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Evaluation of Mercury Environmental Pollution Based on Luminescence Analysis

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The contents of total mercury and dissolved mercury in the water samples and soil samples around the Qin Shihuang mausoleum in Lintong District of Xi'an were measured by cold atomic fluorescence spectrometry. The results showed that the amount of mercury contained in the soil of Qin Shihuang Mausoleum and the surrounding soil was between 41.41-2248.08 ng/g, and the total mercury content (2.04-124.4 ng/L) in the water samples was lower than that in the drinking water (1000 ng/L) of the World Health Organization.

1. Introduction

Mercury (Hg) is a highly toxic element, and it is applied in many ways (Fernández-Martínez et al., 2015; Busto et al., 2016; Syafiqah et al., 2017). Mercury is present in the form of elemental mercury, organic mercury and inorganic mercury, and its toxicity depends on its chemical form (Brombach et al., 2015). In the three forms of mercury, organic mercury compounds, such as methylmercury, are water-soluble, and they have a strong bioaccumulation and biomagnification in the food chain (Brazeau et al., 2013). With the rapid economic development, China's industrial activity and coal consumption increased dramatically, the release of mercury and mercury in the global circulation has caused widespread international attention (Camera et al., 2015). Since industrial activities are generally concentrated in cities and suburbs, it is necessary to determine the mercury content of these areas. Accordingly, the pollution status of the area and the environmental impact of industrial activities can be evaluated (Frentiu et al., 2015). At present, there are many analytical methods for the determination of mercury. It is mainly composed of atomic absorption spectrometry, spectrophotometry, cold atomic fluorescence spectrometry (CVAFS), high performance liquid chromatography, gas chromatography, potentiometry and inductively coupled plasma mass spectrometry ICP-MS) (Almeida et al., 2015).

The mercury content in the environmental samples can reflect the state of environmental pollution. Therefore, this article refers to the United States Environmental Protection Agency EPA Method 1631, Revision standard method and the People's Republic of China national standard GB/T 7468-1987. The mercury content in samples of water samples, soil samples, river sediments and atmospheric deposits in Xi'an, Shaanxi Province was studied, and the environmental pollution situation in the area was evaluated.

2. Experiment

2.1 Experimental apparatus and reagents

Preparation of bromine bromide solution: take 2.7 g of KBr dissolved in 250 mL of concentrated hydrochloric acid, and stir for about 1 h on a magnetic stirrer, and then slowly add 3.8 g of solid $KBrO_3$ with stirring. In the process of adding the $KBrO_3$, the color of the solution is changed from yellow to red, and eventually it is turned to orange, followed by stirring for 1 h. The entire preparation process is carried out in a fume hood.

Preparation of 30% (w/v) spermine hydrochloride: weigh 1.5 g of NHZOH·HCI, dissolve with high purity water and dilute to 1 L.

Preparation of 20% (w/v) stannous chloride: 5 g of $SnCl_2{\cdot}2H_2O$ was dissolved in 2.5 mL of concentrated hydrochloric acid (slightly heated) and then diluted with high purity water in a 25 mL volumetric flask.

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Preparation of secondary mercury standard solution ((1.0 ug/mL): add 50 mL of high purity water and 0.5 mL of BrCI to a 100 mL volumetric flask and add 1.00 mL of 100 g/mL mercury standard solution and dilute it to 100 mL with high purity water. The concentration of mercury standard solution is very stable.
Preparation of mercury working fluid A (10 ng/mL): take 1 mL of the secondary mercury standard solution into a 100 mL volumetric flask and then dilute it to an extent with an aqueous solution containing 0.5% BrCI (v/v).
Preparation of mercury working fluid B (0.10 ng/mL): take 10uL of secondary mercury standard solution into a 100 mL volumetric flask and dilute to a scale with an aqueous solution containing 0.5% BrCI (v/v).
All mercury solutions were stored in a refrigerator at 4°C. Mercury working fluid A, B can be kept for one month.
ZYG-II intelligent cold atomic fluorescence mercury analyzer (Hangzhou Dacheng Photoelectric Instrument Co., Ltd.), agate mortar and 100 mesh sieve (0.154 mm diameter) (Zhejiang Shangyu Du Fuguo yarn sieve factory), 0.45 um microporous membrane (mixed fiber membrane, Shanghai Xinya purification equipment factory), oil-free vacuum pump (Tianjin Aote Saines Instrument Co., Ltd.), SW-CJ-ICU clean bench (Suzhou Aetna Air Technology Co., Ltd.).

