Analysis of trace antimony in water

Complying with Chinese standard methods for atomic absorption spectroscopy - HJ 1046-2019 and HJ 1047-2019

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Goal

To demonstrate the applicability of the Thermo Scientific™ iCE™ 3300 Flame AAS and Thermo Scientific™ iCE™ 3400 Graphite Furnace AAS for determination of antimony in diverse water samples based on Chinese environmental standard methods (*HJ 1046-2019, HJ 1047-2019*) with different application focus.

Introduction

Antimony (Sb) has been used in various manufacturing processes to form hard alloys with copper, lead, and tin as well as in various industrial materials such as glass, semiconductors, and pharmaceutical products. Moreover, soluble pentavalent antimony (Sb[V]) compounds are used as specific therapeutics agents against parasites.[1] Antimony present in water and soil mostly originates from human activities (such as coal burning or with fly ash when antimony-containing ores are smelted), and it is present mainly as insoluble antimony.

At present, antimony is considered a priority pollutant in drinking water in several regions (such as the United States, Canada, and Europe) due to the numerous diseases that it can trigger (for example, cellular damage in the lungs, respiratory tract irritation, and dermatitis), with action levels set to <6 $\mu g \cdot L^{-1}$.

Current analytical methods used for antimony analysis in water include spectrophotometry, electrochemical analysis, and atomic spectroscopy. Atomic absorption spectroscopy in particular is the preferred analytical method mainly due to faster analysis time, higher matrix tolerance, and superior sensitivity that this analytical technique offers.

As an example, by using graphite furnace atomic absorption spectrometry (GF-AAS), antimony detection limits <0.8 $\mu g \cdot L^{-1}$ can be achieved (as required by U.S. EPA Method 204.2)[2].

In 2019, the Ministry of Ecology and Environment (MEE) of the People's Republic of China released two standard HJ methods on antimony analysis, HJ 1046-2019 and HJ 1047-2019, and these were implemented officially in April 2020. HJ 1046-2019 is referenced as a standard method to analyze antimony in water by FL-AAS; by HJ 1047-2019, GF-AAS is the recommended technique. Compared to other technologies, the use of AAS for the determination of trace levels of metals in water offers the advantages of simple, cost effective, rapid, high matrix tolerance, and sensitive operation, making this technology suitable for routine laboratories dealing with large numbers of samples.

In this application note, the performance of the Thermo Scientific™ iCE™ 3300 and 3400 Atomic Absorption Spectrometer (AAS) systems for the analysis of antimony in water samples according to HJ 1046-2019 and HJ 1047-2019 standard methods was assessed. Analytical parameters such as sensitivity, limits of detection, precision, accuracy, and robustness in routine analysis were investigated for the determination of Sb in water samples.

A simplified sample preparation approach using hot plate digestion was employed, avoiding the high salinity steps and associated interferences potentially caused by the introduction of salt-rich matrices. The sample preparation method has been verified and validated following the performance criteria recommended by the HJ 1046-2019 and HJ 1047-2019 environmental standard methods.

A rapid and sensitive method is a necessary condition for studying the morphology, migration, and transformation of antimony in the environment. In this application, two different AAS analytical platforms have been used, FL-AAS and GF-AAS, each platform meeting the required performance criteria specified in the respective HJ standard methods (FL-AAS for HJ 1046, and GF-AAS for HJ 1047).

Part 1

HJ 1046-2019 – Water quality, determination of antimony by flame atomic absorption spectrometry

Flame optimization of instrument parameters

An iCE 3300 FL-AAS operated through the Thermo Scientific™ SOLAAR™ Software was used for all water samples in this study. Wavelength 217.6 nm was selected as recommended by the HJ 1046 method. The configuration with automatically optimized burner height and fuel flow of the FL-AAS is listed in Table 1.

