

Research Article

Precision and trueness of a method for determining antimony content in groundwater using hydride generation-atomic fluorescence spectrometry

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Abstract: At present, there is currently a lack of unified standard methods for the determination of antimony content in groundwater in China. The precision and trueness of related detection technologies have not yet been systematically and quantitatively evaluated, which limits the effective implementation of environmental monitoring. In response to this key technical gap, this study aimed to establish a standardized method for determining antimony in groundwater using Hydride Generation–Atomic Fluorescence Spectrometry (HG-AFS). Ten laboratories participated in inter-laboratory collaborative tests, and the statistical analysis of the test data was carried out in strict accordance with the technical specifications of GB/T 6379.2—2004 and GB/T 6379.4—2006. The consistency and outliers of the data were tested by Mandel's h and k statistics, the Grubbs test and the Cochran test, and the outliers were removed to optimize the data, thereby significantly improving the reliability and accuracy. Based on the optimized data, parameters such as the repeatability limit (r), reproducibility limit (R), and method bias value (δ) were determined, and the trueness of the method was statistically evaluated. At the same time, precision-function relationships were established, and all results met the requirements. The results show that the lower the antimony content, the lower the repeatability limit (r) and reproducibility limit (R), indicating that the measurement error mainly originates from the detection limit of the method and instrument sensitivity. Therefore, improving the instrument sensitivity and reducing the detection limit are the keys to controlling the analytical error and improving precision. This study provides reliable data support and a solid technical foundation for the establishment and evaluation of standardized methods for the determination of antimony content in groundwater.

Keywords: Mandel's h and k statistics; Grubbs test; Cochran test; Repeatability limit; Reproducibility limit; Method bias value

Received: 26 Feb 2025/ Accepted: 10 Oct 2025/ Published: 20 Nov 2025

Introduction

Antimony (Sb) is a metalloid element with significant toxicity and carcinogenicity, mainly existing in trivalent and pentavalent forms (Wang et al.

2023b; Zhang et al. 2021). Excessive antimony can cause severe environmental problems and poses a threat to human, animal and plant health (Wang et al. 2023a; Zhao et al. 2024; Bolan et al. 2022). The World Health Organization (WHO) drinking water quality standard stipulates that the maximum permissible concentration of antimony in drinking water is 0.020 mg/L (Haider et al. 2024). Groundwater is an important source of drinking water, accounting for approximately 65% of global drinking water supplies (Li et al. 2024; Filter et al. 2024). However, excessive mining of antimony-containing ores, metal smelting, and the widespread use of antimony-containing products have led to substantial accumulation of antimony

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DOI: [10.26599/JGSE.2026.9280071](https://doi.org/10.26599/JGSE.2026.9280071)

Liu BB, Zhang L, Li K. 2026. Precision and trueness of a method for determining antimony content in groundwater using hydride generation-atomic fluorescence spectrometry. Journal of Groundwater Science and Engineering, 14(1): 49-58.

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in groundwater (Fu et al. 2023; Lan et al. 2023). China's "Standard for groundwater quality" (GB/T 14848—2017) stipulates that the maximum allowable concentrations of antimony content for Class I and Class II water are 0.0001 mg/L and 0.0005 mg/L, respectively. Therefore, it is necessary to develop methods that can rapidly and accurately determine antimony concentrations in groundwater.

However, there is still a lack of a unified standard method for the determination of antimony content in groundwater in China. Current detection technologies for groundwater antimony have significant limitations in quality evaluation, in terms of precision evaluation, there is a lack of inter-laboratory comparison data, an inadequate basis for method stability assessment, and no systematic determination of repeatability and reproducibility limits; there is also a lack of trueness verification mechanisms and insufficient data from method comparison studies. These problems seriously affect the reliability and comparability of monitoring data and restrict the effective implementation of environmental monitoring. Therefore, it is urgently necessary to establish a unified detection method standard by improving the precision and trueness evaluation system through multi-laboratory collaborative research, so as to enhance the monitoring capacity of antimony pollution in groundwater in China.

The main methods for determining antimony content include Hydride Generation-Atomic Fluorescence Spectrometry (HG-AFS) (Ferreira et al. 2019; Liu et al. 2021), Hydride Generation-Atomic Absorption Spectrometry (HG-AAS) (Correia et al. 2019; Azooz et al. 2024), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Gil-Díaz et al. 2024; Yang, 2019). HG-AAS and ICP-MS necessitate significant investments in instruments and reagents, as well as high operational and maintenance costs, and are therefore less commonly used in laboratories across different regions. In contrast, HG-AFS has the advantages of low instrument cost, simple operation, high sensitivity, and a low detection limit, and is widely applied as one of the routine analysis techniques in laboratories.

Furthermore, the hydride generation-atomic fluorescence spectrometer and its associated standard methods developed in China are at an internationally leading level, with national standards and industry standards for geological, environmental, and metallurgical systems already established (Zhang, 2014; Cui et al. 2014; Li et al. 2017). Therefore, based on HG-AFS, this study conducted

a systematic investigation into the two key performance indicators of the method, namely precision and trueness, to scientifically evaluate the applicability of this analytical method, with the aim of establishing a standardized method for the determination of antimony content in groundwater.

