REPORT OF THE INTER-LABORATORY COMPARISON ON MERCURY AND CHLORIDE DETERMINATION IN WATER

2023

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Title:

Report of the Inter-laboratory Comparison on Mercury and Chloride Determination in Water (2023)

Authors:

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

Standards:

ISO 13528: 2015
Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparison

ISO/IEC 17043:2023
Conformity Assessment - General Requirements for the Competence of Proficiency Testing Providers

Keywords: Inter-laboratory Comparison, Mercury, Chloride, Water

Contents

Summary

The Inter-laboratory Comparison on determining Mercury and Chloride in Water (2023) 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 2023. It is a great honor to undertake this important activity for the fifth round, with full support from the Certification and Accreditation Administration of the People's Republic of China, CNCA (Approved as CNCA[2023]37) and the Alliance of International Science Organizations (ANSO).

This study was conducted to determine the levels of mercury and chloride 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 enhance 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.

Seventy-seven sets of testing sample were sent to 48 different laboratories across 14 countries. Finally, 56 sets of data, including 24 sets for mercury and 32 sets for chloride, were returned from 35 laboratories of 11 countries according to the due time of《Operation Instruction for Testing samples of the 5th Inter-Laboratory Comparison (2023)-Mercury/Chloride》, which were used for the statistical analysis of this report. Results submitted after the due time would be evaluated directly using the assigned value and the standard deviation obtained in this report.

According to the distribution of histogram graph, the classical statistical method was adopted to calculate the mean and standard deviation in this study. The mean indicated the assigned value and the standard deviation indicated standard deviation for proficiency assessment, which could be used to subsequently calculate z-scores.

For the mercury samples (-a and -b), z-scores within ± 2 were obtained by 62.5% of the reporting participants (corresponding to 15 of the total 24 participants).

For the chloride samples (-a and -b), z-scores within ± 2 were obtained by 75.0% of the reporting participants (corresponding to 24 of the total 32 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 fifth 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 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 December 2023 when testing samples were delivered to the laboratories for analysis, and lasted until May 2024 when all testing results were received. A total of 77 sets of testing samples were sent to 48 different laboratories across 14 countries. Finally, 35 laboratories across 11 countries (presented in Figure 1 and Table 1) have submitted the testing results within the due time. A draft report of the study was made available to the participants in July 2024.

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 excellent work and active support to this activity. We will continue this effort, and welcome suggestions from participants to further 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.

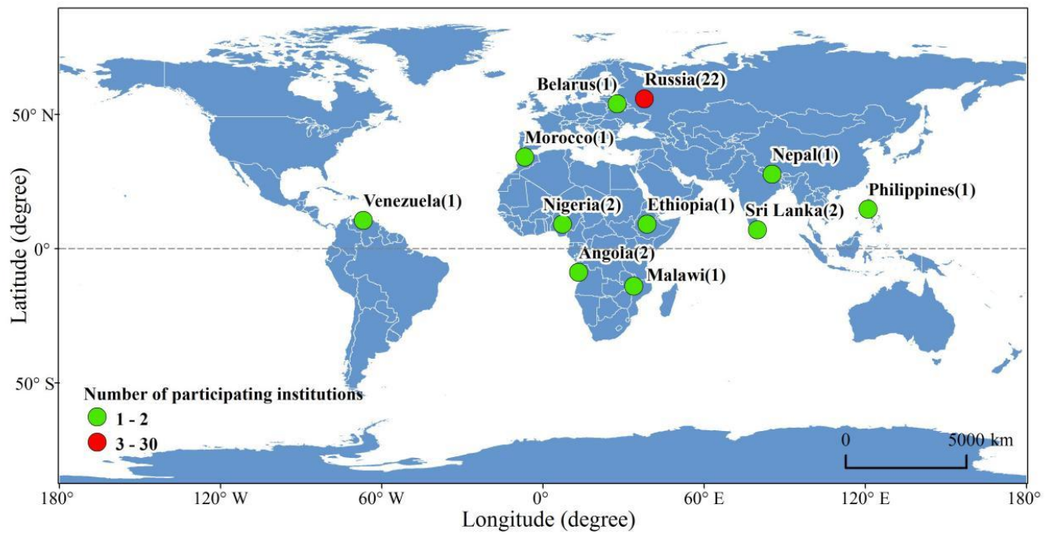

Figure 1 Distribution of the laboratories that reported results in the Inter-laboratory Comparison on Mercury and Chloride Determination in Water 2023

Table 1. Participants that reported results in the Inter-laboratory Comparison on Mercury and Chloride Determination in Water 2023 within the due time

Region	Countries
Asia（3）	Philippines, Sri Lanka, Nepal
Africa（5）	Ethiopia, Nigeria, Malawi, Morocco, Angola
South America（1）	Venezuela
Europe（2）	Russia, Belarus
Total	11 countries (35 laboratories)

Design and practical implementation

Study design and reporting of results

The measurement should be conducted according to 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 Mercury and Chloride Determination in Water 2023

Items	Testing Methods	Countries
Mercury	Atomic Absorption Spectroscopy (AAS)	Nepal (1), Morocco (1), Russia (14), Venezuela (1), Belarus (1)
	Inductively Coupled Plasma Mass Spectrometry（ICP-MS）	Ethiopia (1), Angola (1)
	Inductively Coupled Plasma Optical Emission Spectrometer（ICP-OES）	Sri Lanka (1), Russia (1)
	Electrochemical method	Russia (1)
	Spectrophotometry	Russia (1)
Chloride	Titration	Philippines (1), Malawi (1), Nigeria (2), Nepal (1), Ethiopia (1), Russia(4), Sri Lanka (2), Venezuela (1)
	Ion Chromatography	Morocco (1), Angola (2), Russia (5), Belarus (1)
	Capillary Electrophoresis	Russia (10)

