REPORT OF THE INTER-LABORATORY COMPARISON ON ARSENIC AND AMMONIA NITROGEN DETERMINATION IN WATER

2022

Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

twas
unesco
The World Academy of Sciences

Published by

Water Quality Analysis Laboratory, Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences (CAS)

Centre of Excellence for Water and Environment (CEWE), CAS-TWAS

Title:

Report of the Inter-laboratory Comparison on Arsenic and Ammonia Nitrogen Determination in Water (2022)

Authors:

Min YANG, Hong-yan LI, Bei ZHENG, Xin WANG

Standards:

ISO 13528: 2015

Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparison

CNAS-GL032: 2018

Guidance on the Selection, Review and Use of Proficiency Testing

CNAS-GL002: 2018

Guidance on Statistic Treatment of Proficiency Testing Results and Performance Evaluation

CNAS-GL003: 2018

Guidance on Evaluating the Homogeneity and Stability of Samples Used for Proficiency Testing

Keywords: Inter-laboratory Comparison, Arsenic, Ammonia Nitrogen, Water

Contents

Summary

The Inter-laboratory Comparison on determining Arsenic and Ammonia Nitrogen in Water (2022) was jointly implemented by Water Quality Analysis Laboratory, Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences (CAS) and Centre of Excellence for Water and Environment (CEWE), CAS-TWAS in 2022. It is a great honor to undertake this important activity for the fourth round, with a full support from the Certification and Accreditation Administration of the People's Republic of China, CNCA (Approved as CNCA[2022]31) and the Alliance of International Science Organizations (ANSO-CR-KP-2020-05).

This study was conducted to determine the levels of arsenic and ammonia nitrogen in two different water items. Both water samples were distributed to the participating laboratories with two testing samples at the same concentration, respectively. The objectives of this proficiency testing are summarized below:

A. To offer a proof of ability for quality assurance to the participating laboratories.

B. To assess the reproducibility of inter-laboratory and inner-laboratory.

C. To elevate the quality control system of the laboratories in the countries along the Belt and Road.

D. To provide a general overview of the analytical performance of laboratories in the countries along the Belt and Road.

E. To strengthen inter-laboratory exchange and cooperation on water quality analysis, and promote capacity building and information sharing.

Eighty-five sets of testing sample were sent to 46 different laboratories across 13 countries. Because of the ongoing epidemic prevention and control measures in 2022, 70 sets of data, including 36 sets for arsenic and 34 sets for ammonia nitrogen, have been returned from 39 laboratories of 9 countries.

According to the distribution of histogram graph, the robust analysis - Algorithm A was adopted to calculate the robust average and robust standard deviation in this study. The robust average indicated the assigned value and the robust standard deviation indicated the standard deviation for the proficiency assessment, which could be used to subsequently calculate z-scores.

For the arsenic samples (-a and -b), z-scores within ±2 were obtained by 55.6% of the reporting participants (corresponding to 20 of the total 36 participants).

For the ammonia nitrogen samples (-a and -b), z-scores within ±2 were obtained by 61.8% of the reporting participants (corresponding to 21 total 34 participants).

Introduction

Analytical laboratories need to possess the necessary skills and expertise to perform measurements that are accredited in accordance with ISO or other relevant quality standards. Inter-laboratory comparison is an effective way to improve the quality control system for analytical laboratories using external measures, which has become increasingly important for analytical laboratories in today's globalized economy.

This is the fourth round of the study on water quality analysis in countries along the Belt-and-Road, jointly organized by Water Quality Analysis Laboratory and CAS-TWAS Centre of Excellence for Water and Environment (CAS-TWAS CEWE), both affiliated with the Research Center for Eco-environmental Sciences (RCEES), Chinese Academy of Sciences (CAS).The main objective of the activity is to assess the laboratory reproducibility in water quality analysis and provide a QA/QC tool for each participating laboratory to improve their performance.

This activity was conducted from October 2022 when testing samples were delivered to the laboratories for analysis, and lasted until March 2023 when all reported results were received. A total of 85 testing samples were sent to 46 different laboratories across 13 countries. Finally, 39 laboratories across 9 countries (presented in Figure 1 and Table 1) have submitted the testing results. A draft report of the study was made available to the participants in April 2023.

The global outbreak of COVID-19 posed significant challenges to the implementation of this work in 2022. We would like to express our gratitude to all the participants for their efforts and trust, and to Russian Federal Service for Accreditation (RusAccreditation) for their recognition and support. We sincerely appreciate all the individual analysts for overcoming difficulties and providing support to this activity. We will continue this effort, and welcome suggestions from participants to improve this inter-laboratory comparison program. We look forward to collaborating with more countries to establish a large laboratory network to share knowledge, experiences, and ideas in the future.

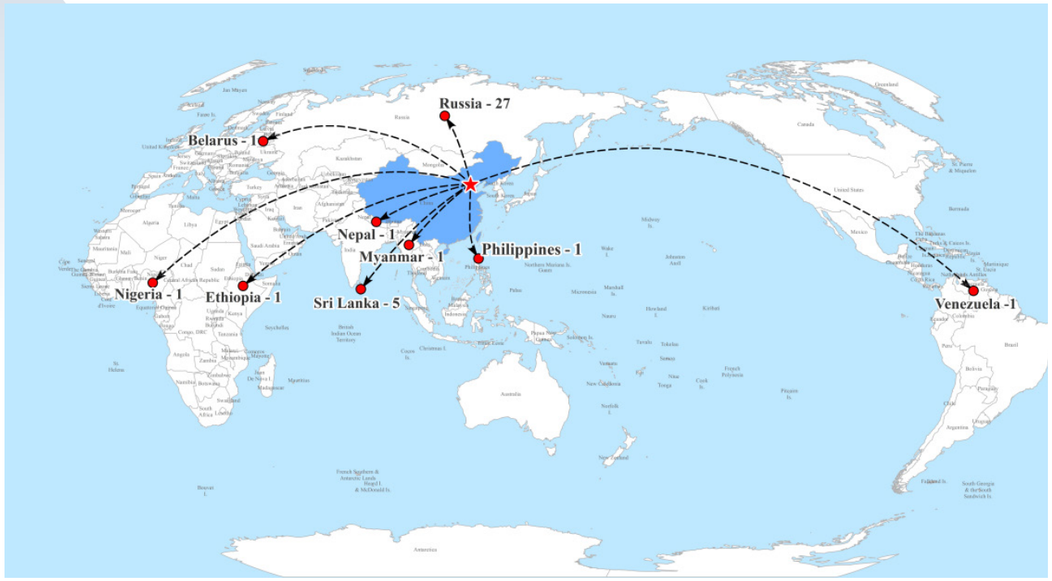

Figure 1 Distribution of the laboratories that reported results in the Inter-laboratory Comparison on Arsenic and Ammonia Nitrogen Determination in Water 2022

Table 1. Participants that reported results in the Inter-laboratory Comparison on Arsenic and Ammonia Nitrogen Determination in Water 2022

Region	Countries
Asia (4)	Philippines, Sri Lanka, Myanmar, Nepal
Africa (2)	Ethiopia, Nigeria
South America (1)	Venezuela
Europe (2)	Russia, Belarus
Total	9 countries (39 laboratories)

Design and practical implementation

Study design and reporting of results

The analysis should be conducted using the laboratories' methods including instrumental analysis, quantification standards, and quantification procedures. The testing methods from the participants who reported results are presented in Table 2. Laboratories were required to report the concentration of each analyte and the corresponding measurement uncertainty according to the Reporting form.

