The dry ashing - AAS method and the microwave digestion - ICP-MS method for determination of lead in plastic packaging bag

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Abstract. A pink plastic packaging bag sample from a enterprise was preliminarily screened via X-ray fluorescence spectroscopy method (XRF), it was found that the lead content exceeded the limit of relevant national standards. Subsequently, the total lead content in the packaging bag was determined via atomic absorption spectrophotometry pretreated by dry ashing method (DA-AAS) and inductively coupled plasma–mass spectrometry with microwave digestion method (MD-ICP-MS), respectively. The working curve equations were obtained by linear least squares method with the calculated linear correlation coefficients r above 0.9998 and the relative standard deviation (RSD) of the determination results from 1.0% to 6.2%, which was in good agreement with the result of XRF.

1. Introduction
Plastic packaging bags are widely used in daily life and industrial production, but their convenience brings long-term harm because they are not easy to degrade. Although the government has issued corresponding policies to limit the use of plastic bags, they are still frequent in daily life for the low requirements of regulations and standards and the lack of enforcement. In addition, in order to expand its application scope and attract the eye of consumers in perception, manufacturers would add various additives, such as plasticizers, stabilizers, colorants, lubricants, antioxidants, etc. These above additives are often harmful to human body, especially colorants, which may contain some heavy metal elements and the potential hazards to the body are greater if are misused in the field of food packaging.

Dry ashing and wet digestion are the frequently-used methods during the pretreatment process of the food-related samples, the pretreated samples are general quantitatively analyzed by atomic absorption spectrophotometry (AAS), inductively coupled plasma emission spectrometry (ICP) or inductively coupled plasma-mass spectrometry (ICP-MS) to obtain the content of the elements to be measured[1]-[5]. In this paper, the total lead content in plastic packaging bag was determined by atomic absorption spectrophotometry pretreated by dry ashing method (DA-AAS) and inductively coupled plasma–mass spectrometry with microwave digestion method (MD-ICP-MS), respectively. We hope to provide some methodological supports for the follow-up research and testing of plastic packaging related industries.
2. Experiment

2.1. Reagents and Samples
Nitric acids and hydrogen peroxide (AR, Chuandong Chemical (Group) Co., Ltd., China) were used. Pb element standard solution (1000 μg/mL) were obtained from the National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (China). A pink plastic packaging bag sample was employed in our experiment.

2.2. Sample Preparation
The preparation of test solution via DA-AAS method: Accurately weighed quantity of sample (about 2.0 g) was transferred to a porcelain crucible, added suitable amount of magnesium nitrate as auxiliaries and ashed in muffle furnace at 450 °C for 4 h with its cap covered. After cooling in the air, the appropriate diluted nitric acid solution (v:v=1:1) was gently dropped and then heated to boil on the electrothermal board for 5 min when the drastic reactions completed in the crucible. The mixture was transferred to a 100 mL volumetric flask after cooling down to room temperature. To rinse the intine and cover of the porcelain crucible for 5 ~ 6 times, transferred together to the above-mentioned volumetric flask up to the mark with ultrapure water and mixed well. At the end of filtering procedures, the mixture solution for AAS analysis was obtained. Each sample was determined in parallel twice and blank solution was prepared along with the above steps.

The preparation of experimental solution via MD-ICP-MS method: About 0.05 g of sample was accurately weighed on an electronic balance to 0.0001 g and placed into the polytetrafluoroethylene (PTFE) digestion jar. Subsequently, 6 mL of nitric acid and 2 mL of hydrogen acid were added into the PTFE digestion tank with the gland and nut-mounted. The temperature-programed settings in the microwave digestion instrument were as follows: room temperature to 140 °C for 10 min, 140 °C heat preservation for 5 min, and 190 °C heat preservation for 10 min. When the digestion process was completed, the sample solution contained in the digestion tank was evaporated on the LabTech electrothermal board at 140 °C and transferred to the 50 mL volumetric flask. The mixture was shaken well for analysis after cooling, and the intine of the digestion tank was flushed 2 ~ 3 times with ultrapure water. Diluted the mixture to the appropriate concentration before measuring and each sample was determined in parallel twice. Blank solution was prepared in a microwave as described above.