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 party. 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 "Statistical methods for use in proficiency testing by interlaboratory comparison ISO 13528: 2015". According to the distribution frequency of the reported results, the distribution of histogram graph is unimodal and symmetric. Then, the classical statistical method could be adopted. By removing outliters after robust statistical methods, the mean ($\bar{x}$) and standard deviation (s) were calculated using the classical statistical method. The mean represents the assigned value(x_{pt}), and the standard deviation (s) represents the standard deviation for proficiency assessment(σ_{pt}). These values were denoted as $\bar{x}$ and s in Table 3, respectively. The value of "$\bar{x}$" and "s" were calculated according to the equation (1) and (2):

$$\bar{x} = \sum_{i=1}^{p} x_i / p \quad \text{.....(1)}$$

$$s = \sqrt{\sum_{i=1}^{p} \frac{(x_i - \bar{x})}{(p-1)}} \quad \text{.....(2)}$$

Where p=number of the remaining data; x_i=reported value; $\bar{x}$=mean of the remaining data; s= standard deviation of the remaining data.

Table 3. The mean and standard deviation of Mercury and Chloride Determination in Water in the Inter-laboratory Comparison 2023

Items	Mercury（μg/L）		Chloride（mg/L）	
	Mercury-a	**Mercury**-b	**Chloride**-a	**Chloride**-b
The mean ($\bar{x}$)	466	470	605	603
The standard deviation (s)	48.1	42.5	33.3	19.6

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 interlaboratory comparison ISO 13528:2015". Z-score was calculated according to the equation (3):

$$z = \frac{x_i - x_{pt}}{\sigma_{pt}} \quad \text{.....(3)}$$

where x_i is the reported value; x_{pt} is the assigned value (hereby the mean, $\bar{x}$); σ_{pt} is the standard deviation for proficiency assessment (hereby the 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.

Table 4. The acceptable range of testing results on Mercury and Chloride Determination in Water in the Inter-laboratory Comparison 2023

Items	Unit	Assigned value/The mean	$\|z\| \leqslant 2.0$	Minimum concentration	Maximum concentration
Mercury-a	**μg/L**	466	Satisfied	370	562
Mercury-b		470		385	555
Chloride-a	**mg/L**	605	Satisfied	538	672
Chloride-b		603		564	642

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 July 2024.

A certificate with analysis results will be provided to each laboratory that contributed to the study by the end of July 2024.

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 of the testing results for mercury and chloride in this activity.

For the samples of mercury, results from 24 laboratories were received. Three kinds of results were obtained including satisfied (15), unsatisfied (7) and problematic (2), accounting for 62.5% ,29.2% and 8.3% of the overall, respectively.

For the samples of chloride, results from 32 laboratories were received. Three kinds of results were reported including satisfied (24), unsatisfied (4) and problematic (4), accounting for 75.0%, 12.5% and 12.5% of the overall, respectively.

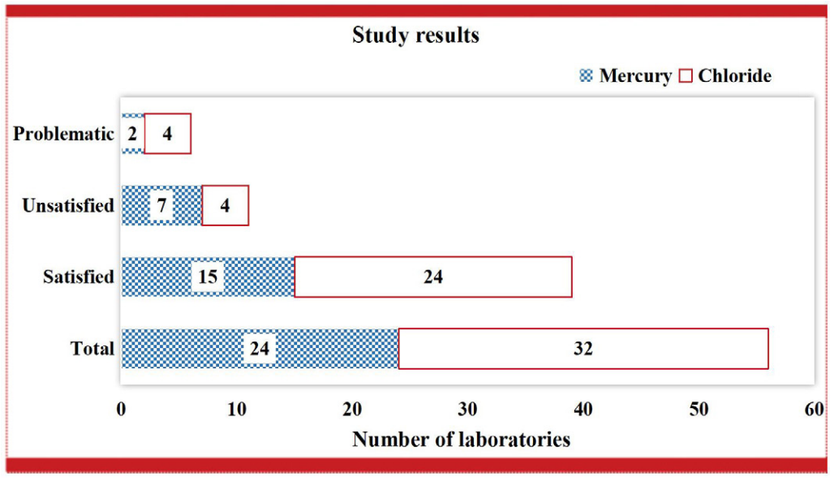

Figure 2 Comprehensive study of the testing results in this activity

Mercury

Figure 3 shows the study results of mercury testing. Among the 24 participating laboratories, 15 of them achieved satisfied results. Within the 7 laboratories who obtained unsatisfied results, 3 laboratories obtained z-scores over ±3.0, and one laboratory submitted the testing results with a z-score of 3.4 for mercury-a as unsatisfied result and with a z-score of 1.0 for mercury-b as satisfied result. In addition, three laboratories submitted testing results where the z-score of one sample fell between 2.0 and 3.0, classified as problematic result, while the z-score of another sample over ±3.0, regarding as unsatisfied result.

One laboratory reported both testing results with the z-score of 2.0 ～ 3.0 as problematic results. One laboratory submitted the testing results where the z-score of one sample was -2.6 as problematic result, and the z-score of another sample was -1.7 as satisfied result. The results of each participant are presented in Appendix F 1-1.

