Verification and confirmation of ICP-MS method for determination of As, Zn and Cr in water

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Abstract. According to the standard method of "Determination of 65 Elements in Water by Inductively Coupled Plasma Mass Spectrometry" (HJ 700-2014), the verification and confirmation of ability of detecting As, Zn and Cr in water were conducted in laboratory. Each element has a good linear relationship in the concentration range of 0 to 500 $\mu$g/L, and the correlation coefficients are all greater than 0.999. The laboratory detection limit of As, Zn and Cr was 0.06 $\mu$g/L, 0.29 $\mu$g/L and 0.03 $\mu$g/L, respectively. Which meet the requirements of corresponding detection limit in standard method (As detection limit: 0.12 $\mu$g/L, Zn detection limit: 0.67 $\mu$g/L, Cr detection limit: 0.11 $\mu$g/L); In the verification of experimental precision and accuracy, the relative deviation is 2.59%~10.1%, the recovery rate is 94.7%~109%, which are all meets the standard requirements of relative deviation should less than 20%, the recovery rate should be 80%~120%. The results confirmed that our laboratory possess the ability using ICP-MS to detect As, Zn and Cr in water.

1. Introduction

According to different pollution sources, water pollution can be divided into organic pollution, heavy metal pollution and microbial pollution. As the industrialization and regional urbanization continue to advance, the discharge of industrial wastewater and domestic sewage continues to increase. The pollution of China's water environment is not optimistic, and the heavy metals pollution of water is particularly serious. Wang evaluate the heavy metal pollution in the main river sediments of China by collecting a large amount of data and using method of the potential ecological hazard index. The results showed that there were different levels of Hg, Cd and mixed heavy metals pollution in the main stream sediments of the Yangtze River, Liaohe River, Yellow River, Pearl River, Songhua River, Haihe River and Huaihe River [1]. Pb and Cu exceed the standard by 62.9% and 25.9%, respectively in China's offshore waters. The content of Cd, Pb, and Zn in the sediments of the Dalian Bay water system exceeded that of quality standards of marine sediments [2]. Heavy metals in water can not only be degraded by microorganisms, but also could be enriched in animals and plants through the bio-chain amplification.
effect. Once ingested into the human body through drinking water or diet, it will seriously threaten human health. Therefore, the development of rapid and accurate heavy metal detection technology is of great significance for the identification of heavy metal pollution in water [3].

At present, the detection methods of metals are becoming more and more diverse, mainly including atomic absorption spectroscopy, atomic emission spectroscopy, atomic fluorescence spectroscopy, etc. The inductively coupled plasma mass spectrometry (ICP-MS) is a new elemental analysis technique. It has been widely developed and applied in the fields of environment, chemical industry, food, biomedicine, due to its high sensitivity, low detection limit, wide range of elements and other outstanding advantages [4, 5]. In order to implement the "Environmental Protection Law of the People's Republic of China" and the "Law on the Prevention of Water Pollution of the People's Republic of China", the Ministry of Ecology and Environment of the People's Republic of China promulgated the environmental standards of "Inductively Coupled Plasma Mass Spectrometry for the Determination of 65 Elements of Water Quality (HJ 700-2014) " for the first time on May 16, 2014. In order to improve the detecting ability and expand the business scope, the verification and confirmation of ability of detecting As, Zn and Cr in water were conducted in the laboratory, the detection limit, experimental precision and accuracy were carried out, according to the "General Requirements for Testing and Calibration Laboratory Capacity GB / T 27025-2008" to verify and confirm the application of this method in this experiment [6].

2. Materials and methods

2.1. Experimental principle
The liquid sample is atomized and sprayed into the atomization chamber by the atomizer at a certain rate in the channel, and the sample aerosol is transported by the carrier gas (argon) into the high-temperature plasma through the injection tube. The sample aerosol is evaporated and dissociated, atomized and ionized into positively charged ions, which enter the high vacuum mass spectrometer through the sample cone interface. All ions were separated and determined by high-speed sequential scanning with quadrupole scanning mass spectrometer according to the different mass to charge ratio (M / E) of elements.

