Analysis of Heavy Metal Elements in Tianjin Tuanbo Lake Water by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) from the Perspective of Water Quality Evaluation

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Abstract. In recent years, water pollution incidents have occurred frequently, affecting people's lives and health in great way. Based on this, in order to explore the pollution situation of Tuanbo Lake, this research uses plasma inductively coupled mass spectrometry (ICP-MS) to analyze the pollution of heavy metals cadmium (Cd), arsenic (As), lead (Pb) and chromium (Cr) in water condition. It was found that chromium was detected in trace amounts, lead was detected more downstream, and neither Cd nor As was detected. According to the "Environmental Quality Standard of Surface Water", the water quality of this area is in the Grade III water quality standard under pb, and the As is in the Grade II water quality standard.

Keywords: Inductive coupling, plasma, mass spectrometry, heavy metal pollution, water quality.

1. Introduction

Tianjin Tuanbo Lake is located at the junction of Tianjin Dagang, Jinghai and Xiqing districts. Due to its large area and numerous birds, it is known as the "Lung of Tianjin" [1]. Tuanbo Lake, which is a water storage source, has developed rapidly in recent years, and many companies have discharged various heavy metals into rivers and lakes without permission. Among them, arsenic and cadmium in sewage can enter the body through the respiratory tract or skin and through the blood circulation, and combine with hemoglobin. It can cause great harm to various functions of human kidney, nervous system, cardiovascular and cerebrovascular [2]. "Bone-Ititai disease" and "Itai-itai disease" are typical hazards caused by cadmium and arsenic to the human body [3]. Therefore, as an important lake in Tianjin, Tuanbo Lake, it is of great practical significance to explore its pollution. At present, the instruments for detecting heavy metals in aqueous solutions mainly include ICP-OES inductively coupled plasma spectrometer, ICP-MS inductively coupled plasma mass spectrometer, fluorescence measurement X-diffraction, electrochemical analysis, etc. Among them, ICP-MS has the advantages of high sensitivity, low background signal, and low detection limit (at sub-ng/L-ppt level), which can accurately detect water pollution. Based on this, this study used the ICP-MS method to determine the heavy metal elements in Tuanbo Lake in Tianjin, and provided a certain reference for the relevant departments to conduct follow-up water quality assessment and monitoring.

2. Materials and Methods

2.1. Sample Extraction

For testing the overall water quality of Tuanbo Lake, the research team selected calm and clear waters and sampled a bottle of water every one to two kilometers. In accordance with the topographic features here, two sampling points are set in the middle reaches, one in the upstream and one in the downstream. A total of four specimens were tested. For strict guarantee of no external error, the sampling bottle should be opened and taken without touching before water sampling, and the number should be marked.

2.2. Apparatus and Reagents

Electronic balance (mettler instrument (Shanghai) co., ltd., al204);

Microwave Digester (US CEM Company, MARS);
Inductively coupled plasma mass spectrometer (RQ, Thermo Fisher Scientific, USA);
Acid analyzer (Beijing Aowei Instrument Co., Ltd., V-2438);
Liquid transfer gun (Eppendorf, Germany, 1000, 200, 50 UL);
Ultra-pure water machine (Shanghai Fusite Instrument Equipment Co., Ltd., FST-III-UP20);
Colorimeter: All of them were soaked in 25%HNO3 solution overnight and washed with ultrapure water for later use. Nitric acid (HNO3, Sinopharm Chemical Reagent Co., Ltd., excellent grade pure)
Cadmium (Cd), arsenic (As), lead (Pb) and chromium (Cr) standard solutions (National Nonferrous Metals and Electronic Materials Analysis and Testing Center, 1000 ug/ml)
Internal standard solution (Bi, Ge, In, Sc, Y, National Nonferrous Metals and Electronic Materials Analysis and Testing Center, 10ug/ml).

3. Steps and Methods

3.1. Pre-experiment Procedure

3.1.1. Idling

For ensuring accuracy and eliminating impurity interference. The digestion tank was subjected to two rounds of idling before the experiment, that is to say, without adding sample solution, 10ml nitric acid was added for microwave digestion. So as to achieve that effect of clean the digestion jar. Then, clean with ultrapure water, and then repeat the above steps for idling again.

3.1.2. Pre-Sampling Procedure

Let the sample stand first, and after mud, sand and other impurities precipitate, accurately take 2ml of the upper clarified water sample into the digestion tank, and add 10ml of excellent grade pure nitric acid to digest it according to the procedure in Table 1. After the digestion is finished, open the lid, put it in an acid-driving instrument, and drive the acid at 130℃ until the liquid in the digestion tank is the size of soybean grains. Transfer the liquid in the digestion tank into a 50ml colorimetric tube, rinse it with 0.5% nitric acid for 3~5 times, and finally set the volume to 50.0ml for ICP-MS.

