Determination of Cr(VI) precipitation in small faucet samples by spectrophotometry and evaluation of the uncertainty

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Abstract. A spectrophotometric method for the determination of Cr(VI) precipitation in small volume faucet samples which were less than 50 mL was established. The method was verified by precision and standard addition recovery, and the uncertainty of the measurement results was evaluated. After analysis, the precipitation of Cr(VI) in the extracting solution of the faucet samples was measured as (50.7±1.7) μg/L, (k=2, P=95%). Small volume detection method which just needs 5 mL samples solution had the advantages of small sample consumption, simple and quick operation, and can meet the requirements of the product, especially the faucet samples with small internal volume.

1. Introduction
As a common appliance in ordinary families and all kinds of public places, the safety of faucet is directly related to the safety of people’s water. Chromate and polychromate are commonly used in the plating layer in the faucet for electroplating, so it is very important to measure the amount of chromium element in the faucet[1]. Especially Cr(VI), it is a carcinogen, which is easily absorbed and accumulated by many tissues in human body, and will harm human health. GB 18145-2014 Ceramic cartridge faucets stipulate that Cr(VI) precipitation of the faucets should be detected by the photometric method of the diphenylcarbonyl dihydrazine spectrophotometric according to GB/T 5750.6-2006 Standard examination methods for drinking water-Metal parameters[2][3]. At present, there is a considerable number of kitchen faucets in the inner cavity volume which are less than 50 mL, or even smaller faucet only a few milliliters. The detection of the concentration of Cr(VI) precipitation in the faucet is not applicable to the method specified in GB/T 5750.6-2006. In this paper, according to the amount of reagent in the diphenylcarbonyl dihydrazine spectrophotometric method, the shrinkage experiment was carried out to establish a small volume (5 mL) method to detect the precipitation of Cr(VI) in the faucet immersion solution, and the method was verified. The uncertainty of the measurement results was analyzed.

2. Experiment

2.1. Materials and instruments
- Shimazu Ultraviolet-visible Spectrophotometer (UV-PROBE)
- Pipette: 5000 μL, 1000 μL, 100 μL
- Standard solution: 1000 mg/L Cr(VI) standard solution
2.2. The measurement method

2.2.1. Extracting the faucet samples. The samples were soaked at (23±2) °C, and the preparation requirements of the extracting solution for the test were prepared according to the preparation requirements of Appendix B of GB 18145-2014. The extracting solution which was collected on the 19th day and kept for 16 h was experiment tested.

2.2.2. Preparation and linear range of standard solution. Transferred 100 μL standard solution of Cr(VI) into a 100 mL volumetric flask, and then got 1 mg/L standard reserve solution of Cr(VI) at constant volume with pure water, and then used pipette to dilute the standard curve solution step by step to a total volume of 5 mL. Then added 0.25 mL (1+7) sulfuric acid solution and 0.25 mL diphenylcarbonyl dihydrazine acetone solution (2.5 g/L), mixed well and placed for 10 min. The average value of each standard solution was measured twice, and a good linear relationship was obtained between the concentration and the absorption value, \( Y = 0.0008X + 0.00025 \), and the correlation coefficient (\( R^2 \)) was greater than 0.9999. The standard solution preparation and test results were shown in Table 1, and the standard curve was shown in Figure 1.

Table 1  Cr(VI) standard curve solution configuration table and corresponding measured absorbance values

| Concentration (X/(μg/L)) | 0   | 4   | 10  | 20  | 40  | 80  | 120 | 160 | 200 |
|-------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Cr(VI) (1mg/L) add-in (μL) | 0   | 20  | 50  | 100 | 200 | 400 | 600 | 800 | 1000|
| Pure Water Addition (mL) | 5.00| 4.98| 4.95| 4.90| 4.80| 4.60| 4.40| 4.20| 4.00|
| Absorbance (Y)           | 0.000| 0.004| 0.008| 0.016| 0.031| 0.064| 0.095| 0.126| 0.159|

Figure 1  The linear relationship between concentration and absorbance

3. Methods validation

3.1. Standard addition recovery
Each 5 mL sample solution were added with 10 μL, 20 μL, 40 μL Cr(VI) solution with a concentration of 10 μg/mL, respectively, and the standard recovery experiment was carried out. The calculated recovery rate was within the range of deviation[4], and the results were shown in Table 2.
Table 2 Cr(Ⅵ) solution recovery rate results

| Original (μg/L) | Added (μg/L) | Found (μg/L) | Recovery (%) |
|----------------|--------------|--------------|--------------|
| 39.666         | 20           | 60.319       | 103.27       |
| 39.666         | 40           | 80.890       | 103.06       |
| 39.666         | 80           | 117.780      | 97.64        |

3.2. Precision measurement

Under the same conditions, 5 mL of standard Cr(VI) solution (10 μg/L, 80 μg/L, 160 μg/L) were taken separately and repeated for 6 times by the same method, calculating the relative standard deviation of Cr(VI) was 3.53%, 1.54%, 0.59%. It showed that the instrument has good repeatability in this established method, the data results can be seen in Table 3.