Table 1. Instrument configuration of the iCE 3300 FL-AAS for antimony in water analysis

Parameter	Value
Wavelength	217.6 nm
Lamp current	10 mA
Bandpass	0.2 nm
Background	D_2 background correction
Burner height	6.4 mm
Flame type	Air-acetylene
Fuel flow	1.3 $L \cdot min^{-1}$
Resamples	3
Measurement time	4.0 s

Method development

Sample and standard preparation (FL-AAS) according to HJ 1046-2019:

(The described sample preparation protocol requires the use of hazardous chemicals. Appropriate personal protective gear such as lab coat, safety glasses, and gloves are required.)

River water samples were collected daily from a pollution control monitoring area in Bremen, Germany. Three sample collections per day (morning, noon, and evening) during a two days period were performed. The sampling volume was 250 mL. The river water samples were acidified immediately with 2.5 mL concentrated HNO_3 (Fisher Scientific™ TraceMetal™ grade).

The industrial wastewater samples, which were collected downstream of the discharge points from an industrial area in Bremen, were prepared by a hot plate digestion method. A volume of 25 mL of water sample was acidified with 2.0 mL concentrated HNO_3 and 6.0 mL concentrated HCl (TraceMetal grade). The sample was heated on an electric hot plate digestion system (Magnetic hotplate stirrer, RCT basic IKAMAG™) in a fume extraction hood until the solution became clear and transparent. After cooling to room temperature, the sample was transferred to a

50 mL volumetric flask, the inner wall of the Erlenmeyer flask was rinsed with ultra-pure water (18.2 Megaohm, Thermo Scientific™ Barnstead™ water purification system) and the rinse solution transferred to the volumetric flask to a final volume of 50 mL. Figure 1 shows the industrial wastewater sample before and after hot plate digestion procedure.

Linearity assessment

To accurately determine the amount of Sb in the water samples, a six-point calibration curve was generated using Sb stock solution (Sb 1000 mg·L^{-1}, Spex Certiprep, Metuchen, NJ) that was serially diluted to obtain the following concentrations: 2 mg·L^{-1}, 4 mg·L^{-1}, 8 mg·L^{-1}, 16 mg·L^{-1}, 32 mg·L^{-1}, and 40 mg·L^{-1}. From low concentration to high concentration, the standards' absorbance was sequentially measured, and each standard was analyzed in triplicate. The mass concentration was used as the X-axis and the corresponding absorbance as the Y-axis to establish the standard curve. Figure 2 shows the 6-point standard curve. The correlation coefficient, R^2, achieved was 0.9993 with the detection limit 0.18 mg·L^{-1}. The detection limit was 3× the standard deviation of the six concentration blank.