According to the requirements of "Accuracy (trueness and precision) of measurement methods and results- Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method" (GB/T 6379.2—2004) and "Accuracy (trueness and precision) of measurement methods and results-Part 4: Basic methods for the determination of the trueness of a standard measurement method" (GB/T 6379.4—2006), ten authoritative laboratories were organized to conduct collaborative tests and perform statistical analysis of the test data. Outliers in the test data were identified and screened using Mandel's h and k statistics, Grubbs test, and Cochran test. The repeatability limit (r), reproducibility limit (R), and precision-function relationships of the method were systematically established, and a comprehensive statistical evaluation of trueness was carried out.

This paper provides, for the first time, a scientifically robust and reliable precision and trueness evaluation system for the determination of antimony content in groundwater by HG-AFS, offering reliable data support and a solid technical basis for the establishment and evaluation of standard methods for determining antimony in groundwater. This research not only fills the technical gap in the verification of standard methods in this field in China, but also lays a solid theoretical and practical foundation for the establishment of a standard method for antimony content determination in groundwater with international comparability. It has significant scientific value and application prospects for enhancing the country's environmental monitoring capabilities.

1 Experiment

1.1 Selection and preparation of collaborative test samples

To ensure the accuracy and validity of the collaborative test data, groundwater samples were collected from routine monitoring programs in multiple regions, including Hebei, Yunnan, Inner Mongolia, Qinghai, and Tibet. Comprehensive water quality analysis was conducted to determine the total dissolved solids content and identify the

hydrochemical types of each sample. Preliminary determination of antimony content was performed using HG-AFS. Based on the antimony content and comprehensive evaluation of the samples, five representative samples were selected.

An antimony standard solution was added to the samples according to preliminary analytical results to ensure that the Sb content in different water samples spanned the high, medium, and low ranges of the calibration curve. The sample matrix was maintained in 2% nitric acid, followed by thorough stirring and settling to achieve complete homogenization, thereby guaranteeing excellent uniformity and stability of the samples. Details of the sample are provided in Table 1.

In accordance with the sample preservation regulations in the "Standard for groundwater quality" (GB/T 14848—2017) and "Methods for analysis of groundwater quality-Part 2: Collection and preservation of water samples" (DZ/T 0064.2—2021), the water samples were acidified immediately after collection with nitric acid to a pH < 2 and stored in the dark at 4°C for up to 30 days. The antimony concentration in the five collaborative test samples ranged from 0.10 µg/L to 5.0 µg/L, effectively covering the typical concentration range found in groundwater and meeting the determination requirements of the proposed standard method.

1.2 Instruments and reagents

Atomic fluorescence spectrometer (model AFS-3100, Beijing HaiGuang Instrument Co., Ltd.), and an antimony hollow cathode lamp were used.

Antimony standard stock solution (100 mg/L, GBW(E)080545, National Institute of Metrology, China). Antimony standard intermediate solution (2.00 mg/L): Take 2.00 mL of antimony standard stock solution into a 100 mL volumetric flask, add 20 mL of 50% hydrochloric acid solution, then dilute to volume with pure water, and mix thoroughly.

Antimony standard working solution (50.0 µg/L): Take 2.50 mL of antimony standard intermediate solution into a 100 mL volumetric flask, add 20 mL of 50% hydrochloric acid solution, then dilute to volume with pure water, and mix thor-

oughly.

Hydrochloric acid ($\rho = 1.19$ g/mL), guaranteed reagent; sodium hydroxide, sodium borohydride, thiourea and ascorbic acid, analytical reagent grade.

Thiourea-ascorbic acid solution: Weigh 2.5 g of thiourea, add about 80 mL of pure water, heat to dissolve, cool and then add 12.5 g of ascorbic acid, dilute to 100 mL, mix thoroughly, and prepare freshly before use.

Sodium hydroxide solution (2 g/L): Weigh 1.0 g of sodium hydroxide, dissolve in pure water and dilute to 500 mL.

Sodium borohydride solution (20 g/L): Weigh 10.0 g of sodium borohydride, dissolve in 500 mL of the sodium hydroxide solution (2 g/L), mix thoroughly, and prepare freshly before use.

Argon gas: Purity $\geq 99.99\%$. The water used in the experiment was deionized water.

1.3 Instrument working conditions

Lamp current: 75 mA; photomultiplier tube negative high voltage: 310 V; carrier gas flow rate: 400 mL/min; shielding gas flow rate: 900 mL/min; atomizer height: 8.5 mm.

1.4 Collaborative test method

Preparation of standard solution series: 0 mL, 0.10 mL, 0.25 mL, 0.50 mL, 1.00 mL, and 2.50 mL of the antimony standard working solution (50.0 µg/L) were accurately pipetted into 25 mL volumetric flasks. Then, 5 mL of 50% hydrochloric acid solution were added, and the mixture was diluted to volume with purified water and mixed thoroughly. Subsequently, 10.00 mL of each standard series solution were transferred into dry 10 mL colorimetric tubes. The corresponding antimony masses were 0 µg, 0.002 µg, 0.005 µg, 0.010 µg, 0.020 µg, and 0.050 µg, respectively.

