ISSN: 2710-0588

Determination of Trace Mercury in Geological Samples by Atomic Fluorescence Spectrometry

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Abstract

An atomic fluorescence method was established for the determination of mercury in geological samples. After sample digestion, mercury reacts with potassium borohydride in a specific medium to produce volatile hydride. The fluorescence of characteristic wavelength is emitted under the irradiation of argon loaded quartz atomizer light source, and the fluorescence intensity is proportional to the content of elements.

Keywords

Atomic Fluorescence; Geological Samples; Mercury.

1. Introduction

Mercury is a toxic element with strong accumulation. There are silver salt colorimetric method, spectrophotometry, atomic absorption spectrometry, atomic fluorescence spectrometry and other atomic fluorescence techniques[1-3] are developing rapidly in recent years. Hg is a toxic element commonly contained in many herbal foods. Both inorganic and organic Hg compounds are accumulated in kidney and brain and exhibit serious of the poisonousness [4]. Hg also is genotoxic which will increase the risk of chromosomal aberrations.

Mercury is widely distributed in nature, with high toxicity and bioaccumulation. It has been included in the blacklist of priority pollutants in China's environment and has become one of the necessary items for routine monitoring in environmental monitoring.

At present, the main methods for determining mercury include cold atomic absorption spectroscopy, cold atomic fluorescence spectroscopy, inductively coupled plasma emission spectroscopy (ICP-AES), hydride generation atomic fluorescence spectroscopy (HG-AFS), and so on. HG-AFS has the advantages of simple spectral lines, high sensitivity, low detection limit, low interference, and wide linear range. The key to using HG-AFS to determine mercury in soil is the digestion of soil samples before measurement. The methods of soil digestion include ultrasonic assisted extraction, water bath digestion, electric thermal digestion, etc. These methods have many problems such as long analysis time, incomplete digestion, cumbersome operation, or easy mercury loss. Microwave digestion technology R has been widely used in various sample pretreatment methods. Microwave digestion method has the advantages of fast, efficient, low sample loss, and low reagent consumption.

2. Experimence

2.1. Instrument and Reagents

Atomic fluorescence spectrophotometer; Merury hollow cathode lamp; The carrier gas and shield gas were N-50 purity compressed argon (99.999%) of BOC GAZY (China). 18.2MΩ.cm de-ionized water from a Mille-Q system (Millipore, Milford, MA, USA). The commercial standard stock solutions were purchased from the National Standard Material Center of China(1.0 g L-1 of Hg) and stored in the refrigerator at 4℃. The Hg working standard solutions were in 5% (v/v) HCl, diluted by the stock solutions. Potassium tetrahydroborate solution was in 1% (w/w)

ISSN: 2710-0588

KOH solution, and dissolving the solid KBH4 of Xi'an Chemicals Co., China. The HCl solution was prepared by GR grade HCl from Xi'an Chemicals Co., China.

2.2. Sample Processing

The collected soil samples are air dried and dried at 105 ℃ to remove foreign objects. They are then crushed with a grinder to prepare a 100 mesh sample. Accurately weigh 0.2000 (± 0.000 2) g of soil sample into the inner tank of the microwave digestion tank, add HNO, 5mL, HCl 5mL, and HF2mL respectively, mix well, seal, and place the digestion tank into the microwave digestion instrument. Digest the soil sample according to the working conditions of microwave digestion in Table 1 at a microwave power of 7OOW and a maximum pressure of 2Mpa. After the digestion is completed, when the temperature drops below 80 ℃, remove the digestion tank and transfer the digestion solution to a polytetrafluoroethylene 30 jar, Wash the digestion tank with a small amount of ultrapure water, merge the washing solution into the cyanotic snail, place the polytetrafluoroethylene cyanotic snail on an electric heating plate, gradually heat and drive the acid to about 2mL, cool down, transfer the digestion solution to a 25mL volumetric flask, wash the snail with 2% HNO, merge the washing solution, and use 2% HNO; Dilute to 25mL and shake well for testing. Simultaneously conduct a blank test. Microwave digestible.

