Report of the Inter-laboratory Comparison on Nitrite and Lead in Water 2019

THE FIRST ROUND OF AN INTERNATIONAL STUDY

Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

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

Title:

Report of the Inter-laboratory Comparison on Nitrite and Lead in Water 2019

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Standards:

GB/T 27043-2012
Conformity Assessment-General Requirements for Proficiency Testing

JJF 1117.1-2012
Measurement Comparison of Chemical Quantity

JJF 1343-2012
General and Statistical Principles for Characterization of Reference Materials

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

CNAS-GL02：2014
Guidance on Statistic Treatment of Proficiency Testing Results and Performance Evaluation

Key words: Inter-laboratory Comparison, Nitrite, Lead, Water

Contents

Summary

The first round of the Inter-laboratory Comparison on Nitrite and Lead in Water was jointly conducted by Water Quality Analysis Laboratory, RCEES, CAS and Centre of Excellence for Water and Environment (CEWE), CAS-TWAS in 2019. We was supported by Certification and Accreditation Administration of People's Republic of China, CNCA.

This study included the determination of nitrite-N and lead in two different water items, which were both distributed to the participating laboratories at two concentration levels. The objectives of this inter-laboratory comparison study were

A. To offer a tool for quality assurance to the participating laboratories.

B. To assess the between laboratory reproducibility.

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

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

Thirty two test samples were sent to 19 different laboratories from 15 countries along the Belt and Road, with 29 sets of data returned from 17 laboratories of 13 countries. This report presents the reported results for 15 test samples of lead (each was prepared at two concentration levels) and 14 test samples of nitrite (each at two concentration levels).

The assigned concentration for each analyte in the test samples was determined by National Institute of Metrology, China. All values exceeding ±50% of the assigned concentrations were removed from the calculation. The consensus mean and the standard deviation (SD) were calculated from the remaining data, while this SD and the assigned concentration were used to subsequently calculate Z-scores because only 14/15 reported results for each analyte were collected and the outliers would contribute to a large degree.

For the samples of Lead-a, Z-scores within ±1 were obtained by 46.7% of the reporting participants, and Z-scores within ±2 were achieved by 60% of the participants (corresponding to 9 of the total 15 participants). For the samples of Lead-b, Z-scores within ±1 were obtained by 46.7% of the reporting participants, and Z-scores within ±2 were achieved by 66.7% of the participants (corresponding

to 10 of the total 15 participants).

For the samples of Nitrite-a (calculated in nitrite-N, hereby Nitrite-N-a), Z-scores within ±1 and ±2 were obtained by 64.3% of the reporting participants (corresponding to 9 of the total 14 participants). For the samples of Nitrite-b (calculated in nitrite-N, hereby Nitrite-N-b), Z-scores within ±1 were obtained by 57.1% of the reporting participants, and Z-scores within ±2 were achieved by 71.4% of the participants (corresponding to 10 of the total 14 participants).

Introduction

The analytical laboratories with skills and abilities are required to perform related measurements that are accredited according to ISO standards or some other related standards. Inter-laboratory Comparison is an effective way to improve the quality control system for the analytical laboratories through external measures, which is particularly becoming of increasing importance in the context of globalization of world economy.

This is the first round of the inter-laboratory comparison study on water quality analysis in the 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 of which are 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 between laboratory reproducibility on water quality analysis, and to provide a QA/QC tool for each participating laboratories to improve their performance.

This activity took place from July 2019 when the samples were shipped to the laboratories for analysis, and ended in October 2019 when all the reports with results were received. A draft report was made available to the participants till on March 2020.

Table 1 Participants that reported results in the first round of the Inter-laboratory Comparison on Nitrite and Lead in Water 2019

Region	Countries
Asia	Vietnam, Sri Lanka, Philippines, Burma, Nepal, Indonesia
Africa	Ethiopia, Nigeria, South Africa, Malawi, Tunisia
South America	Trinidad and Tobago, Venezuela
Total	13 countries (17 laboratories)

Finally, seventeen laboratories from 13 countries (presented in Table 1) along the Belt and Road submitted results, and thereby contributed to the study results.

Design and practical implementation

Study design and reporting of results

The analysis should be performed using the laboratories' own methods for instrumental analysis, their own quantification standards and quantification procedures. Table 2 showed the testing method from the participants that reported results.