2.2. Experimental instruments and chemicals
The ICP-MS (inductively coupled plasma mass spectrometry), Multi-element mixed standard solution, Multi-element mixed internal standard solution and Mixed tuning solution were products of Agilent Technologies. Ultra-pure water machine was brought from Millipore, the Pipette were products of Eppendorf, other chemicals such as sulfuric acid, Nitric acid were purchased from Sinopharm Group Chemical Reagent Co., Ltd. The purity of Argon and Helium were greater than 99.995%. All the instruments involved in this experiment are in good condition.

2.3. Experimental procedure

2.3.1. Sample pretreatment. After sample was collected, it is filtered with a 0.45 μm water-based filter membrane, immediately, and the filtered sample is added with an appropriate amount of nitric acid, adjusted to pH <2, waiting to be tested.

2.3.2. Standard curve preparation. Stepwise dilution and gravimetric method were used to prepare the standard curve. The 5% nitric acid solution was used to dilute the multi-element mixed standard solution.

2.3.3. Instrument debugging and analysis test. The instrument parameters for commissioning the instrument are shown in Table 3. After the helium gas is purged for about 20 minutes, the plasma is ignited. After the instrument is stabilized for 30 minutes, the sensitivity, oxide, and double charge of the instrument are optimized with the tuning fluid to ensure the best analysis status of the instrument. After
tuning, establish a method, set up a standard curve and batch of samples to be tested, and add a queue to start analysis and testing.

3. Results

3.1. Linear range
A standard curve is drawn with the measured signal intensity as the ordinate and the concentration (μg/L) as the abscissa. The summary of standard curve for determination of water As, Zn and Cr is shown in table 1. The data shows that each element has a good linear relationship in the concentration range of 0 to 500 μg/L, and the correlation coefficients are greater than 0.999.

Table 1. Summary of the standard curve

| Element | Concentration range (μg/L) | Linear equation | Correlation coefficient |
|---------|---------------------------|-----------------|------------------------|
| As      | (0, 0.2, 1, 5, 10, 20, 50, 100, 200) | y=9.791*10^-4x+0.0016 | 1.0000 |
| Zn      | (0, 0.2, 1, 5, 10, 20, 50, 100, 200, 500) | y=0.0011x+0.0037 | 0.9996 |
| Cr      | (0, 0.2, 1, 5, 10, 20, 50, 100, 200, 500) | y=0.0057x+8.6756*10^-4 | 0.9996 |

3.2. Determination of detection limit
According to the relevant provisions of “Technical Guidelines for Environmental Monitoring and Analysis Method Standards” (HJ 168-2010). Blank experiment was conducted for seven times, the standard deviation of seven parallel determinations was calculated. The detection limit was calculated according to the formula 1. The data were summarized in Table 2. The data shows that the detection limit of each element were is lower than or equal to the method detection limit, indicating that the measurement of As, Zn and Cr in this laboratory could meet the method requirements.

\[
\text{MDL} = t_{(n-1,0.99)} \times S
\]  

MDL—detection limit
n—number of parallel measurements
t—t distribution with n-1 degree of freedom and 99% confidence level (one-sided)
S—the standard deviation of parallel measurements.

Table 2. Summary of detection limit and lower limit of determination

| Element | Average x̄ (μg/L) | Standard deviations (μg/L) | Detection limit (μg/L) | Detection limit of the method (μg/L) |
|---------|------------------|-----------------------------|------------------------|------------------------------------|
| As      | 0.08             | 0.019                       | 0.06                   | 0.12                               |
| Zn      | 3.12             | 0.091                       | 0.29                   | 0.67                               |
| Cr      | 0.45             | 0.010                       | 0.03                   | 0.11                               |

3.3. Method precision
Three water samples with different concentration level were used to conduct method precision analysis. Each sample was measured in parallel six times. For the data summarized in table 3, the parameters such as the average value, maximum value, minimum value and relative deviation of different samples were calculated. The maximum and minimum values in the six parallel measurement were used to calculate the relative deviation, which is the maximum relative deviation in the set of data. Calculate the relative deviation according to formula 2.
\[ RD = \left| \frac{A - B}{(A + B)} \right| \times 100\% \]  

(2)

RD—Relative deviation;  
A—the maximum value;  
B—the minimum value;

