

# Fast ICP-MS method for determination of heavy elements in different types of food matrices

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## Overview

In this work, the concentrations of seven trace level heavy elements (As, Cd, Cr, Ni, Pb, Se and Tl) in different types of foodstuffs were determined using inductively coupled plasma mass spectrometry (ICP-MS). The food samples were prepared using microwave digestion method with nitric acid. A fast and versatile ICP-MS method using helium collision mode was developed. The method accuracy was verified by comparison of analysis results from different isotopes and validated using spike recovery test in a variety of food matrices to demonstrate its robustness and suitability for routine food safety analysis.

## 1. Introduction

Food safety may occur in food planting, processing and packaging. It has drawn great concerns due to air and soil pollution, environmental contamination and misuses of additives and materials in food processing and other human activities. Metal toxicity can be acute or chronic, depending upon one's dietary intake and duration of exposure. Toxic elements such as As, Cd, Pb and Tl are well known as they are among the most hazardous materials present in food chain based on their prevalence and the severity of their toxicity. Even at low concentration, these heavy metals could be potential threats to human health. Cr, Ni, Se are either required for plant growth or considered as essential micronutrient elements. However, they would become toxic at high concentrations. The determination of trace level metals in food is critical for food safety and human health [1, 2]. Among various techniques for heavy metal analysis, ICP-MS is the most ideal and reliable technique for measuring toxic elements in food due to its superior low detection limit, high throughput, wide linearity range and less interferences.



Figure 1: ICPMS-2030

## 2. Experimental

### 2.1 Sample preparation

Three food samples representing different food types were selected in this work. They are rice, Chinese noodle (processed food from dried plain flour) and onion (vegetable), which were obtained from the local market. The samples were dried in an oven at 60°C for 24 hours for dehydration. Approximately 0.5 g of each sample was weighed and transferred into pre-cleaned PTFE sample vessels. Mixture of 4.0 mL HNO<sub>3</sub> (Merck, 65% Suprapur®) and 1.0 mL H<sub>2</sub>O<sub>2</sub> (Kanto, 35-37%, Ultrapur-100) were then added. Wait for 10 minutes to let the sample to cool down before transferring the vessels into Milestone ETHOS EASY microwave digester. A multistep temperature program was applied for digestion as shown in Table 1. Sample blank was prepared by processing the solution which consists of the HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> plus 1mL ultrapure DI water through the same microwave digestion program. Transparent solutions were achieved for all the food samples and therefore filtration was not needed. The digested solutions were transferred into polypropylene tubes and topped up to 25 mL with ultrapure DI water. The sample solutions were further diluted by 4x before introduced into ICP-MS for measurement. An internal standard mixture of Sc, Rh and Ce was added using online internal standard addition kit to compensate matrix interferences during sample introduction. The addition of caesium as internal standard would also work as an ionization suppressant for ionization of interferences.

Table 1: Microwave digestion program of food samples

| Step | Temp              | Power | Time |
|------|-------------------|-------|------|
| 1    | Ramp to 120 °C    | 1200  | 5    |
| 2    | Hold at 120°C     | 1200  | 10   |
| 3    | Ramp to 200 °C    | 1800  | 5    |
| 4    | Hold at 200°C     | 1800  | 10   |
| 5    | cool down to 25°C | 0     | 20   |

### 2.2 Analytical conditions

All measurements were performed on Shimadzu ICPMS-2030 coupled with a mini torch and an AS-10 autosampler. A helium collision cell employed provides an effective way to remove polyatomic spectral interferences. In this study, the collision cell mode was applied to all targeted analytes to reduce the transition time from normal mode to collision mode for each standard and sample. Multiple isotopes were measured at the same time and compared for Cd, Cr, Ni and Pb. The detailed instrument configuration and the operating parameters are summarized in Table 2.

Table 2: Analytical conditions and parameters of ICPMS-2030

| Parameter           | Setting           |
|---------------------|-------------------|
| RF Frequency Power  | 1.20 kW           |
| Sampling Depth      | 6.0 mm            |
| Plasma Gas          | Ar 8.0 L/min      |
| Auxiliary Gas       | Ar 1.10 L/min     |
| Carrier Gas         | Ar 0.70 L/min     |
| Torch               | Mini-Torch, ICPMS |
| Nebulizer           | Nebulizer, 07UES  |
| Chamber             | Cyclone Chamber   |
| Chamber Temperature | 5°C               |
| No. of Scans        | 10 times          |
| Cell Gas (He)       | 6.0 mL/min        |
| Cell Voltage        | -21.0 V           |
| Energy Filter       | 7.0 V             |

## 3. Results and Discussion

### 3.1 Calibration curves

The metal concentrations were determined against calibration standards prepared in the sample matrix. Calibration standards and internal standards were prepared by mixing single element stock solution (1000 mg/L) following by dilution. The ranges of calibration curves for the targeted elements were up to 10 ppb except for Ni, which is calibrated up to 50 ppb to enclose the high concentration in onion sample into the calibration range.