Table 1. Microwave Digestion

Steps	Power	Rramp-up	Temperature	Heating time
1	800	5	110	5
2	800	3	130	5
3	800	3	150	25

3.1.3. Internal standard

In this research, the internal standard method is used to reduce matrix interference. Select inert elements with similar mass numbers to the target elements and without affecting the concentration of the target elements. Generally, Li, Se, Rh, Ho, Bi, Tb and other elements are recommended Internal standard elements. By comparing various internal standard elements, it is found that four internal standard elements such as Bi, Ge, Sc and in have ideal effects.

4. Results

4.1. Drawing Standard Curve

Four kinds of heavy metal mixed standard solutions (2.0, 4.0, 8.01, 2.0 and 16.0 ng/ml) were prepared to measure the ratios of different heavy metal elements to the corresponding internal standards at different concentrations, and the standard curves were drawn. The regression equations are shown in Table 2, and it can be seen that the correlation coefficients are all greater than 0.9990, indicating that the linear relationship of each element is good within the response range. And that

detection limit of four element is low, especially the detection limit of cd is as low as 0.0008ng/ml. It indicates that ICP-ICP has high sensitivity to these heavy metals, and meets the analysis requirements.

Table 2. Detection limits and regression curves of four heavy metals

Elementes	Linear Regression	Correlation coefficient (R2)	Detection limit (ng/ml)
52Cr	16245.8603*x+3589.3340	0.9990	0.0041
75AS	1406.2387*x+16.8411	0.9997	0.0020
111Cd	7779.1501*x+11.6603	0.9999	0.0008
208Pb	147417.2003*x+26784.1200	0.9997	0.0036

4.2. Precision

As shown in Table 3, the relative standard deviation of each element at different concentrations shows that the average value is 0.3-2.0%, which has high precision and can meet the simultaneous determination of multiple elements.

Table 3. Precision Test Results of Four Heavy Metal Elements

Items		RSD
0.005mg/l	Cd	1.4%
	Pb	0.8%
	As	0.8%
	Cr	0.8%
0.01mg/l	Cd	1.3%
	Pb	1.5%
	As	1.3%
	Cr	2.0%
0.016mg/l	Cd	1.7%
	Pb	0.9%
	As	1.7%
	Cr	1.4%
0.028mg/l	Cd	0.3%
	Pb	1.1%
	As	1.0%
	Cr	0.8%
0.04mg/l	Cd	0.7%
	Pb	1.2%
	As	1.4%
	Cr	1.2%

4.3. Element Content of Sampling sites

The element contents of four parallel samples to be paralleled determination are shown in Table 4, and the data are analyzed for water quality grade. The results are evaluated according to "Surface Water Environmental Quality Standard" [4], see Table 5 for details, and the water quality grades of different sampling points can be obtained from the analysis as shown in Table 6.

Table 4. Different element contents of sampling sites

sample	Cr(mg/l)	As(mg/l)	Cd(mg/l)	Pb(mg/l)
blank	0.0222	0.0004	—	0,0091
upstream 1	0.0045	0.0021	—	0.0076
upstream 2	0.0040	0.0021	—	0.0078
middle 11	—	0.0010	—	—
middle 12	—	0.0012	—	—
middle 21	0.0187	00016	—	—
middle 22	0.0200	0.0017	—	—
lower 1	—	0.0015	—	0.0177
lower 2	—	0.0017	—	0.0188

Note: "—"indicates that it is not detected.

Table 5. Definition of Water Quality Grades of Different Elements in Surface Water Environmental Quality Standard

Water quality grade	Cr	As	Cd	Pb
I	≤0.01	≤0.05	≤0.001	≤0.01
II	≤0.05	≤0.05	≤0.005	≤0.01
III	≤0.05	≤0.05	≤0.005	≤0.05
IV	≤0.05	≤0.1	≤0.005	≤0.05
V	≤0.1	≤0.1	≤0.01	≤0.1
Concentration unit	mg/L	mg/L	mg/L	mg/L

Table 6. Water quality grades corresponding to different element contents in sampling sites

sample	Cr	As	Cd	Pb
upstream1	I	I	I	I
middle 1	I	I	I	I
middle 2	II	I	I	I
lower	I	I	I	III

5. Discussion

The results showed that the content of heavy metals in the upper reaches of Tuanbo Lake was generally low, and all of them reached the first-class water quality standard. Only about 0.0010mg/l of arsenic was detected in a sample in the middle reaches, which was lower than that in other samples. The other sample from the middle reaches of the river detected a high cadmium content, reaching the water quality standard of Grade II. The lead pollution in the lower reaches is serious, and the water quality is Grade III.