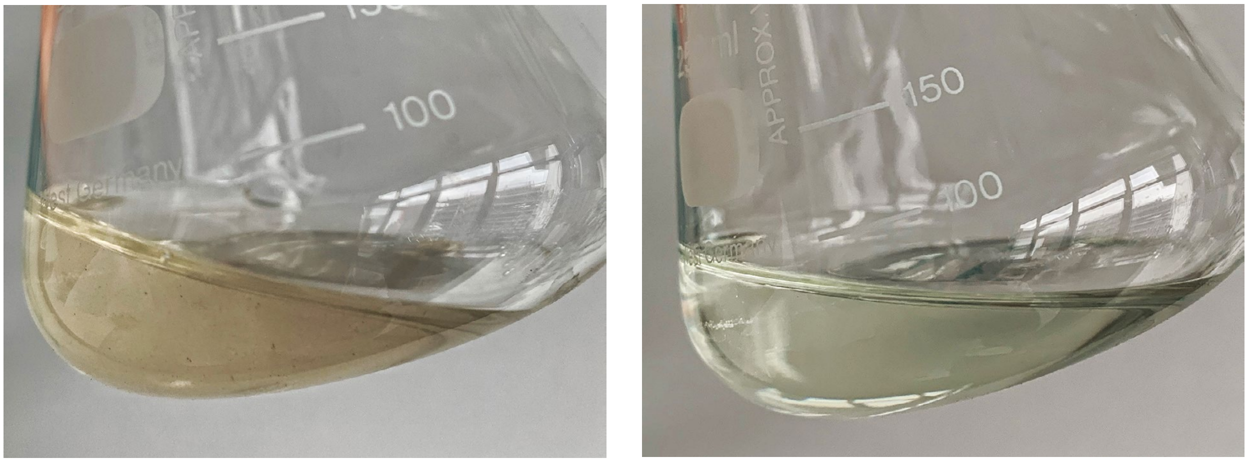
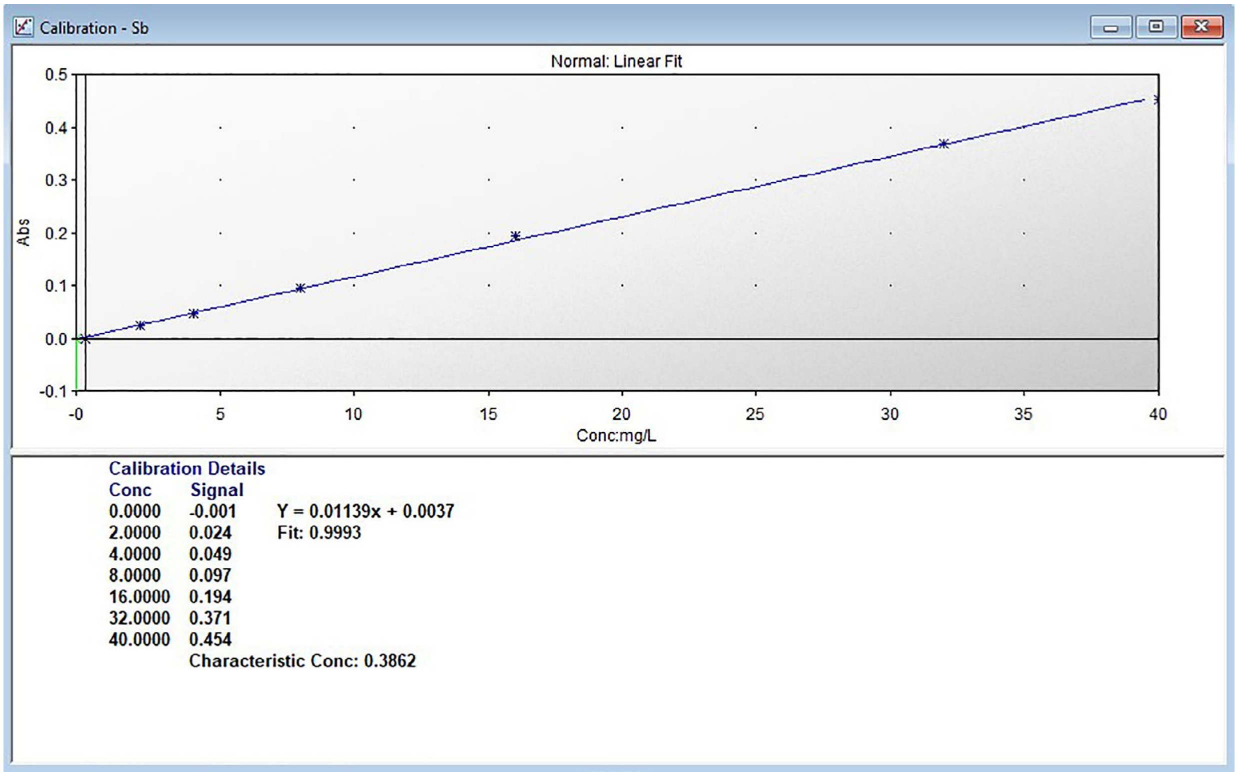


Figure 1. Wastewater samples before (left) and after (right) hot plate digestion procedure



Calibration Details

Conc	Signal	
0.0000	-0.001	Y = 0.01139x + 0.0037
2.0000	0.024	Fit: 0.9993
4.0000	0.049	
8.0000	0.097	
16.0000	0.194	
32.0000	0.371	
40.0000	0.454	

Characteristic Conc: 0.3862

Figure 2. Sb calibration curve obtained on an iCE 3300 FL-AAS system over 6-point standards

Results and discussion for Part 1

To meet the requirement specified in the HJ 1046-2019 method, the fowling tests were performed:

- Detection limit (DL): the HJ 1046-2019 standard method requires a detection limit of Sb in wastewater of at least 0.3 mg·L^{-1}. This should be determined by analyzing a spiked real water sample in triplicate with relative standard deviation calculated from these replicates ≤1.2%.