Table 3. Summary of the maximum, the minimum value and Relative deviation of As, Zn, Cr

| Element | Concentration Level | Parallel measurement (μg/L) | A (μg) | B (μg) | RD (%) | Deviation requirements (%) |
|---------|---------------------|-----------------------------|--------|--------|--------|---------------------------|
| As      | 1                   | 1.91 1.95 2.00 2.03 2.11 2.17 1.91 | 6.37   |        |        | ≤20                       |
|         | 2                   | 2.75 3.12 2.82 2.55 3.01 3.05 2.55 | 10.1   |        |        | ≤20                       |
|         | 3                   | 6.04 5.60 5.56 4.98 5.62 5.96 5.98 6.04 | 9.62   |        |        | ≤20                       |
| Zn      | 1                   | 9.18 9.04 9.20 8.51 8.89 9.29 8.51 | 4.38   |        |        | ≤20                       |
|         | 2                   | 5.78 5.80 5.85 5.86 5.86 5.87 5.78 5.87 | 0.77   |        |        | ≤20                       |
|         | 3                   | 17.9 18.0 18.2 18.3 18.5 18.5 18.5 | 1.65   |        |        | ≤20                       |
| Cr      | 1                   | 19.78 19.88 19.98 20.0 19.89 19.87 19.87 19.78 | 2.59   |        |        | ≤20                       |
|         | 2                   | 6.64 6.65 6.65 6.65 6.66 6.69 6.69 6.64 | 0.38   |        |        | ≤20                       |
|         | 3                   | 18.9 19.0 19.2 19.2 19.5 19.6 19.6 19.8 | 1.82   |        |        | ≤20                       |

The maximum relative deviations of As, Zn and Cr in water by inductively coupled plasma mass spectrometry are 10.1%, 4.38%, and 2.59%, respectively, which meet the requirements in "Determination of 65 Elements in Water Quality by Inductively Coupled Plasma Mass Spectrometry HJ 700-2014" that the relative deviation of parallel samples should be less than 20%.

3.4. Method accuracy

The method precision analysis was carried out by adding certain concentration of multi-element mixed standard solution into three actual samples with different concentrations. Each sample was measured 6 times in parallel. The data was summarized in table 4. The average value of before and after adding certain concentration of multi-element mixed standard solution were measured, and the recovery rate was calculated.

Table 4. Summary of recovery rate of As, Zn, Cr

| Element Sample | Average \( \bar{x} \) (μg/L) Before adding | Detected adding amount (μg) | Actual adding amount(μg) | Recovery rate (%) |
|----------------|-------------------------------------------|-----------------------------|--------------------------|-------------------|
| As             |                                            |                             |                          |                   |
| 1              | 2.03                                      | 0.084                       | 0.08                     | 105               |
| 2              | 2.88                                      | 0.093                       | 0.09                     | 104               |
| 3              | 5.63                                      | 0.102                       | 0.10                     | 102               |
| Zn             |                                            |                             |                          |                   |
| 1              | 9.02                                      | 0.100                       | 0.1                      | 100               |
| 2              | 5.84                                      | 0.109                       | 0.1                      | 109               |
| 3              | 18.2                                      | 0.0985                      | 0.1                      | 99.0              |
| Cr             |                                            |                             |                          |                   |
| 1              | 10.0                                      | 0.0947                      | 0.1                      | 94.7              |
| 2              | 6.66                                      | 0.0962                      | 0.1                      | 96.2              |
| 3              | 19.2                                      | 0.0951                      | 0.1                      | 95.1              |

The inductively coupled plasma mass spectrometry was used to determine As, Zn, Cr in three actual water samples. The recovery rate of the standard was 94.7% -109%, which met the standard requirements of the recovery rate should be 80% - 120%.
4. Conclusion

According to the standard method of "Determination of 65 Elements in Water by Inductively Coupled Plasma Mass Spectrometry (HJ 700-2014)", the detection limit, experimental precision and accuracy of detecting As, Zn, Cr in water were carried out, and the results show that the detection limit, relative deviation and recovery rate measured and calculated in this experiment all meet the requirement of standard method. Which verified and confirmed that our laboratory possess the ability using ICP-MS to detect As, Zn and Cr in water.

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