Affirmation of the Method that Determination of Water Heavy Metals by Flame Atomic Absorption Spectrophotometry

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Abstract. For the FAAS determination of water heavy metal elements to confirm the method to determine whether the laboratory had the ability to detect the method. According to General Requirements for the Competence of Testing and Calibration Laboratories, GB/T 27025-2008” in the relevant requirements of personnel qualifications, facilities, environmental conditions and equipment. The results had shown that the standard curve of each element was R = 0.999 or more, and detection limits, accuracy, precision results were in line with standard requirements. The results confirmed that the laboratory had the ability to develop this method.

1. Introduction
China had abundant water resources. With the rapid development of social economy, the problem of water environmental pollution had become increasingly prominent. Heavy metal damage to China's water environment had caused the country's high attention. February 2012, the State Council promulgated and implemented the State Council's Opinions on Implementing the Most Stringent Water Resources Management System, for the treatment of heavy metal pollution in the water environment, ensuring drinking water safety, water supply security and ecological safety had extremely important practical significance and promoting .Therefore, it was particularly important to strengthen the research and monitoring of heavy metal pollution [1].

The laboratory had included the Water Quality - Determination of Copper, Zinc, Lead and Cadmium - Atomic Absorption Spectrophotometry, GB 7475-1987 within the scope of qualification certification. And according to General Requirements for the Competence of Testing and Calibration Laboratories, GB/T 27025-2008 and Environmental Monitoring-Technical Guideline on Drawing and Revising Analytical Method Standards, HJ 168-2010, the method was confirmed [2-4]. Method validation included detection limits, precision, accuracy, and actual sample determination, as well as assessment of personnel qualifications, environmental conditions, and equipment and equipment. Test
data and results were statistically processed to determine whether the laboratory had the ability to perform this method.

2. Overview

2.1. Cope of application
This study was applicable to the determination of copper, zinc, lead and cadmium in water.

2.2. Principle
After the water sample was pretreated, it was detected by a flame atomic absorption spectrophotometer. Pre-set drying, ashing, atomization, and other temperature-raising procedures evaporated the co-existing matrix components. At the same time, lead and cadmium compounded dissociate into ground state atomic vapor. The instrument selectively absorbed the characteristic lines emitted by the hollow cathode lamp and determined the concentration of the measured element in the sample.

3. Materials and methods

3.1. Instruments and reagents

3.1.1. The main reagent
(1) Standard copper solution substance (GBW08615), Standard zinc solution substance (GBW08620), Standard lead solution substance (GBW08619), Standard cadmium solution substance (GBW08612). The concentrations were all 1000 mg/L, China Institute of Metrology production.
(2) Trace element standard substance in water (GBW08607), China Institute of Metrology production.
(3) Nitric acid (HNO3): Excellent grade (Sino pharm Group Chemical Reagent Co., Ltd.).
(4) Per chloric acid (HClO4): Excellent grade (Sino pharm Group Chemical Reagent Co., Ltd.).
(5) Test water: Ultra-pure water, purified by Milli-Q System, resistivity not less than 18.2 MΩ•cm.

3.1.2. Instrument and working conditions. Atomic absorption spectrophotometer: Zeenit 700P, German Jena Company, Flame-Graphite Furnace Compact Design. The main working conditions were shown in the table 1.

| Element | Wavelength (nm) | Lamp current (mA) | Acetylene flow (L/h) | Air flow (L/h) | Slit width (nm) | Burner height (mm) |
|---------|-----------------|-------------------|----------------------|----------------|----------------|-------------------|
| Cu      | 324.8           | 2                 | 210                  | 50             | 1.2            | 6                 |
| Zn      | 213.9           | 2                 | 230                  | 50             | 0.5            | 6                 |
| Pb      | 283             | 2                 | 250                  | 65             | 1.2            | 6                 |
| Cd      | 228.8           | 2                 | 250                  | 50             | 1.2            | 6                 |

3.2. Experiment metho

3.2.1. Standard curve line. Draw 10mL single element solution standard substance and 1000mL PTFE volumetric flask, and use 1% HNO3 to make it into volume. This is 10 mg/L standard single-use solution. Drain the standard single-use solution into a 100mL PTFE volumetric flask, copper, zinc and lead elements formulated as a standard series of six calibration points, such as 0 mg/L, 0.1 mg/L, 0.3 mg/L, 0.5 mg/L, 0.8 mg/L, 1 mg/L. Standard series of six calibration points for cadmium 0 mg/L, 0.01 mg/L, 0.02 mg/L, 0.05 mg/L, 0.08 mg/L, 0.10 mg/L. Both were fixed with 1% HNO3.
3.2.2. Sample preparation. Took 100 mL water sample and add 5 mL HNO₃. Heated to about 10 mL, add 5 mL of HNO₃ and 2 mL of HClO₄ to continue heating and digestion to about 1 mL. Repeatedly purging with water, transfer the filtrate to a constant volume in a 100 mL volumetric flask. Prepare blank samples in the same way.

3.2.3. Instrument determination. After completing the self-test of the instrument, the instrument installed the corresponding element hollow cathode lamp, selected the corresponding method, and adjusted each indicator of the instrument. It established the analytical method, set up the sample batch and added it to the queue, and the instrument started the analysis.