2.3. The Key Instruments and Setting
After preliminary semiquantitative tests carried out by the XSORT hand-held X-ray fluorescence spectrometer (XRF) (SPECTRO analytical instruments company, Germany), the dry ashing and wet digesting pretreatment procedures of the sample were conducted in the muffle and the MARS 6 microwave digestion instrument (Pynn Corp, United States of America) respectively. The concentration of Pb in the sample was determined via PinAAcle 900T atomic absorption spectrometer (AAS) (PerkinElmer Co., Ltd., United States of America) and Agilent 7700 x inductively coupled plasma mass spectrometer (ICP-MS) (Agilent Technologies Inc., United States of America) respectively, and key parameter settings were as follows (Table 1):

2.4. Work Curves
The preparation of standard solution via DA-AAS method: 1000 μg/mL Pb element standard stock solution was diluted stepwise to obtain three diverse-levels concentration gradient of 100 μg/mL, 10 μg/mL and 1 μg/mL. Afterwards 2.0, 5.0 mL (100 μg/mL) and 1.5, 2.0 mL (1000 μg/mL) were quantificationally transferred to four 100 mL volumetric flasks respectively, added to the graduated line of the volumetric flasks with ultrapure water and mixed well. In the end seven different-levels Pb standard solution of 0.0, 1.0, 2.0, 5.0, 10.0, 15.0, 20.0 μg/mL were obtained.

The preparation of standard solution via MD-ICP-MS method: Diluted the above 1 μg/mL of Pb standard diluted solution to 100 ng/mL, transferred 1.0, 2.0, 5.0 mL (1 μg/mL) and 1.0, 5.0 mL (100
ng/mL) Pb standard diluted solution to five volumetric flask respectively, and diluted with ultrapure water up to 100mL making five different-levels Pb standard solution of 1.0, 5.0, 10.0, 20.0 and 50.0 ng/mL, and finally shaken well.

Table 1. The operating settings of PinAAcle 900T atomic absorption spectrophotometry (AAS) and 7700x inductively coupled plasma mass spectrometer (ICP-MS).

| Parameter                          | PinAAcle 900T atomic absorption spectrophotometry (AAS) | 7700x inductively coupled plasma mass spectrometer (ICP-MS) |
|------------------------------------|--------------------------------------------------------|-------------------------------------------------------------|
| Wavelength                        | 283.31 nm                                               | 1550W                                                       |
| Slit                               | 0.7 nm                                                  | Plasma gas 15.00L/min                                        |
| Current                            | 10 mA                                                   | RF power 10.0mm                                              |
| Oxidant                            | Air                                                     | Sampling depth 10.0mm                                         |
| Oxidizer flow rate                 | 10.0L/min                                               | Carrier gas 1.05L/min                                        |
| Repetition number                  | 3 times                                                 | He gas 4.3L/min                                              |
| Flow rate                          | Acetylene flow rate                                     | Peristaltic pump 0.10rps                                     |
| Sample depth                       | Hollow-cathode lamp                                     | Atomizer chamber temperature 2℃                              |
| Lamp                               | Pb (C-HCL)                                              |                                                             |

3. Results and Discussions

3.1. The Calculated Linear Regression Equation

The least squares method for a unitary linear regression model were employed to obtain a calculation table of parameter estimation between the different-levels Pb standard solution concentration and the corresponding absorbance by DA-AAS method (Table 2).

Table 2. The regression calculation table of parameter estimation between the different-levels Pb standard solution concentration and the corresponding absorbance by DA-AAS method.

| Test Number/n | \(x_i\) | \(y_i\) | \(x_i^2\) | \(y_i^2\) | \(x_i y_i\) | \(I_{xx}\) | \(I_{xy}\) | \(I_{yy}\) |
|---------------|--------|--------|----------|----------|-----------|----------|----------|----------|
| 1             | 1      | 1      | 0.0228   | 0.0005   | 0.0228    |          |          |          |
| 2             | 2      | 2      | 0.0450   | 0.0020   | 0.0900    |          |          |          |
| 3             | 5      | 5      | 0.1023   | 0.0105   | 0.5115    |          |          |          |
| 4             | 10     | 10     | 0.2015   | 0.0406   | 2.0150    |          |          |          |
| 5             | 15     | 15     | 0.2937   | 0.0863   | 4.4055    |          |          |          |
| 6             | 20     | 20     | 0.3828   | 0.1465   | 7.6560    |          |          |          |
| Sum           | 53     | 53     | 1.0481   | 0.2864   | 14.7008   |          |          |          |
| Average       | 8.8333 | 0.1747 | —        | —        | —         |          |          |          |

From the above table, the relationship between the concentration of Pb standard solution \(x_i\) (μg/mL) and the absorbance corresponding \(y_i\) can be expressed by:

\[ y = \hat{\beta}_0 + \hat{\beta}_1 x \]  (1)

