Determination of trace heavy metals in seawater with 8-hydroxyquinoline solid phase extraction by ICP-OES

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Abstract. The determination of trace heavy metals in seawater with 8-hydroxyquinoline solid phase extraction by ICP-OES was studied. In ammonium acetate buffer with pH 5.0, 8-hydroxyquinoline chelated with trace heavy metal ions 15 min. The chelate compound can be enriched by C18 solid phase extraction column. The chelate can be eluted quantitatively by methanol, and then determined by ICP-OES method after digestion. The method can be used for quantitative analysis of trace heavy metal ions in high salinity. The data are reliable, which meets the marine monitoring standards.

1. Introduction
With the rapid development of coastal economy and the increasing dependence on marine resources in China, pollution in coastal waters is growing serious, and heavy metal pollutions are also deteriorating. Heavy metals accumulate in algae and sediment, which in turn enrich the organism through the food chain, destroying the marine ecology, and ultimately causing great harm to human health. Due to the low concentration of heavy metal ions in seawater, the matrices are complex and there are extremely high chloride and sodium ions, which causes them are difficult to detect and analyze. In traditional analytical methods, the determination of these elements is seriously interfered by spectra or below the detection limit of the instrument. Quantitative analysis of these elements is very difficult. It must be separated and enriched step by step before it can be analyzed [1-3].

At present, solid phase extraction (SPE) has been widely used in analytical chemistry, but there are few applications in the analysis of inorganic and metal elements. 8-hydroxyquinoline, as an anionic ligand with double ligands (N, O), can form chelates with metal ions [4-6]. The chelate can be separated and enriched by solid phase extraction, which is convenient for batch processing of seawater. Then, the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) method was used to determine six trace heavy metals in seawater, namely, chromium, cadmium, lead, copper, zinc and nickel, by solid phase extraction with 8-hydroxyquinoline. So, an ICP-OES method for the simultaneous determination of six trace heavy metals, chromium, cadmium, lead, copper, zinc and nickel, in seawater by 8-hydroxyquinoline solid phase extraction was established.

2. Materials and methods

2.1. Instruments and reagents
ICP-OES (Thermo 7400).
Waters Sep-Pak C18 solid phase extraction column (3 ml/500 mg), the column was soaked with methanol about 5ml, the residual methanol on the column was washed with ultra-pure water, and then the sample could be extracted.

Gilson GX-274ASPEC.

Six kinds of 1.0mg/ml reserves of chromium, cadmium, lead, copper, zinc and nickel (Shanghai Anpu Experimental Science and Technology Co., Ltd.), which diluted by 2% nitric acid to standard solutions for use.

8-hydroxyquinoline (99%, Beijing Bailingwei Technology Co., Ltd.), which mixed with 95% ethanol to 0.1% solution.

Ultra-pure water (Millipore), 18.2 MΩ•cm\(^{-1}\).

Standard Seawater (salinity 35).

The buffer solution of ammonium acetate (pH = 4, 5, 6, 7, 8).

### 2.2. Test methods

Accurate extraction of 200 ml Standard Seawater in 250 ml beaker, adding appropriate amount of standard solution of chromium, cadmium, lead, copper, zinc and nickel, then adding 10 ml ammonium acetate buffer solution and 5 ml 0.1% 8-hydroxyquinoline solution. After stirring reaction, the sample was carried out at a flow rate of 10 mL/min in the activated C18 solid phase extraction column. After enrichment, centrifugal dehydration of small column was carried out. The column was eluted with 5.0 mL methanol at a flow rate of 5 mL/min. The methanol eluent was concentrated about 1.0 ml by nitrogen blower. Adding 1 ml concentrated nitric acid to digest for 2 minutes, then adding ultrapure water to make the solution volume is 5 ml. Finally the contents of chromium, cadmium, lead, copper, zinc and nickel were determined by ICP-OES.

### 3. Results and discussion

#### 3.1. pH selection

In solid phase extraction, the pH of solution is an important parameter for quantitative recovery of target analyte [7-9]. Chelating reaction of 8-Hydroxyquinoline with heavy metal ions was influenced by the PH value of solution. The form of 8-hydroxyquinoline in aqueous phase is significantly affected by pH, too high acidity is not conducive to its dissociation, and the dissociated 8-hydroxyquinoline can chelate with heavy gold ions, but when the pH exceeds a certain value, heavy metal ions will hydrolyse and deposit on the wall [10-12].

![Figure 1. Recovery test at different Ph.](image-url)
When pH=4, 5, 6, 7 and 8, 20 ug/L standard solutions of chromium, cadmium, lead, copper, zinc and nickel were added to standard seawater. The recovery rate of heavy metal ions was determined by experiment 1.2 method, as shown in figure 1. It can be found that the recovery rate of different heavy metal ions is affected by the pH difference. Considering that the method needs to meet the requirements of all heavy metal ions, the pH value of 5.0 is chosen as the optimal value, and subsequent studies are carried out at this pH value.