Table 2 Testing methods from the participants in the first round of the Inter-laboratory Comparison on Nitrite and Lead in Water 2019

Items	Testing Methods	Countries
Pb	Atomic Absorption Spectroscopy(AAS)	Vietnam, Ethiopia, Trinidad and Tobago, Nepal, Malawi, Indonesia, Nigeria
	Spectrophotometry	Venezuela
	ICP	Sri Lanka, Philippines, Burma, South Africa, Tunisia
NO_2-N	Spectrophotometry	Vietnam, Ethiopia, Nigeria, Sri Lanka, Nepal, Trinidad and Tobago, Malawi, Indonesia, Venezuela
	Ion Chromatography(IC)	Sri Lanka, Tunisia

The laboratories were to report the concentration of each analyte and the uncertainty according to the Report forms.

Confidentiality

Each participating laboratory was given an exclusion laboratory code by coordinators. In the present report, the participants are presented in the tables and figures by their unique codes. The participants have access to their own code only, and laboratory codes were not revealed to any third parties. Both the testing samples distribution and results are transmitted by code. When received by the coordinators, the raw data from the laboratories were entered into a database for the report draft.

Statistical analysis

Outliers were defined as those values outside $\pm$ 50% of the assigned concentrations and were removed from the data set before the calculation of mean and SD, according to the equation (1) and (2):

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

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

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

Because limited number of laboratories reported results (n=14-15), we have chosen the assigned concentration of each analyte and SD for the calculation of Z-scores according to the equation (3):

$$z = \frac{x - X}{\hat{\sigma}} \quad \text{.....（3）}$$

Where x=reported value; X=assigned value, which was determined by National Institute of Metrology, China; $\hat{\sigma}$=SD.

$|z| \leq 2.0$ means a satisfied result; $2.0 < |z| < 3.0$ means a problematic result; $|z| \geq 3.0$ means an unsatisfied result.

The final report and certificate

The final report was drafted by the coordinators and published in March 2020.

A certificate of participation will be sent to each laboratory who has contributed to the results by the end of October 2019.

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:

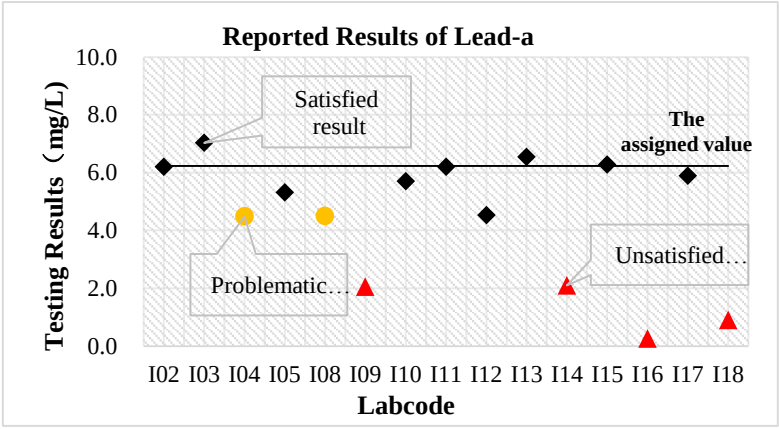
Dr. Hongyan LI, Senior engineer
Prof. Min YANG, Director
szfxsys@126.com; cas_twas@rcees.ac.cn