2.2 The principle of measurement

Mercury vapor has a strong absorption effect on ultraviolet light with a wavelength of 253.7 nm, and the mercury vapor concentration is proportional to the fluorescence value (Reis, et al., 2015). The samples were digested with potassium permanganate and potassium persulfate, or the samples were digested with potassium permanganate and potassium an admixture (sodium chloride) to convert all of the mercury contained to divalent mercury. The excess oxidant is reduced with hydrochloric acid amine, and the divalent mercury is reduced to elemental mercury by excess stannous chloride. At room temperature, a hydrogen or nitrogen stream is introduced. The generated mercury vapor is ejected from the atomic nozzle with the carrier gas and is irradiated by the excitation light of 253.7 nm emitted by the low pressure mercury lamp. The ground state mercury atoms are excited to high energy states and emit resonant fluorescence when returning to ground state. Based on the measured fluorescence values, the mercury content in the sample can be determined.

$$HgCL_2 + SnCl_4 \rightarrow SnCl_4 + Hg \quad (1)$$

2.3 Sample processing

(1) Treatment of water samples
a. Remove the water sample and filter it with a 0.45um filter, and insert it into a 100 mL glass bottle (for the determination of dissolved mercury).
b. The water samples were protected by adding 5.0 mL/L 12N HCl or 5 mL/L BrCI solution within 4 h of recovery. In this experiment, BrCI solution was used. If the water sample does not add BrCI protective solution, the following amount of BrCI can be added, tighten the cap, digest it for more than 12h at room temperature, so that it can be measured.
For clear or filtered water samples, add BrCI to 0.5 mL/100 mL of water; for brown or turbid water samples, add BrCI to 1.0 mL / 100 mL of water. The presence of organic or sulfide also consumes BrCI, and if the water sample disappears, it is necessary to continue to add BrCI until the water sample does not disappear within 12 hours.
For water samples with high organic substrate content (eg effluent effluent), the amount of BrCI required is increased (eg 5.0 mL/100 mL), the duration of oxidation is increased, or the oxidation temperature is increased (eg, the sealed vials were digested in an oven at 50 °C for 6 h).
(2) Treatment of soil samples
a. After removal of stones, plants and other substances in soil samples, soil samples were dried at room temperature for about four weeks. Then, it was crushed in an agate mortar and sieved on a 100 mesh sieve. After mixing, the soil samples were dried in a 40°C oven for 48 h.
b. Weigh 0.25 g of soil samples in 25 mL of colorimetric tubes, add 5.0 mL of high purity water and 5.0 mL of aqua regia. Then, it was placed in an oven at 95 ° C for 2 h, and the shaking was continued during the period to complete the digestion of the sample. After cooling the sample, dilute it with high purity water to 25 mL for the determination of total mercury.

3. Results and discussion

3.1 Working curve

(1) The working curve of mercury in small mercury generator.

A standard solution of 0, 50, 100, 200, 300, 400 (ng / L) mercury was prepared with high purity water containing 0.5% (v/v) BrCI in different volumes. The working curve was shown in Figure 1. The linear equation was Y=0.62X + 46.49 (X units ng/L), the correlation coefficient was 0.9998, and the detection limit was 11 ng/L. The standard solution of 100 ng / L mercury was subjected to seven parallel determinations, and the relative standard deviation (RSD) was 3.2%.