The results of this test demonstrated that the iCE 3300 FL-AAS detection limits were as low as 0.18 mg·L^{-1}, exceeding the expected DL level. Thanks to the high stability of the system, the %RSD of the measurement as calculated from three replicate analyses of an industrial wastewater sample was 0.3%, much lower than the expected value.

- Precision test: for testing the precision of the system, the HJ 1046-2019 standard method requires a six-replicate test of standard solutions, from low, middle, to high concentration, and a six-replicate test of the industry wastewater sample as well. The expected RSD ranges are listed in the Table 2. All precision test results obtained by the iCE 3300 FL-AAS system are within the required range.

Table 2. Precision test results. Each sample has been measured with six replicates.

Standard sample (mg·L^{-1})	RSD % (expected range)	RSD % (determined range)
4	1.2–3.6	0.9
16	0.9–2.2	0.5
32	0.3–2.9	0.3
Industry wastewater	1.6–4.5	0.3

- Accuracy test: to assess the accuracy of the system, as per the HJ 1046-2019 requirement, triplicate analysis of real samples spiked with 2 mg·L^{-1} of Sb were performed. The results of this test were in line with the expected recovery range and are listed in the Table 3.

Table 3. Accuracy test results of spiked samples

Sample	Recovery % (expected range)	Recovery % (measured)
River	93.7–101	100.3
Tap water	93.7–101	97.9
Industrial wastewater	93.7–101	99.8

- QC test: as part of the QC validation required by the HJ 1046-2019 standard method, a QC standard solution containing Sb at 16 mg·L^{-1} was monitored regularly (every 20 real samples). A summary of this experiment is shown in Table 4 with average concentration deviation values of <3.2% (from n=3 measurements), well within the required range (10%). This demonstrates the suitability of the iCE 3300 FL-AAS system for routine analysis of trace elements.

Table 4. Results of QC control sample

QC (mg·L^{-1})	Standard deviation (expected)	Standard deviation (measured)
16.4484	±10%	+2.8%
16.5366	±10%	+3.4%
16.5283	±10%	+3.3%
16.5044		**+3.2%**

In summary, these results demonstrate that the iCE 3300 FL-AAS system is suitable for routine analysis of Sb in industrial wastewater samples and that all performance requirements of the HJ 1046-2019 standard method are met. This method is appropriate for laboratories that need to analyze Sb in water samples following the HJ 1046-2019 standard method with a detection limit range of up to 0.3 mg·L^{-1}, making the iCE 3300 FL-AAS system a cost-effective analytical platform that allows for high-throughput analysis with accurate and robust results obtained.

Part 2

HJ 1047-2019 – Water quality, determination of antimony by graphite furnace atomic absorption spectrometry (GF-AAS)

An iCE 3400 GF-AAS system operated under SOLAAR Software was used to analyze Sb in environmental wastewater samples following the HJ 1047-2019 method requirements. Typically, environment water samples contain high concentrations of alkali metals, such as sodium, potassium, and calcium. These ubiquitous elements can interfere with antimony and cause significant background effects that could result in erroneous quantification of Sb. To address this background, correction with deuterium and adding matrix modifiers to samples are common practice.

To ensure selective analysis of Sb, a 217.6 nm wavelength was used and the sample was mixed with a 5 µL matrix modifier stock solution (1000 mg·L^{-1} magnesium nitrate and 900 mg·L^{-1} palladium nitrate (SPEX CertiPrep, Metuchen, NJ, USA)). Moreover, a deuterium (D$_2$) correction was also employed. Following these steps, excellent peak shape and selectivity was obtained for Sb as demonstrated in Figure 3 for 40 µL·L^{-1} Sb signal.