4. Results and discussion

4.1. Standard curve and linear regression equation
According to the content range of the sample element, a standard curve was drawn. The elements to be measured had a good linearity within the measured concentration range. The correlation coefficients were all above 0.999 (Table 2).

| Element | Measurement range (mg/L) | Slope/b | Intercept/a | Correlation index/R² | Correlation coefficient/R |
|---------|--------------------------|---------|-------------|----------------------|--------------------------|
| Cu      | 0~1.0                    | 1.92×10⁻¹ | 1.49×10⁻³  | 0.9997               | 0.9999                   |
| Zn      | 0~1.0                    | 6.31×10⁻¹ | 1.70×10⁻²  | 0.9989               | 0.9995                   |
| Pb      | 0~1.0                    | 1.82×10⁻² | 1.97×10⁻⁵  | 0.9981               | 0.9991                   |
| Cd      | 0~0.10                   | 6.54×10⁻¹ | 7.94×10⁻⁴  | 0.9995               | 0.9998                   |

4.2. Method detection limit
According to sample analysis all steps, repeated n (n ≥ 7) blank tests. The result of the measurement was converted into the concentration in the sample, and calculated the standard deviation of n parallel measurements. Calculated the method detection limit according to the following formula. The lower limit of detection was 4 times the detection limit. The result was judged reasonable [8].

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

The detection limit and the lower limit of determination for each element method were shown in Table 3. Visible from Table 3, the detection limit of each element was lower than the detection limit required by GB 7475-1987. Detection limit met measurement requirements.

| Element | Detection limit calculation (mg/L) | Lower limit calculation (mg/L) | Lower limit element by GB 7475-1987 (mg/L) | Conclusion |
|---------|-----------------------------------|--------------------------------|---------------------------------------------|------------|
| Cu      | 0.01                              | 0.04                           | 0.05                                        | pass       |
| Zn      | 0.01                              | 0.04                           | 0.05                                        | pass       |
| Pb      | 0.05                              | 0.20                           | 0.2                                         | pass       |
| Cd      | 0.01                              | 0.04                           | 0.05                                        | pass       |

4.3. Method precision
Perform 15 parallel measurements on the same sample. The result was calculated relative standard deviation to determine its precision. The result was shown in Figure 6. Table 4 showed the precision of the measured values of each element. The results were less than the standard reference relative standard deviation. Method precision met measurement requirements.
### Table 4. Precision test results

| Element | Test results(mg/L) | Relative standard deviation | Relative standard deviation by GB 7475-1987 | Conclusion |
|---------|--------------------|------------------------------|--------------------------------------------|------------|
| Cu      | 0.501              | 0.94%                        | 3.13%                                      | pass       |
| Zn      | 0.589              | 1.21%                        | 1.60%                                      | pass       |
| Pb      | 0.602              | 1.55%                        | 3.61%                                      | pass       |
| Cd      | 0.0584             | 1.76%                        | 5.88%                                      | pass       |

4.4. Method accuracy

Certified Reference Material (China Institute of Metrology) was repeatedly measured six times. Result calculated relative error. The relative error results were shown in Table 5. The mean value of each element was within the standard value range. The relative error was less than 5%. Method accuracy met measurement requirements.

### Table 5. Accuracy test result element (Trace elements in water/GBW08607)

| Element | Mean value (mg/L) | Standard value (mg/L) | Relative error (REi%) | Conclusion |
|---------|-------------------|-----------------------|-----------------------|------------|
| Cu      | 1.02              | 1.03±0.01             | 0.97                  | pass       |
| Zn      | 5.12              | 5.15±0.05             | 0.58                  | pass       |
| Pb      | 1.00              | 1.01±0.02             | 0.99                  | pass       |
| Cd      | 0.102             | 0.104±0.02            | 1.92                  | pass       |

4.5. Sample spike recovery

A sample was tested as a background. The sample was added with different concentrations of low, medium and high concentrations of the standard solution and measured 3 times. Result calculated the spike recovery rate. The test results were shown in Table 6. The recovery rate of this study was between 95.0% and 105%, indicating that this method had better accuracy [5].

### Table 6. Spiking Recovery Test Results

| Element | Background mean (mg/L) | Scalar (μg) | Recovery rate (p%) | Scalar (μg) | Recovery rate (p%) | Scalar (μg) | Recovery rate (p%) | Conclusion |
|---------|------------------------|-------------|-------------------|-------------|-------------------|-------------|-------------------|------------|
| Cu      | 0.2004                 | 10.0        | 101               | 20.0        | 102               | 30.0        | 98                | pass       |
| Zn      | 0.2018                 | 10.0        | 102               | 20.0        | 101               | 30.0        | 100               | pass       |
| Pb      | 0.2122                 | 10.0        | 105               | 20.0        | 102               | 30.0        | 102               | pass       |
| Cd      | 0.0509                 | 17.5        | 99                | 22.5        | 99                | 27.5        | 99                | pass       |

5. Conclusion

This laboratory was based on the relevant requirements of General Requirements for Testing and Calibration Laboratory Capabilities, GB/T 27025-2008. The flame atomic absorption spectrophotometric method for the determination of heavy metals in water was confirmed by means of method detection limits, precision, addition and recovery tests, environmental conditions, instrumentation and so on. The confirmation results had shown that the relevant results met the standards and the laboratory had the ability to carry out this method.

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