Sample preparation: 10 mL of the water sample were transferred into a dry colorimetric tube.

Determination procedure: 1 mL of thiourea-ascorbic acid solution (125 g/L) and 1 mL of hydrochloric acid were added to both the standard series and sample tubes. The mixture was mixed thoroughly and allowed to stand for 60 min. Using sodium borohydride solution (20 g/L) as the reduc-

Table 1 Sample information

Sample number	YP-1	YP-2	YP-3	YP-4	YP-5
pH	8.37	8.38	7.35	7.95	7.86
Hydrochemical type	HCO ₃ +Cl-Na	HCO ₃ -Na	HCO ₃ +SO ₄ -Ca+Mg	HCO ₃ -Ca	HCO ₃ -Ca
Antimony content (µg/L)	0.10–0.30	0.50–1.00	1.20–1.80	2.00–3.00	3.00–5.00

ing agent and 5% hydrochloric acid solution as the carrier stream, the standard solution series and samples were analyzed on the atomic fluorescence spectrometer, and the fluorescence intensity values were recorded. The calibration curve was plotted with the antimony mass as the x-axis and fluorescence intensity as the y-axis. The antimony mass in the water sample was determined from the calibration curve, and its mass concentration was calculated accordingly. Between each determination, the sample introduction system was rinsed thoroughly with 5% hydrochloric acid solution.

1.5 Implementation of collaborative tests

A total of 10 laboratories were invited to conduct collaborative tests following the procedure described in Section 1.2. Each of the five samples was independently analyzed five times. All samples were distributed in coded form to the participating laboratories. To verify the compatibility and applicability of the method, the laboratories were located in various testing centers and research institutes across the Beijing-Tianjin-Hebei region, as well as in Shandong, Hubei, Henan, and Anhui provinces.

2 Result discussion and statistical analysis

2.1 Method validation

2.1.1 Detection limit and quantification limit

Twelve blank spiked samples were taken throughout the experimental process. The instrument was

adjusted to optimal operating conditions according to Section 1.4. Independent determinations were made, and the method detection limit was calculated as three times the standard deviation of the measurement results, while the limit of quantification was defined as three times the detection limit. The detection limit of antimony was 0.02 µg/L, and the quantification limit was 0.06 µg/L, satisfying the detection requirements for the antimony limit value (0.0001 mg/L) for Class I water according to the "Standard for groundwater quality" (GB/T 14848—2017).

2.1.2 Precision and trueness

Within the same laboratory, precision experiments were conducted using three different concentration levels of antimony standard solutions: low, medium, and high. The antimony concentrations of the standard solutions selected for this experiment were 0.50 µg/L, 1.00 µg/L, and 3.00 µg/L, respectively. Each concentration was measured 12 times independently, and the relative standard deviations were 1.34%–2.46%.

Additionally, two water samples with different Total Dissolved Solids (TDS) were selected to perform recovery tests at antimony concentrations of 0.30 µg/L, 1.00 µg/L, and 3.00 µg/L. Twelve parallel samples were measured for each concentration level, and the results are presented in Table 2. The recovery rate ranged from 95.11% to 105.7%.

2.1.3 Method comparison and applicability analysis

To evaluate the applicability of HG-AFS in the detecting antimony in groundwater, this study conducted a comparison of the performance of the established method with HG-AAS and ICP-MS reported in the literature. The results are shown in Table 3.

Table 2 Method trueness test

Sample number	Background value (µg/L)	Added value (µg/L)	Measured value (µg/L)	Recovery rate (%)
1#	N.D	0.30	0.3021, 0.3104, 0.3068, 0.3113, 0.3124, 0.2943, 0.3081, 0.3108, 0.3056, 0.3099, 0.3011, 0.3142	98.10%–104.7%
		1.00	0.9874, 1.0196, 1.0296, 0.9851, 0.9644, 0.9661, 1.0281, 1.0574, 0.9996, 1.0471, 1.0056, 0.9620	96.20%–105.7%
		3.00	2.9761, 2.9914, 2.9414, 3.0499, 3.0309, 3.0354, 3.0980, 3.0695, 3.0662, 3.1142, 2.9856, 3.0304	98.05%–103.8%
		0.30	0.3072, 0.3121, 0.3078, 0.2906, 0.2964, 0.2933, 0.3110, 0.2873, 0.3024, 0.3018, 0.3128, 0.3115	95.77%–104.3%
		1.00	0.9654, 0.9511, 0.9758, 0.9882, 1.0274, 1.0447, 1.0115, 1.0083, 1.0356, 1.0298, 1.0059, 0.9627	95.11%–104.5%
		3.00	3.1055, 3.0631, 2.9652, 3.0321, 3.0615, 3.0629, 2.9881, 3.0054, 3.0015, 3.0445, 2.9653, 2.9155	97.18%–103.5%