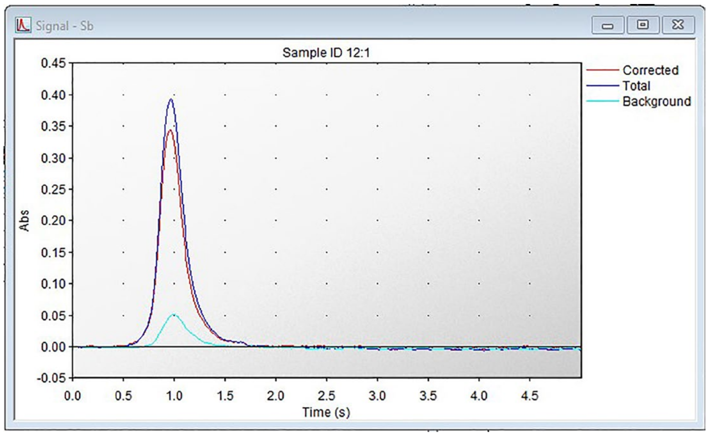


Figure 3. Example of Sb signal obtained on an iCE 3400 GF-AAS system at 40 µL·L^{-1} level (standard), showing no spectral interferences from other background elements

To ensure robust analysis, pyrolytic-coated graphite tube cuvettes with a 10 µL sample volume were used throughout the analysis. The final set of spectrometer parameters used is shown in Table 5, and the details of furnace temperature parameters are shown in Table 6.

Table 5. Instrument configuration for antimony in water analysis.

Parameter	Value
Wavelength	217.6 nm
Band pass	0.2 nm
Background correction (BGC)	D$_2$
Lamp current	10 mA
Signal measurement	Peak height
Sample volume	10 µL
Analysis time	108 s
Replicates	3

Table 6. iCE 3400 GF-AAS temperature method parameters used for Sb analysis in water samples

Phase	Temp. (°C)	Time (s)	Ramp (°C·s^{-1})	Argon gas flow (L·min^{-1})
Dry	110	50	10	0.2
Ash	1200	20	100	0.2
Atomize	2350	5	0	0
Clean	2600	3	0	0.2

Data acquisition and processing

SOLAAR Software allows quick and easy optimization and method development with the Graphite Furnace Television (GFTV), which allows to view at the sample inside the cuvette to make sure the sample are placed into the cuvette properly (Figure 4). The quality control (QC) test function is implemented on SOLAAR Software and indicates a flag on the results if the QC sample has out of range results.

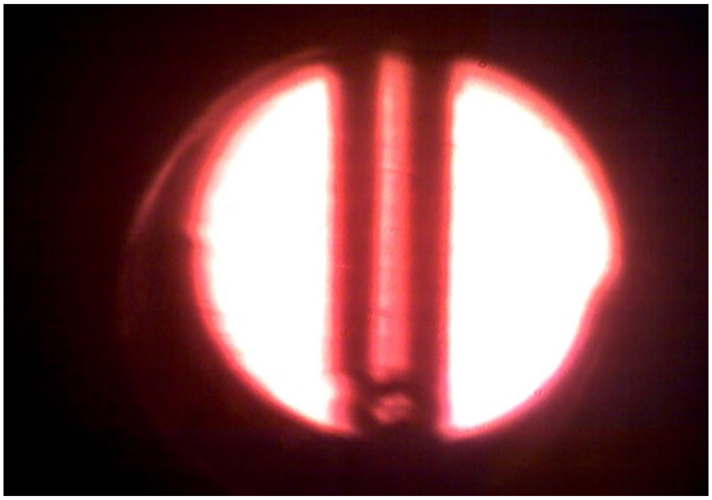


Figure 4. Monitoring the sample injection process on GFTV

Samples and standard preparation

An external calibration curve was prepared using an antimony stock solution at 1000 mg·L^{-1} acidified with 2% v/v HNO$_3$ (Fisher Scientific™, Optima™ grade). The calibration concentration range was from 10 µg·L^{-1} to 150 µg·L^{-1} as required by the HJ 1047-2019 method.