Table 2. Testing methods from the participants in the Inter-laboratory Comparison on Arsenic and Ammonia Nitrogen Determination in Water 2022

Items	Testing Methods	Countries
Arsenic	Atomic Fluorescence Spectroscopy (AFS)	Sri Lanka (1)
	Atomic Absorption Spectroscopy (AAS)	Myanmar (1), Russia (11), Nepal (1), Belarus (1)
	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	Russia (2)
	Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)	Sri Lanka (2), Russia (5)
	Voltammetry	Russia (8)
	Spectrophotometry	Russia (1), Venezuela (1), Nigeria (1), Sri Lanka (1)
Ammonia Nitrogen	Spectrophotometry	Russia (23), Sri Lanka (4), Nepal (1), Ethiopia (1), Venezuela (1), Nigeria (1)
	Ion Selective Electrode	Philippines (1)
	Ion Chromatography	Belarus (1)
	Capillary Electrophoresis	Russia (1)

Confidentiality

To ensure the impartiality of this inter-laboratory comparison activity, each participating laboratory was assigned a random laboratory code by coordinators. Participants were only provided access to their respective codes, and laboratory codes were not disclosed to any third parties. The distribution and result for each paired sample are transmitted by code. When received by the coordinators, the raw data from participating laboratories were imported into a database for analysis and the report draft. In this report, the participants are presented in the tables and figures by their unique codes.

Statistical analysis and evaluation

Statistical analysis

The statistical method for this inter-laboratory comparison is based on the "Guidance on the selection, review and use of proficiency testing CNAS-GL032:2018". According to the distribution frequency of the reported results, the distribution of histogram graph is unimodal and symmetric, as shown in Appendix B. Then, the robust analysis - Algorithm A (as shown in Appendix C) could be adopted. The robust average and robust standard deviation were calculated using the Algorithm A. The robust average represents the assigned value, while the robust standard deviation represents the standard deviation for the proficiency assessment. These values were denoted as x^* and s^* in Table 3, respectively.

Table 3. The robust average and robust standard deviation of Arsenic and Ammonia Nitrogen Determination in Water in the Inter-laboratory Comparison 2022

Items	Arsenic		Ammonia Nitrogen	
	Arsenic-a	Arsenic-b	Ammonia Nitrogen-a	Ammonia Nitrogen-b
The robust average (x^*)	4.91 μg/L	4.91 μg/L	0.308 mg/L	0.308 mg/L
The robust standard deviation (s^*)	0.281	0.268	0.0197	0.0197
The standard uncertainty of the robust average ($u(x_{pt})$)	0.04 μg/L	0.03 μg/L	0.003 mg/L	0.003 mg/L
0.3 s^*	0.084	0.080	0.006	0.006

Result evaluation

Z-score was adopted to evaluate the results in the inter-laboratory comparison, according to "Statistical methods for use in proficiency testing by inter-laboratory comparison ISO 13528:2015". Z-score was calculated according to the equation (1):

$$z = \frac{x_i - x_{pt}}{\sigma_{pt}} \quad \text{.....(1)}$$

where x_i is the reported value; x_{pt} is the assigned value (hereby the robust average, x^*); σ_{pt} is the standard deviation for proficiency assessment (hereby the robust standard deviation, s^*). $|z| \leqslant 2.0$ means a satisfied result; $2.0<|z|<3.0$ means a problematic result; $|z| \geqslant 3.0$ means an unsatisfied result.

When the standard uncertainty of the assigned value ($u(x_{pt})$) is larger than the standard deviation for proficiency assessment (σ_{pt}), there is a risk that some participants will receive problematic result or unsatisfied result because of inaccuracy of the assigned value, rather than internal reasons from the participant. If the $u(x_{pt})<0.3\sigma_{pt}$, then the uncertainty of the assigned value may be considered negligible and may not need to be included in the interpretation of the results of the round of proficiency testing (as shown in Table 3).

There were three kinds of evaluation results: satisfied, problematic, and unsatisfied. A satisfied result will be achieved for each laboratory only when paired sample (both sample-a and sample-b) meet the condition of "$|z| \leqslant 2.0$". Otherwise, the result will be evaluated as problematic or unsatisfied. Table 4 shows the acceptable range of testing results for arsenic and ammonia nitrogen in water.

Table 4. The acceptable range of testing results on Arsenic and Ammonia Nitrogen Determination in Water in the Inter-laboratory Comparison 2022

Items	Unit	Assigned value/The robust average	$\|z\| \leqslant 2.0$	Minimum concentration	Maximum concentration
Arsenic-a	μg/L	4.91	Satisfied	4.35	5.47
Arsenic-b		4.91		4.37	5.45
Ammonia Nitrogen-a	mg/L	0.308	Satisfied	0.269	0.347
Ammonia Nitrogen-b		0.308		0.269	0.347

If the participating laboratory obtained a result of "unsatisfied" or "problematic", we would offer additional sample deliveries for retesting based on the principle of voluntary participation. All the analysis results for each laboratory in this report were based on the initially returned testing results. The retesting results were evaluated according to the above statistical analysis results directly with no further calculation, while the retesting evaluation would be supplemented by the notice of the study results.

The final report and certificate

The final report was drafted by the coordinators and published in April 2023.

A certificate with analysis results will be provided to each laboratory that contributed to the study by the end of April 2023.

Coordination

This activity was initiated by CNCA and RCEES, and jointly carried out by the Water Quality Analysis Laboratory and CAS-TWAS Centre of Excellence for Water and Environment (CEWE), RCEES. Members of the coordination committee were:

Prof. Hongyan LI,
Prof. Min YANG,
szfxsys@126.com; cas_twas@rcees.ac.cn

Results

General

Figure 2 shows the results of comprehensive assessment to the testing results of arsenic and ammonia nitrogen in this activity.

For the samples of arsenic, results from 36 laboratories were received. Three kinds of results were obtained including satisfied (20), unsatisfied (10) and problematic (6), accounting for 55.6% ,27.8% and 16.7% of the overall, respectively.

For the samples of ammonia nitrogen, results from 34 laboratories were received. Three kinds of results were reported including satisfied (21), unsatisfied (11) and problematic (2), accounting for 61.8%, 32.4% and 5.88% of the overall, respectively.