Which the slope \(\hat{\beta}_1\) and intercept \(\hat{\beta}_0\) can be calculated by Equation 2 and Equation 3 respectively. Here, \(\bar{x}, \bar{y}\) were a average value of \(x_i, y_i\) respectively.
Then the linear correlation coefficient $r$ was expressed as follows:

$$
\hat{\beta}_1 = \frac{\sum_{i=1}^{n} x_i y_i - n \bar{x} \bar{y}}{\sum_{i=1}^{n} x_i^2 - n \bar{x}^2}
$$

(2)

$$
\hat{\beta}_0 = \bar{y} - \hat{\beta}_1 \bar{x}
$$

(3)

According to the related parameters in the above table, formulas (1) ~ (4) were carried out to obtain the linear regression equation: $y = 0.00707 + 0.01897x$ ($r = 0.9998$). In the same way, the linear regression equation between the different-levles concentration of Pb standard solution and its corresponding absorbance determined by MD-ICP-MS method was obtained: $y = 40124 + 70572x$ ($r = 0.9999$). The linear regression equation, lower control limit (LCL) and upper control limit (UCL) were shown in Figure 1 and Figure 2.

![Figure 1. The linear regression equation, lower control limit (LCL) and upper control limit (UCL) via DA-AAS method.](image-url)
Figure 2. The linear regression equation, lower control limit (LCL) and upper control limit (UCL) via MD-ICP-MS method.

3.2. Interference Correction
In order to calibrate the changes of the response sign and eliminate the sampling error 205Tl was selected as online internal standard (ISTD) solutions during the MD-ICP-MS method determination. The relative standard deviation (RSD) of counts per second (CPS) ranged from 1.5% to 7.4% and the percent recovery were 100.0% - 104.3%. These aforementioned experimental facts testified that the stability and reliability of the measurement process were satisfactory.

3.3. Determination Results of Sample
The prepared sample solutions were analyzed via AAS and ICP-MS respectively. Statistical test results showed that there was no significant difference between the two methods, which were in good agreement with the result of X-ray fluorescence spectroscopy (XRF). The results of different methods were shown in Table 3.

| Method          | Parallel determination times | Work curves      | Linear correlation coefficient/r | Determination results of sample/(mg/kg) | RSD/ (%) |
|-----------------|------------------------------|------------------|----------------------------------|----------------------------------------|----------|
| XRF             | 1                            | -                |                                  | 1450                                   | -        |
| DA-AAS          | 2                            | $y=0.00707+0.01897x$ | 0.9998                          | 1190                                   | 1.4      |
|                 |                              |                  |                                  | 1207                                   | 1.0      |
| MD-ICP-MS       | 2                            | $y=40124+70572x$  | 0.9999                          | 1282                                   | 3.3      |
|                 |                              |                  |                                  | 1258                                   | 6.2      |

4. Conclusion
In this paper, dry ashing combined with atomic absorption spectrometry method (DA-AAS) and wet microwave digestion with inductively coupled plasma mass spectrometry method (MD-ICP-MS) were used to determine the lead content in plastic bags, and the working curve was calculated by linear least square method. The determined results of sample showed that the two methods were in good agreement with the result of X-ray fluorescence spectroscopy (XRF). This method is expected to provide a reference for the research and detection of similar materials.
References

[1] M. H. Peng, Z. H. Ming, L. G. Rong. Determination of Pb, Cr, Cd, and As in aluminum-plastic packaging materials via inductively coupled plasma–mass spectrometry with microwave digestion, Spectrosc. Spectral Anal. 37 (2017) 646-650.

[2] A. E. Fathabad, N. Shariatifar, M. Moazzen, Determination of heavy metal content of processed fruit products from Tehran's market using ICP- OES: A risk assessment study, Food Chem. Toxicol. 115 (2018) 436-446.

[3] M. Türkmen, D. Budur, Heavy metal contaminants in edible wild mushroom species from Turkey’s Black Sea region, Food Chem. 254 (2018) 256-259.

[4] S. L. Jackson, J. Spence, D. J. Janssen, A. R. S. Rossac, Determination of Mn, Fe, Ni, Cu, Zn, Cd and Pb in seawater using offline extraction and triple quadrupole ICP-MS/MS, J. Anal. At. Spectrom. 2 (2018) 304-313.

[5] G. M. Dico, F. Galvano, G. Dugo, Toxic metal levels in cocoa powder and chocolate by ICP-MS method after microwave-assisted digestion, Food Chem. 245 (2018) 1163-1168.