To evaluate the system performance with relevant sample matrices, a certified reference material was used (SLRS-5, river water, National Research Council of Canada). Tap water samples (collected from north of Bremen, Germany) as well as six surface river (stream) water samples (collected from Bremen) were collected for two consecutive days at three different time intervals (morning, noon, and evening, samples named A to F) and used for determination of their Sb content. All samples were acidified with 2% v/v HNO_3 (Fisher Scientific, nitric acid, TraceMetal grade) after collecting samples, as the HJ 1047 method required. In addition, the six river water samples were filtered with a 0.45 µm membrane to remove visible particles (Figure 5). Moreover, to test Sb recovery, the SLRS-5 and drinking water samples were spiked with 8 $\mu g{\cdot}L^{-1}$ Sb.

Table 7. Calibration range used to test Sb linearity on the iCE3400 GF-AAS system. A Sb concentration of 80 $\mu g{\cdot}L^{-1}$ was used as a QC standard.

Standard group	Concentration ($\mu g{\cdot}L^{-1}$)
Calibration curve	0, 10, 20, 40, 80, 100, and 150
QC (CCV)	80

Results and discussion for Part 2

The analytical performance of the iCE 3400 GF-AAS system was assessed using both solvent standards and real water samples in accordance to the HJ 1047-2019 standard method requirements. Antimony linearity, sensitivity, selectivity, and method performance with real samples were tested.

Figure 5. Collection of river water samples and sample filtration

Linearity

The results of the linearity test for antimony is shown in Figure 6. Good linearity was obtained over the concentration range analysed (10 – 150 µg·L^{-1}) as indicated by the coefficient of determination (R^2> 0.998).

Sensitivity

Antimony sensitivity obtained with the iCE 3400 GF-AAS system was demonstrated with the concentration detection limit, defined as three times the blank standard deviation (3Σ), was 0.3 µg·L^{-1}, exceeding the expected detection limit requirements of the HJ 1047-2019 method (8 µg·L^{-1} is maximum contamination allowance).