Table 3 Comparison of HG-AFS, HG-AAS and ICP-MS methods

Performance indicators	This method (HG-AFS)	HG-AAS (Li et al. 2008)	ICP-MS (Zhang et al. 2016)
Detection limit (µg/L)	0.02	0.31	0.03
Precision (RSD,%)	1.34–2.46	2.2–4.2	0.36–1.15
Linear range (µg/L)	0–5.0	0–20.0	0–50.0
Matrix interference	Transition metals (Cu, Ni, etc.)	Transition metals, hydride-forming elements	Mass spectrometry interference
Analysis costs	Low	Intermediate	Very High

As shown in Table 3, the HG-AFS method established in this study significantly outperforms HG-AAS in terms of detection limit and precision, and has a detection limit comparable to ICP-MS, with similar precision. Although its linear range is relatively narrow, its performance fully satisfies and, in most cases, exceeds national standard requirements for the routine groundwater monitoring tasks. For groundwater samples with abnormally high antimony content, appropriate dilution is required prior to measurement.

All three methods face different types of matrix interference. HG-AFS is mainly affected by transition metals. In this study, the thiourea-ascorbic acid system was used as both a pre-reducing agent and masking agent, effectively suppressing such interference and ensuring the accuracy of the method in actual water samples. Its applicability in high-sanity groundwater samples is superior to ICP-MS.

Therefore, HG-AFS is a cost-effective, efficient, and reliable method for the determination of antimony content in groundwater in laboratories at all levels, especially for grassroots laboratories performing large-scale routine monitoring tasks.

2.2 Unit mean and dispersion

A mathematical and statistical analysis was performed on the raw data from the collaborative tests for antimony content determination. For each laboratory, the data from a single concentration level were treated as one analytical unit. The mean and standard deviation within each unit were calculated, with the results presented in Table 4. The standard deviation reflects the degree of dispersion of data within each unit, serving as an indicator of how far the data within the unit deviate from the mean. A smaller standard deviation indicates that the data within the unit are more closely clustered around the mean.

2.3 Consistency and outlier tests

To thoroughly assess the precision and trueness of the standard method, it is essential to verify the consistency and identify outliers in the raw data from the collaborative tests for antimony content determination. Statistical analysis of the raw data was conducted using the "Geological Analysis

Table 4 Mean and standard deviation of antimony content analysis results for each unit

Unit: µg/L

Laboratory number	Level									
	1		2		3		4		5	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
1	0.256	0.017	0.832	0.016	1.520	0.037	2.254	0.064	4.620	0.051
2	0.248	0.014	0.932	0.040	1.542	0.077	2.176	0.092	4.556	0.189
3	0.252	0.008	0.796	0.027	1.482	0.036	2.270	0.061	4.616	0.129
4	0.244	0.017	0.816	0.015	1.562	0.015	2.272	0.051	4.606	0.103
5	0.230	0.010	0.824	0.023	1.546	0.036	2.250	0.043	4.762	0.049
6	0.314	0.009	0.876	0.005	1.542	0.064	2.260	0.068	4.530	0.114
7	0.252	0.019	0.728	0.002	1.376	0.021	2.130	0.046	4.416	0.034
8	0.274	0.011	0.860	0.016	1.406	0.017	2.232	0.022	4.546	0.027
9	0.324	0.018	0.732	0.013	1.364	0.015	2.020	0.020	4.148	0.038
10	0.257	0.004	0.787	0.010	1.482	0.019	2.195	0.021	4.563	0.030

Standard Method Information Management System" software developed by the National Research Center for Geoanalysis. The analysis primarily included Mandel's h and k statistics, Grubbs test, and Cochran test. The main purpose of these four testing methods is to identify laboratories whose results significantly deviate from those of other laboratories, thereby excluding inconsistent results and ensuring the verification of data consistency and identification of outliers.

Among all the testing methods, Mandel's h and k statistics are the most commonly used. These graphical methods are easy to interpret and effectively highlight consistency issues. Mandel's h statistic measures inter-laboratory variation, while the k statistic estimates intra-laboratory variation (Wu and Qian, 2020; Flores et al. 2021). Figs. 1 and 2 present the results of Mandel's h and k statistics grouped by laboratory. The horizontal dashed

