HJ

NATIONAL ENVIRONMENTAL PROTECTION STANDARD

OF THE PEOPLE'S REPUBLIC OF CHINA

HJ 694-2014

Water Quality - Determination of Mercury, Arsenic, Selenium, Bismuth and Antimony – Atomic Fluorescence Spectrometry

水质 汞、砷、硒、铋和锑的测定

原子荧光法

Issued on: March 13, 2014 **Implemented on: July 01, 2014**

Issued by: Ministry of Environmental Protection

Table of Contents

Announcement

2014 No. 17

Ministry of Environmental Protection of the People's Republic of China

To implement the “Environmental Protection Law of the People's Republic of China”, protect the environment, protect human health, and regulate environmental monitoring, two standards, including “Water Quality - Determination of Mercury, Arsenic, Selenium, Bismuth and Antimony - Atomic Fluorescence Spectrometry”, are approved as national environmental protection standards, and are published.

The standard names and numbers are as follows:

1. “Water Quality - Determination of Mercury, Arsenic, Selenium, Bismuth and Antimony - Atomic Fluorescence Spectrometry” (HJ 694-2014);

2. “Soil - Determination of organic carbon - Combustion oxidation nondispersive infrared absorption method” (HJ 695-2014).

Above standards are implemented since July 1, 2014, and are published by China Environmental Press. The standard content can be inquired at the website of the Ministry of Environmental Protection (bz.mep.gov.cn).

Notice is hereby given.

Ministry of Environmental Protection

March 13, 2014

Foreword

To implement the “Environmental Protection Law of the People's Republic of China” and "Water Pollution Prevention Law of the People's Republic of China”, protect the environment, protect human health, and regulate the monitoring methods of mercury, arsenic, selenium, antimony, and bismuth in water, this Standard is formulated.

This Standard specifies the atomic fluorescence spectrometry for determination of mercury, arsenic, selenium, bismuth, and antimony in water.

This Standard is released for the first time.

Annex A of this Standard is informative.

This Standard was formulated by the Department of Science, Technology and Standards of Ministry of Environment Protection.

Main drafting organization of this Standard: Nanjing Environmental Monitoring Center.

Verification organizations of this Standard: Jiangsu Environment Monitoring Center, Jiangsu Physical and Chemical Testing Center, Wuxi Environmental Monitoring Center Station, Changzhou Environmental Monitoring Center, Zhenjiang Environmental Monitoring Center Station, and Taizhou Environmental Monitoring Center.

This Standard was approved by the Ministry of Environmental Protection on March 13, 2014.

This Standard shall be implemented from July 1, 2014.

This Standard shall be interpreted by the Ministry of Environmental Protection.

Water Quality - Determination of Mercury, Arsenic, Selenium, Bismuth and Antimony – Atomic Fluorescence Spectrometry

Warning: nitric acid, hydrochloric acid, and perchloric acid have a strong corrosivity and a strong oxidability, so it shall wear protective equipment when operating, so as to avoid contact with skin and clothing. The pretreatment process of all samples shall be carried out in a fume hood.

1 Application scope

This Standard specifies the atomic fluorescence spectrometry for the determination of mercury, arsenic, selenium, bismuth, and antimony in water.

This Standard applies to the determination of soluble [Translator: dissolved-state] and total quantity of mercury, arsenic, selenium, bismuth, and antimony in surface water, groundwater, sewage, and industrial waste water.

According to the method of this Standard, the detection limit of mercury is 0.04μg/L, the determination lower limit of mercury is 0.16μg/L; the detection limit of arsenic is 0.3μg/L, the determination lower limit of arsenic is 1.2μg/L; the detection limit of selenium is 0.4μg/L, the determination lower limit of selenium is 1.6μg/L; the detection limit of bismuth and antimony is 0.2μg/L, the determination lower limit of bismuth is 0.8μg/L.

2 Normative references

This Standard references the following documents or its terms. For undated references, the latest version applies to this Standard.

GB/T 21191 Atomic fluorescence spectrometer

HJ/T 91 Technical specifications requirements for monitoring of surface water and waste water

HJ/T 164 Technical specifications for environmental monitoring of groundwater

HJ 493 Water quality - Technical regulation of the preservation and handling of samples

HJ 494 Water quality - Guidance on sampling techniques

3 Terms and definitions

The following terms and definitions apply to this Standard.

3.1

Soluble mercury, arsenic, selenium, bismuth and antimony

It refers to the content of mercury, arsenic, selenium, bismuth, and antimony determined in the filtrate of the not-acidified sample, after being filtered through the filter membrane with a pore size of 0.45μg.