Repeatability of measurement

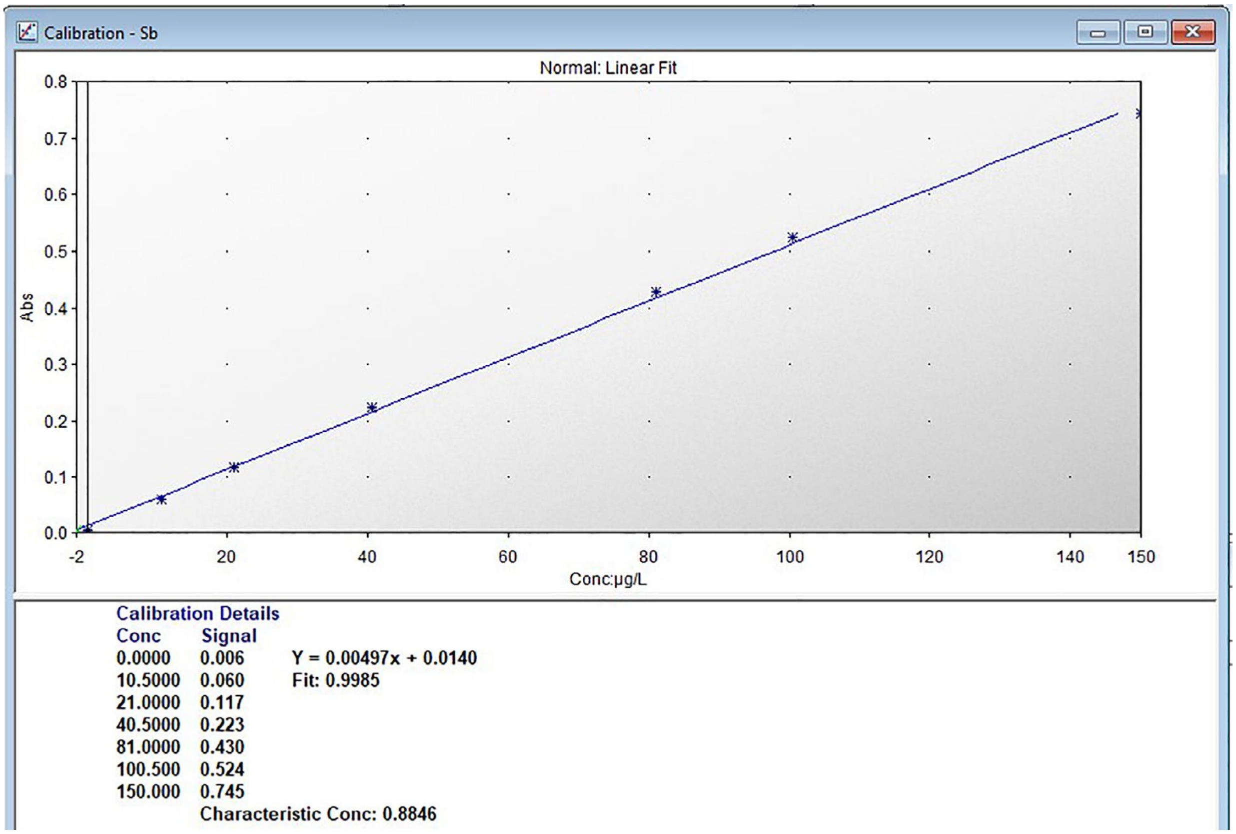
Repeatability of measurement was assessed using antimony standards at 10, 40, and 100 µg·L^{-1} concentration levels, which were analyzed in replicates (n=6 each). The results of these experiments demonstrated excellent precision of measurement with % RSD values <3.5, meeting the HJ 1047-2019 method precision requirement (Table 8).

Table 8. Repeatability as demonstrated by precision of measurement of n=6 replicate analysis of Sb standards analyzed at 10, 40, and 100 µ·L-^{1} level

	10 µg·L^{-1}	**40 µg·L^{-1}**	**100 µg·L^{-1}**
Run-1	10.0	39.3	100.5
Run-2	9.9	38.4	101.9
Run-3	10.1	39.4	105.8
Run-4	10.8	36.9	105.3
Run-5	10.1	39.4	104.2
Run-6	10.6	40.0	102.6
RSD (%)	**3.5**	**2.8**	**2.0**

Quantification of Sb in water samples

The performance of the iCE 3400 GF-AA system for Sb analysis was tested using river water and drinking water samples. Antimony was detected and quantified in these samples, and the results are reported in Table 9. None of the river water samples had Sb levels higher than 1.6 µg·L^{-1} and no Sb was detected in the drinking water sample.



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Calibration Details
Conc      Signal
0.0000    0.006      Y = 0.00497x + 0.0140
10.5000   0.060      Fit: 0.9985
21.0000   0.117
40.5000   0.223
81.0000   0.430
100.500   0.524
150.000   0.745
          Characteristic Conc: 0.8846
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Figure 6. Sb calibration curve obtained on an iCE 3400 GF-AAS system over a 6-points standard curve with concentration ranging from 10 – 150 µg·L^{-1}. Excellent linear response was obtained with coefficient of determination R^2 > 0.998.

Table 9. Antimony analysis result in environmental water samples

Sample name	Measured (µg·L^{-1})	% Recovery
River water CRM SLRS-5	< LOD	-
SRS5 spiked with 8 µg·L^{-1}	8.2	99.6
Drinking water	< LOD	-
River water A	1.6	-
River water B	1.5	-
River water C	1.2	-
River water D	0.99	-
River water E	1.1	-
River water F	1.1	-

The certified reference material SLRS-5 spiked with 8 µg·L^{-1} Sb (as this is the maximum antimony contamination level allowed as per the HJ 1047-2019 method) was also analyzed to evaluate the accuracy of results. Good agreement between the measured and certified concentration (0.3 µg·L^{-1}) in the CRM was obtained. The spike recovery was 99.6%.