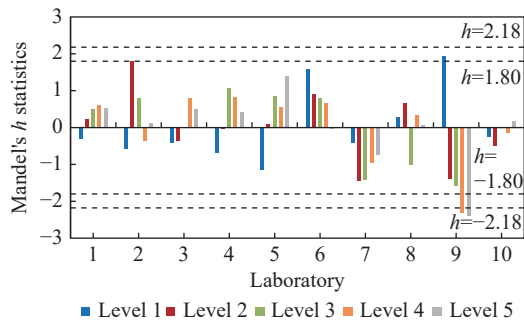


Fig. 1 Mandel's h statistics grouped by laboratory

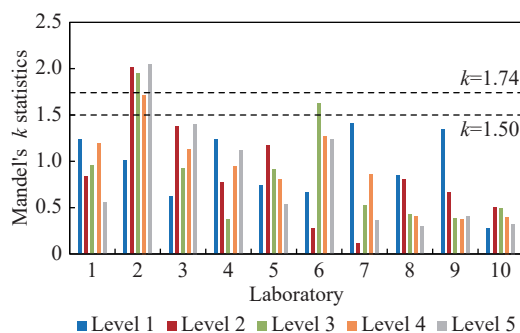


Fig. 2 Mandel's k statistic grouped by laboratory

Table 5 Grubbs and Cochran test results

	Collaborative sample number	YP-1	YP-2	YP-3	YP-4	YP-5
Grubbs test	Gp	1.928	1.375	1.138	0.926	1.829
	G1	1.149	1.517	1.47	1.964	1.694
	1% critical value	2.482	2.387	2.387	2.387	2.274
	5% critical value	2.29	2.215	2.215	2.215	2.126
Cochran test	C	0.197	0.316	0.424	0.298	0.348
	1% critical value	0.393	0.425	0.425	0.425	0.463
	5% critical value	0.331	0.358	0.358	0.358	0.391

lines in the figures represented the critical values of Mandel's h and k statistics at 1% and 5% significance levels, respectively.

The Mandel's h statistic graph indicated that two levels of Laboratory 9 were outliers. The Mandel's k statistic showed the five test results of each laboratory, with three levels from Laboratory 2 identified as outliers. These outliers may result from factors such as low instrument accuracy or insufficient reagent purity during analysis. After the exclusion of outliers, while retaining stragglers, all remaining data successfully passed the tests.

The Grubbs test and the Cochran test are primarily used for outlier detection and are classic statistical methods widely applied. The Grubbs test is an inter-laboratory analytical method based on mean differences, while the Cochran test focuses on variance differences within individual laboratories (Flores et al. 2018b). Table 5 presents the results of Grubbs and Cochran tests in this study. After testing the raw data using Mandel's h and k statistics and removing outliers (while retaining stragglers), all remaining data were below the 5% critical value for the Grubbs test and the 1% critical value for the Cochran test, thereby passing both tests.

After removing all outliers, the four test methods were reapplied for verification. Among them, the Mandel's k statistic showed that one level of Laboratory 6 became an outlier again. This outlier was removed once more, and the remaining data continued to be included in the subsequent calculations.

2.4 Statistical analysis of precision and trueness

Repeatability and reproducibility are two critical indicators for evaluating the precision of a standard analytical method, serving as essential foundations for establishing its validity. Trueness is a key factor in assessing the reliability of a standard method and ensuring the accuracy of experimental results (Peta et al. 2024; Flores et al. 2018a; Xiong,

2017; Zhang et al. 2023).

The determination data of antimony content from five-level samples across ten laboratories were subjected to consistency and outlier tests. After eliminating the outliers, the grand mean (m), repeatability standard deviation (s_r), reproducibility standard deviation (s_R), repeatability limit (r), reproducibility limit (R), and method bias value (δ) were calculated in accordance with the requirements of "Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method" (GB/T 6379.2—2004) and "Accuracy (trueness and precision) of measurement methods and results - Part 4: Basic method for the determination of trueness of a standard measurement method" (GB/T 6379.4—2006), and the trueness of the method was statistically evaluated.

The results are presented in Table 6. It was observed that as the antimony content in groundwater samples increased, both the repeatability limit (r) and the repeatability standard deviation (s_r) increased correspondingly. Conversely, lower antimony content was associated with reduced values for both the repeatability limit (r) and the repeatability standard deviation (s_r). Additionally, the reproducibility limit (R) and reproducibility standard deviation (s_R) generally followed a similar trend, increasing with higher antimony content in the samples. Furthermore, for each sample level tested, the repeatability limit (r) was consistently

less than the reproducibility limit (R), accounting for 100% of cases.

Trueness is expressed as the degree of agreement between the mean of a large number of determinations and an acceptable reference value, typically represented by bias (δ). This experiment primarily investigated the bias of the determination method, specifically focusing on the degree of agreement between the grand mean (m) of determination results at the same level and the acceptable reference value (μ). If an approximate 95% confidence interval for the method bias ($\delta - A \cdot s_R \leq \delta \leq \delta + A \cdot s_R$, where A is the uncertainty coefficient) includes zero, it indicates that the method bias is not significant; otherwise, the bias is considered significant. If the method bias value satisfies Formula (1), the bias is deemed insignificant.