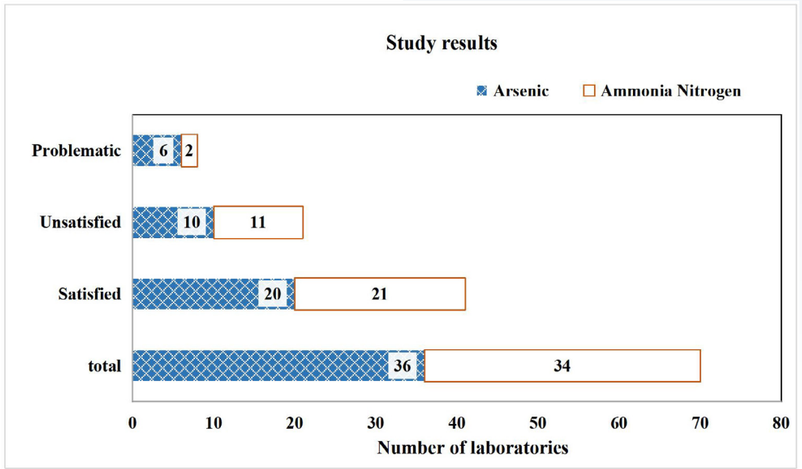

Figure 2 Comprehensive study of the testing results in this activity

Arsenic

Figure 3 shows the study results of arsenic testing. Among the 36 participating laboratories, 20 of them achieved satisfied results. Within the 10 laboratories who obtained unsatisfied results, 9 laboratories obtained z-scores over ±3.0, and one laboratory submitted the testing results with a z-score of 3.58 for arsenic-a as unsatisfied result and with a z-score of 2.74 for arsenic-b as problematic result.

One laboratory reported both testing results with the z-score of 2.0~3.0 as problematic results. Five laboratories submitted the testing results where the z-score of one sample was 2.0~3.0 as problematic result, and the z-score of another sample was within ±2.0 as satisfied result. The results of each participant are presented in Appendix G 1-1.

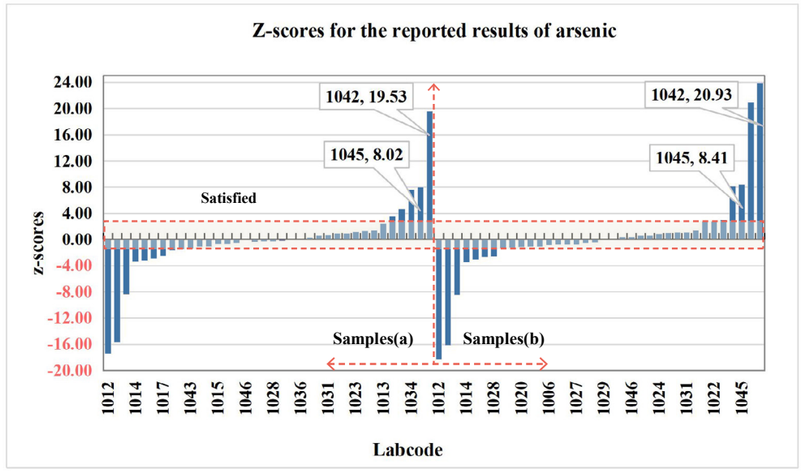

Figure 3 Study results of arsenic testing

(Note: To reduce the impact of larger z score on the overall distribution of data, the z-scores of 1042 and 1045 in this figure are 1/20 of the original)

Ammonia Nitrogen

Figure 4 shows the results of ammonia nitrogen measurement. It was observed that 21 of total participating laboratories achieved the satisfied results, while 11 laboratories obtained unsatisfied results, 8 of them obtained the z-scores over ±3.0. Furthermore, it should be noted that two laboratories submitted testing results with one z-score exceeding ±3.0, classified as an unsatisfactory result, and another z-score falling within the range of 2.0 to 3.0, classified as a problematic result. In addition, one laboratory submitted the testing results with a z-score of 8.54 for ammonia nitrogen-a as unsatisfied result and a z-score of -1.94 for ammonia nitrogen-b as satisfied result.

Moreover, it should be highlighted that two laboratories submitted testing results where the z-score of one sample fell between 2.0 and 3.0, classified as a problematic result, and the z-score of another sample fell within the range of ±2.0, regarding as a satisfactory result. The overall results are presented in Appendix G 1-2.

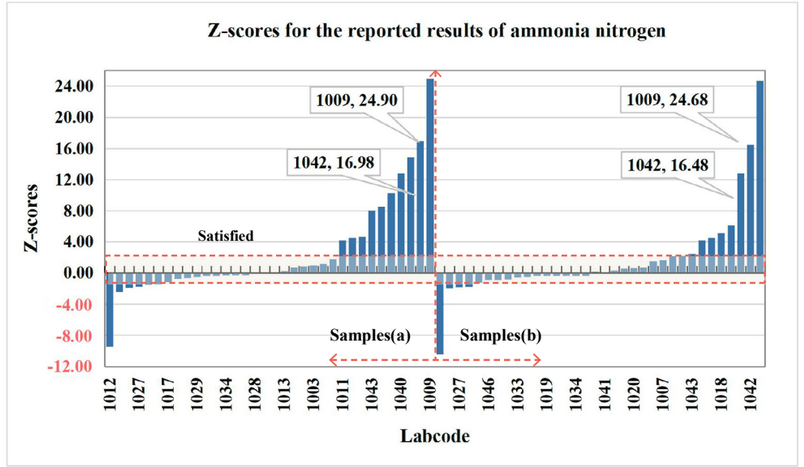

Figure 4 Study results of ammonia nitrogen testing

(Note: To reduce the impact of larger z score on the overall distribution of data, the z-scores of 1009 and 1042 in this figure are 1/20 of the original)

Statistics of testing methods

Based on the technical traceability of original records, the assessment results with respect to different testing methods performed by all participating laboratories are summarized in Figure 5 and Figure 6.

For the measurement of arsenic in water, six kinds of methods including AFS (1), AAS (14), ICP - MS (2), ICP - OES (7), voltammetry (8) and spectrophotometry (4) were adopted. AAS was identified as the most commonly used method for arsenic analysis, achieving a high proportion of 71.4% in the satisfied results category in this study followed by the methods of voltammetry and ICP – OES.

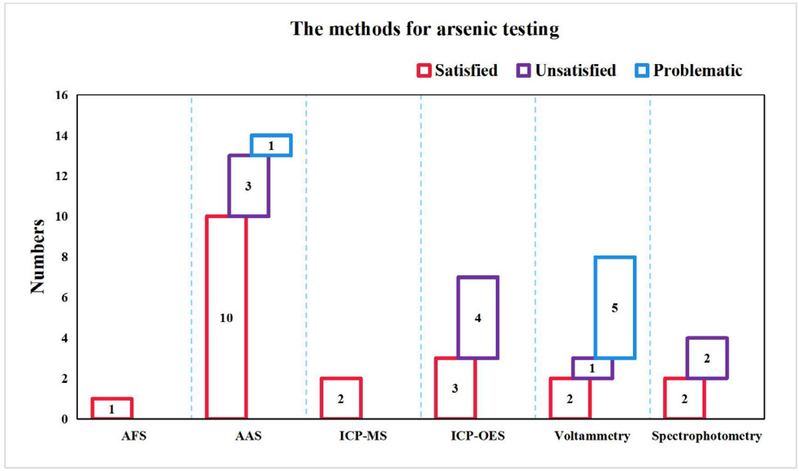

Figure 5 Category statistics of the testing methods for arsenic

In terms of the determination of ammonia nitrogen, four kinds of methods including spectrophotometry (31), ion selective electrode (1), IC (1) and capillary electrophoresis (1) were adopted for testing. Spectrophotometry is the predominant testing method for ammonia nitrogen analysis, which achieved a proportion of 64.5% as satisfied results in this study.