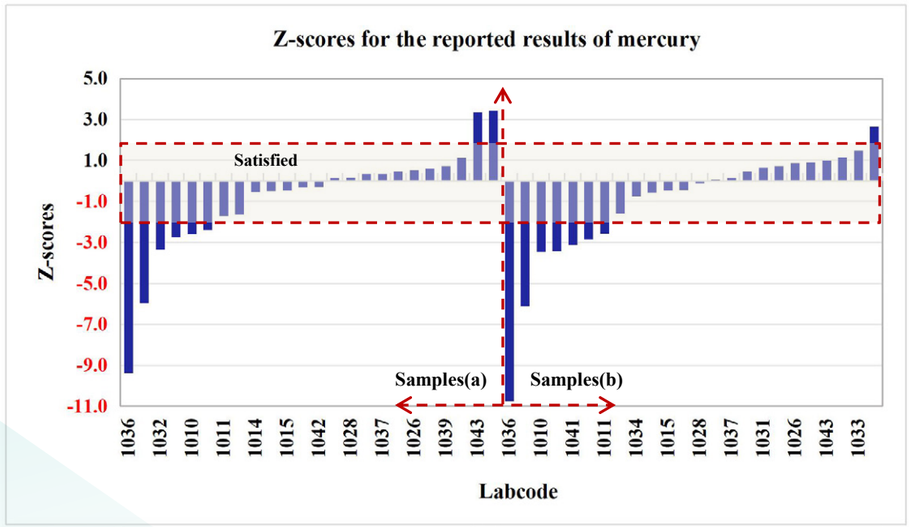

Figure 3 Study results of mercury testing

Chloride

Figure 4 shows the results of chloride measurement. It was observed that 24 of total participating laboratories achieved the satisfied results, while 4 laboratories obtained unsatisfied results and 1 of them obtained the z-scores over ±3.0. One laboratory submitted the testing results where the z-score of one sample was 3.6 as unsatisfied result, and the z-score of another sample was 1.6 as satisfied result, and one laboratory submitted the testing results with a z-score of 2.9 for chloride-a as problematic result and with a z-score of 4.9 for chloride-b as unsatisfied result. In addition, there is one laboratory that submitted only one testing result, which obtained the z-score of 9.2, classified as an unsatisfied result.

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

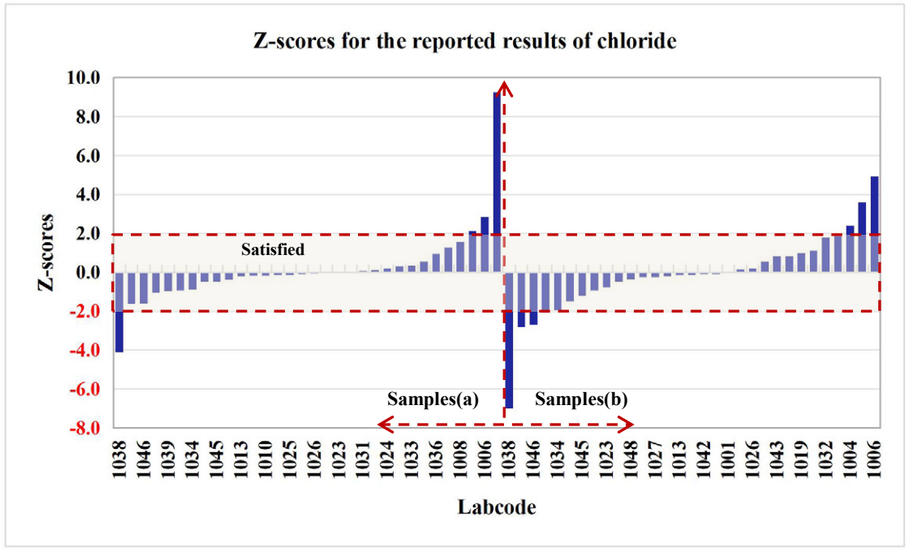

Figure 4 Study results of chloride testing

（Note: To reduce the impact of larger z score on the overall distribution of data, the z-scores of 1038 in this figure are 1/4 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 mercury in water, five kinds of techniques including AAS (18), ICP - MS (2), ICP - OES (2), electrochemical method (1) and spectrophotometry (1) were adopted. AAS was identified as the most commonly used technique for mercury analysis, which achieved a proportion of 61.1% as satisfied results in this study. Recently, ICP - MS and ICP - OES have become increasingly applied for metal analysis. Compared to those, when AAS is used for the measurement of mercury, no flame or electric heating is required to atomize the targeted element. In addition, the spectral lines of atomic absorption are very narrow because it only occurs in the principal lines, therefore the spectral interference is small, which consequently improve the testing sensitivity.

When analyzing the elements that can emit fluorescence and can be synthesized to gaseous hydrides at room temperature, like Hg, As, Se, Sb and so on, atomic fluorescence spectrometer (AFS) is another noteworthy technique with high sensitivity, in which hydrides is decomposed that makes the targeted elements release more ground-state atoms in orders magnitude.