3.2

Total quantity of mercury, arsenic, selenium, bismuth and antimony

It refers to the content of mercury, arsenic, selenium, bismuth, and antimony determined in the unfiltered sample, after being dissolved.

3.3

Determined elements

It refers to mercury, arsenic, selenium, bismuth, and antimony elements.

4 Principle of the method

The test solution after pretreatment is put into the atomic fluorescence spectrometer; under potassium borohydride (or sodium borohydride)'s reducing effects at acidic conditions, it generates arsine, bismuthine, antimony hydrogen, hydrogen selenide, and mercury atoms; the hydride forms ground-state atoms in argon and hydrogen flames; its ground-state atoms and mercury atoms generate atomic fluorescence by the excitation of the light emitted by element (mercury, arsenic, selenium, bismuth, and antimony) lights; the atomic fluorescence intensity is in direct proportion to the content of determined elements in the sample solution within a certain range.

5 Interference and elimination

5.1 The elements in acidic medium, that can react with potassium borohydride and generate hydride, would affect each other and produce interference; adding thiourea + ascorbic acid solution (6.20) can substantially eliminate the interference.

5.2 Copper and other transition metals that are above a certain concentration may interfere to the determination; adding thiourea + ascorbic acid solution (6.20) can eliminate most of the interference. Under the experimental conditions of this Standard, samples containing less than 100mg/L of Cu^{2+}, less than 50mg/L of Fe^{2+}, less than

1mg/L of Co^{2+}, less than 10mg/L of Pb^{2+} (5mg/L for selenium), and less than 150mg/L of Mn^{2+} (2mg/L for selenium) do not affect the determination.

5.3 Common anions do not interfere to the determination.

5.4 Physical interference elimination. Select two-layer-structure quartz tube atomizer; with the outer and inner layers filled with argon gas, form a protective outer layer to isolate air, so that the ground-state atom of determined elements do not collide with oxygen and nitrogen in the air, so as to reduce the fluorescence quenching effect on the determination.

6 Reagents and materials

Unless otherwise indicated, use analytically chemical reagents that comply with national standards when analyzing, water for test is freshly prepared deionized or distilled water.

6.1 Hydrochloric acid: ρ(HCl) = 1.19g/ml, guarantee reagent.

6.2 Nitric acid: ρ(HNO_3) = 1.42g/ml, guarantee reagent.

6.3 Perchloric acid: ρ($HClO_4$) = 1.68g/ml, guarantee reagent.

6.4 Hydrogen sodium hydride (NaOH).

6.5 Potassium borohydride (KBH_4).

6.6 Thiourea (CH_4N_2S).

6.7 Ascorbic acid ($C_6H_8O_6$).

6.8 Potassium dichromate ($K_2Cr_2O_7$): guarantee reagent.

6.9 Mercuric chloride ($HgCl_2$): guarantee reagent.

6.10 Arsenic trioxide (As_2O_3): guarantee reagent.

6.11 Selenium powder: high-purity (the mass fraction is more than 99.99%).

6.12 Bismuth: high-purity (the mass fraction is more than 99.99%).

6.13 Antimony trioxide (Sb_2O_3), guarantee reagent.

6.14 Hydrochloric acid solution: 1 + 1.

6.15 Hydrochloric acid solution: 5 + 95.

6.16 Nitric acid solution: 1 + 1.

6.17 Hydrochloric acid - nitric acid solution

Weigh 300ml of hydrochloric acid (6.1) and 100ml of nitrate (6.2) respectively; add to 400ml of water; mix well.

6.18 Mixture acid of nitric acid - perchloric acid

Prepare by mixing an equal volumes of nitric acid (6.2) and perchloric acid (6.3). Prepare it when it is to be used.

6.19 Reducing agents

6.19.1 Potassium borohydride Solution A

Weigh 0.5g of sodium hydroxide (6.4); dissolve in 100ml of water; add 1.0g of potassium borohydride (6.5); mix well. This solution is used for the determination of mercury; prepare it when it is to be used; stored in a plastic bottle.

6.19.2 Potassium borohydride solution B

Weigh 0.5g of sodium hydroxide (6.4); dissolve in 100ml of water; add 2.0g of potassium borohydride (6.5); mix well. This solution is used for the determination of arsenic, selenium, bismuth, and antimony; prepare it when it is to be used; stored in a plastic bottle.

Note: It can also use potassium hydroxide, potassium borohydride to prepare reducing agents.

