp(1,1)}^2 + u_{tp(1,2)}^2 + u_{tp(2,1)}^2 + u_{tp(2,2)}^2 + u_{tp(2,2)}^2 + u_{tp(5,1)}^2 + u_{tp(5,2)}^2 + u_{tp(10,1)}^2 + u_{tp(10,2)}^2 + 9u_{f(50,1)}^2 + 9u_{f(50,2)}^2} = 1.29\times 10^{-2}$$

2.2.4 Uncertainty components introduced by standard working solution preparation

$$u_2 = \sqrt{u_b^2 + u_{tp}^2 + u_f^2 + u_s^2} = 1.85\times 10\text{-}2$$

In this experiment, 8 standard levels of standard solutions (3 times for each concentration) were measured on-line using the internal standard method. The ratio of the response value of the measured solution to the response value of the internal standard solution (Y) to the standard working solution concentration (C) was The regression equation and the linear correlation coefficient are obtained together (see [7]). Six samples of hot melt adhesive were measured to obtain the concentration of four heavy metals in the sample (see [7]). The relative standard uncertainty for the introduction of four heavy metals in hot melt samples was calculated using a fitted line:

$$u_3 = \frac{S_R}{b \times \bar{C}} \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(\bar{C} - \bar{C}_0)^2}{\sum_{i=1}^{n} (C_{0i} - \bar{C}_0)^2}} \quad \text{in which} \quad S_R = \sqrt{\frac{\sum_i^n (Y_i - Y)^2}{n-2}}$$

In the formula, the residual standard deviation of the SR-standard curve; b-slope (see [7]); p—the number of repeated measurements of the sample to be tested; n—the total number of pairs of data for the fitted line, $\bar{C}$ — the concentration of the sample to be measured Average value (see [7]); $\bar{C}_0$ - Average value of the concentration of each point of the standard working solution; C_{0i} - The concentration value of each point of the standard working solution; Y_i - The actual ratio of the response value of each standard working solution to the internal standard solution; Y - Each standard working solution the theoretical ratio of the response value to the internal standard solution.

The relative standard uncertainties for the introduction of four heavy metals in hot melt samples are:

$S_{R(Cr)}$=1.19×10-3，$S_{R(Ni)}$=8.69×10-4，$S_{R(As)}$=2.64×10-4，$S_{R(Pb)}$=7.24×10-4,

$u_{3(Cr)}$=3.64×10-2，$u_{3(Ni)}$=1.64×10-1，$u_{3(As)}$=2.77×10-1，$u_{3(Pb)}$=1.72×10-1.

A sample of hot melt adhesive was measured in parallel for 6 times to obtain the relative standard deviations of the four heavy metal contents of Cr, Ni, As, and Pb (see [7]). According to $u_4=\frac{RSD}{\sqrt{n}}$（n=6）, four heavy metals were obtained respectively. The relative standard uncertainty component introduced by repetitiveness: $u_{4(Cr)}$=1.49×10-2，$u_{4(Ni)}$=1.19×10-2，$u_{4(As)}$=1.84×10-2，$u_{4(Pb)}$=8.33×10-3.

According to $u_c = \overline{C} \times \sqrt{u_1^2 + u_2^2 + u_3^2 + u_4^2}$,, the combined standard uncertainty for the determination results of Cr, Ni, As, and Pb in hot melt adhesive samples was: $1u_{c(Cr)}$=1.60×10-2μg/g，$u_{c(Ni)}$=5.11×10-3μg/g，$u_{c(As)}$=2.84×10-3μg/g，$u_{c(Pb)}$=5.29×10-3μg/g

According to the confidence probability P = 0.95, if the inclusion factor k = 2 is taken, then the expanded uncertainty is: $U_{(Cr)} = 3.21 \times 10\text{-}2\,\mu g/g$, $U_{(Ni)} = 1.02 \times 10\text{-}2\,\mu g/g$, $U_{(As)} = 5.68 \times 10\text{-}3\mu g/g$, $U_{(Pb)} = 1.06 \times 10\text{-}2.\ \mu g/g$.

The residual amounts of Cr, Ni, As, and Pb in the hot melt adhesive samples were: (0.3555±0.0321)μg/g, (0.0308±0.0102)μg/g, (0.0102±0.0057)μg/g, (0.0305±0.0106)μg/g.