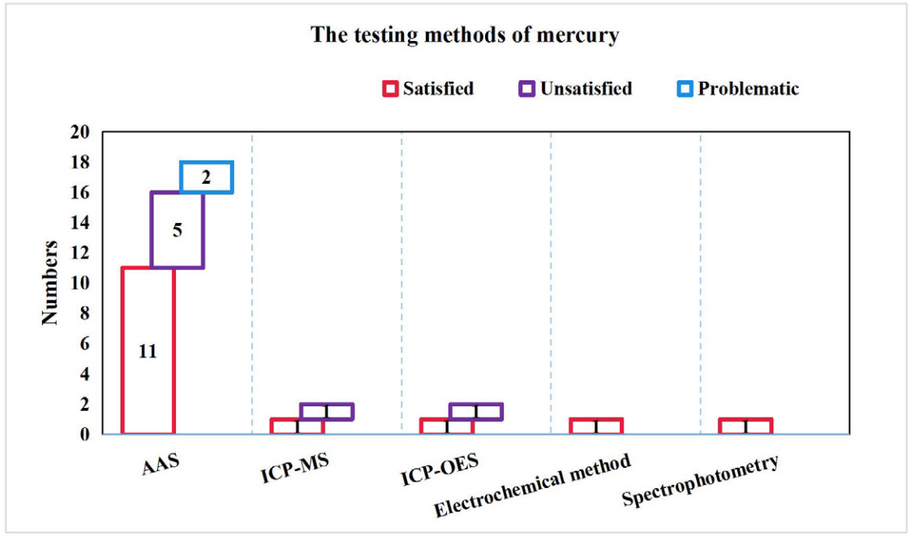

Figure 5 Category statistics of the testing methods for mercury

In terms of the determination of chloride, three kinds of techniques including titration (13), ion chromatography (9) and capillary electrophoresis (10) were adopted for testing. Titration is the predominant technique for chloride analysis, which achieved a proportion of 53.8% as satisfied results in this study. Ion Chromatography (IC) has become a preferred technique for determining anionic compounds due to its high sensitivity, good accuracy and simultaneous measurement of multi-component elements, which has been widely applied for testing chloride in water. In this study, a proportion of 88.9% as satisfied results was obtained for the laboratories using IC.

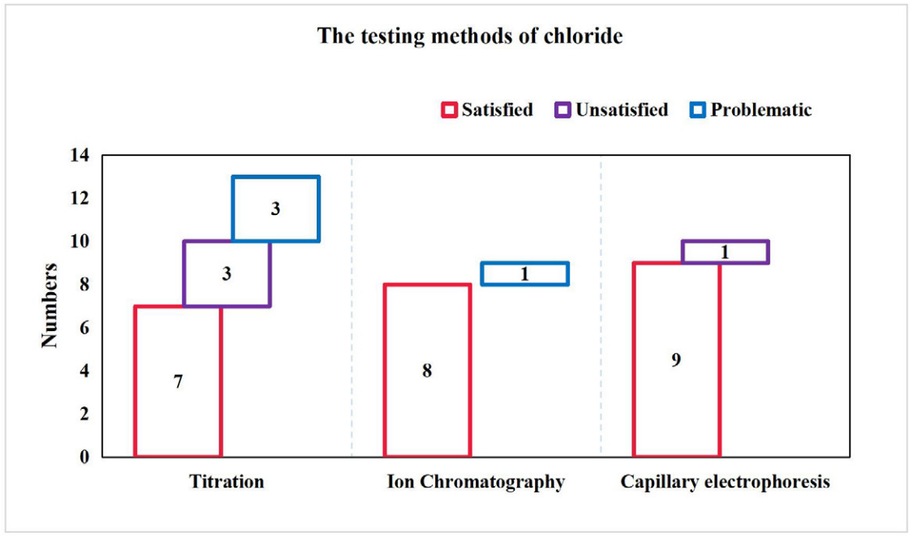

Figure 6 Category statistics of the testing methods for chloride

In conclusion，upon technical analysis and traceability of the original records, it was discovered that blank titration and reagent calibration were often overlooked when titration was utilized for water quality analysis, despite it being a widespread and convenient technique. The memory effect caused by the adsorption of mercury on the injection system when using ICP-MS/OES should be avoided. In case of ICP-MS analysis, the strength of internal standard should be monitored and its response value should be between 70% and 130% of that of the calibration curve.

Conclusion and suggestion

In the Inter-laboratory Comparison on Mercury and Chloride Determination in Water 2023, 35 laboratories across 11 countries submitted the testing results within the due time. The satisfaction rates for mercury and chloride in water were 62.5% and 75.0%, respectively. Atomic absorption spectrometry and titration were employed as the primary detection methods for mercury and chloride, respectively.

With the aim of improving the quality of results and making the inter-laboratory comparison more effective and useful for laboratories, a few recommendations are listed below:

Pay more attention to the integrity of the original records so that it can be traced back to the source when data deviates. Out of the 35 participants, 20 laboratories provided their original records along with the testing results, which was highly beneficial for technical traceability, especially in cases that problematic or unsatisfied results were identified.

Strictly implement the quality control measures required in the standard method, and ensure the accuracy of the data through a variety of quality control measures when necessary. Usually, when the number of samples is less than 20, it is recommended to arrange 2 blank samples for testing and the results of blank should be lower than the method detection limit, otherwise, the quality of experimental water and reagents, vessel cleanliness and the instrument performance should be checked and confirmed. In addition, we also recommend that laboratories pay more attention to the matching of the calibration curve and the measured concentration of samples.

Strengthen personnel technical capabilities and continuously ensure testing capabilities through proficiency testing and other methods. Under favorable conditions, it is advisable to replace manual operations with automated equipment to reduce personal error.

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. We 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. [2023] 37), the Alliance of International Science Organizations (ANSO) and the Federal Service for Accreditation (Rus Accreditation).