Table 3 Precision results

| Concentration(μg/L) | 10 μg/L | 80 μg/L | 160 μg/L |
|---------------------|---------|---------|----------|
| 1                   | 10.910  | 81.617  | 162.135  |
| 2                   | 11.455  | 81.891  | 159.568  |
| 3                   | 10.684  | 79.813  | 159.983  |
| 4                   | 10.565  | 79.004  | 160.545  |
| 5                   | 11.494  | 79.141  | 159.783  |
| 6                   | 10.928  | 79.951  | 159.947  |
| Average value       | 11.006  | 80.236  | 160.327  |
| STDEV               | 0.388   | 1.235   | 0.943    |
| RSD                 | 3.53%   | 1.54%   | 0.59%    |

3.3. Method validation results analysis

The results showed that there was a good linear relationship between the concentration of the solution and the absorbance value in the standard curve, and the correlation coefficient was greater than 0.9999. The results showed that the standard addition recoveries of the three groups of Cr(VI) samples were 103.27%, 103.06% and 97.64%, respectively, which were within the range of method recovery deviation. The relative standard deviations of Cr(VI) were calculated to be 3.53%, 1.54% and 0.59%, respectively, for the data of 10 μg/L, 80 μg/L and 160 μg/L standard solution for 6 repeated measurements, which indicated that the analytical data of this method was accurate and reliable.

4. Uncertainty analysis

The uncertainty of measuring Cr(VI) content in faucet samples mainly comes from the following sources: the repeatability of measurement, the uncertainty of measuring instrument, the uncertainty of standard material, the uncertainty of standard curve preparation, the uncertainty of temperature change and the uncertainty of curve fitting.

4.1. Evaluation of uncertain components

4.1.1. Relative standard uncertainty of measurement repeatability \( u_{rel}(R) \). The same sample solution was repeated for 9 times and the measured concentrations were as follows: 50.278 μg/L, 49.977 μg/L, 49.273 μg/L, 48.639 μg/L, 52.711 μg/L, 52.039 μg/L, 50.773 μg/L, 50.615 μg/L, 51.885 μg/L, repeatability measurement was evaluated according to Class A standard uncertainty [5].
Average concentration of sample was \( \bar{X} = \frac{\sum_{i=1}^{n} X_i}{9} = 50.688 \mu g/L \)

Standard deviation of sample determination results was \( S = \sqrt{\frac{\sum_{i=1}^{n-1} (X_i - \bar{X})^2}{n-1}} = 1.334 \mu g/L \)

Standard uncertainty due to measurement repeatability was \( u(R) = \frac{S}{\sqrt{n}} = \frac{1.334}{\sqrt{9}} = 0.445 \mu g/L \)

Relative standard uncertainty due to measurement repeatability was \( u_{rel}(R) = \frac{u(R)}{\bar{X}} = 0.00877 \).

4.1.2. The relative standard uncertainty of the measuring instrument \( u_{rel}(Y) \). According to the verification certificate of UV-Vis spectrophotometer, the extended uncertainty of the error of the instrument's transmission ratio was 0.8%, \( k=2 \), and its relative standard uncertainty was \( u_{rel}(Y) = \frac{U(Y)}{k} = 0.004 \).

4.1.3. Relative standard uncertainty \( u_{rel}(W) \) for standard reserve solutions. The solution of Cr(VI) reference substance used in this experiment was 1000 mg/L (GBW(E)082820), and the relative extended uncertainty was obtained by inquiry 1%, \( k=2 \), and the relative standard uncertainty introduced by the standard solution was calculated as \( u_{rel}(W) = \frac{1\%}{2} = 0.005 \).

4.1.4. Relative standard uncertainty introduced by standard curve configuration \( u_{rel}(Q) \). Three kinds of pipette with nominal capacity of 5000 μL, 1000 μL and 100 μL were used for the preparation of standard solution. The pipette gauges were used to calibrate the introduced uncertain devices according to the rectangular distribution. The allowable errors of the pipette capacity of 5000 μL, 1000 μL and 100 μL were obtained as 0.6%, 1% and 2% [6]. The calculation was as follows:

- Standard uncertainty of 5000 μL pipette gun was \( u(Q_1) = 0.0173 \) mL
- Standard uncertainty of 1000 μL pipette gun was \( u(Q_2) = 0.00577 \) mL
- Standard uncertainty of 100 μL pipette gun was \( u(Q_3) = 0.00116 \) mL

Since each uncertainty component was not related to each other, the relative uncertainty introduced by the pipette gun gauge calibration was as follows:

\[
u(Q) = \sqrt{9 \times u(Q_1)^2 + 6 \times u(Q_2)^2 + 3 \times u(Q_3)^2} = 0.0539 \text{ mL}
\]

\[
u_{rel}(Q) = \frac{0.0539}{5} = 0.0108
\]

In the formula, "9×", "6×" and "3×" represent the number of times pipette gun was used in the experiment.