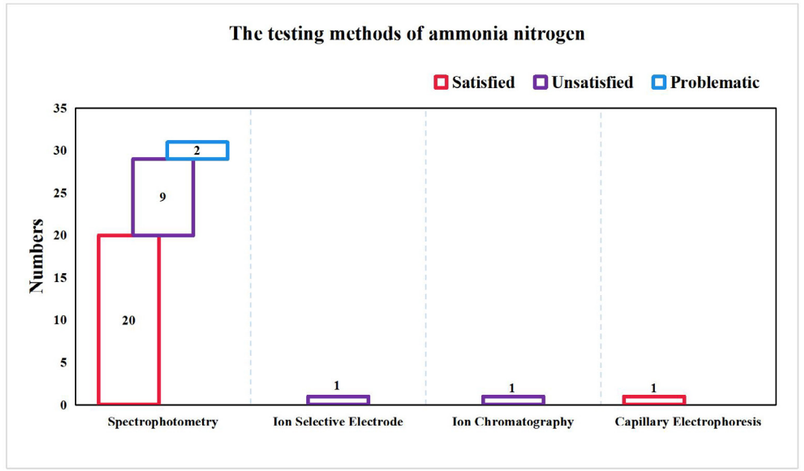

Figure 6 Category statistics of the testing methods for ammonia nitrogen

Out of the 39 participants, 19 laboratories provided their original records alongside their testing results, which was highly beneficial for technical traceability, especially in cases where problematic or unsatisfactory results were identified. It is recommended that laboratories prioritize the traceability of their original records, as these records can provide insight into both managerial and technical issues that may affect the accuracy of their testing results. Managerial issues such as transcription errors and decimal point mistakes can be identified through original record analysis, as well as technical issues such as problems with measuring methods, internal quality control, or poor condition of equipment.

Upon technical analysis and traceability of the original records, it was discovered that reagent blank calibration was often overlooked when spectrographic methods were utilized for water quality analysis, despite it being a widespread and convenient technique. In addition, we also recommend that laboratories pay more attention to the correction of calibration curves and measurement recovery. Futhermore, voltametric methods have the advantage of high sensitivity for heavy metals analysis, whereas its accuracy and sensitivity highly depend on the working conditions of electrode, therefore, maintaining long-term stability is vital to ensure the accuracy and reliability of voltametric methods.

Acknowledgment

We would like to express our sincere appreciation to the participating laboratories for their involvement in this inter-laboratory comparison and their commitment to its overarching objectives, and also extend our gratitude to all the individual analysts for their significant contributions to the results.Appreciation is extended for the assistance provided by Certification and Accreditation Administration (Grant No. [2022] 31), the Alliance of International Science Organizations (Grant No. ANSO-CR-KP-2020-05) and the Russian Federal Service for Accreditation (RusAccreditation); Thank Prof. Jingbo CHAO from the National Institute of Metrology, China, for providing the standard solutions and her technical guidance.

国家认证认可监督管理委员会

认秘函〔2022〕31 号

认监委秘书处关于组织开展水质、铁矿石和石灰石国际检验检测机构能力验证活动的通知

中国合格评定国家认可中心，中国科学院生态环境研究中心，北京中实国金国际实验室能力验证研究有限公司，各有关检验检测机构：

为充分发挥检验检测、认证认可对国际贸易和“一带一路”建设的技术支撑作用，经研究，认监委决定在水质、铁矿石和石灰石检验检测领域组织开展国际能力验证活动，组织国内相关检验检测机构并邀请“一带一路”沿线国家检验检测机构参与，推动标准和检测结果联通，为后续相关业务交流和技术能力提升奠定基础。现将有关事项通知如下：

一、能力验证项目和参加要求

本次能力验证活动委托中国合格评定国家认可中心提供技术支撑，委托中国科学院生态环境研究中心水质分析实验室具体承担“水中砷和氨氮的测定”项目实施，委托北京中实国金国际实验室能力验证研究有限公司承担“铁矿石中 TFe、SiO_2、P、S 的测定”和“石灰石中 SiO_2、CaO、MgO、Fe_2O_3、Al_2O_3 的测定”项目实施。

具备相关检测项目技术能力的国家产品质检中心应积极报名参加相关能力验证项目。因故不能参加的，需向项目承担单位提交书面情况说明。

项目承担单位负责联系和邀请“一带一路”沿线国家和地区的检验检测机构参加本次能力验证。

二、检测标准和样品信息

（一）“水中砷和氨氮的测定”能力验证项目

水中砷的测定可采用 ISO 17378-2:2014《Water quality — Determination of arsenic and antimony—Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)》；GB/T 5750.6-2006 6.1《氢化物原子荧光法》；GB/T 5750.6-2006 6.5《电感耦合等离子体发射光谱法》；GB/T 5750.6-2006 6.6《电感耦合等离子体质谱法》。

水中氨氮的测定可采用 ISO 11732:2005《Water quality — Determination of ammonium nitrogen — Method by flow analysis (CFA and FIA) and spectrometric detection》；ISO 6778:1984《Water quality — Determination of ammonium — Potentiometric method》；ISO 7150-1:1984《Water quality — Determination of ammonium — Part 1: Manual spectrometric method》；ISO 5664:1984《Water quality — Determination of ammonium — Distillation and titration method》；GB/T 5750.5-2006 9.1《纳氏试剂分光光度法》；GB/T 5750.5-2006