6.20 Thiourea - ascorbic acid solution

Weigh 5.0g of sulfur urea (6.6) and ascorbic acid (6.7) respectively; dissolve with 100ml of water; mix well. Prepare it at the day of determination.

6.21 Mercury standard solution

6.21.1 Mercury standard fixative

Weigh 0.5g of potassium dichromate (6.8) and dissolve in 950ml of water; add 50ml of nitric acid (6.2); mix well.

6.21.2 Mercury standard stock solution: ρ(Hg) = 100mg/L.

Purchase the commercially available certified reference materials; or weigh 0.1354g of mercuric chloride (6.9) that has been placed on a silica dryer overnight; transfer into a 1000ml flask after dissolved with a small amount of mercury standard fixative (6.21.1); dilute with mercury standard fixative (6.21.1) to the mark; mix well. Store in a glass bottle. It can be stored at 4°C for 2 years.

6.21.3 Mercury standard intermediate solution: ρ(Hg) = 1.00mg/L.

Pipette 5.00ml of mercury standard solution (6.21.2) into a 500ml volumetric flask; add 50ml of hydrochloric acid (6.14); use mercury standard fixative (6.21.1) to dilute to the mark; mix well. Store in a glass bottle. It can be stored at 4°C for 100 d [Translator: days].

6.21.4 Mercury standard using solution: ρ(Hg) = 10.0g/L.

Pipette 5.00ml of mercury standard intermediate solution (6.21.3) into a 500ml volumetric flask; add 50ml of hydrochloric acid (6.14); dilute with water to the mark; mix well. Store in a glass bottle. Prepare it when it is to be used.

6.22 Arsenic standard solution

6.22.1 Arsenic standard stock solution: ρ(As) = 100mg/L.

Purchase the commercially available certified reference materials; or weigh 0.1320g of guarantee-reagent arsenic trioxide (6.10) that has been dried at 105°C for 2h; dissolve in 5ml of 1mol/L sodium hydroxide solution; use 1mol/L hydrochloric acid to neutralize until phenolphthalein red fades off; transfer into a 1000ml volumetric flask; dilute with water to the mark; mix well. Store in a glass bottle. It can be stored at 4°C for 2 years.

6.22.2 Arsenic intermediate standard solution: ρ(As) = 1.00mg/L.

Pipette 5.00ml of arsenic standard stock solution (6.22.1) into a 500ml volumetric flask; add 100ml of hydrochloric acid (6.14); dilute with water to the mark ; mix well. It can be stored at 4°C for 1 year.

6.22.3 Arsenic standard using solution: ρ(As) = 100μg/L.

Pipette 10.00ml of arsenic standard intermediate solution (6.22.2) into a 100ml volumetric flask; add 20ml of hydrochloric acid (6.14); dilute with water to the mark; mix well. It can be stored at 4°C for 30 d.

6.23 Selenium standard solution

6.23.1 Selenium standard stock solution: ρ(Se) = 100mg/L.

Purchase the commercially available certified reference materials; or weigh 0.1000g of high-purity selenium powder (6.11) in a 100ml beaker; add 20ml of nitric acid (6.2); heat at a low temperature to dissolve; cool to room temperature; transfer into a 1000ml volumetric flask; dilute with water to the mark; mix well. Stored in a glass bottle. It can be stored at 4°C for 2 years.

6.23.2 Selenium standard intermediate solution: ρ(Se) = 1.00mg/L.

Pipette 5.00ml of selenium standard stock solution (6.23.1) into a 500ml volumetric flask; add 150ml of hydrochloric acid (6.14); dilute with water to the mark; mix well. It

can be stored at 4°C for 100 d.

6.23.3 Selenium standard using solution: ρ(Se) = 10.0μg/L.

Pipette 5.00ml of selenium standard intermediate solution (6.23.2) into a 500ml volumetric flask; add 150ml of hydrochloric acid (6.14); dilute with water to the mark; mix well. Prepare it when it is to be used.

6.24 Bismuth standard solution

6.24.1 Bismuth standard stock solution: ρ(Bi) = 100mg/L.

Purchase the commercially available certified reference materials; or weigh 0.1000g of high-purity mental bismuth (6.12) in a 100ml beaker; add 20ml of nitric acid (6.2); heat at a low temperature to dissolve completely; cool down; transfer into a 1000ml volumetric flask; dilute with water to the mark; mix well. Store in a glass bottle. It can be stored at 4°C for 2 years.