As presented in Table 6, the confidence intervals for Levels 1-5 all encompassed zero. Furthermore, the method bias values satisfied Formula (1), indicating that there is no significant bias present. Therefore, the method exhibited no significant bias across Levels 1-5, and the results of the statistical analysis regarding method trueness were satisfactory.

$$|\delta| \leq 2 \sqrt{\frac{s_R^2 - (1 - 1/n) s_r^2}{p}} \quad (1)$$

2.5 Correlation of precision parameters

In the inter-laboratory collaborative tests, as

Table 6 Statistical analysis results of method precision and trueness parameters

Statistical parameters	Level				
	1	2	3	4	5
Number of accepted laboratories (p)	10	9	8	9	8
Number of test replicates (n)	5	5	5	5	5
Grand mean (m)/(μg/L)	0.265	0.806	1.47	2.23	4.58
Acceptable reference value (μ)/(μg/L)	0.26	0.80	1.50	2.20	4.55
Repeatability standard deviation (s_r)/(μg/L)	0.014	0.016	0.026	0.056	0.078
Repeatability coefficient of variation/%	5.09	1.99	1.79	2.52	1.69
Repeatability limit (r)/(μg/L)	0.038	0.045	0.074	0.159	0.219
Reproducibility standard deviation (s_R)/(μg/L)	0.033	0.053	0.080	0.070	0.120
Reproducibility coefficient of variation/%	12.41	6.59	5.47	3.16	2.62
Reproducibility limit (R)/(μg/L)	0.093	0.150	0.227	0.199	0.340
$\gamma = s_R/s_r$	2.429	3.311	3.048	1.250	1.551
Uncertainty coefficient (A)	0.630	0.625	0.626	0.658	0.645
Method bias value (δ)/(μg/L)	0.005	0.006	-0.033	0.027	0.032
$\delta - A \cdot s_R$ /(μg/L)	-0.016	-0.027	-0.083	-0.020	-0.045
$\delta + A \cdot s_R$ /(μg/L)	0.026	0.039	0.018	0.073	0.110

presented in Table 6, the calculated precision-related parameters demonstrated that the mean level (m) correlated with both the repeatability limit (r) and the reproducibility limit (R). Therefore, it is essential to establish functional relationships between r and R in relation to the mean level (m). This is crucial for accurately characterizing method precision.

Three data fitting approaches were applied using statistical software, with the results illustrated in Figs. 3 and 4. Taking the reproducibility limit (R) as an example:

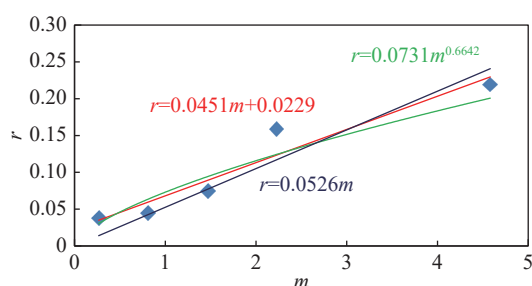


Fig. 3 Data fitting relationship between r and m

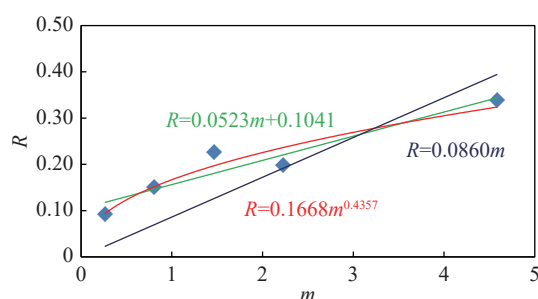


Fig. 4 Data fitting relationship between R and m

① $R = a + b \cdot m$ (a straight line with a positive intercept);

② $R = c \cdot m^d$, $d \leq 1$ (an exponential relationship);

③ $R = b \cdot m$ (a straight line passing through the origin).

In most cases, at least one of these three data fitting relationships provides an adequate fit. The results indicated that for the repeatability limit (r), relationship ① yielded the highest degree of fit and the best performance, whereas for the reproducibility limit (R), relationship ② provided the optimal

fit. Thus, within the range of antimony content mean level (m) from 0.26 $\mu\text{g/L}$ to 4.55 $\mu\text{g/L}$, the functional relationships of r and R with m - representing the method precision results - are presented in Table 7.

Under correct experimental conditions, the absolute difference between two determinations of antimony content in the same groundwater sample by the same laboratory should be less than

$$r = 0.0451 m + 0.0229,$$

and the absolute difference between two determinations in the same groundwater sample by different laboratories should be less than

$$R = 0.1668 m^{0.4357}.$$

3 Conclusion

This study demonstrated through method validation experiments, that HG-AFS is a highly suitable method for the determination of antimony content in groundwater. The collaborative test data were strictly screened using Mandel's h and k statistics, Grubbs test, and Cochran test, efficiently optimizing the original data and significantly improving the reliability and accuracy of the measured data.

It was observed that lower antimony content corresponded to lower the repeatability limit (r) and reproducibility limit (R). This suggests that the analytical error in antimony determination primarily arises from the method detection limit and instrument sensitivity. Therefore, enhancing instrument sensitivity and reducing the detection limit are critical for controlling analytical error within acceptable ranges.

This study provides a scientific basis for establishing a standard method for determining antimony content in groundwater, offering valuable reference for the development and improvement of related technical specifications. Furthermore, it provides theoretical guidance for quality control in practical environmental monitoring applications.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (Project No. 42307555).