Appendix A Document from CNCA

附件：1. 水中砷和氨氮的测定能力验证报名表

2. 铁矿石中 TFe、SiO_2、P、S 的测定能力验证报名表

3. 石灰石中 SiO_2、CaO、MgO、Fe_2O_3、Al_2O_3 的测定能力验证报名表

国家认证认可监督管理委员会 秘书处

认监委秘书处

2022 年 8 月 18 日

（此件公开发布）

— 5 —

Appendix B Distribution Histogram of Returned Testing Results

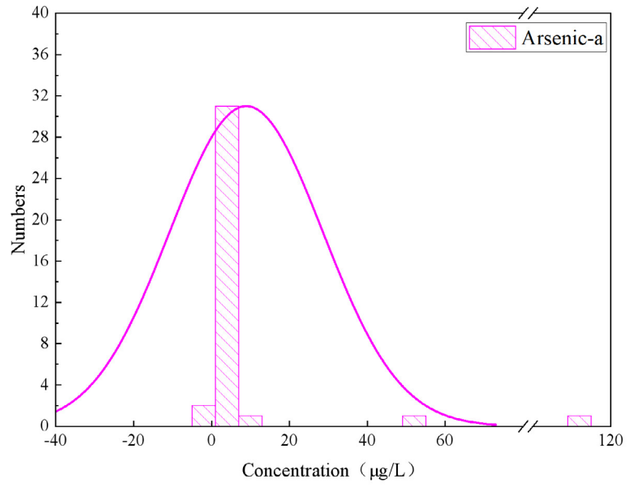

Figure B-1 Distribution histogram of testing results of arsenic-a

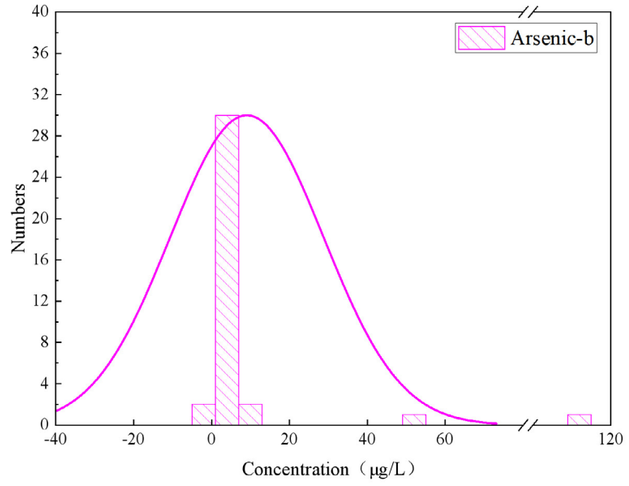

Figure B-2 Distribution histogram of testing results of arsenic-b

Appendix B Distribution Histogram of Returned Testing Results

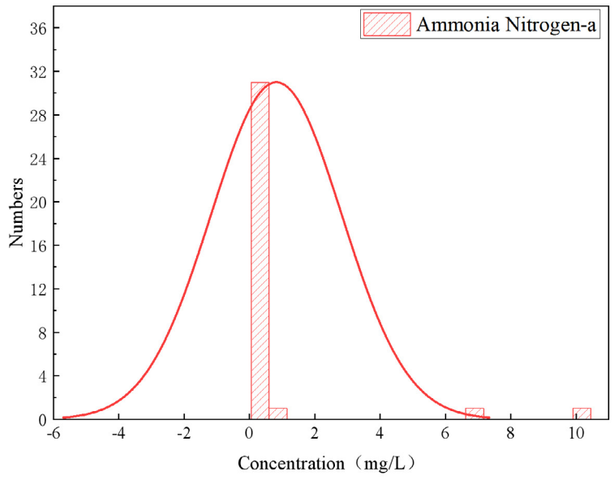

Figure B-3 Distribution histogram of testing results of ammonia nitrogen-a

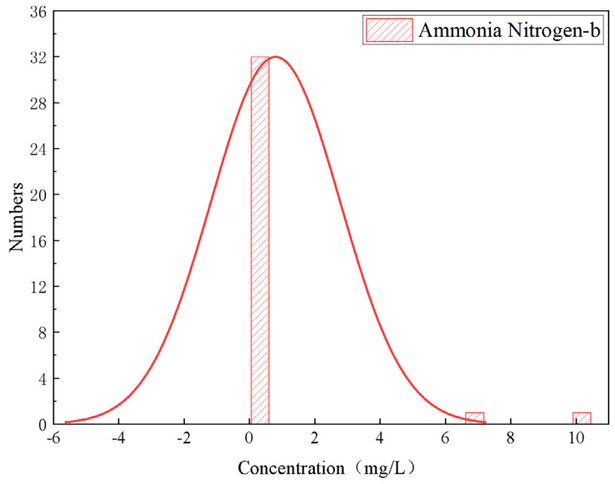

Figure B-4 Distribution histogram of testing results of ammonia nitrogen-b

Appendix C Robust Analysis : Algorithm A

This algorithm yields robust estimates of the mean and standard deviation of the data to which it is applied.

Denote the p items of data , sorted into increasing order, by :

$x_{\{1\}}, x_{\{2\}}, ..., x_{\{p\}}$

Denote the robust average and robust standard deviation of these data by x^* and s^*.

Calculate initial values for x^* and s^* as:

x^* =*median of* x_i (i =*1, 2 , ..., p*) ……(1)

s^* =1.483 *median of* $\{|x_i - x^*|\}$ with (i =*1, 2 , ..., p*) ……..(2)

Up date the values of x^* and s^* a s follows. Calculate:

$\delta = 1.5 s^*$……..(3)

For each x_i (i=1,2…….p), calculate:

$$x_i^* = \begin{cases} x^* - \delta, & when\ x_i < x^* - \delta \\ x^* + \delta, & when\ x_i > x^* + \delta \\ x_i, & otherwise \end{cases} \quad \text{.....(4)}$$

$x^* = \sum x^*/p$……..(5)

$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2/(p-1)}$……..(6)

where the summation is over i.

The robust estimates x^* and s^* may be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times using the modified data in equations (3) to (6), until the process converges. Convergence may be assumed when there is no change from one iteration to the next in the third significant figures of the robust mean and robust standard deviation (x^* and s^*). Alter native convergence criteria can be determined according to the design and reporting requirements for proficiency test results.

Appendix D 1-1 Operation Instruction for Testing of Arsenic

Operation Instruction for Testing Samples of the 4th Inter-Laboratory Comparison (2022)- Arsenic

Participating laboratories:

The 4th Inter-laboratory Comparison on Water Quality Analysis (2022), which is focused on the Proficiency Testing of Arsenic and Ammonia Nitrogen in Water, is organized and implemented by the CAS-TWAS Center of Excellence for Water and Environment (CAS-TWAS CEWE) and Water Quality Analysis Laboratory, Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences. In this project, your laboratory code is **1×××**. The relevant information of the project is as follows:

To ensure the smooth implementation of the proficiency testing, please read the following instructions carefully before testing:

1. Description of the testing samples

1.1 This operation instruction is prepared for the testing of **Arsenic in water**, and the testing samples will be provided randomly according to the registration information.

1.2 **Two** samples provided for this test are packaged in bottles with volume about 20 mL, numbered **S1×××a** and **S1×××b**. The matrix is 1% HNO_3. The reference concentration of the Arsenic in samples is between 1.00 μg/L~10.0 μg/L (after the dilution).

1.3 The samples will be delivered from the CAS-TWAS Center of Excellence for Water and Environment, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

1.4 Upon receipt, please confirm that all the samples are in good condition. Please fill in the **Confirmation Form for the Receiving Status of Testing Samples** within 7 days after receipt, and then please send the scanned copy of this form to **szfxsys@126.com**. If the sample received is damaged, please contact us through email **szfxsys@126.com** in time and apply for replacement (Note: The replacement is only for damage caused by transportation, but not that caused by experimental operations).