Appendix

Appendix A Document from CNCA

国家认证认可监督管理委员会

认秘函〔2023〕37 号

国家认监委秘书处关于开展水质和矿产国际检验检测机构能力验证活动的通知

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对国际贸易和“一带一路”建设的技术支撑作用，经研究，国家认监委决定在水质、矿产检验检测领域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，“水中汞和氯化物的测定”委托中国科学院生态环境研究中心水质分析实验室承担项目实施，“萤石中 CaF_2、SiO_2、TFe 的测定”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项目实施。

具备相关检测项目技术能力的国家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，需提交书面情况说明。具备相关检测项目技术能力的其他资质认定检验检测机构鼓励参加。

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。本次能力验证活动不收取费用。

二、检测标准和样品信息

（一）“水中汞和氯化物的测定”能力验证项目

水中汞的测定可采用 ISO 12846:2012《Water quality — Determination of mercury — Method using atomic absorption spectrometry (AAS) with and without enrichment》; ISO 17852:2006《Water quality — Determination of mercury — Method using atomic fluorescence spectrometry》; EPA Method 6010C: Inductively Coupled Plasma-Atomic Emission Spectrometry; EPA Method 200.15: Determination of Metals and Trace Elements in Water by Ultrasonic Nebulization Inductively Coupled Plasma-Atomic Emission Spectrometry; EPA Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry; GB/T 5750.6 — 2023 11.1《原子荧光法》; GB/T 5750.6 — 2023 11.2《冷原子吸收法》; GB/T 5750.6 — 2023 11.3《双硫腙分光光度法》; GB/T 5750.6 — 2023 11.4《电感耦合等离子体质谱法》; GB/T 7469 — 87《水质　总汞的测定　高锰酸钾—过硫酸钾消解法　双硫腙分光光度法》等标准方法。

水中氯化物的测定可采用 ISO 15682:2000《Water quality — Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection》; ISO 10304-1:2007《Water quality — Determination of dissolved anions by liquid chromatography of ions-Part 1: Determination of bromide，chloride，fluoride，nitrate，nitrite， phosphate and sulfate》; ISO 9297:1989《Water quality — Determination of chloride — Silver nitrate titration with chromate indicator (Mohr's method)》; EPA Method 9212: Potentiometric Determination of Chloride in Aqueous Samples with Ion-Selective Electrode; GB/T 5750.5 — 2023 5.1《硝酸银容量法》; GB/T 5750.5 — 2023 5.2《离子色谱法》; GB/T 5750.5 — 2023 5.3《硝酸汞容量法》; GB 11896 — 89《水质　氯化物的测定　硝酸银滴定法》等标准方法。

“水中汞和氯化物的测定”能力验证项目测试样品为水溶液，其中汞样品基质为 3%硝酸，氯化物样品基质为纯水，样品规格 20 毫升/瓶，每个检验检测机构随机发 1 个浓度水平样品 2 瓶。

（二）“萤石中 CaF_2、SiO_2、TFe 的测定”能力验证项目

“萤石中 CaF_2、SiO_2、TFe 的测定”可采用 ASTM E815-2017b《Standard Test Method for Determination of Calcium Fluoride in Fluorspar by EDTA Complexometric Titrimetry》; ASTM E463-2021《Standard Test Method for Determination of Silica in Fluorspar by Silico-Molybdate Visible Spectrophotometry》; GOST 7619.3-1981

《 Fluorite. Method for the determination of calcium fluoride content》; GOST 7619.4-1981《Fluorite. Method for the determination of silicon dioxide content》; GOST 7619.6-1981《Fluorite. Method for the determination of iron content》； GB/T 5195 系列萤石化学分析方法等标准。

