

Laboratory Method Validation of Hexavalent Chromium in Water

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Abstract

Hexavalent chromium is a key indicator in the evaluation of drinking water quality. This paper mainly tests the method for the determination of hexavalent chromium in water by diphenylcarbazide spectrophotometry in GB/T 5750.7-2006. The results showed that the detection limit of the assay was 3.0µg/L; the three actual water samples were tested in parallel for 6 times, the relative deviations were 3.5%, 2.8%, and 2.3%, respectively; for the nationally certified standard sample numbered BY400024 The measurement was performed in parallel for 6 times, and the average value was 78.2 µg/L. The above measurement results all meet the method requirements. It is determined that the determination of hexavalent chromium in water can be carried out and applied in this laboratory.

Keywords

Hexavalent chromium, Method validation, Diphenylcarbazide spectrophotometry.

1. Introduction

Chromium is one of the essential trace elements in nature[1]. It is usually in the form of Cr(III) and Cr(VI) in nature. The former is less harmful, and the proper amount of Cr(III) promotes the metabolism of biological cells, while Cr(VI) It is a highly toxic heavy metal with a toxicity of about 100 times that of trivalent chromium. It is a strong carcinogen and never degrades in living organisms. Hexavalent chromium usually comes from industrial wastewater generated by metal processing and leather industries, which seriously pollutes the aquatic environment and thus affects human health[2]. Water is the source of life. Paying attention to the safety and health of drinking water is the top priority. Therefore, hexavalent chromium is a key indicator in the evaluation of drinking water quality[3]. At present, there are many methods for quantitative detection of hexavalent chromium, and the spectrophotometry is favored because of its low cost, simple operation, less interference, and high sensitivity[4]. China's domestic drinking water Cr (VI) is determined by the national standard "Standards for the Determination of Drinking Water Standards" (GB/T 5750.6-2006), namely diphenylcarbazide spectrophotometry.

This paper is based on the national standard "Metal Indicators for the Standardization of Drinking Water Standards" (GB/T 5750.6-2006) and the "Technical Guidelines for Environmental Monitoring and Analysis Methods Standards and Revisions" (HJ 168-2010). On the basis of the existing equipment and personnel technology, it is verified whether the

laboratory has the method to determine the water quality Cr(VI) by measuring the specific limits such as detection limit, accuracy and precision.

2. Experimental Process

2.1. Experimental Principle

In an acidic environment, Cr(VI) in solution has strong oxidizing properties, which can oxidize diphenylcarbazine to diphenyl azocarbohydrazide, which in turn forms a magenta complex with Cr(III). The signal value at 540 nm is the largest with a 3 cm cuvette colorimetric.

2.2. Experimental Reagents and Instruments

Acetone (analytical grade), diphenylcarbazine (analytical grade), sulfuric acid (excellent grade), potassium dichromate (excellent grade), hexavalent chromium standard solution (standard material GBW (E) 082820), standard Sample-hexavalent chromium (standard material, BY400024).

UV-Vis Spectrophotometer (752N)

2.3. Analysis Steps

(1) Pipette 50mL of water sample and place it in a 50mL colorimetric tube. If the concentration of hexavalent chromium in the water sample is too high, it should be diluted as appropriate. Add 2.5 mL of sulfuric acid solution and 2.5 mL of diphenylcarbazine acetone solution to the water sample, and let stand for 10 min.

(2) Take another 50mL colorimetric tube, add 1 μ g/mL hexavalent chromium standard solution 0mL, 0.20mL, 0.50mL, 1.00mL, 2.00mL, 4.00mL, 6.00mL, 8.00mL, 10.00mL, add pure Water to the mark, and the color reaction is carried out with reference to (1).

(3) The absorbance was measured at a wavelength of 540 nm using a 3 cm cuvette with pure water as a reference.

(4) If the actual water sample has color, the water sample is pretreated according to the national standard "Metal Index for Domestic Drinking Water Standard Test Method" (GB/T 5750.6-2006).

(5) Draw a standard curve and find the mass of hexavalent chromium in the sample tube on the curve.

3. Experimental Results

3.1. Linear Range

The measured signal intensity is plotted on the abscissa and the mass (μ g) is plotted on the ordinate. A standard curve was prepared for a standard solution of hexavalent chromium content of 0 μ g, 0.5 μ g, 1.0 μ g, 2.0 μ g, 4.0 μ g, 6.0 μ g, 8.0 μ g, and 10.0 μ g. The calibration curve equation is a calibration curve equation of $y = 35.088x - 0.5099$. The correlation coefficient is 0.9993.

3.2. Determination of Method Detection Limit and Determination Lower Limit

According to the relevant provisions of the Technical Guidelines for the Standardization and Revision of Environmental Monitoring and Analysis Methods (HJ 168-2010). According to all the steps of sample analysis, the laboratory pure water was added to the hexavalent chromium standard solution (additional concentration was 10 μ g/L), that is, the sample with the concentration content of 2.5 times the detection limit of the standard method was performed 7 times. Parallel measurement, calculate the standard deviation of 7 parallel determinations, and

calculate the detection limit according to formula 1. The data summary table is shown in Table 1.

$$MDL=t (n-1, 0.99) \times S \quad (\text{Formula 1})$$

Where: MDL - method detection limit;

n-the number of parallel measurements of the sample;

T-degree of freedom is n-1, and the confidence distribution is 99% of the t distribution (one side);

S-Standard deviation of n parallel determinations.

Among them, when the degree of freedom is 6, the value of t with a confidence of 99% is 3.143.