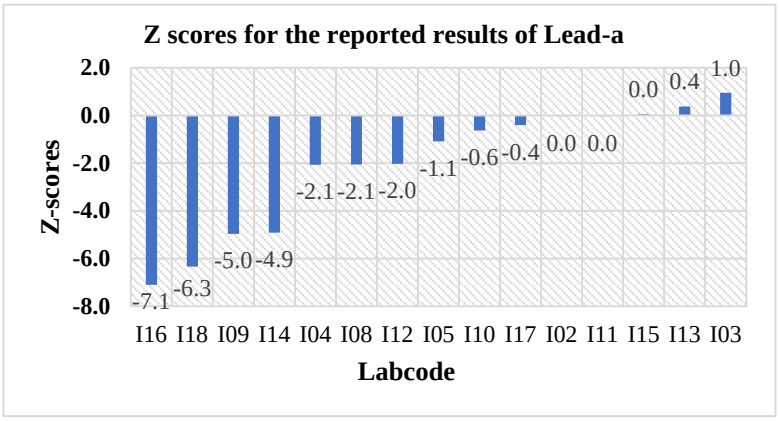
Results

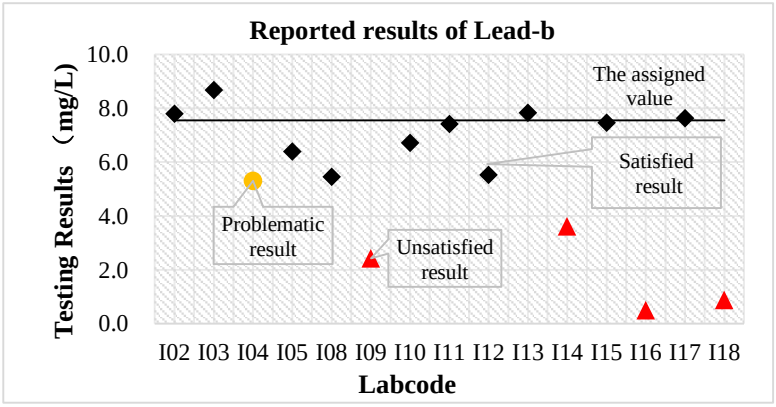
Lead

For the samples of lead, results from 15 laboratories were received. The assigned concentrations of lead are 6.23 mg/L (Lead-a) and 7.55 mg/L (Lead-b), and their uncertainties are 1.2% and 1.8%, respectively. SD was 0.841and 1.079 for Lead-a and

Lead-b respectively after outliers were removed.







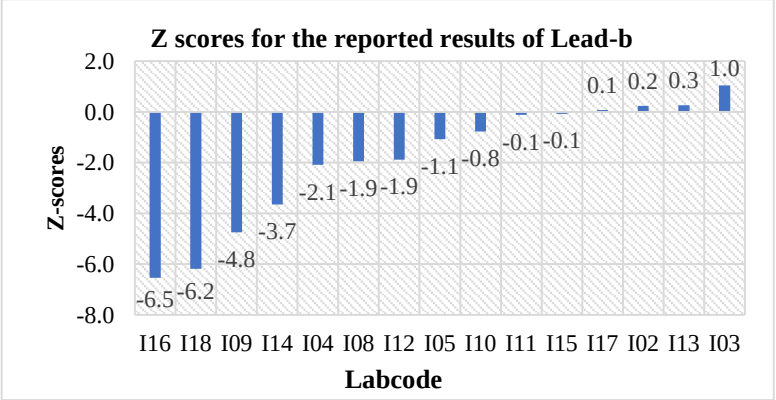


Figure 1 Study results of Lead (-a and -b)

Figure 1 showed the study results of lead (-a and -b). It could be seen that of the 15 participating laboratories, 9 achieved Z-scores within ±2 as satisfied results, and 4 obtained Z-scores over ±3 as unsatisfied results. In addition, one laboratory reported both testing results with Z-score of 2.1 as problematic result, and another laboratory submitted the testing results with Z-score of 2.1 for Lead-a and Z-score of 1.9 for Lead-b. Result of each participant were presented in Appendix 1.

In Table 3 Z scores for the reported results of lead are analyzed based on different testing methods. It could be found that atomic absorption spectrometer (AAS) and inductively coupled plasma optical emission spectrometer (ICP) were both popular technologies to determine lead in water, while 3 laboratories reported results using AAS method obtained unsatisfied Z scores. From the technical point of view, the AAS is a traditional instrument, but its linear range is narrow and thus higher abilities and skills is required. ICP can not only complete multi-elements determination at one time, but also make the technical operation more simple and reliable.

Only one laboratory determined the testing samples using spectrophotometric method, which is generally considered to be a rougher testing method compared to AAS and ICP. Fortunately, results of both Lead-a and Lead-b from this laboratory presented high scores. This clearly demonstrates that this laboratory performance is of good quality control.