测试样品为 1 种含量水平的萤石粉末样品，样品规格 15 克/瓶，用玻璃瓶包装，每个检验检测机构发放 1 瓶样品。

三、时间安排

（一）报名：2023 年 8-10 月；

（二）样品发放：2023 年 11-12 月；

（三）检测结果反馈：2024 年 1 月；

（四）初步技术分析报告：2024 年 4 月；

（五）结果发布：2024 年 6 月。

四、其他事宜

（一）报名参加的检验检测机构应填写报名表（见附件），通过发送电子邮件方式进行报名。

（二）联系方式

1.“水中汞和氯化物的测定”能力验证项目

中国科学院生态环境研究中心水质分析实验室

郑蓓，李红岩，+86-10-62849466，szfxsys@126.com

2.“萤石中 CaF_2、SiO_2、TFe 的测定”能力验证项目

北京中实国金国际实验室能力验证研究有限公司

朱生慧，唐凌天，+86-10-62185713，zsh@analysis.org.cn

附件：1. 水中汞和氯化物的测定能力验证报名表

2. 萤石中 CaF_2、SiO_2、TFe 的测定能力验证报名表

国家认监委秘书处

2023 年 8 月 18 日

（此件公开发布）

Appendix B Distribution Histogram of Returned Testing Results

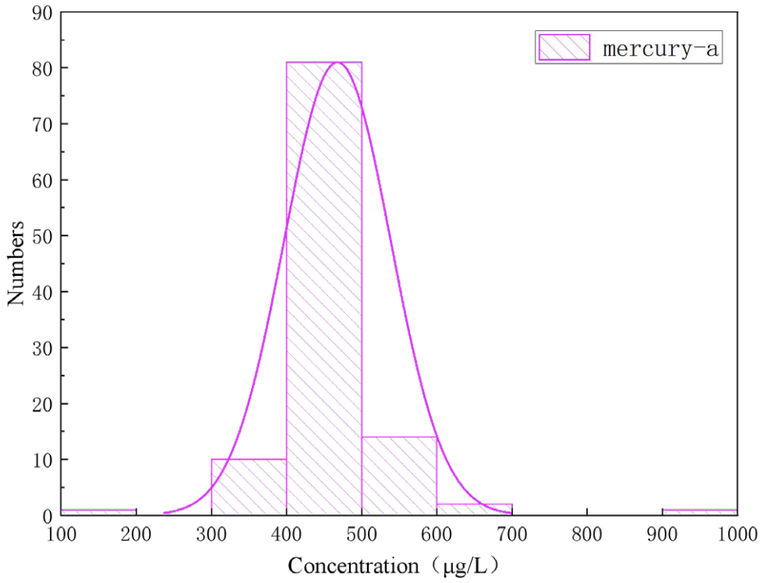

Figure B-1 Distribution histogram of testing results of mercury-a

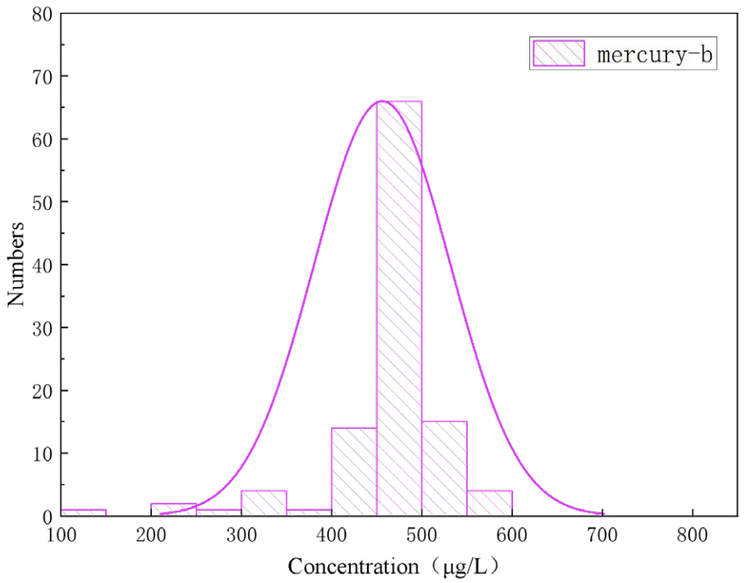

Figure B-2 Distribution histogram of testing results of mercury-b

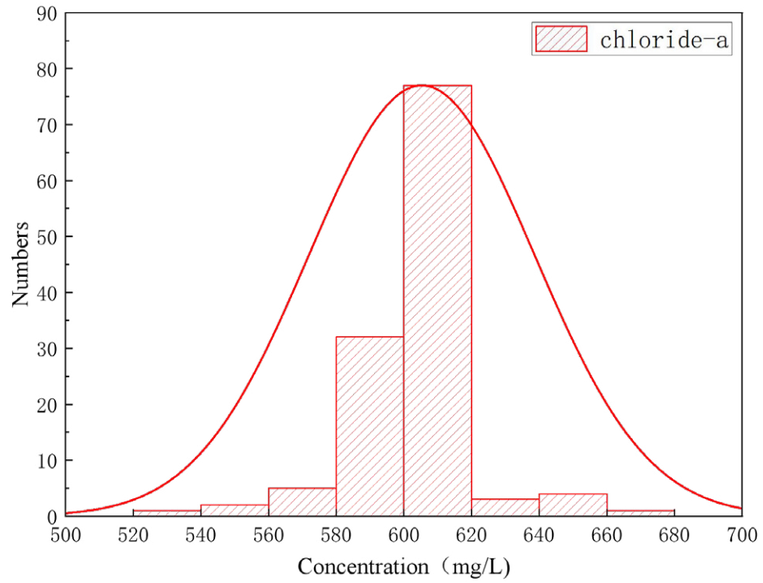

Figure B-3 Distribution histogram of testing results of chloride-a

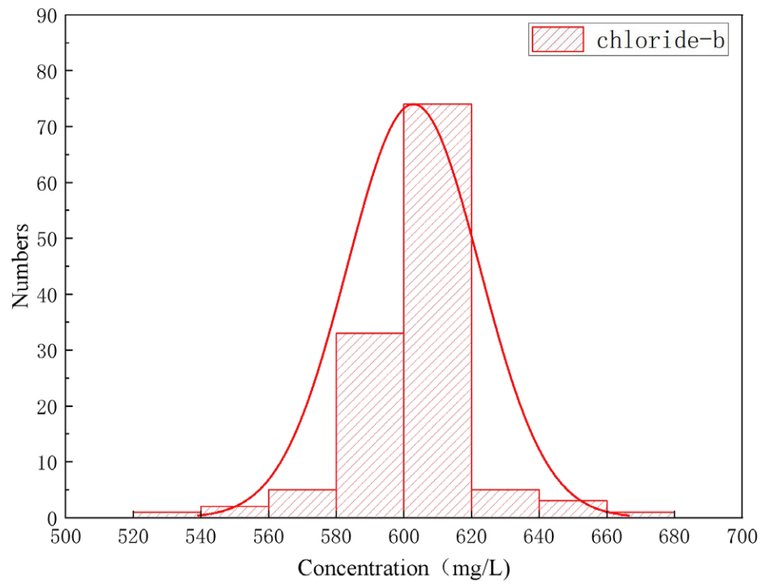

Figure B-4 Distribution histogram of testing results of chloride-b

Appendix C 1-1 Operation Instruction for Testing of Mercury

Operation Instruction for Testing Samples of the 5th Inter-Laboratory Comparison (2023)- Mercury

