Determination of Total Mercury in Rain Water by Chemical Vapor Atomic Fluorescence Spectrometry

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Abstract. We report a facile method to determine total mercury in rain water by chemical vapor atomic fluorescence spectrometry and optimize the method conditions, which were carrier gas flow rate, Shielding gas flow rate, Hydrochloric acid concentration, Potassium borohydride concentration, etc. In the optimal conditions, the Correlation coefficient(r) was more than 0.998, detection limit is less than 0.0005ng/mL, and the recovery was from 93%.

1. Introduction

It was well known that mercury was a highly toxic heavy metal element to people’s health. Mercury is considered a global pollutant, as it can travel long distances in the atmosphere. Different forms of mercury entered into the atmosphere, and then they could enter into water or terrestrial ecosystems by precipitation, which could cause harm to human body.

So it was very important to accurately detect mercury in rain water. In order to ensure the sensitivity of detection, it was most popular to determine mercury by ICP-MS [1, 2] or CV-AFS [3-5]. In the paper, we detected total mercury in rain water by chemical vapor atomic fluorescence spectrometry.

2. Experiment

2.1. Reagents

The used reagents were analytical-reagent grade. 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 from National Standard Material Center of China (1.0 g L⁻¹ of Hg) were stored in the refrigerator at 4°C. The Hg working standard solutions were in 10% (v/v) HCl, diluted by the stock solutions. Potassium
tetrahydroborate solution was in 5% (w/w) KOH solution, and dissolving the solid KBH₄ of Xi’an shunda chemical reagent instrument co. LTD, China. The GR grade HCl and HNO₃ from Xi’an shunda chemical reagent instrument co. LTD, China.

2.2. Instrument
The method was studied by AFS-9760 atomic fluorescence spectrometer (Beijing haiguang instrument co. LTD). The Hg hollow cathode lamp was specially made for AFS as the radiation sources (General Research Institute for Nonferrous Metals). The instrument working program was described in Table 1.

| Working program | PMT (V) | Lamp Current (mA) | Reading time (s) | Delay time (s) |
|-----------------|---------|-------------------|-----------------|---------------|
| Settings Hg     | 280     | 30                | 9               | 1             |

2.3. Sample pretreatment
50 ml rain water was put into a 100ml beaker, added 10ml Aqua regia, mixed it evenly, placed it in a water bath and slowly heated it at low temperature until the solution volume was left 15ml. After cooling completely, the solution was transferred to a 50ml volumetric flask, diluted it with ultra-pure water and shook it well. The content of total mercury in the sample was directly determined by chemical vapor atomic fluorescence spectrometry after being shaken well.

3. Results and discussion

3.1. Determination of optimal carrier gas and shield gas flow rates
The carrier gas and shield gas were 99.999% pure argon. We studied the effect of the flow rates of carrier gas and shield gas. The effect of carrier gas velocity (0-600mL/min) on Hg atomic fluorescence signal was discussed. The experimental results were shown that when the carrier gas was between 0-300mL/min, the atomic fluorescence signal increased with the increase of the carrier gas velocity, while the carrier gas velocity was between 300-600mL/min, the Hg signal decreased with the increase of the carrier gas. It is recommended 300mL/min carrier gas for the experiment.

The main role of shielding gas in the determination of Hg by chemical vapor generation - atomic fluorescence spectrometry is to isolate mercury vapor from the air around the atomizer, which could reduce fluorescence quenching and the interference of water vapor. In this paper, the effect of shielding gas (0-1200mL/min) on Hg signal was studied. The results are shown that when the shielded gas changed from 0-800mL/min, the atomic fluorescence signal increased with the flow rate of shielded gas, and when the shielded gas changed from 800-1200mL/min, the fluorescence signal decreased with the increase of the flow rate of shielded gas. The flow rate of shielded gas was suggested to be 800mL/min.

3.2. Concentration optimization of HCl
We studied the effect of the concentration of HCl. When the concentration of hydrochloric acid (V/V) increased from 5% to 20% (V/V), mercury signal had no significant change. Because of reagent blank, cost, interference factors and the stability of mercury, hydrochloric acid concentration of 10% (V/V) was selected.

3.3. Concentration optimization of KBH₄
In this paper, the effect of KBH₄ concentration on Hg atomic fluorescence signal was studied. The experimental results were shown that when KBH₄ concentration was from 0 to 0.5g/L, the Hg atomic fluorescence signal increased with the increase of KBH₄ concentration. When KBH₄ concentration changed at 0.5-4g/L, the Hg signal formed a platform with little change. When KBH₄ concentration increased continuously, Hg fluorescence signal decreased obviously. The recommended KBH₄ concentration was 0.2-0.5g/L.
3.4. Analytical figures of merit
The method characteristics were described in Table 2. It was very obvious that the calibration functions, detection limits and precision of the proposed were excellent.

| Element | Calibration functions | Corr. coefficient | RSD (%) (n=7) | Detection limit (ng/mL) |
|---------|-----------------------|-------------------|---------------|-------------------------|
| Hg I$_1$=687.5C$_{Hg}$+31.4 | 0.9991 | 1.89 | 0.00448 |

The established method was used to determine Hg in rainwater. The results were shown in table 3, and the method established in this paper was compared with ICP-MS. In addition, the result of recycling experiment was good.

**Table 3.** Determination result of rain water and recycling experiment.

| Sample   | element | Determination value (μg/L, n=3) | Recovery rate (%) |
|----------|---------|--------------------------------|-------------------|
|          |         | This method | ICP-MS            |
| Rain water | Hg      | 0.059      | 0.063             | 93               |

3.5. Conclusion
In this paper, an analytical method for the determination of Hg in rainwater was explored, and the experimental conditions were optimized. Under the experimental conditions, the linearity, precision and detection limit of the proposed method were good.

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References
[1] Yang C.Q, Zhang S.S, Wu N., et al. Feasibility study on content determination of mercury and arsenic in high organic anthracite by microwave digestion-hydride generation-atomic fluorescence spectrometry and mass spectrometry [J]. Rock and Mineral Analysis, 2016, 35(5):481-487.
[2] Liu H., Qian Q., Studies on determination of mercury in foods by inductively coupled plasma-mass spectrometry with microwave digestion [J]. Farm Products Processing, 2016, (6):55-60.
[3] Maria L. A., Carmela P., Elisabetta M., et al. Simple and rapid method for the determination of mercury in human hair by cold vapour generation atomic fluorescence spectrometry [J]. Microchemical Journal, 2019, 150.
[4] Xia H., Li C.H., Chen H.J., Green preparation of CuI particles in dielectric barrier discharge for colorimetric determination of trace mercury in comparison with atomic fluorescence spectrometric determination [J]. Microchemical Journal, 2019, 146: 1169-1172.
[5] Yao M.L., Feng P. Z., Bao Y.J., et al. Automated dispersive liquid-liquid microextraction coupled to high performance liquid chromatography – cold vapour atomic fluorescence spectroscopy for the determination of mercury species in natural water samples [J]. Journal of Chromatography A, 2017, 1493(14): 1-9.