6.24.2 Bismuth standard intermediate solution: ρ(Bi) = 1.00mg/L.

Pipette 5.00ml of bismuth stock standard solution (6.24.1) into a 500ml volumetric flask; add 100ml of hydrochloric acid (6.14); dilute with water to the mark; mix well. It can be stored at 4°C for 1 year.

6.24.3 Bismuth standard using solution: ρ(Bi) = 100μg/L.

Pipette 10.00ml of bismuth standard intermediate solution (6.24.2) into a 100ml volumetric flask; add 20ml of hydrochloric acid (6.14); dilute with water to the mark; mix well. Prepare it when it is to be used.

6.25 Antimony standard solution

6.25.1 Antimony standard stock solution: ρ(Sb) = 100mg/L.

Purchase the commercially available certified reference materials; or weigh 0.1197g of antimony trioxide (6.13) that has been dried at 105°C for 2h; dissolve in 80ml of hydrochloric acid (6.1); transfer into a 1000ml volumetric flask; add 120ml of hydrochloric acid (6.1); dilute with water to the mark; mix well. Stored in a glass bottle. It can be stored at 4°C for 2 years.

6.25.2 Antimony standard intermediate solution: ρ(Sb) = 1.00mg/L.

Pipette 5.00ml of antimony standard stock solution (6.25.1) into a 500ml volumetric flask; add 100ml of hydrochloric acid (6.14); dilute with water to the mark; mix well. It can be stored at 4°C for 1 year.

6.25.3 Antimony standard using solution: ρ(Sb) = 100μg/L.

Pipette 10.00ml of antimony standard intermediate solution (6.25.2) into a 100ml

volumetric flask; add 20ml of hydrochloric acid (6.14); dilute with water to the mark; mix well. Prepare it when it is to be used.

6.26 Argon: purity ≥ 99.999%.

7 Instruments and equipment

7.1 Atomic fluorescence spectrometer: Instrument performance indicators shall comply with specifications of GB/T 21191.

7.2 Element light (mercury, arsenic, selenium, bismuth, antimony).

7.3 Thermostat heating plate.

7.4 Thermostatic water bath device: temperature control accuracy is ±1°C.

7.5 Filtration device: water-system microporous filter membrane with a pore size of 0.45μm.

7.6 Analytical balance: accuracy is 0.0001g.

7.7 Sample container: hard glass bottles or polyethylene bottles (barrels).

7.8 Commonly used laboratory ware: grade-A glass gauges and glassware that comply with the national standard.

8 Samples

8.1 Sample collection

Sample collection is conducted by referring to the relevant specifications of HJ/T 91 and HJ/T 164. Soluble samples and total quantity samples are collected separately.

8.2 Sample preservation

Sample preservation is conducted by referring to the relevant specifications of HJ 493.

8.2.1 Filterable mercury, arsenic, selenium, bismuth, antimony samples

Filter the sample with 0.45μm filter membrane (7.5) as soon as possible after sample collection; discard the initial 50ml of filtrate; clean sample bottle with a small amount of the filtrate; collect the filtrate in the sample bottle. Determine mercury samples; if the water sample is neutral, add hydrochloric acid in a ratio of adding 5ml of hydrochloric acid (6.1) per liter of water sample; determine arsenic, selenium, antimony, bismuth samples; add hydrochloric acid in a ratio of adding 2ml of hydrochloric acid (6.1) per liter of water sample. Sample preservation period is 14 d.

8.2.2 Total quantity samples of mercury, arsenic, selenium, bismuth, antimony

Except that samples are not filtered after collection, other treatment methods and preservation period are same as 8.2.1.

8.3 Sample preparation

8.3.1 Mercury

Weigh 5.0ml of mixed sample (8.2.1) or (8.2.2) in a 10ml colorimetric tube; add 1ml of hydrochloric acid - nitric acid solution (6.17); put on a stopper and mix well; place in boiling water bath to heat to dissolve for 1h; shake for 1 to 2 times during heating, and open the stopper to deflate. Cool down; dilute with water to the mark; mix well for test.

8.3.2 Arsenic, selenium, bismuth, antimony

Weigh 50.0ml of mixed sample (8.2.1) or (8.2.2) in a 150ml conical flask; add 5ml of mixture acid of nitric acid - perchloric acid (6.18); heat on a heating plate until white smoke emits; cool down. Then add 5ml of hydrochloric acid solution (6.14); heat until brown smoke disappears; transfer into a 50ml volumetric flask after cooling down; diluted with water to constant volume; mix well for test.

8.3.3 Blank samples

Use water to replace the sample, prepare blank samples according to the steps of 8.3.