Participating laboratories:

The 5th Inter-laboratory Comparison on Water Quality Analysis (2023), which is focused on the Proficiency Testing of Mercury and Chloride 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 **1xxx**. 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 **Mercury 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 **M1xxxa** and **M1xxxb**. The matrix is 5% HCl The reference concentration of the Mercury in samples is between 100 μg/L~1000 μg/L (before 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 5% HCl 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 "**Mercury in water**" should be reported in μg/L with **the concentration before dilution** in the **Results Form for the 5th Inter-laboratory Comparison (2023).** 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 5th Inter-laboratory Comparison (2023)**, **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 and 3.2) 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: YU Miao
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 C 1-2 Operation Instruction for Testing of Chloride

Operation Instruction for Testing Samples of the 5th Inter-Laboratory Comparison (2023)-Chloride

Participating laboratories:

The 5th Inter-laboratory Comparison on Water Quality Analysis (2023), which is focused on the Proficiency Testing of Mercury and Chloride 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 **1xxx**. 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 **Chloride 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 **C1xxxa** and **C1xxxb**. The matrix is H_2O. The reference concentration of the Chloride in samples is between 100 mg/L~1000 mg/L (before 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 100 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 "**Chloride in water**" should be reported in mg/L with **the concentration before dilution** in the **Results Form for the 5th Inter-laboratory Comparison (2023)**. 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 5th Inter-laboratory Comparison (2023)**, **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 and 3.2) 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: YU Miao
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 D Testing Results for the 5th Inter-laboratory Comparison (2023)

Testing Results for the 5th Inter-laboratory Comparison (2023)

"Mercury"

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 5th Inter-laboratory Comparison (2023)

"Chloride"

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 E 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 F 1-1 Z-scores of Results for Mercury

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
1008	satisfied	M1008a	404.38	369.47	386.73	-1.6	satisfied	M1008b	400.08	420.13	402.23	-1.6	satisfied
1010	unsatisfied	M1010a	340	341	340.50	-2.6*	problematic	M1010b	322	323	322.50	-3.5§	unsatisfied
1011	problematic	M1011a	404.07	361.893	382.98	-1.7	satisfied	M1011b	338.73	381.16	359.95	-2.6*	problematic
1012	satisfied	M1012a	449	451	450	-0.3	satisfied	M1012b	449	452	451	-0.4	satisfied
1014	satisfied	M1014a	441	436	439	-0.6	satisfied	M1014b	476	468	472	0.0	satisfied
1015	satisfied	M1015a	432	454	443	-0.5	satisfied	M1015b	461	438	450	-0.5	satisfied
1026	satisfied	M1026a	492.2	488.2	490.2	0.5	satisfied	M1026b	507.2	507.0	507.1	0.9	satisfied
1027	satisfied	M1027a	478.6	465.7	472.2	0.1	satisfied	M1027b	482.8	534.2	508.5	0.9	satisfied
1028	satisfied	M1028a	472	476	474	0.2	satisfied	M1028b	460	470	465	-0.1	satisfied
1029	satisfied	M1029a	475	488	482	0.3	satisfied	M1029b	490	489	490	0.5	satisfied
1031	satisfied	M1031a	495.8	492.1	494	0.6	satisfied	M1031b	497.9	495.9	497	0.6	satisfied
1032	unsatisfied	M1032a	302	306	304	-3.4§	unsatisfied	M1032b	322	326	324	-3.4§	unsatisfied
1033	satisfied	M1033a	478	499	488	0.5	satisfied	M1033b	535	532	533	1.5	satisfied
1034	satisfied	M1034a	441	443	442	-0.5	satisfied	M1034b	437	440	438	-0.8	satisfied
1036	unsatisfied	M1036a	15.387	14.469	14.928	-9.4§	unsatisfied	M1036b	13.590	13.551	13.570	-10.7§	unsatisfied
1037	satisfied	M1037a	489	474	482	0.3	satisfied	M1037b	484	486	476	0.1	satisfied
1038	unsatisfied	M1038a	183	177	180	-5.9§	unsatisfied	M1038b	215	206	210	-6.1§	unsatisfied
1039	satisfied	M1039a	490	510	500	0.7	satisfied	M1039b	490	510	500	0.7	satisfied
1041	unsatisfied	M1041a	329	337	333	-2.8*	problematic	M1041b	338	336	337	-3.1§	unsatisfied
1042	satisfied	M1042a	451	453	452	-0.3	satisfied	M1042b	443	448	445	-0.6	satisfied
1043	unsatisfied	M1043a	583	673	628	3.4§	unsatisfied	M1043b	537	488	512	1.0	satisfied
1045	problematic	M1045a	349	351	350	-2.4*	problematic	M1045b	348	347	348	-2.9*	problematic
1046	unsatisfied	M1046a	629.8591	633.0421	631.4506	3.4§	unsatisfied	M1046b	581.9678	582.2557	582.1175	2.6*	problematic
1048	satisfied	M1048a	520	520	520	1.1	satisfied	M1048b	519	519	519	1.2	satisfied

Notes Mercury-a testing: the assigned value = 466 μg/L, the standard deviation for proficiency assessment of Mercury-a = 48.1. Mercury-b testing: the assigned value =470 μg/L, the standard deviation for proficiency assessment of Mercury-b = 42.5. $|z| \leq 2.0$ means a satisfied result; $2.0 < |z| < 3.0$ means a problematic result, which is marked with * in the table; $|z| \geq 3.0$ means an unsatisfied result, which is marked with § in the table. The evaluation is "unsatisfied", when any result in the paired sample gets a $|z| \geq 3.0$.