4.1.5. Relative standard uncertainty introduced by temperature change \( u_{rel}(T) \). The measured sample and the standard curve solution prepared were both 5 mL, the laboratory temperature was controlled at 20±5°C, the expansion coefficient of water was 2.1x10⁻⁴ mL/°C, distributed in a rectangular way, and the resulting relative standard uncertainty was \( u_{rel}(T) = \frac{2.1 \times 10^{-4} x 5}{5 \times 5^{\frac{1}{2}}} = 0.000121 \).

4.1.6. Relative standard uncertainty introduced by curve fitting \( u_{rel}(X) \). In the experiment, 9 concentration points were used as the solution of Cr(VI) standard curve series, and the readings of each concentration point were taken twice to take the average value. The results were shown in Table 1. The regression line equation was obtained by fitting as follows: \( Y = 0.0008X + 0.00025 \), and the correlation coefficient \( R^2 = 0.99993 \). The residual standard deviation of the standard curve was:

\[
S(Y) = \sqrt{\frac{\sum_{i=1}^{n_1} (Y_i - (a + bX_i))^2}{n_1 - 2}} = 0.000650 \mu g/L
\]
Standard uncertainty caused by standard curves:

\[ u(X) = \frac{s(Y)}{b} \sqrt{\frac{1}{n_1} + \frac{1}{n_2} + \frac{(c-X)^2}{\sum_{i=1}^{n_1}(x_i-X)^2}} = 0.343 \ \text{μg/L} \]

In the formula, "Y" refers to the average measured punctuation value, "X" refers to the concentration of each punctuation, "n_1" refers to the number of standard curves, "n_2" refers to the total number of standard curve measurements, "a" refers to 0.00025, "b" refers to 0.0008, "c" refers to the average concentration of the sample solution.

The relative standard uncertainty introduced by the standard curve was: \( u_{rel}(X) = 0.00677 \)

4.2. The composition of uncertainty of each component

4.2.1. The relative uncertainty of each component. The relative uncertainty of each component in this established method was shown in Table 4.

| Component | \( u_{rel}(R) \) | \( u_{rel}(Y) \) | \( u_{rel}(W) \) | \( u_{rel}(Q) \) | \( u_{rel}(T) \) | \( u_{rel}(X) \) |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|           | 0.00877         | 0.004           | 0.005           | 0.0108          | 0.000121        | 0.00677         |

4.2.2. Composition of relative uncertainty \( u_{rel} \). The related combined standard uncertainty of the above uncertainty components was:

\[ u_{rel} = \sqrt{u_{rel}(R)^2 + u_{rel}(Y)^2 + u_{rel}(W)^2 + u_{rel}(Q)^2 + u_{rel}(T)^2 + u_{rel}(X)^2} = 0.0167 \]

4.3. Extend uncertainty

The extended uncertainty took the inclusion factor \( k=2 \), then the extended uncertainty \( U = 0.0167 \times 50.7 \times 2 = 1.7 \ \text{μg/L} \).

4.4. Result representation

The measurement result of Cr(VI) in a small volume sample of 5 mL was \((50.7 \pm 1.7) \ \text{μg/L}, \ (k=2, \ P=95\%)\) by diphenylcarbonyl dihydrazine spectrophotometric method.

5. Conclusions

In this study, a diphenylcarbonyl dihydrazine spectrophotometric spectrophotometric method was established to determine the detection method of Cr(VI) in small-volume faucet samples, which was verified by the method of mark-up recovery rate and repeatability, which showed that the method was feasible. This method just required 5 mL sample solution. At the same time, the method mainly used pipetting gun to prepare standard curve solution and remove sample solution, which was simpler and faster than measuring instruments such as volumetric flask and colorimetric cylinder.

The uncertainty analysis was shown that the main sources of the uncertainty in the measurement of faucet samples by the compressed volume method were the repeatability of the measurement, the preparation and fitting of the standard curve. Compared with the relative standard uncertainty between the standard curve prepared by the 50 mL large-volume detection method and the sample measurement results, the 5 mL small-volume sample solution detection method can meet the testing requirements of the products, which indicates that the 5 mL small-volume method for measuring the concentration of Cr(VI) was feasible when the sample volume was less than 50 mL.

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