1.5 Store in dark at room temperature, please test as soon as possible after opening.

2. Testing

2.1 Dilution method: Use a clean and dry pipette to accurately remove 10 mL of the sample from the bottle, transfer it to a 250 mL volumetric flask, dilute to volume with ultrapure water or as required by the test method, and test immediately after mixing. Each sample must be tested in duplicate.

2.2 The actual testing methods of each laboratory should be consistent with that in the Registration Form. If there is any change, instructions for the change should be submitted and the Registration Form should be resubmitted.

Note: If the recommended method or international standard methods are not used, you need to send the testing methods (in English) to **szfxsys@126.com** when the results are submitted.

3. Result report

3.1 The results of "**Arsenic in water**" should be reported in μg/L with **the concentration after dilution** in the **Results Form for the 4th Inter-laboratory Comparison (2022).** At the same time, the average results should be calculated (submit testing results for only one method) and **retained 3-digit valid numbers**. Given the extended uncertainty (U) (k=2), please evaluate the uncertainty of the results in the Results Form as well.

3.2 Each laboratory please send the completed **Results Form for the 4th Inter-laboratory Comparison (2022)**, **reference standards for testing methods (in English), and the detailed original records** to **szfxsys@126.com** within 30 natural days (including weekends and national holidays) since the receipt of the samples. The results will not be counted and evaluated if the Results Form is not returned in time.

3.3 All laboratories that apply for replacement samples due to **sample damage caused by transportation** or **retest**, please submit results and relevant materials (required in **3.1**) within **10 natural days** since the receipt of the samples.

3.4 During the implementation of this proficiency testing program, each laboratory should pay attention to confidentiality, independently complete the experiment and submit the report.

Note: The original records please include instrumental conditions, spike recovery, preparation of standard solution and reference reagents, standard curve, quality control samples, parallel samples, and other quality control measures. Quality control measures should reflect the reliability of test results.

4. Contact information

If you have any questions during the proficiency testing process, please contact with the CAS-TWAS Center of Excellence for Water and Environment, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Contact: Si, Ludan

Contact number: +86-10-62849800

E-mail: cas_twas@rcees.ac.cn

Contact address: CAS-TWAS Center of Excellence for Water and Environment,

Research Center for Eco-environmental Sciences, Chinese Academy of Sciences,
Beijing 100085, CHINA

Operation Instruction for Testing Samples of the 4th Inter-Laboratory Comparison (2022)-Ammonia Nitrogen

Participating laboratories:

The 4th Inter-laboratory Comparison on Water Quality Analysis (2022), which is focused on the Proficiency Testing of Arsenic and Ammonia Nitrogen in Water, is organized and implemented by the CAS-TWAS Center of Excellence for Water and Environment (CAS-TWAS CEWE) and Water Quality Analysis Laboratory, Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences. In this project, your laboratory code is **1×××**. The relevant information of the project is as follows:

To ensure the smooth implementation of the proficiency testing, please read the following instructions carefully before testing:

1. Description of the testing samples

1.1 This operation instruction is prepared for the testing of **Ammonia Nitrogen in water**, and the testing samples will be provided randomly according to the registration information.

1.2 Two samples provided for this test are packaged in bottles with volume about 20 mL, numbered **A1×××a** and **A1×××b**. The matrix is H_2O. The reference concentration of the Ammonia Nitrogen in samples is between 0.100 mg/L~1.00 mg/L (after the dilution).

1.3 The samples will be delivered from the CAS-TWAS Center of Excellence for Water and Environment, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

1.4 Upon receipt, please confirm that all the samples are in good condition. Please fill in the **Confirmation Form for the Receiving Status of Testing Samples** within 7 days after receipt, and then please send the scanned copy of this form to **szfxsys@126.com**. If the sample received is damaged, please contact us through email **szfxsys@126.com** in time and apply for replacement (Note: The replacement is only for damage caused by transportation, but not that caused by experimental operations).

1.5 Store in dark at room temperature, please test as soon as possible after opening.

2. Testing

2.1 Dilution method: Use a clean and dry pipette to accurately remove 10 mL of the sample from the bottle, transfer it to a 250 mL volumetric flask, dilute to volume with ultrapure water or as required by the test method, and test immediately after mixing. Each sample must be tested in duplicate.

2.2 The actual testing methods of each laboratory should be consistent with that in the Registration Form. If there is any change, instructions for the change should be submitted and the Registration Form should be resubmitted.

Note: If the recommended method or international standard methods are not used, you need to send the testing methods (in English) to **szfxsys@126.com** when the results are submitted.

3. Result report

3.1 The results of "**Ammonia Nitrogen in water**" should be reported in mg/L with **the concentration after dilution** in the **Results Form for the 4th Inter-laboratory Comparison (2022)**. At the same time, the average results should be calculated (submit testing results for only one method) and **retained 3-digit valid numbers**. Given the extended uncertainty (U) (k=2), please evaluate the uncertainty of the results in the Results Form as well.

3.2 Each laboratory please send the completed **Results Form for the 4th Inter-laboratory Comparison (2022)**, **reference standards for testing methods (in English), and the detailed original records** to **szfxsys@126.com** within 30 natural days (including weekends and national holidays) since the receipt of the samples. The results will not be counted and evaluated if the Results Form is not returned in time.

3.3 All laboratories that apply for replacement samples due to **sample damage caused by transportation** or **retest**, please submit results and relevant materials (required in **3.1**) within **10 natural days** since the receipt of the samples.

3.4 During the implementation of this proficiency testing program, each laboratory should pay attention to confidentiality, independently complete the experiment and submit the report.

Note: The original records please include instrumental conditions, spike recovery, preparation of standard solution and reference reagents, standard curve, quality control samples, parallel samples, and other quality control measures. Quality control measures should reflect the reliability of test results.

4. Contact information

If you have any questions during the proficiency testing process, please contact with the CAS-TWAS Center of Excellence for Water and Environment, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Contact: Si, Ludan

Contact number: +86-10-62849800

E-mail: cas_twas@rcees.ac.cn

Contact address: CAS-TWAS Center of Excellence for Water and Environment,

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences,

Beijing 100085, CHINA

Appendix E Testing Results for the 4th Inter-laboratory Comparison (2022)

Testing Results for the 4th Inter-laboratory Comparison (2022)

"Arsenic"

Laboratory: _____ Laboratory code:_____

Report date: _____

Sample number	Testing results (μg/L)			Extended uncertainty（k=2）	Title and issued No. of the testing method	Ambient temperature	Instrument and model	Date of inspection	Signature of the inspector	Signature of the certifier
	1	2	Average							

Problems or anomalies that occur during the experiment：_____

_____（Not enough, please attach a page）

Person in charge（signature）：

Official seal：

Testing Results for the 4th Inter-laboratory Comparison (2022)

"Ammonia Nitrogen (as N)"