### 3.2 Quantitative results of food samples

Quantitative results of the 7 targeted elements in the three foodstuffs (rice, noodle and onion) were determined and shown in Table 3. For Cd, Cr, Ni and Pb, the concentrations results measured with different isotopes were compared.

Table 3: Heavy metal contents determined in different food samples and the method detection limit (MDL).

| Isotope | Rice (µg/kg) | Noodle (processed) (µg/kg) | Onion (µg/kg) | MDL (µg/kg) |
|---------|--------------|----------------------------|---------------|-------------|
| As 75   | 85.6         | 4.9                        | 26.5          | 0.38        |
| Cd 111  | 8.7          | 27.4                       | 21.0          | 0.20        |
| Cd 112  | 9.7          | 28.3                       | 21.7          | 0.16        |
| Cd 114  | 9.5          | 28.0                       | 21.3          | 0.16        |
| Cr 52   | 21.7         | 43.9                       | 34.0          | 1.62        |
| Cr 53   | 22.6         | 41.0                       | 32.6          | 3.51        |
| Ni 60   | 510          | 105                        | 1768          | 1.08        |
| Ni 62   | 508          | 107                        | 1742          | 2.00        |
| Pb 206  | 45.1         | 59.0                       | 43.6          | 0.52        |
| Pb 207  | 42.6         | 55.5                       | 40.5          | 0.24        |
| Pb 208  | 45.4         | 59.7                       | 43.3          | 0.29        |
| Se 78   | 27.3         | 414                        | 7.2           | 9.60        |
| Tl 205  | 9.9          | 0.1                        | 1.3           | 0.02        |

It is known that Arsenic is one of the most toxic trace elements. The total As concentration in the rice sample was detected to be 85.5 µg/kg. This is the highest As concentration among the three tested samples. Though it was below the maximum allowed level (200 µg/kg) defined by European Commission (EC) 2006/1881 [2] for milled rice, the high arsenic content in rice sample indicated the potential of soil or water contamination where the rice was produced or during its processing.

Cadmium is a naturally occurring toxic heavy metal and a potent cell poison [3]. According to EU regulation for contaminants in foodstuffs [2], the maximum Cd level should be less than 200 µg/kg for rice and wheat grains, and less than 50 µg/kg for vegetables. As shown in Table 3, the concentration determined for Cd were all below the allowed concentration.

Similar Pb contents were detected in rice, noodle and onion samples at 45~60 µg/kg. The maximum allowed level for Pb contamination is defined by the EU regulation to be no more than 100 µg/kg in vegetables.

### 3.3 Evaluation of Method Performance

#### 3.3.1 Calibration linearity and detection limits

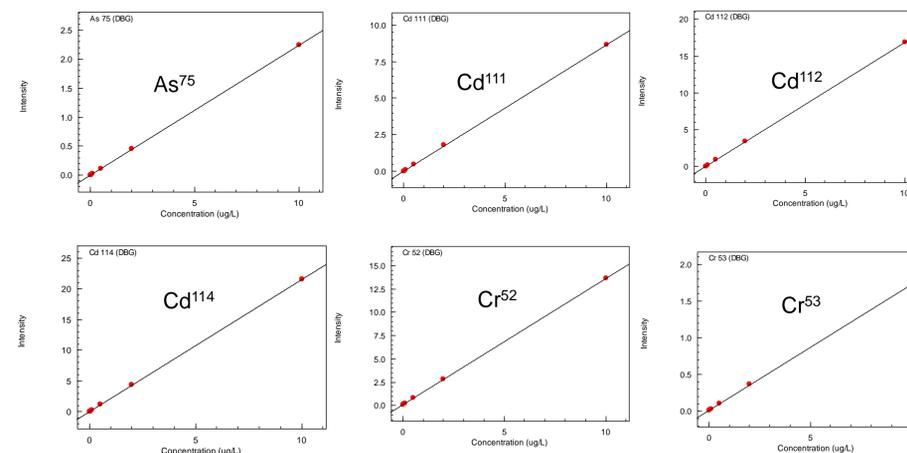

 Figure 2: Calibration curves for As<sup>75</sup>, Cd<sup>111</sup>, Cd<sup>112</sup>, Cd<sup>114</sup>, Cr<sup>52</sup> and Cr<sup>53</sup>.

Figure 2 shows the calibration curves of selected analytes with their isotopes. As shown in Table 4, the limit of quantitation (LOQs) were at ppt or sub ppb level, indicating the capability to determine trace levels of toxic and micronutrient elements in food with a large dilution factor (200x). Good linearities were established with correlation coefficients  $r > 0.9999$  for calibration curves of all analytes and isotopes.