QC test

The HJ 1047-2019 method specifies exact performance criteria and acceptance ranges for long term analyses using a selected quality control (QC). As part of QC validation, a QC standard containing Sb at 80 µg·L^{-1} was continuously monitored and used as a continuing calibration verification (CCV). Additionally, two blank samples were analyzed before and after each water sample as continuing calibration blank (CCB) to check for potential carry-over that should be below the detection limit. Moreover, an 8 µg·L^{-1} spiked CRM SLRS-5 river water sample was used as the laboratory control standard (LCS). All QCs (CCV, CCB, and LCS) were analyzed across the sample batch after every twenty water samples.

In total, 50 water samples (river water as well as drinking water) were analyzed in a single batch that also contained the QC samples (CCV, CCB, and LCS), and the entire duration of the analysis exceeded 6.5 hours of continuous acquisition.

The results summary of QC performance is shown in Table 10. The CCB levels did not exceed the limit of detection in any of the blanks analyzed.

Table 10. Summary of QCs results in HJ 1047-2019 criteria

	Analysis results	HJ 1047-2019 criteria	Results
CCB	< LOD	< LOD	Pass
CCV	+4.0%	< ±10%	Pass
LCS	+4.8%	< ±20%	Pass

Also, the CCV demonstrated very close values to the expected with concentration deviation of <4%. The certified reference material samples used as LCS also show calculated concentrations of Sb with values <5% of the theoretical, exceeding the HJ 1047-2019 requirements of ±20%.

All QC results show excellent RSD (%) to be able to confirm that using the fully automated iCE 3400 GF-AAS functionality meets the analysis requirement for HJ 1047/1019 and suitable configuration for 24/7 analysis.

In summary, all experimental results of Sb in water samples by using the iCE 3400 GF-AAS system meet the requirements of the HJ 1047-2019 standard method. When there is a requirement to analyze Sb in water samples based on HJ 1047-2019 with a detection limit range at the µg·L^{-1} level, the iCE 3400 GF-AAS system with its high sensitivity, low detection limit, accuracy, precision, and competitive price will be the best choice.

Conclusion

Antimony is an emerging contaminant, and because of that, a strong focus is put on the analysis of this element in environmental samples such as water to assure water quality and avoid potential hazards due to its toxicity.

This application note demonstrates that antimony can be determined accurately and precisely using atomic absorption, with either a flame or a graphite furnace excitation source. However, there are differences in the achievable detection limits (as well as the required analysis time per sample), so that the choice for either technique depends on the required limits and the sample nature.

- A graphite furnace system can achieve detection limits in the single digit µg·L^{-1} concentration range, and therefore allow the determination of low levels of antimony, for example, in drinking waters for human consumption. However, a flame system is more suitable for laboratories focusing on rapid screening of large numbers of samples, such as effluents or wastewater samples, which may allow higher concentrations of this important element.

- Further improvements of the detection limits of the iCE 3300 FL-AAS system are possible through the use of hydride generation as an accessory.

- For laboratories that need to analyze Sb in water samples according to the HJ 1046-2019 standard method, the iCE 3300 FL-AAS system is suitable and meets all the method requirements.

- For laboratories looking for lower Sb limits of detection and following the HJ 1047-2019 standard method requirements, the iCE 3400 GF AAS system with dedicated graphite furnace part is perfectly suited.

- Taken together, the results of the experiments described in this application note demonstrate that AAS represents an efficient alternative to determine trace (FL-ASS) and ultratrace (GF-AAS) amounts of antimony in environmental samples.

- Laboratories that aim to analyze Sb in water samples following both the HJ 1046 and HJ 1047 methods, the combined dual flame and furnace Thermo Scientific™ iCE™ 3500 AAS system can offer a full turn-key solution without the need of individual analytical platforms.

References

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