4. Discussion

Through the analysis and evaluation of the ICP-MS method for the simultaneous determination of the uncertainty of Cr, Ni, As, and Pb content in hot melt adhesives for cigarettes, it was found that the uncertainty introduced by the standard working curve fitting accounted for the largest weight (especially for The concentration of low-concentration elements is relatively large, followed by the uncertainty of the formulation and repetitive introduction of standard working solutions. The uncertainty introduced by sample preparation accounts for the smallest weight. Therefore, using this method to determine the contents of Cr, Ni, As, and Pb in hot melt adhesives for cigarettes, the key control points lie in the fitting of standard working curves and the preparation of everyday working solutions [7].

In order to reduce the uncertainty introduced by the curve fitting, especially for low concentration elements, the concentration range of the target work curve can be appropriately reduced according to the concentration of the target element of the test object, and the correlation coefficient can be increased to improve the accuracy of the analysis[9]; due to the low content of heavy metal elements in the hot melt adhesive, the preparation of standard working solution often requires progressive dilution, the error will increase with the increase of dilution steps, so in actual work, in order to reduce the standard working solution preparation To introduce the uncertainty, under the premise of ensuring the concentration range of the standard working solution, the dilution step should be minimized, and a high-precision measuring instrument should be selected to obtain a high-accuracy standard working solution[11].

The uncertainty introduced by repetitiveness is primarily due to the accuracy and performance of the instrument. It should be controlled and maintained by the instrument to reduce this uncertainty so as to ensure the accuracy and reliability of the measurement results. In order to decrease the uncertainty of sample preparation, the key to this experiment is to control the digestion process. The appropriate digestion method should try to select a relatively single reagent digestion system (to reduce the number of sample digestion and element loss). Introduce pollution opportunities) and avoid complicating digestion steps to increase recovery rate [11].

As an important content of prevailing error theory, the evaluation of uncertainty directly reflects the source of error in the quantitative analysis process, and provides a basis for reducing the error of the measurement procedure and improving the accuracy of the measurement result. This experiment uses ICP-MS to determine Cr, Ni, As, and Pb content in hot melt adhesives for cigarettes. In order to obtain measurement results that are closer to the true value, after the uncertainty evaluation, the everyday work curve should be fitted to the standard work. The procedure of solution preparation, repeatability measurement, and sample digestion should be carefully controlled [11].

References

[1] YC/T 187-2004 Cigarette hot melt adhesive[S].

[2] Li Zhongkai, Tang Gangling, Chen Zaigen, et al. Evaluation of Uncertainty in Determination of Benzene in Cigarette Packaging Materials by Headspace-GC-MS] [J]. Chinese Journal of Mass Spectrometry, 2009, 30 (6): 359-363.

[3] China National Accreditation Board for Laboratories. Evaluation Guide for Uncertainty in Chemical Analysis [M]. Beijing: China Measurement Press, 2002.

[4] Tang Xuemei. Application of Uncertainty Assessment in Quantitative Chemical Analysis [D]. Beijing: Beijing Jiaotong University, 2004: 4-8.

[5] Huang Shufang, Li Xiaozhong, Wang Xiuqi, et al. Evaluation of Uncertainty for Determination of Heavy Metal Lead in Tobacco Products by GFAAS[J]. Chinese Journal of Spectroscopy Laboratory, 2011, 28 (6): 3271-3276.

[6] JJF (Tobacco) 4.1-2010 Tobacco and Tobacco Products - Guidelines for the Evaluation of Uncertainty in the Measurement of General Chemical Compositions by the Continuous Flow Method Part 1: Water-Soluble Sugars [S].

[7] Simultaneous determination of chromium, nickel, arsenic and lead in hot-melt adhesives for cigarette by inductively coupled plasma mass spectrometry, Tobacco Science, 2015 (sup): 71-75.

[8] JJF 1059.1-2012 Evaluation and Expression of Measurement Uncertainty [S].

[9] Huang Huizhen, Jiang Jinfeng, Liang Hui, et al. Determination of the Uncertainty of Butyl Acetate in Tobacco Used Tip Paper by Headspace-Gas Chromatography[J]. Tobacco Science & Technology, 2014, 325(8): 38-41.

[10] JJG 196-2006 Common Glass Gauges [S].

[11] Wang Xinmei, Wang Ke, Ji Shen. Evaluation of uncertainty in determination of copper, arsenic, cadmium, mercury and lead in Chinese traditional medicine by ICP-MS[J]. Qilu Pharmaceutical Affairs, 2012, 31 (3): 136- 140.