Table 4: Correlation coefficients (r), LOD and LOQ in collision gas mode for elements at different masses.

| Element | Mass | Mode     | r       | LOD (ppb) | LOQ (ppb) |
|---------|------|----------|---------|-----------|-----------|
| As      | 75   | Cell gas | 1.00000 | 0.002     | 0.006     |
| Cd      | 111  | Cell gas | 0.99998 | 0.001     | 0.003     |
| Cd      | 112  | Cell gas | 0.99999 | 0.001     | 0.003     |
| Cd      | 114  | Cell gas | 0.99999 | 0.001     | 0.003     |
| Cr      | 52   | Cell gas | 0.99999 | 0.008     | 0.027     |
| Cr      | 53   | Cell gas | 0.99999 | 0.018     | 0.059     |
| Ni      | 60   | Cell gas | 1.00000 | 0.005     | 0.018     |
| Ni      | 62   | Cell gas | 1.00000 | 0.010     | 0.033     |
| Pb      | 206  | Cell gas | 0.99998 | 0.003     | 0.009     |
| Pb      | 207  | Cell gas | 0.99997 | 0.001     | 0.004     |
| Pb      | 208  | Cell gas | 0.99990 | 0.001     | 0.005     |
| Se      | 78   | Cell gas | 0.99998 | 0.048     | 0.160     |
| Tl      | 205  | Cell gas | 0.99990 | 0.0001    | 0.0003    |

### 3.3.2 Accuracy and Repeatability

Method accuracy was assessed by spiking 1 ppb of the 7 elements into the three food matrices. Satisfactory recovery rates of 91-108% in rice, 90-114% in noodle and 88-112% in onion sample were achieved, indicating the robustness of the ICP-MS method to handle a variety of food samples. Repeatability of spiked samples were of RSD% (n=3) less than 2.5% for majority of elements/isotopes with a few exceptions of up to 4%.

Table 5: Repeatability (n=3) and recovery of 7 heavy metals spiked in rice, Chinese noodle and onion.

| Isotope | Rice |           | Noodle (processed) |           | Onion |           |
|---------|------|-----------|--------------------|-----------|-------|-----------|
|         | RSD% | Recovery* | RSD%               | Recovery* | RSD%  | Recovery* |
| As 75   | 0.8  | 95%       | 0.6                | 103%      | 0.6   | 103%      |
| Cd 111  | 1.3  | 96%       | 1.5                | 97%       | 1.5   | 97%       |
| Cd 112  | 0.2  | 96%       | 0.8                | 98%       | 0.8   | 98%       |
| Cd 114  | 0.5  | 95%       | 1.2                | 97%       | 1.2   | 97%       |
| Cr 52   | 0.3  | 104%      | 0.8                | 114%      | 0.8   | 114%      |
| Cr 53   | 4.0  | 108%      | 0.7                | 114%      | 0.7   | 114%      |
| Ni 60   | 0.9  | 100%      | 1.4                | 105%      | 1.4   | 105%      |
| Ni 62   | 0.3  | 101%      | 2.5                | 101%      | 2.5   | 101%      |
| Pb 206  | 1.8  | 96%       | 1.2                | 91%       | 1.2   | 91%       |
| Pb 207  | 2.5  | 96%       | 0.8                | 90%       | 0.8   | 90%       |
| Pb 208  | 2.1  | 98%       | 2.0                | 92%       | 2.0   | 92%       |
| Se 78   | 3.2  | 88%       | 0.9                | 109%      | 0.9   | 109%      |
| Tl 205  | 1.4  | 104%      | 2.8                | 97%       | 2.8   | 97%       |

\* The data was calculated by subtraction of the residual elements as shown in Table 2.

Multiple isotopes for Cd, Cr, Ni and Pb were monitored and the results were compared in the three food matrices. The results are well agreed for different isotopes, indicating the absence of isobaric and polyatomic interferences in the analysis. The efficiency of applying helium gas to suppress polyatomic interferences were confirmed in different food samples.

## 4. Conclusions

A fast ICP-MS method was developed and applied to analyse seven heavy metal contents (As, Cd, Cr, Ni, Pb, Se and Tl) in rice, noodle and onion. The content levels of As, Cd and Pb are far below the maximum allowed level defined by EC 2006/1881. These three heavy metals and Tl are regarded as toxic elements and monitored for food safety. The other three elements (Ni, Cr and Se) are micronutrients for human health, but high levels being harmful. The ICP-MS method established exhibits good performance, with good linearity ( $r > 0.9999$ ) and low method quantitation limits at ppb to sub-ppb levels. Satisfactory recovery rates were obtained at 85% to 115% in three food matrices.

## References

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