Appendix F 1-2 Z-scores of Results for Chloride

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
1001	satisfied	C1001a	603	605	604	0.0	satisfied	C1001b	602	606	604	0.1	satisfied
1003	unsatisfied	C1003a	1000	825	912.7	9.2§	unsatisfied	C1003b	/	/	/	/	/
1004	problematic	C1004a	650.000	645.000	647.500	1.3	satisfied	C1004b	650.000	650.000	650.000	2.4*	problematic
1006	unsatisfied	C1006a	700	700	700	2.9*	problematic	C1006b	700	700	700	4.9§	unsatisfied
1008	unsatisfied	C1008a	664.37	650.24	657.304	1.6	satisfied	C1008b	680.832	666.64	673.73	3.6§	unsatisfied
1010	satisfied	C1010a	599	600	599.50	-0.2	satisfied	C1010b	600	600	600.00	-0.2	satisfied
1011	satisfied	C1011a	599.7975	599.6787	599.74	-0.2	satisfied	C1011b	601.1103	600.9767	601.04	-0.1	satisfied
1012	satisfied	C1012a	599	599	599	-0.2	satisfied	C1012b	599	598	598	-0.3	satisfied
1013	satisfied	C1013a	598	599	598	-0.2	satisfied	C1013b	601	599	600	-0.2	satisfied
1017	satisfied	C1017a	571	571	571	-1.0	satisfied	C1017b	588	588	588	-0.8	satisfied
1019	satisfied	C1019a	623	623	623	0.5	satisfied	C1019b	623	650	622	1.0	satisfied
1023	satisfied	C1023a	610	600	605	0.0	satisfied	C1023b	586	590	588	-0.8	satisfied
1024	satisfied	C1024a	616	608	612	0.2	satisfied	C1024b	619	619	619	0.8	satisfied
1025	satisfied	C1025a	600.3	600.5	600.40	-0.1	satisfied	C1025b	592.2	595	593.60	-0.5	satisfied
1026	satisfied	C1026a	593.2	612.5	603	-0.1	satisfied	C1026b	586.2	627.7	607	0.2	satisfied
1027	satisfied	C1027a	603.5	600.2	601.9	-0.1	satisfied	C1027b	597.4	599.0	598.0	-0.3	satisfied
1029	satisfied	C1029a	606	606	606	0.0	satisfied	C1029b	605	606	606	0.2	satisfied
1031	satisfied	C1031a	608	605	607	0.1	satisfied	C1031b	612	615	614	0.6	satisfied
1032	problematic	C1032a	677	674	676	2.1*	problematic	C1032b	640	635	638	1.8	satisfied
1033	satisfied	C1033a	613	619	616	0.3	satisfied	C1033b	622	628	625	1.1	satisfied
1034	satisfied	C1034a	574	578	576	-0.9	satisfied	C1034b	553	574	565	-1.9	satisfied
1036	satisfied	C1036a	630.000	642.852	636.426	0.9	satisfied	C1036b	636.364	642.852	639.608	1.9	satisfied
1037	problematic	C1037a	550	552	551	-1.6	satisfied	C1037b	548	548	548	-2.8*	problematic
1038	unsatisfied	C1038a	56.63	56.62	57	-16.5§	unsatisfied	C1038b	52.60	52.61	53	-28.1§	unsatisfied
1039	satisfied	C1039a	573	573	573	-1.0	satisfied	C1039b	563	563	563	-2.0	satisfied
1041	satisfied	C1041a	589	589	589	-0.5	satisfied	C1041b	586	583	585	-0.9	satisfied
1042	satisfied	C1042a	616	614	615	0.3	satisfied	C1042b	600	602	601	-0.1	satisfied
1043	satisfied	C1043a	603	615	609	0.1	satisfied	C1043b	620	619	619	0.8	satisfied
1044	satisfied	C1044a	574.0	574.0	574.0	-0.9	satisfied	C1044b	574.0	574.0	574.0	-1.5	satisfied
1045	satisfied	C1045a	588.94	589.57	589.26	-0.5	satisfied	C1045b	579.08	579.99	579.54	-1.2	satisfied
1046	problematic	C1046a	547.0996	556.0687	551.5842	-1.6	satisfied	C1046b	544.8576	556.0687	550.4632	-2.7*	problematic
1048	satisfied	C1048a	592	592	592	-0.4	satisfied	C1048b	596	596	596	-0.4	satisfied
Notes	Chloride-a testing: the assigned value =605 mg/L, the standard deviation for proficiency assessment of Chloride-a =33.3. Chloride-b testing: the assigned value =603 mg/L, the standard deviation for proficiency assessment of Chloride-b = 19.6. $\|z\| \leq 2.0$ means a satisfied result; $2.0 < \|z\| < 3.0$ means a problematic result, which is marked with * in the table; $\|z\| \geq 3.0$ means an unsatisfied result, which is marked with § in the table. The evaluation is "unsatisfied", when any result in the paired sample gets a $\|z\| \geq 3.0$.												