9 Analysis steps

9.1 Instrument adjustment

Adjust the instrument to the optimal working condition according to instrument's instructions for use. Reference measurement conditions are shown in Table 1.

Table 1 Reference measurement conditions

Elements	Negative high voltage/ V	Light current/ mA	Atomizer preheat temperature/ °C	Carrier gas flow/ (ml/min)	Shielding gas flow/ (ml/min)	Integration method
Hg	240~280	15~30	200	400	900~1000	Peak area
As	260~300	40~60	200	400	900~1000	Peak area
Se	260~300	80~100	200	400	900~1000	Peak area
Sb	260~300	60~80	200	400	900~1000	Peak area
Bi	260~300	60~80	200	400	900~1000	Peak area

9.2 Calibration

9.2.1 Preparation of calibration standard series

9.2.1.1 Mercury

Pipette respectively 0ml, 1.00ml, 2.00ml, 5.00ml, 7.00ml, 10.00ml of mercury standard using solution (6.21.4) in 100ml volumetric flasks; add 10.0ml of hydrochloric acid - nitric acid solution respectively; dilute with water to the mark; mix well.

9.2.1.2 Arsenic

Pipette respectively 0ml, 0.50ml, 1.00ml, 2.00ml, 3.00ml, 5.00ml of arsenic standard using solution (6.22.3) in 50ml volumetric flasks; add respectively 10ml of hydrochloric acid solution (6.14) and 10ml of thiourea - ascorbic acid solution (6.20); place at room temperature for 30min (when room temperature is lower than 15°C, place in 30°C water bath for 30min); dilute with water to constant volume; mix well.

9.2.1.3 Selenium

Pipette respectively 0ml, 2.00ml, 4.00ml, 6.00ml, 8.00ml, 10.00ml of selenium standard using solution (6.23.3) in 50ml volumetric flasks; add 10ml of hydrochloric acid solution (6.14) respectively; dilute with water to constant volume; mix well.

9.2.1.4 Bismuth

Pipette respectively 0ml, 0.50ml, 1.00ml, 2.00ml, 3.00ml, 5.00ml of bismuth standard using solution (6.24.3) in 50ml volumetric flasks; add 10ml of hydrochloric acid solution (6.14) respectively; dilute with water to constant volume; mix well.

9.2.1.5 Antimony

Pipette respectively 0ml, 0.50ml, 1.00ml, 2.00ml, 3.00ml, 5.00ml of antimony standard using solution (6.25.3) in 50ml volumetric flasks; add respectively 10ml of hydrochloric acid solution (6.14) and 10ml of thiourea - ascorbic acid solution (6.20); place at room temperature for 30min (when room temperature is lower than 15°C, place in 30°C water bath for 30min); dilute with water to constant volume; mix well.

Mass concentrations of mercury, arsenic, selenium, bismuth, antimony standard series are shown in Table 2.

Table 2 Mass concentrations of standard series Unit: μg/L

Elements	Mass concentrations of standard series					
Hg	0	0.10	0.20	0.50	0.70	1.00
As	0	1.0	2.0	4.0	6.0	10.0
Se	0	0.4	0.8	1.2	1.6	2.0
Bi	0	1.0	2.0	4.0	6.0	10.0
Sb	0	1.0	2.0	4.0	6.0	10.0

9.2.2 Drawing of calibration curves

9.2.2.1 Mercury

Reference to measurement conditions (9.1) or use self-determined optimal measurement conditions; use hydrochloric acid solution (6.15) as the carrier; use potassium borohydride solution A (6.19.1) as the reducing agent; determine the atomic fluorescence intensity of mercury standard series from low to high concentration; take the atomic fluorescence intensity as ordinate and the mass concentration of mercury as abscissa, to draw the calibration curve.

9.2.2.2 Arsenic, selenium, bismuth, antimony

Reference to measurement conditions (9.1) or use self-determined optimal measurement conditions; use hydrochloric acid solution (6.15) as the carrier; use potassium borohydride solution B (6.19.2) as the reducing agent; determine the atomic fluorescence intensity of each element standard series from low to high concentration; take the atomic fluorescence intensity as ordinate and the mass concentration of the corresponding elements as abscissa, to draw the calibration curve.

9.3 Sample determination

9.3.1 Mercury

Determine the atomic fluorescence intensity of the sample (8.3.1) according to the same conditions of drawing calibration curves. For samples that exceed the high concentration points of the calibration curve, determine again after diluting its digestion solution, the dilution multiple is f.