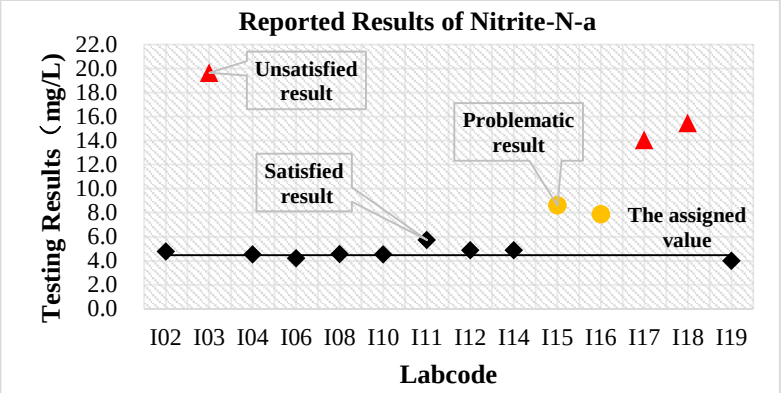
Table 3 Z scores for the reported results of Lead with different testing methods

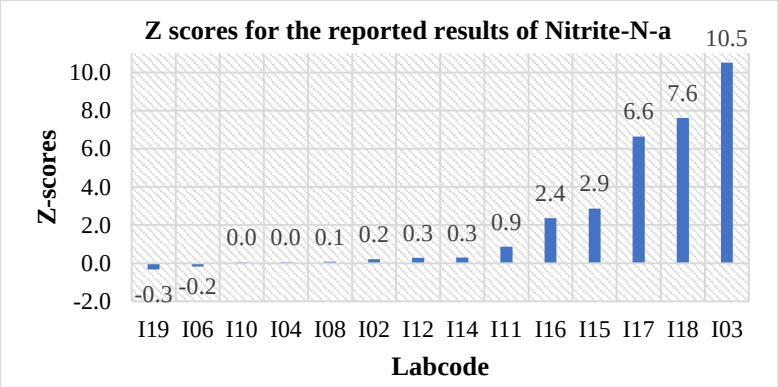
Testing Methods	Lab Number	|z| ≤2.0		2.0< |z| <3.0		|z| ≥3.0	
		Lab Number	Percentage %	Lab Number	Percentage %	Lab Number	Percentage %
Atomic Absorption Spectroscopy(AAS)	7	4	57.1	/	/	3	42.9
Spectrophotometry	1	1	100.0	/	/	/	/
ICP-OES	7	a-4 b-5	a-57.1 b-71.4	a-2 b-1	a-28.6 b-14.3	1	14.3

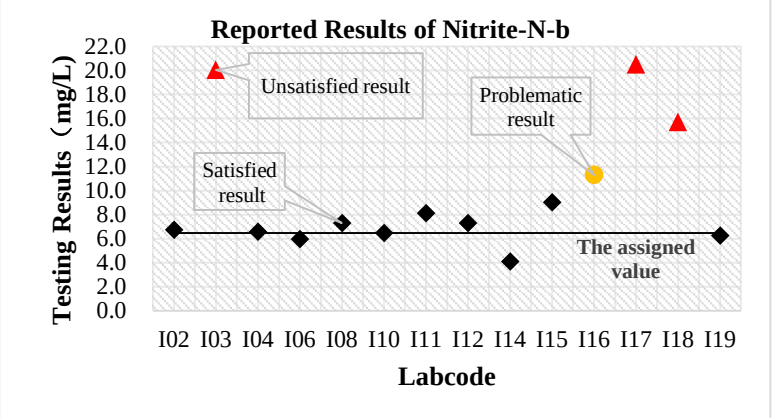
Nitrite

For the samples of nitrite, results from 14 laboratories were received. The assigned concentrations of nitrite-N are 4.46 mg/L (Nitrite-a) and 6.48 mg/L (Nitrite-b), and their uncertainties are 1.0% and 0.9%, respectively. SD was 1.445 and 1.767 for Nitrite-N-a and Nitrite-N-b respectively after outliers were removed.

Figure 2 showed the study results of nitrite-N (-a and -b). It could be seen that of







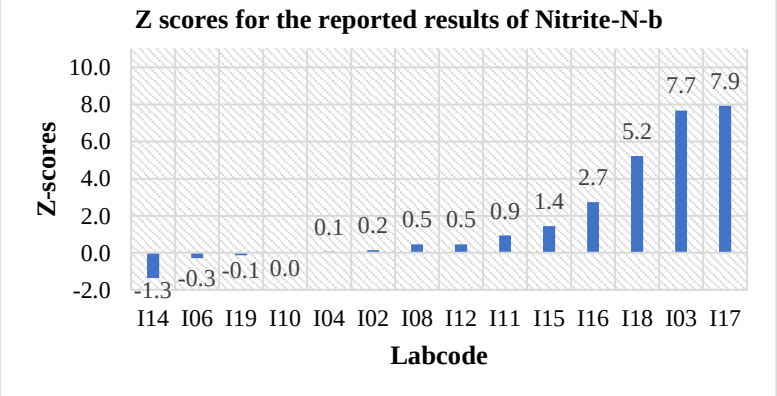


Figure 2 Study results of Nitrite-N (-a and -b)