Table 7 Inter-laboratory precision

Unit: $\mu\text{g/L}$

Element	Mean level (m)	Repeatability limit (r)	Reproducibility limit (R)
Antimony	0.26–4.55	$r = 0.0451 m + 0.0229$	$R = 0.1668 m^{0.4357}$

Note: The precision was determined in accordance with GB/T 6379.2, based on statistical analysis of data from ten laboratories, each performing five replicate determinations for five concentration levels under repeatability conditions, after the elimination of outliers.

References

- Azooz EA, Al-Murshedi AYM, Abodiame AAM, et al. 2024. A novel green cloud point extraction-based switchable hydrophilicity solvent method for antimony separation and quantification from various bottled beverages by HGAAS. *Microchemical Journal*, 207: 111824. DOI: [10.1016/j.microc.2024.111824](https://doi.org/10.1016/j.microc.2024.111824).
- Bolan N, Kumar M, Singh E, et al. 2022. Antimony contamination and its risk management in complex environmental settings: A review. *Environment International*, 158: 106908. DOI: [10.1016/j.envint.2021.106908](https://doi.org/10.1016/j.envint.2021.106908).
- Correia FO, Almeida TS, Garcia RL, et al. 2019. Sequential determination and chemical speciation analysis of inorganic As and Sb in airborne particulate matter collected in outdoor and indoor environments using slurry sampling and detection by HG AAS. *Environmental Science and Pollution Research*, 26(21): 21416–21424. DOI: [10.1007/s11356-019-04638-9](https://doi.org/10.1007/s11356-019-04638-9).
- Cui J, Zhao XH, Wang Y, et al. 2014. Research on optimization of mathematical model of flow injection-hydride generation-atomic fluorescence spectrometry. *Spectroscopy and Spectral Analysis*, 34(1): 246–251. (in Chinese) DOI: [10.3964/j.issn.1000-0593\(2014\)01-0246-06](https://doi.org/10.3964/j.issn.1000-0593(2014)01-0246-06).
- Ferreira SLC, Anjos JP, Felix CSA, et al. 2019. Speciation analysis of antimony in environmental samples employing atomic fluorescence spectrometry-Review. *TrAC Trends in Analytical Chemistry*, 110: 335–343. DOI: [10.1016/j.trac.2018.11.017](https://doi.org/10.1016/j.trac.2018.11.017).
- Filter J, Schröder C, El-Athman F, et al. 2024. Nitrate-induced mobilization of trace elements in reduced groundwater environments. *Science of The Total Environment*, 927: 171961. DOI: [10.1016/j.scitotenv.2024.171961](https://doi.org/10.1016/j.scitotenv.2024.171961).
- Flores M, Fernández-Casal R, Naya S, et al. 2018a. ILS: An R package for statistical analysis in Interlaboratory Studies. *Chemometrics and Intelligent Laboratory Systems*, 181: 11–20. DOI: [10.1016/j.chemolab.2018.07.013](https://doi.org/10.1016/j.chemolab.2018.07.013).
- Flores M, Moreno G, Solórzano C, et al. 2021. Robust bootstrapped Mandel's h and k statistics for outlier detection in interlaboratory studies. *Chemometrics and Intelligent Laboratory Systems*, 219: 104429. DOI: [10.1016/j.chemolab.2021.104429](https://doi.org/10.1016/j.chemolab.2021.104429).
- Flores M, Tarrío-Saavedra J, Fernández-Casal R, et al. 2018b. Functional extensions of Mandel's h and k statistics for outlier detection in interlaboratory studies. *Chemometrics and Intelligent Laboratory Systems*, 176: 134–148. DOI: [10.1016/j.chemolab.2018.03.016](https://doi.org/10.1016/j.chemolab.2018.03.016).
- Fu XX, Xie XJ, Charlet L, et al. 2023. A review on distribution, biogeochemistry of antimony in water and its environmental risk. *Journal of Hydrology*, 625: 130043. DOI: [10.1016/j.jhydrol.2023.130043](https://doi.org/10.1016/j.jhydrol.2023.130043).
- Gil-Díaz T, Pougnet F, Dutruch L, et al. 2024. Reactivity and fluxes of antimony in a macrotidal estuarine salinity gradient: Insights from single and triple quadrupole ICP-MS performances. *Marine Chemistry*, 267: 104465. DOI: [10.1016/j.marchem.2024.104465](https://doi.org/10.1016/j.marchem.2024.104465).
- Haider FU, Zulfikar U, Ain NU, et al. 2024. Managing antimony pollution: Insights into soil–plant system dynamics and remediation strategies. *Chemosphere*, 362: 142694. DOI: [10.1016/j.chemosphere.2024.142694](https://doi.org/10.1016/j.chemosphere.2024.142694).
- Lan JM, Jiang T, Mei JH, et al. 2023. Characterization and causes of interannual variation of antimony contamination in groundwater of a typical antimony mining area. *Hydrogeology and Engineering Geology*, 50(5): 192–202. (in Chinese) DOI: [10.16030/j.cnki.issn.1000-3665.202302052](https://doi.org/10.16030/j.cnki.issn.1000-3665.202302052).
- Li JQ, Zhou JT, Song XR. 2008. Determination of Sb(III) and Sb(V) by atomic absorption spectrometry with hydride generation. *Physical Testing and Chemical Analysis (Part B (Chemical Analysis))*, 44(2): 168–170. (in Chinese)
- Li R, Yan YT, Xu JQ, et al. 2024. Evaluate the groundwater quality and human health risks for sustainable drinking and irrigation purposes in mountainous region of Chongqing, Southwest China. *Journal of Contaminant Hydrology*, 264: 104344. DOI: [10.1016/j.jconhyd.2024.104344](https://doi.org/10.1016/j.jconhyd.2024.104344).
- Li YJ, Yang ZJ, Dong GF, et al. 2017. Simultaneous determination of arsenic and antimony in