9.3.2 Arsenic, antimony

Weigh 5.0ml of sample (8.3.2) in a 10ml colorimetric tube; add 2ml of hydrochloric acid solution (6.14) and 2ml of thiourea - ascorbic acid solution (6.20); place at room temperature for 30min (when room temperature is lower than 15°C, place in 30°C water bath for 30min); dilute with water to constant volume; mix well; determine according to the same conditions of drawing calibration curves. For samples that exceed the high concentration points of the calibration curve, determine again after diluting its digestion solution, the dilution multiple is f.

9.3.3 Selenium, bismuth

Weigh 5.0ml of sample (8.3.2) in a 10ml colorimetric tube; add 2ml of hydrochloric acid solution (6.14); dilute with water to constant volume; mix well; determine according to the same conditions of drawing calibration curves. For samples that exceed the high concentration points of the calibration curve, determine after diluting its digestion solution, the dilution multiple is f.

9.4 Blank test

Determine the blank sample according to the same procedure of determination (9.2).

10 Result calculation and representation

10.1 Result calculation

The mass concentration ρ of the determined element in the sample is calculated according to equation (1):

$$\rho = \frac{\rho_1 \times f \times V_1}{V} \quad (1)$$

Where:

ρ - The mass concentration of the determined element in the sample, μg/L;

ρ_1 - The mas concentration of the determined element in the sample obtained from the calibration curve, μg/L;

f - Sample dilution multiple (if the sample has been diluted);

V_1 - The constant volume of sample after pipetted, ml;

V - The volume of pipetted sample, ml.

10.2 Result presentation

When the determination result of mercury is less than 1μg/L, retain to two decimal places; when the determination result of mercury is greater than 1μg/L, retain three significant figures.

When the determination result of arsenic, smashing, bismuth, antimony is less than 10μg/L, retain to one decimal place; when the determination result of arsenic, smashing, bismuth, antimony is greater than 10μg/L, retain three significant figures.

11 Precision and accuracy

11.1 Precision

Six laboratories have tested the unified sample that contains mercury, arsenic, selenium, bismuth, antimony of different concentration levels. Test results of method precision are shown in Table A.1.

Six laboratories have determined the unified sample that contains mercury of four kinds of concentrations, i.e. 0.10μg/L, 0.20μg/L, 0.40μg/L, and 0.80μg/L. The relative standard deviations among laboratories are 3.3%~10.9%, 2.0%~7.5%, 1.5%~3.7%, and 1.5%~2.9% respectively; the relative standard deviations among laboratories are 8.5%, 2.8%, 1.9%, and 1.4%; the repeatability limits are 0.03μg/L, 0.03μg/L, 0.03μg/L, and 0.05μg/L; the reproducibility limits are 0.03μg/L, 0.03μg/L, 0.04μg/L, and

0.06μg/L.

Six laboratories have determined the unified sample that contains arsenic of three kinds of concentrations, i.e. 1.0μg/L, 4.0μg/L, and 8.0μg/L. The relative standard deviations among laboratories are 6.0%~7.0%, 2.3%~5.4%, and 0.9%~3.4%; the relative standard deviations among laboratories are 4.1%, 1.6%, and 1.5%; the repeatability limits are 0.2μg/L, 0.4μg/L, and 0.5μg/L; the reproducibility limits are 0.2μg/L, 0.4μg/L, and 0.6μg/L.

Six laboratories have determined the unified sample that contains selenium of three kinds of concentrations, i.e. 1.0μg/L, 2.0μg/L, and 8.0μg/L. The relative standard deviations among laboratories are 4.1%~8.9%, 1.2%~4.9%, and 0.3%~3.6%; the relative standard deviations among laboratories are 4.1%, 2.6%, and 2.7%; the repeatability limits are 0.2μg/L, 0.2μg/L, and 0.6μg/L; the reproducibility limits are 0.2μg/L, 0.2μg/L, and 0.8μg/L.

Six laboratories have determined the unified sample that contains bismuth of three kinds of concentrations, i.e. 0.5μg/L, 2.0μg/L, and 4.0μg/L. The relative standard deviations among laboratories are 4.8%~8.0%, 2.8%~4.7%, and 2.7%~4.0%; the relative standard deviations among laboratories are 4.5%, 3.6%, and 1.5%; the repeatability limits are 0.1μg/L, 0.2μg/L, and 0.4μg/L; the reproducibility limits are 0.1μg/L, 0.3μg/L, and 0.4μg/L.