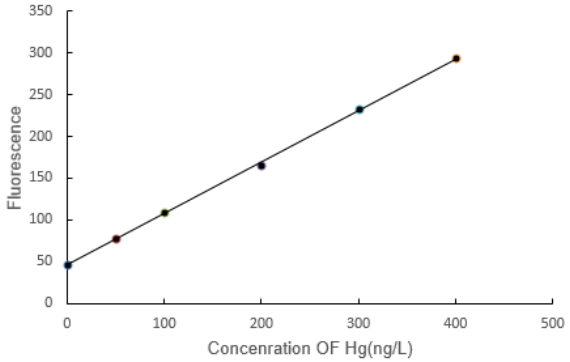

Figure 1: The working curve of mercury in small mercury generator.

(2) The working curve of mercury in big mercury generator.
Take 0, 0.5 mL of mercury working solution B in 100 mL of large mercury generator, add high water to 100 mL scale mercury concentration of 0, 0.5 ng/L solution. Then, take a different volume of mercury working solution A in 100 mL of the big bubbler, add high water to 100 mL scale. The mercury concentration was 1.0, 1.5, 2.0, 2.5 ng/L, respectively. The working curve is shown in Figure 2. The linear equation was Y=307X+94.5 (X units is ng/L), the correlation coefficient was 0.9937, and the detection limit was 3.3 *10^5ng/L. The standard solution of 1.5 ng / L mercury was measured three times in parallel. The relative standard deviation (RSD) was 3.9%.

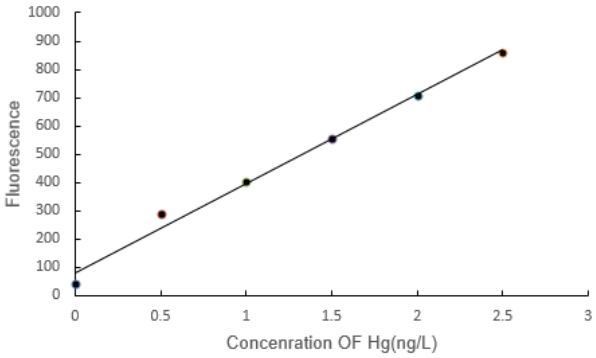

Figure 2: The working curve of mercury in big mercury generator.

(3) The working curve of mercury in soil and sediment samples.
Dilute 100 μg/mL of mercury standard solution to 50 ng/mL with 5.0% (v/v) HNO_3. Then, take different volumes of the concentration of mercury standard solution, with 10% (v/v) HNO_3 to prepare it, and the concentration of 0,500, 1000, 1500. 2000, 2500 ng/L mercury standard solution was obtained respectively. The working curve is shown in Figure 3. The linear equation is Y=0.29X+24.8 (X units is ng/L), the correlation coefficient is 0.9995, and the detection limit is 31 ng/L. The standard solution of 1500 ng/mL of mercury was measured three times in parallel, and the relative standard deviation (RSD) was 2.8%.

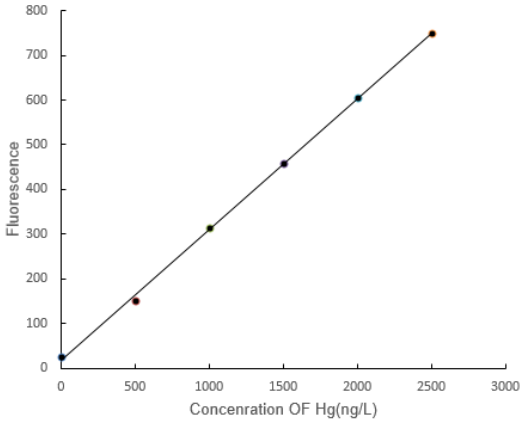

Figure 3: The working curve of mercury in soil and sediment samples.

3.2 Analysis of the results

There are pomegranates on the tomb of Qin Shihuang. This study collected water from pomegranate pomegranates in pomegranate trees grown on mausoleum (October 2016). The trenches of the tap water and the surrounding area of the water samples (October 2016) were measured. At the same time, we collected soil samples around mausoleum and mausoleum, and we carried out measurement. W represents water sample, and S represents soil sample. The water sample of W1-W10 is the water in the bag of pomegranate grown on the tree. A, C water samples are well water, and B water samples are tap water. S1-S12 is a soil sample that collected from Mausoleum of the First Qin Emperor. At the same time, soil samples were collected in A orchard and C village in the southeast of the mausoleum.