Analysis of the geographical location shows that the downstream of Tuanbo Lake is near Yaoqiang Zhenyuan Steel Pipe Factory, Yilong Steel Structure Processing Factory and Seamless Steel Pipe Factory. These factory wastewaters mainly come from acidic leaching, extraction and other technological processes in wet smelting, and generally contain a lot of heavy metals, especially cadmium and lead. The substandard discharge or stolen discharge of these wastewaters will pose a threat to the overall ecology of Tuanbo Lake.

Moreover, there are many residential areas, farmhouses and aquaculture near Tuanbo Lake. Domestic sewage will also make the lake eutrophic, which will lead to the decrease of water self-purification capacity and water pollution.

Meanwhile, there have been many cases of construction waste left unattended by Tuanbo Lake [5]. During the stacking and landfill of construction waste, the sewage-leachate or leachate percolated by

fermentation, leaching and erosion of rainwater, and soaking of surface water and groundwater will cause pollution of surrounding surface water and groundwater.

Water intake will lead to the decrease of Tuanbo Lake water volume, which will affect the depth of water body and the carrying capacity of environment to pollution, and then lead to the decrease of self-purification capacity of water body. This is the main reason that industrial wastewater and domestic sewage may cause arsenic and lead pollution in the middle and lower reaches.

Lead is the most common toxic substance. The inorganic lead and its compounds in the environment are very stable, and once they are produced, they will exist in the environment for a long time. Some experiments show that when the water body is polluted by lead, it will destroy the chlorophyll, mitochondria and nuclear structure of aquatic plants, reduce the content of chlorophyll and ascorbic acid, reduce the activities of nitrate reductase and dehydroreductase, hinder the respiratory metabolism and photosynthesis of finger, and affect the quality and biomass of plants, thus inhibiting the self-purification ability of water [6] Thus, it is imperative to prevent and control lead.

Ecological point of view, when sampling, it was found that there were more algae in the middle reaches of the first sample water. Because of the strong ability of algae to enrich heavy metals, the use of microalgae to remediate heavy metal polluted water bodies has received extensive attention in the world. The system of Utomo et al. [7] verified the strong biosorption and rapid adsorption ability of algae, indicating that algae is a potential wastewater treatment method. As a result, when analyzing heavy metal elements in water samples, the content of heavy metal elements in this area is low.

6. Conclusion

Through ICP-MS inductively coupled plasma mass spectrometer, the pollution of four water samples in Tuanbo Lake was measured, the data were analyzed, and then the heavy metal pollution in water body was judged according to "Surface Water Environmental Quality Standard". We found that the water quality of As and Cd was in good condition, and the pollution of Cr and Pb elements still existed. Cr was the second-grade water quality standard, while Pb was the third-grade water quality standard. Accordingly, the author suggests that relevant departments should strengthen the monitoring and control of Pb and Cr in this water area.

Regernces

[1] Fang Rongle, Zhu Xiaoming, Zhang Suyuan et al. biological productivity and fishery exploitation in the water bodies of Tuanpohua Reservoir, Tianjin [J]. Journal of Lake Sciences, 1992, 4 (2): 38 - 45.

[2] Luo Yanan, Yu Yuesheng, Tao Chen, et al. Research progress on the biohazard effect and mechanism of environmental cadmium pollution [J]. Journal of Qiannan Medical College for Nationalities, 2011, 24 (4): 306 - 308.

[3] Zhang Juanping, Zhang Xifeng. A preliminary investigation on the harm of cadmium pollution to human body [J]. Value Engineering, 2013, 25 (42): 282 - 283.

[4] Zhang P, Liang R F, Zhao P X, et al. The Hydraulic Driving Mechanisms of Cyanobacteria Accumulation and the Effects of Flow Pattern on Ecological Restoration in Lake Dianchi Caohai [J]. Environ Res Public Health. 2019, 16 (3): 361.

[5] Sun Qiming. How to crack the "garbage around the lake" in Tuanbo Lake [N]. Today, Newspaper, 2021 (4).

[6] Chu Yi Dan, Zhao Shu Min. Effects of lead on aquatic plants [J]. Guangdong Chemical Industry, 2014, 41 (16): 98 - 99.

[7] Yang Ying, Liu Liwen, Li Jianhong. A review on the mechanism of heavy metal enrichment by microalgae and its application in environmental remediation [J]. Jiangsu Agricultural Science, 2019, 47 (21): 88 - 94.