Six laboratories have determined the unified sample that contains mercury of four kinds of concentrations, i.e. 0.5μg/L, 1.0μg/L, 2.0μg/L, and 4.0μg/L. The relative standard deviations among laboratories are 6.4%~11.6%, 3.9%~6.7%, 3.2%~4.7%, and 1.7%~3.8%; the relative standard deviations among laboratories are 4.4%, 4.5%, 2.6%, and 2.7%; the repeatability limits are 0.1g/L, 0.1g/L, 0.2g/L, and 0.3g/L; the reproducibility limits are 0.1μg/L, 0.2μg/L, 0.2μg/L, and 0.4μg/L.

11.2 Accuracy

Six laboratories have tested the certified reference samples of mercury, arsenic, selenium of two kinds of concentrations; and conduct spiked recovery test of three spiked quantity to the unified sample of mercury, arsenic, selenium, bismuth, antimony. Test data of method accuracy is shown in Table A.2.1 and Table A.2.2 in Annex A.

The relative error of the determination results of mercury's certified reference materials (concentration of 16.0μg/L ± 1.4μg/L) by six laboratories is -2.8%~0.9%, the final value of relative error is -0.4% ± 2.8%; the relative error of the determination results of mercury's certified reference materials (concentration of 11.4μg/L ± 1.1μg/L) is -5.6%~0.0%, the final value of relative error is -3.6% ± 4.0%.

The relative error of the determination results of arsenic's certified reference materials (concentration of 60.6μg/L ± 4.2μg/L) by six laboratories is -1.9%~1.7%, the final value of relative error is -0.4% ± 3.2%; the relative error of the determination results of arsenic's certified reference materials (concentration of 75.1μg/L ± 5.3μg/L) is

-4.7%~-0.9%, the final value of relative error is -2.3% ± 3.0%.

The relative error of the determination results of selenium's certified reference materials (concentration of 11.2μg/L ± 1.1μg/L) by six laboratories is -1.5%~3.1%, the final value of relative error is 0% ± 8.8%; the relative error of the determination results of selenium's certified reference materials (concentration of 26.2μg/L ± 2.4μg/L) is -1.5%~3.1%, the final value of relative error is -0.6% ± 3.2%.

Six laboratories have conducted spiked determination to unified industrial waste water, the spiked quantities of mercury are 0.20μg/L, 0.40μg/L, 0.60μg/L, the spiked recoveries are 91.5%~104%, 91.2%~99.6%, and 98.6%~107% respectively; the final values of spiked recovery rates are 98.2% ± 9.4%, 96.6% ± 6.2%, and 102% ± 6.2% respectively.

Six laboratories have conducted spiked determination to unified industrial waste water, the spiked quantities of arsenic are 2.0μg/L, 4.0μg/L, 6.0μg/L, the spiked recoveries are 92.0%~109%, 96.5%~106%, and 94.3%~103% respectively; the final values of spiked recovery rates are 97.1% ± 12.2%, 100% ± 8.2%, and 99.4% ± 5.8% respectively.

Six laboratories have conducted spiked determination to unified industrial waste water, the spiked quantities of selenium are 1.0μg/L, 2.0μg/L, 3.0μg/L, the spiked recoveries are 90.0%~102%, 96.0%~102%, and 98.7%~107% respectively; the final values of spiked recovery rates are 95.0% ± 9.4%, 98.2% ± 4.6%, and 102% ± 6.8%.

Six laboratories have conducted spiked determination to unified industrial waste water, the spiked quantities of bismuth are 1.0μg/L, 2.0μg/L, 4.0μg/L, the spiked recoveries are 90.0%~103%, 93.5%~104%, and 93.0%~101% respectively; the final values of spiked recovery rates are 94.8% ± 11.4%, 97.6% ± 7.6%, and 97.0% ± 6.4%.

Six laboratories have conducted spiked determination to unified industrial waste water, the spiked quantities of antimony are 1.0μg/L, 2.0μg/L, 4.0μg/L, the spiked recoveries are 94.0%~108%, 92.0%~105%, and 94.0%~100% respectively; the final values of spiked recovery rates are 101% ± 11.4%, 97.4% ± 10.8%, and 96.2% ± 4.4%.

12 Quality assurance and quality control

12.1 Sampling, storage and management of samples shall be conducted according to HJ 494 and HJ 493.

12.2 It shall add one determination of laboratory blank, after determinations of 20 samples. It shall determine two laboratory blanks when the batch is less than 20 samples. The determination results of full blank shall be less than the method detection limit.

12.3 It shall draw calibration curve in each sample analysis. The correlation coefficient

of the calibration curve shall be greater than or equal to 0.995.