Table 1 is the total amount of total mercury in the water samples collected from the tombs of Qin Shihuang. The total mercury content in the bag of pomegranate pomegranate was between 2.04-124.4 ng / L and the total mercury content was 37.13 ng / L. The total mercury of 40 meters' northwest of the Qinling orchard well water A (depth is about 28 m), the tap water B of Qinling (water is the southwest of the village of Qinling wells, and the well depth is about 100 m), and the water of 700 meters southeast of Qin Shihuang tomb (the well depth is about 180m) were 21.6 ng / L, 26.5 ng / L, 16.1 ng / L, respectively. According to the literature, the concentration of mercury in groundwater in other areas of our country is mostly around 0.01 ug / L (Zhang, et al., 2016). The total mercury content of the well water near the Qinling area is reached the requirements of the national groundwater quality standard (GB / T14848-93) (<1ug / L), and it is also reached the hygiene of the drinking water of the World Health Organization and China.

Table 1: The total mercury content in the water samples of Qin Shihuang Mausoleum and its surroundings.

Samples	Total mercury (ng/L)
W1	14.28
W2	3.06
W3	2.04
W4	124.44
W5	37.74
W6	88.74
W7	53.04
W8	3.06
W9	21.42
W10	23.46
A(W)	21.624
B(W)	26.52
C(W)	16.116

It can be seen from the data in Table 1 that the highest point of total mercury in the water sample is 130 m in the northwest corner of the Qinling Mountains and the W6 and W7 mercury levels are also higher. One of the reasons may be the pomegranate rupture in the bag. Another reason may be the cause of Qinling

underground mercury. According to the literature, Qinling groundwater flow is southeast to northwest, the water brought out some of the mercury movement (Vasile et al., 2016). Therefore, there is a high level of mercury in the northwest of Qinling.

Table 2 is the total amount of total mercury in the soil samples taken during and around the tomb of Qin Shihuang. The total mercury content of the soil samples in the southeastern villages and the northwest orchards was 54.6 ng/g and 45.1 ng/g, respectively. The total mercury content of the soil samples on the mausoleum varies greatly from 41.41-2248.08 ng/g. The average mercury content is 451.044ng/g. The high total mercury content (S3, S4, S5) is mainly concentrated in the northeastern part of the mausoleum, and the average content of total mercury is 1334.364ng/g. The highest total mercury content S4 exceeded 1.5 times the tertiary standard (1500ng/g) of the national soil environmental quality standard (GB 15618-1995). The total mercury content of other soil samples on the mausoleum is below the secondary standard (1000ng/g) stipulated by the national soil environmental quality standard. The total mercury content of the soil samples that taken from the northwest orchard (A) and the southeastern village (C) is lower than that of the national soil environmental quality standard (150 ng/g).

Table 2: The total mercury content of the soil samples taken from the tombs of Qin Shihuang

Samples	Total mercury (ng/L)
S1	101.49
S2	63.036
S3	1041.42
S4	2248.08
S5	713.592
S6	257.958
S7	41.412
S8	88.434
S9	74.97
S10	94.656
S11	93.228
S12	593.64
A(S)	46.002
C-1(S)	61.608
C-2(S)	35.7
C-3(S)	69.666

4. Conclusions

In this paper, the contents of total mercury and dissolved mercury in river water samples, soil samples and sediment samples in Xi'an area were determined by cold atomic fluorescence spectrometry, and the mercury pollution in this area was studied. Through the experiment, the results show that although there is a large amount of mercury buried in the mausoleum of Emperor Qin Shihuang, the groundwater and surface soil around it are not affected. Mercury in water did not exceed the allowable amount of mercury in the World Health Organization, the European Union, the United States and China's drinking water standards. The mercury content in the soil on the mausoleum is within the scope of the secondary and tertiary standards stipulated by the National Soil Environmental Quality Standard. The mercury content in the soil around the mausoleum is within the primary standard of the soil environmental quality standard.

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