- lead ingot by hydride generation-atomic fluorescence spectrometry. *Metallurgical Analysis*, 37(11): 75–79. (in Chinese) DOI: [10.13228/j.boyuan.issn1000-7571.010172](https://doi.org/10.13228/j.boyuan.issn1000-7571.010172).
- Liu BB, Liu J, Zhang CL, et al. 2021. Determination of trace antimony in environmental water by hydride generation-atomic fluorescence spectrometry. *Water Purification Technology*, 40(8): 40–43, 96. (in Chinese) DOI: [10.15890/j.cnki.jsjs.2021.08.006](https://doi.org/10.15890/j.cnki.jsjs.2021.08.006).
- Peta K, Love G, Brown CA. 2024. Comparing repeatability and reproducibility of topographic measurement types directly using linear regression analyses of measured heights. *Precision Engineering*, 88: 192–203. DOI: [10.1016/j.precisioneng.2024.02.009](https://doi.org/10.1016/j.precisioneng.2024.02.009).
- Xiong Y, Dong YN, Pei RH, et al. 2017. Precision determination and evaluation of antimony ore chemical phase analysis method. *Metallurgical Analysis*, 37(3): 13–20. (in Chinese) DOI: [10.13228/j.boyuan.issn1000-7571.010002](https://doi.org/10.13228/j.boyuan.issn1000-7571.010002).
- Wang WQ, Cheng XY, Song YY, et al. 2023a. Elevated antimony concentration stimulates rare taxa of potential autotrophic bacteria in the Xikuangshan groundwater. *Science of The Total Environment*, 864: 161105. DOI: [10.1016/j.scitotenv.2022.161105](https://doi.org/10.1016/j.scitotenv.2022.161105).
- Wang WQ, Lei JW, Li M, et al. 2023b. Archaea are better adapted to antimony stress than their bacterial counterparts in Xikuangshan groundwater. *Science of The Total Environment*, 905: 166999. DOI: [10.1016/j.scitotenv.2023.166999](https://doi.org/10.1016/j.scitotenv.2023.166999).
- Wu BW, Qian Y. 2020. Explore methods for testing outliers in inter-laboratory comparison test results. *China Fiber Inspection*, (4): 82–86. (in Chinese) DOI: [10.14162/j.cnki.11-4772/t.2020.04.023](https://doi.org/10.14162/j.cnki.11-4772/t.2020.04.023).
- Yang YM. 2019. Determination of silver, copper, arsenic, antimony, bismuth and cadmium in stream sediment by inductively coupled plasma mass spectrometry. *Metallurgical Analysis*, 39(7): 58–64. (in Chinese) DOI: [10.13228/j.boyuan.issn1000-7571.010632](https://doi.org/10.13228/j.boyuan.issn1000-7571.010632).
- Zhang M, Cai YM, Xiao L, et al. 2023. Discussion on the precision evaluation method of serpentine phase quantitative analysis by X-ray diffraction. *Rock and Mineral Analysis*, 42(3): 513–522. (in Chinese) DOI: [10.15898/j.cnki.11-2131/td.202101180010](https://doi.org/10.15898/j.cnki.11-2131/td.202101180010).
- Zhang S. 2014. Development and application of high sensitivity atomic fluorescence spectrometry instrument. Ph. D. thesis. Xiamen: Xiamen University: 8–22. (in Chinese)
- Zhang XY, Gu XM, Zhou MF, et al. 2016. Comparison between AFS and ICP-MS in the determination of antimony in water. *Environmental Monitoring and Forewarning*, 8(6): 26–28. (in Chinese) DOI: [10.3969/j.issn.1674-6732.2016.06.007](https://doi.org/10.3969/j.issn.1674-6732.2016.06.007).
- Zhang Y, Ding CX, Gong DX, et al. 2021. A review of the environmental chemical behavior, detection and treatment of antimony. *Environmental Technology & Innovation*, 24: 102026. DOI: [10.1016/j.eti.2021.102026](https://doi.org/10.1016/j.eti.2021.102026).
- Zhao QY, Zhang ZM, Tan Z, et al. 2024. Speciation and environmental pollution characteristics in three typical antimony mining areas of southwest China. *Research of Environmental Sciences*, 37(7): 1612–1625. (in Chinese) DOI: [10.13198/j.issn.1001-6929.2024.03.05](https://doi.org/10.13198/j.issn.1001-6929.2024.03.05).