Laboratory: _____ Laboratory code:_____

Report date: _____

Sample number	Testing results (mg/L)			Extended uncertainty（k=2）	Title and issued No. of the testing method	Ambient temperature	Instrument and model	Date of inspection	Signature of the inspector	Signature of the certifier
	1	2	Average							

Problems or anomalies that occur during the experiment：_____

_____（Not enough, please attach a page）

Person in charge（signature）：

Official seal：

Appendix F Confirmation Form for the Receiving Status of Testing Samples

Confirmation Form for the Receiving Status of Testing Samples

Laboratory		
Code of Laboratory		
Accepted Date		
Accepted Samples	Amount of Samples	☐ 2 ☐ 4
	No. of Samples	
	Status of Samples	☐ in good condition ☐ broken Note: If the samples are broken, please attach photos of the sample when returning this form.
Recipient	Name	
	E-Mail	

Appendix G 1-1 Z-scores of Results for Arsenic

Lab code	Comprehensive assessment conclusion	Sample code	Conc 1 (μg/L)	Conc 2 (μg/L)	Mean value (μg/L)	z-scores	Conclusion	Sample code	Conc 1 (μg/L)	Conc 2 (μg/L)	Mean value (μg/L)	z-scores	Conclusion
1001	unsatisfied	S1001a	5.928	5.906	5.917	3.58§	unsatisfied	S1001b	5.805	5.481	5.643	2.74*	problematic
1002	satisfied	S1002a	4.99	5.12	5.06	0.53	satisfied	S1002b	4.99	4.98	4.99	0.30	satisfied
1003	problematic	S1003a	4.21	3.95	4.08	-2.95*	problematic	S1003b	3.97	4.42	4.20	-2.65*	problematic
1004	unsatisfied	S1004a	3.99	4.01	4.00	-3.24§	unsatisfied	S1004b	4.12	4.06	4.09	-3.06§	unsatisfied
1006	satisfied	S1006a	4.854	4.842	4.848	-0.22	satisfied	S1006b	4.675	4.678	4.676	-0.87	satisfied
1007	unsatisfied	S1007a	6.09	6.35	6.22	4.66§	unsatisfied	S1007b	11.6	11.0	11.3	23.84§	unsatisfied
1011	satisfied	S1011a	4.75	4.75	4.75	-0.57	satisfied	S1011b	5.17	5.42	5.30	1.46	satisfied
1012	unsatisfied	S1012a	0.0045	0.0045	0.0045	-17.46§	unsatisfied	S1012b	0.0060	0.0060	0.0060	-18.30§	unsatisfied
1013	problematic	S1013a	4.75	6.41	5.58	2.38*	problematic	S1013b	4.32	5.78	5.05	0.52	satisfied
1014	unsatisfied	S1014a	3.947	3.997	3.972	-3.34§	unsatisfied	S1014b	3.883	4.051	3.967	-3.52§	unsatisfied
1015	satisfied	S1015a	4.65	4.76	4.7	-0.75	satisfied	S1015b	4.75	4.77	4.8	-0.41	satisfied
1016	unsatisfied	S1016a	2.341	2.78	2.561	-8.36§	unsatisfied	S1016b	2.412	2.891	2.652	-8.43§	unsatisfied
1017	problematic	S1017a	4.28	4.12	4.20	-2.53*	problematic	S1017b	4.66	4.54	4.60	-1.16	satisfied
1018	satisfied	S1018a	4.82	4.81	4.82	-0.32	satisfied	S1018b	5.18	5.18	5.18	1.01	satisfied
1019	satisfied	S1019a	4.931	4.836	4.883	-0.10	satisfied	S1019b	4.775	4.719	4.747	-0.61	satisfied
1020	satisfied	S1020a	4.596	4.589	4.59	-1.14	satisfied	S1020b	4.482	4.692	4.59	-1.19	satisfied
1021	problematic	S1021a	5.01	4.20	4.61	-1.07	satisfied	S1021b	5.30	6.10	5.70	2.95*	problematic
1022	problematic	S1022a	5.10	5.50	5.30	1.39	satisfied	S1022b	5.50	5.80	5.65	2.76*	problematic
1023	satisfied	S1023a	5.236	5.249 5.212	5.230	1.14	satisfied	S1023b	5.246	5.265 5.077	5.200	1.08	satisfied
1024	satisfied	S1024a	5.144	5.195	5.17	0.93	satisfied	S1024b	5.083	5.192	5.14	0.86	satisfied
1027	satisfied	S1027a	4.70	4.70	4.70	-0.75	satisfied	S1027b	4.70	4.70	4.70	-0.78	satisfied
1028	problematic	S1028a	4.25	5.39	4.82	-0.32	satisfied	S1028b	3.64	4.80	4.22	-2.57*	problematic
1029	satisfied	S1029a	5.04	5.31	5.175	0.94	satisfied	S1029b	4.75	5.02	4.885	-0.09	satisfied
1030	satisfied	S1030a	4.47	4.50	4.49	-1.49	satisfied	S1030b	4.53	4.55	4.54	-1.38	satisfied
1031	satisfied	S1031a	5.00	5.20	5.10	0.68	satisfied	S1031b	5.40	5.0	5.20	1.08	satisfied
1032	satisfied	S1032a	4.52	6.09	5.31	1.42	satisfied	S1032b	4.55	4.59	4.57	-1.27	satisfied
1033	satisfied	S1033a	4.59	5.03	4.81	-0.36	satisfied	S1033b	4.71	5.43	5.07	0.60	satisfied
1034	unsatisfied	S1034a	7.08	7.02	7.05	7.62§	unsatisfied	S1034b	7.2	6.95	7.08	8.10§	unsatisfied
1035	satisfied	S1035a	4.96	5.01	4.99	0.28	satisfied	S1035b	4.79	4.58	4.69	-0.82	satisfied
1036	satisfied	S1036a	4.85	4.92	4.89	-0.07	satisfied	S1036b	4.93	4.86	4.90	-0.04	satisfied
1038	satisfied	S1038a	4.43	4.47	4.45	-1.64	satisfied	S1038b	4.58	4.62	4.60	-1.16	satisfied
1040	unsatisfied	S1040a	0.483	0.503	0.493	-15.72§	unsatisfied	S1040b	0.623	0.548	0.586	-16.13§	unsatisfied
1042	unsatisfied	S1042a	113.76	113.48 116.70	114.65	390.53§	unsatisfied	S1042b	115.62	116.83 118.80	117.08	418.54§	unsatisfied
1043	satisfied	S1043a	4.33	4.71	4.52	-1.39	satisfied	S1043b	4.50	4.88	4.69	-0.82	satisfied
1045	unsatisfied	S1045a	50.0	50.0	50.0	160.46§	unsatisfied	S1045b	50.0	50.0	50.0	168.25§	unsatisfied
1046	satisfied	S1046a	4.8	5.0	4.9	-0.04	satisfied	S1046b	5.1	4.9	5.0	0.34	satisfied
Notes	Arsenic-a testing: the assigned value = 4.91 μg/L, the standard deviation for proficiency assessment of Arsenic-a = 0.281. Arsenic-b testing: the assigned value = 4.91 μg/L, the standard deviation for proficiency assessment of Arsenic-b = 0.268. $\|z\| \leqslant 2.0$ means a satisfied result; $2.0 < \|z\| < 3.0$ means a problematic result, which is marked with * in the table; $\|z\| \geqslant 3.0$ means an unsatisfied result, which is marked with § in the table. The evaluation is "unsatisfactory", when any result in the paired sample gets a $\|z\| \geqslant 3.0$.												