12.4 Conduct one verification to the zero-point and mid-point concentration of calibration curve after determinations of 20 samples, the relative deviation of the test results shall not exceed 20%.

12.5 Determine at least 10% of parallel double-samples to each batch of samples. When the sample number is less than 10, determine at least one parallel double-sample. The relative deviation of the test results shall not be greater than 20%.

12.6 Determine at least 10% of spiked samples to each batch of samples. When the sample number is less than 10, determine at least one spiked sample. Spiked recovery rate shall be controlled between 70%~130%.

13 Waste disposal

Waste liquors and waste matters generated in the experiment can not be dumped at-will, which shall be placed in sealed containers to store, and entrust qualified organizations to process.

14 Notes

14.1 Potassium borohydride is a strong reducing agent, which is easily to react with oxygen and carbon dioxide in the air, and easily to decompose and produce hydrogen in neutral and acidic solutions, therefore, when preparing potassium borohydride reducing agent, it shall dissolve the solid potassium borohydride in sodium hydroxide solution, and prepare it when it is to be used.

14.2 Glassware used in laboratory must be soaked in nitric acid solution (6.16) for 24h, or rinsed with hot nitric acid. When washing, clean with running water and deionized water successively.

Annex A

(Informative)

Summary table of precision and accuracy

The precision and accuracy data determined by six laboratories are shown in Table A.1, Table A.2.1, and Table A.2.2.

Table A.1 Method precision

Element name	Concentration/ (μg/L)	Relative standard deviation in laboratory/%	Relative standard deviation among laboratories/%	Repeatability limit r/ (μg/L)	Reproducibility limit R/(μg/L)
Mercury	0.10	3.3~10.9	8.5	0.03	0.03
	0.20	2.0~7.5	2.8	0.03	0.03
	0.40	1.5~3.7	1.9	0.03	0.04
	0.80	1.5~2.9	1.4	0.05	0.06
Arsenic	1.0	6.0~7.0	4.1	0.2	0.2
	4.0	2.3~5.4	1.6	0.4	0.4
	8.0	0.9~3.9	1.5	0.5	0.6
Selenium	1.0	4.1~8.9	4.1	0.2	0.2
	2.0	1.2~4.9	2.6	0.2	0.2
	8.0	0.3~3.6	2.7	0.6	0.8
Bismuth	0.5	4.8~8.0	4.5	0.1	0.1
	2.0	2.8~4.7	3.6	0.2	0.3
	4.0	2.7~4.0	1.5	0.4	0.4
Antimony	0.5	6.4~11.6	4.4	0.1	0.1
	1.0	3.9~6.7	4.5	0.1	0.2
	2.0	3.2~4.7	2.6	0.2	0.2
	4.0	1.7~3.8	2.7	0.3	0.4

Table A.2.1 Method accuracy (certified reference material test)

Element name	Concentration of certified reference material/(μg/L)	Relative error/%	Final value of relative error/%
Mercury	16.0±1.4	-2.8~0.9	-0.4±2.8
	11.4±1.1	-5.6~0.0	-3.6±4.0
Arsenic	60.6±4.2	-1.9~1.7	-0.4±3.2
	75.1±5.3	-4.7~-0.9	-2.3±3.0
Selenium	11.2±1.1	-5.4~6.2	0.0±8.8
	26.2±2.4	-1.5~3.1	0.6±3.2

Table A.2.2 Method accuracy (spiked recovery test)

Element name	Sample concentration / (μg/L)	Spiked concentration / (μg/L)	Spiked recovery rate / %	Final value of spiked recovery rate / %
Mercury	0.39	0.20	91.5~104	98.2±9.4
	0.39	0.40	91.2~99.6	96.6±6.2
	0.39	0.60	98.6~107	102±6.2
Arsenic	3.9	2.00	92.0~109	97.1±12.2
	3.9	4.00	96.5~104	100±8.2
	3.9	6.00	94.3~103	99.4±5.8
Selenium	2.0	1.00	90.0~102	95.0±9.4
	2.0	2.00	96.0~102	98.2±4.6
	2.0	3.00	98.7~107	102±6.8
Bismuth	2.0	1.00	90.0~103	94.8±11.4
	2.0	2.00	93.5~104	97.6±7.6
	2.0	4.00	93.0~101	97.0±6.4
Antimony	2.0	1.00	94.0~108	101±11.4
	2.0	2.00	92.5~105	97.4±10.8
	2.0	4.00	94.0~100	96.2±4.4

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