3.2. Determination of stirring reaction time
20 μg/L standard solution of chromium, cadmium, lead, copper, zinc and nickel is added to the standard seawater. The effect of different stirring reaction time on the recovery rate is shown in figure 2. There is a certain difference in the chelation rate between different heavy metal ions and 8-hydroxyquinoline. After the reaction time exceeds 15 min, the recovery of all heavy metal ions tends to be stable, so the stirring reaction time is selected to be 15 min.

3.3. Recovery and precision determination
Adding 2 levels of standard solutions of chromium, cadmium, lead, copper, zinc and nickel to 200 ml standard seawater (5, 20 μg/L), and each level is measured 5 times according to the 1.2 test method. The result is shown in table 1. It can be seen that the recovery is 85.2-88.08% with the addition of 5 μg/L, and relative standard deviation (RSD) is about 4.5% except for lead. With the addition of 20 μg/L, the recoveries were more than 90%. RSD was all 1.5% except for lead. It is indicated that the solid phase extraction-ICP-OES method for the determination of trace heavy metal ions in chromium, cadmium, lead, copper, zinc and nickel in seawater is stable, feasible and reliable, which meets the marine monitoring norms.

![Figure 2. Recovery test at different stirring reaction time.](image)

| Element | Adding standard solution amount (μg/L) | Average value (μg/L) | Recovery rate (%) | RSD (%) |
|---------|----------------------------------------|----------------------|-------------------|---------|
| Cd      | 5.0                                    | 4.16                 | 83.20             | 4.98    |
|         | 20.0                                   | 17.92                | 89.60             | 1.07    |
| Cr      | 5.0                                    | 4.10                 | 82.00             | 4.56    |
|         | 20.0                                   | 18.12                | 90.59             | 0.90    |
| Cu      | 5.0                                    | 4.18                 | 83.60             | 3.93    |
|         | 20.0                                   | 18.32                | 91.60             | 1.18    |
3.4. Method detection limit

Taking 200 ml Standard Seawater and adding a certain amount of standard solution of chromium, cadmium, lead, copper, zinc and nickel, the concentration was 1-5 times of the expected MDL value. The concentration was determined by 1.2 test method.

According to the determination method of MDL such as Liu Lijun, the calculation formula of MDL is as follows [13]:

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

Where \( n \) = number of replicate samples; \( S = n \) times the standard deviation of the concentration was determined; \( t \) = Student's t value when the degree of freedom is \( n - 1 \) (obtained by the table); \( 1-a \) is the confidence level.

It can be seen from table 2, that the detection limit of dissolved heavy metal elements in standard seawater with solid phase extraction by ICP-OES is low, and the detection limit of lead removal is slightly higher than that of other countries. It proves that the method meets the analysis requirements of dissolved trace heavy metals in coastal seawater.

| Element | Cd  | Cr  | Cu  | Ni  | Pb  | Zn  |
|---------|-----|-----|-----|-----|-----|-----|
| MDL     | 0.2 | 0.5 | 0.2 | 0.8 | 3.0 | 0.2 |

3.5. Determination of seawater samples

Using this method, the content of chromium, cadmium, lead, copper, zinc and nickel in the actual seawater samples were measured. The measured heavy metal content in seawater was consistent with the related reports [14,15]. At the same time, the recovery experiments were carried out which shown in table 3. It was found that the recoveries of the six trace heavy metal ions were all above 80%.

| Element | Measured value | Adding standard solution amount | Measured value after adding standard solution amount | Recovery data (%) |
|---------|----------------|--------------------------------|---------------------------------------------------|-------------------|
| Cd      | 0.61           | 5                              | 4.74                                              | 82.60             |
| Cr      | 15.86          | 20                             | 33.53                                             | 88.35             |
| Cu      | 8.23           | 20                             | 26.56                                             | 91.65             |
| Ni      | 5.32           | 20                             | 23.11                                             | 88.95             |
| Pb      | Not detected   | 20                             | 18.56                                             | 92.80             |
| Zn      | 20.36          | 20                             | 38.17                                             | 89.05             |

4. Conclusion

In this study, determination of trace heavy metals in seawater with 8-hydroxyquinoline-solid phase extraction by ICP-OES was established. The method has good separation and enrichment effect, high sensitivity, simple operation and stable and reliable results. The detection of trace heavy metal ions is not disturbed by high salt. Moreover, it can be carried out in batches without additional special equipment. The existing laboratory equipment can meet the detection requirements of trace heavy metal ions in high salt (sea water) samples.
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