Appendix G 1-2 Z-scores of Results for Ammonia Nitrogen

Lab code	Comprehensive assessment conclusion	Sample code	Conc 1 (mg/L)	Conc 2 (mg/L)	Mean value (mg/L)	z-scores	Conclusion	Sample code	Conc 1 (mg/L)	Conc 2 (mg/L)	Mean value (mg/L)	z-scores	Conclusion
1003	satisfied	A1003a	0.326	0.328	0.327	0.96	satisfied	A1003b	0.322	0.319	0.321	0.66	satisfied
1006	unsatisfied	A1006a	0.4713	0.4814	0.4763	8.54§	unsatisfied	A1006b	0.2877	0.2518	0.2697	-1.94	satisfied
1007	satisfied	A1007a	0.32	0.33	0.325	0.86	satisfied	A1007b	0.34	0.34	0.34	1.62	satisfied
1009	unsatisfied	A1009a	10.21	10.03	10.12	498.07§	unsatisfied	A1009b	10.03	10.03	10.03	493.50§	unsatisfied
1011	unsatisfied	A1011a	0.39	0.38	0.39	4.16§	unsatisfied	A1011b	0.39	0.39	0.39	4.16§	unsatisfied
1012	unsatisfied	A1012a	0.120	0.126	0.123	-9.39§	unsatisfied	A1012b	0.100	0.105	0.103	-10.41§	unsatisfied
1013	satisfied	A1013a	0.309	0.317	0.313	0.25	satisfied	A1013b	0.332	0.341	0.337	1.47	satisfied
1014	unsatisfied	A1014a	0.393	0.399	0.396	4.47§	unsatisfied	A1014b	0.401	0.390	0.396	4.47§	unsatisfied
1015	satisfied	A1015a	0.283	0.285	0.28	-1.42	satisfied	A1015b	0.285	0.289	0.29	-0.91	satisfied
1016	satisfied	A1016a	0.321	0.323	0.322	0.71	satisfied	A1016b	0.320	0.318	0.319	0.56	satisfied
1017	satisfied	A1017a	0.289	0.281	0.285	-1.17	satisfied	A1017b	0.281	0.285	0.283	-1.27	satisfied
1018	unsatisfied	A1018a	0.39	0.40	0.40	4.67§	unsatisfied	A1018b	0.40	0.41	0.41	5.18§	unsatisfied
1019	satisfied	A1019a	0.295	0.311	0.303	-0.25	satisfied	A1019b	0.306	0.295	0.300	-0.41	satisfied
1020	satisfied	A1020a	0.31	0.35	0.33	1.12	satisfied	A1020b	0.30	0.34	0.32	0.61	satisfied
1021	satisfied	A1021a	0.29	0.30	0.30	-0.41	satisfied	A1021b	0.30	0.30	0.30	-0.41	satisfied
1022	problematic	A1022a	0.343	0.343	0.343	1.78	satisfied	A1022b	0.351	0.351	0.351	2.18*	problematic
1023	satisfied	A1023a	0.278	0.278	0.278	-1.52	satisfied	A1023b	0.275	0.270	0.273	-1.78	satisfied
1024	satisfied	A1024a	0.310	0.310	0.310	0.10	satisfied	A1024b	0.308	0.310	0.309	0.05	satisfied
1027	satisfied	A1027a	0.274	0.275	0.274	-1.73	satisfied	A1027b	0.274	0.268	0.271	-1.88	satisfied
1028	satisfied	A1028a	0.3071	0.3100	0.3085	0.03	satisfied	A1028b	0.2985	0.3014	0.2999	-0.41	satisfied
1029	satisfied	A1029a	0.307	0.289	0.298	-0.51	satisfied	A1029b	0.310	0.317	0.314	0.30	satisfied
1030	satisfied	A1030a	0.293	0.293	0.293	-0.76	satisfied	A1030b	0.296	0.286	0.291	-0.86	satisfied
1031	satisfied	A1031a	0.296	0.304	0.300	-0.41	satisfied	A1031b	0.296	0.300	0.298	-0.51	satisfied
1032	satisfied	A1032a	0.301	0.304	0.303	-0.25	satisfied	A1032b	0.298	0.301	0.300	-0.41	satisfied
1033	satisfied	A1033a	0.293	0.298	0.296	-0.61	satisfied	A1033b	0.295	0.299	0.297	-0.56	satisfied
1034	satisfied	A1034a	0.297	0.305	0.301	-0.36	satisfied	A1034b	0.288	0.312	0.300	-0.41	satisfied
1036	satisfied	A1036a	0.31	0.30	0.31	0.10	satisfied	A1036b	0.30	0.29	0.30	-0.41	satisfied
1040	unsatisfied	A1040a	0.560	0.560	0.560	12.79§	unsatisfied	A1040b	0.560	0.560	0.560	12.79§	unsatisfied
1041	satisfied	A1041a	0.27	0.27	0.27	-1.93	satisfied	A1041b	0.31	0.31	0.31	0.10	satisfied
1042	unsatisfied	A1042a	6.9	6.9 7.2	7.0	339.70§	unsatisfied	A1042b	6.8	6.5 7.1	6.8	329.54§	unsatisfied
1043	unsatisfied	A1043a	0.457	0.474	0.466	8.02§	unsatisfied	A1043b	0.363	0.348	0.356	2.44*	problematic
1044	unsatisfied	A1044a	0.50	0.52	0.51	10.25§	unsatisfied	A1044b	0.43	0.42	0.43	6.19§	unsatisfied
1045	unsatisfied	A1045a	0.60	0.60	0.60	14.82§	unsatisfied	A1045b	0.35	0.35	0.35	2.13*	problematic
1046	problematic	A1046a	0.26	0.26	0.26	-2.44*	problematic	A1046b	0.29	0.29	0.29	-0.91	satisfied
Notes	Ammonia Nitrogen-a/b testing: the assigned value = 0.308 mg/L, the standard deviation for proficiency assessment of Ammonia Nitrogen -a/b = 0.0197. $\|z\| \leqslant 2.0$ means a satisfied result; $2.0 < \|z\| < 3.0$ means a problematic result, which is marked with * in the table; $\|z\| \geqslant 3.0$ means an unsatisfied result, which is marked with § in the table. The evaluation is “unsatisfactory”, when any result in the paired sample gets a $\|z\| \geqslant 3.0$.												