Table 1. Method detection limit, lower limit test data sheet

Parallel sample number	Sample
	1
	2
	3
The measurement results ($\mu\text{g/L}$)	4
	5
	6
	7
average value ($\mu\text{g/L}$)	10.8
standard deviation ($\mu\text{g/L}$)	0.944
The detection limit ($\mu\text{g/L}$)	3.0
Lower limit of measurement ($\mu\text{g/L}$)	11.9

The concentration of hexavalent chromium in the parallel water sample was $10.8 \mu\text{g/L}$, and the sample concentration was less than 10 times the calculated detection limit of the method, which met the requirements. The metal standard GB/T 5750.6-2006 for drinking water standard test method stipulates that the minimum detection quality of this method is $0.2 \mu\text{g}$, that is, the lowest detection mass concentration is $4.0 \mu\text{g/L}$, and the lower limit of determination is $16.0 \mu\text{g/L}$. The detection limit of hexavalent chromium in water by diphenylcarbazide spectrophotometry was $3.0 \mu\text{g/L}$, and the lower limit of determination was $11.9 \mu\text{g/L}$. The test results met the standard requirements.

3.3. Determination of Method Precision

Precision refers to the degree of agreement between independent test results. HJ 168-2010 indicates that the verification laboratory should select uniform samples of 1-3 concentration levels and perform parallel determinations 6 times according to the whole procedure (for colored water samples, reference standards are added. The acid heat treatment was performed to eliminate the interference), and the parameters such as the average value, the standard deviation, the relative deviation, and the relative standard deviation were calculated, and the measurement results were evaluated. As shown in Table 2 below.

Table 2. Precision test data

Parallel sample number	Sample (low concentration)	sample (medium concentration)	sample (high concentration)
The measurement results ($\mu\text{g/L}$)	1	25.6	113.3
	2	24.2	108.4
	3	27.0	104.2
	4	23.5	101.4
	5	25.6	109.8
	6	24.9	105.6
average value ($\mu\text{g/L}$)	25.1	107.1	218.4
standard deviation ($\mu\text{g/L}$)	1.2	4.3	7.2
relative standard deviation RSD (%)	4.9	4.0	3.3
Relative deviation RD (%)	3.5	2.8	2.3

For the actual samples with the content levels of $25.1\mu\text{g/L}$, $107.1\mu\text{g/L}$, and $218.4\mu\text{g/L}$, the hexavalent chromium was determined by diphenylcarbazide spectrophotometry with a standard deviation of $1.2\mu\text{g/L}$, $4.3\mu\text{g/L}$, $7.2\mu\text{g/L}$, relative deviations were: 3.5%, 2.8%, 2.3%. The measurement results meet the requirements of precision in the quality control of water quality analysis GB/T 5750.3-2006 (the concentration level is $10\mu\text{g/L}\sim 1000\mu\text{g/L}$, and the relative deviation of parallel samples is 5%~10%).

3.4. Determination of Method Accuracy

The laboratory uses a certified reference material sample for analytical determination to determine accuracy. The water sample of the certified reference material sample was analyzed and determined, and the measurement was carried out according to all the steps of the sample analysis, and the parallel determination was performed 6 times. The data summary table is shown in Table 3. The detailed process data is shown in the attached original record sheet. Calculate the average value, standard deviation, relative error and other parameters of the samples with different concentrations of certified reference materials.

Table 3. Test data of certified standard samples

Parallel number	Certified standard sample (BY400024)	
The measurement results ($\mu\text{g/L}$)	1	77.5
	2	79.6
	3	81.0
	4	78.2
	5	77.5
	6	75.4
average value ($\mu\text{g/L}$)	78.2	
Certified standard sample concentration μ^a ($\mu\text{g/L}$)	79.6 ± 4.0	
Absolute error ($\mu\text{g/L}$)	1.4	
Relative error RE_i (%)	1.7	
μ^a : Standard value of national certified standard samples \pm uncertainty.		

For the content of the standard substance with a content level of $79.6 \pm 4.0 \mu\text{g/L}$, the hexavalent chromium was determined by diphenylcarbazide spectrophotometry. The average value of the measured value was $78.2 \mu\text{g/L}$, and the relative error was 1.7%. The error is: $1.4 \mu\text{g/L}$, which satisfies the requirements of the extended standard uncertainty ($k=2$) $\pm 4.0 \mu\text{g/L}$ (BY400024).

4. Conclusion

The laboratory verified the method for the determination of hexavalent chromium in water by diphenylcarbazide spectrophotometry in GB/T 5750.6-2006. The parameters such as detection limit, precision and accuracy were verified. The detection limit of hexavalent chromium in water was $3.0 \mu\text{g/L}$, which was less than the required detection limit of $4 \mu\text{g/L}$. The samples with different levels were used for the determination of hexavalent chromium. The relative deviations were 3.5% and 2.8, respectively. %, 2.3%, the measured results all meet the relative deviation allowable values of the parallel samples required by the "Standard for Quality Analysis of Drinking Water Standards for Water Quality Analysis GB/T 5750.3-2006"; the content level is determined by diphenylcarbazide spectrophotometry For the determination of hexavalent chromium in the water of $79.6 \pm 4.0 \mu\text{g/L}$ certified reference material, the average value of the measured value is $78.2 \mu\text{g/L}$, and the measurement result satisfies the uncertainty of the extended standard ($k=2$) $\pm 4.0 \mu\text{g/L}$. (BY400024) requirements. After verification in the laboratory, the results show that the determination of hexavalent chromium in water by diphenylcarbazide spectrophotometry in GB/T 5750.6-2006 can be applied in this laboratory.

References

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