3. Results and Discussion

(1) The selective fluorescence intensity of the lamp current and negative high voltage increases with the increase of the lamp current and negative high voltage of the photomultiplier tube. The increase of negative high voltage is beneficial to the improvement of sensitivity, but the reduction of linear range is considered comprehensively. The lamp current is 20 mA and negative high voltage is 270V.

Observation height was very important to the fluorescence signals of Hg, which is the distance from the top of the atomizer to the point where the atomic fluorescence signal is generated. For Hg element, the intensities were decreased slowly. Take signal-to-noise ratio into consideration of this method and signal intensities, the observation height was selected at 8 mm.

(2) The results of potassium borocyanide dosage show that too low or too high concentration of potassium borocyanide will lead to the decrease of sensitivity, the concentration of potassium borocyanide at 0.05%~0.5% is more stable, so the concentration of potassium borocyanide at 0.5% is used as a reducing agent.

(3) In this method, hydrochloric acid was selected as the carrier. Since the generation efficiency of chemical vapors extremely depended on the acidity of the reaction solution, the intensity of analyzed elements can be affected by the concentration of HCl. Moreover, the stability of the reaction system is related to the concentration of HCl as well. When the concentration of hydrochloric acid was 1% and 10%, the fluorescence intensity was stable, and 5% hydrochloric acid was used as the medium.

(4) Standard Curve

There was a linear relationship between fluorescence intensity and concentration, when Hg was 1~10.00μg/L. Linear equation was Y=798.4x+54.89, r=0.997.

(5) Precision test

The relative standard deviation (RSD%) of amylase samples was calculated for 7 times, and the relative standard deviation (RSD%) of mercury was 2.3%.

(6) Standard addition and recycling experiment

The mercury standard solution was added to amylase samples, and the mercury standard recovery 95.4%, which indicated high method accuracy.

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4. Conclusion

(1) The selection test of instrument working conditions found that the fluorescence intensity of mercury standard solution significantly increased with the increase of negative high voltage of the photomultiplier tube, but the noise also increased accordingly. Under the condition of meeting the sensitivity requirements, 270V was selected. The current of the hollow cathode lamp increases, and the mercury fluorescence intensity also increases. However, an excessive lamp current will shorten the lamp's service life. Through experiments, the lamp current was selected to be 30 mA.

(2) Selection of hydride generation conditions

1) The selection of current carrying concentration was tested for the variation of fluorescence intensity within the range of 1% to 6% of nitric acid concentration. As the concentration of nitric acid increases, the fluorescence intensity increases. Under the condition of meeting the sensitivity requirements of the experiment, the principle of selecting a low acidity is to choose a nitric acid concentration of 2%.

2) Selection of reducing agent concentration The concentration of potassium borohydride has a direct impact on the fluorescence intensity. When the amount of potassium borohydride is insufficient, it cannot be completely reduced; If the dosage is too large, excessive hydrogen gas is generated to dilute the hydride, resulting in a decrease in sensitivity. Under optimized experimental conditions, the effect of potassium borohydride concentration in the range of 0.2% to 5% on fluorescence intensity was measured with 2% nitric acid as the carrier current in a 10ug/mercury standard solution. As the concentration of KBHa increases, the fluorescence intensity also increases; The fluorescence intensity does not change significantly at a concentration of 1% to 2%, but gradually decreases as the KBH concentration continues to increase. 1% KBH was selected as the reducing agent in the experiment.

(3) Summary: Under optimized experimental conditions, the mercury content in soil was determined using the HG-AFS method using a 1% potassium borohydride -0.5% potassium hydroxide solution as the reducing agent and 2% nitric acid as the carrier current. This method has the advantages of simple sample processing, low detection limit, high sensitivity, and wide linear range, making it suitable for the determination of mercury in soil.

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