the 14 participating laboratories, 9 achieved Z-scores within ±2 as satisfied results,

and 3 obtained Z-scores over ±3 as unsatisfied results. In addition, one laboratory submitted the testing results with Z-score of 2.9 for Nitrite-N-a as problematic result and Z-score of 1.4 for Nitrite-N-b as satisfied result. Another laboratory reported testing results with Z-score of 2.4 for Nitrite-N-a and with Z-score of 2.7 for Nitrite-N-b as problematic result. Result of each participant were presented in Appendix 2.

In Table 4 Z scores for the reported results of nitrite-N are analyzed based on different testing methods. Of the 12 laboratories reported testing results using the spectrophotometric method, 2 laboratories obtained unsatisfied Z scores. Ion Chromatography (IC) were employed by 2 laboratories, while one laboratory obtained unsatisfied Z scores for both Nitrite-N-a and Nitrite-N-b. IC and spectrophotometric method are both traditional way to determine nitrite-N, most participating laboratories could manage their analytical performance. It is recommended that the laboratories presented unsatisfied results carefully evaluated the factors that unfavorably may contribute to their performance.

Table 4 Z scores for the reported results of Nitrite with different testing methods

Testing Methods	Lab Number	|z| ≤2.0		2.0< |z| <3.0		|z| ≥3.0	
		Lab Number	Percentage %	Lab Number	Percentage %	Lab Number	Percentage %
Spectrophotometry	12	a-8 b-9	a-66.6 b-75.0	a-2 b-1	a-16.7 b-8.3	2	16.7
Ion Chromatography	2	1	a-50.0 b-50.0	/	/	1	50.0

Acknowledgement

The laboratories are acknowledged for their participation in this inter-laboratory comparison and in their interest in its overall objectives. All the individual analysts are acknowledged for their contributions to the results.

We thank Prof. Xiaohong WAN from the Water Environment Monitoring Assessment and Research Center, Ministry of Water Resources, China, for providing the standard solutions for this activity and Prof. Yanchun Tong from China NIL Research Center for Proficiency Testing for her valuable help of statistical analysis.

Appendix 1 Presentation of results for Lead

Lab code	Item	Testing method	Sample code	Conc 1 (mg/L)	Conc 2 (mg/L)	Mean values (mg/L)	z-score	Conclusion	Sample code	Conc 1 (mg/L)	Conc 2 (mg/L)	Mean values (mg/L)	z-score	Conclusion
I02	Pb	AAS	P02a	/	/	6.2	0.0	satisfied	P02b	/	/	7.8	0.2	satisfied
I03			P03a	7.04	7.02	7.03	1.0	satisfied	P03b	8.70	8.65	8.68	1.0	satisfied
I04		ICP	P04a	4.489	4.485	4.487	-2.1*	problematic	P04b	5.355	5.234	5.295	-2.1*	problematic
I05			P05a	5.406	5.219	5.313	-1.1	satisfied	P05b	6.331	6.461	6.396	-1.1	satisfied
I08			P08a	4.509	4.490	4.499	-2.1*	problematic	P08b	5.471	5.441	5.456	-1.9	satisfied
I09			P09a	2.049	2.047	2.048	-5.0§	unsatisfied	P09b	2.420	2.427	2.423	-4.8§	unsatisfied
I10		AAS	P10a	5.78	5.62	5.7	-0.6	satisfied	P10b	6.68	6.76	6.72	-0.8	satisfied
I11		Spectrophotometry	P11a	6.20	/	6.20	0.0	satisfied	P11b	7.42	/	7.42	-0.1	satisfied
I12		ICP	P12a	4.52.	4.521	4.522	-2.0	satisfied	P12b	5.530	5.520	5.525	-1.9	satisfied
I13			P13a	6.54	/	6.54	0.4	satisfied	P13b	7.83	/	7.83	0.3	satisfied
I14		AAS	P14a	2.010	2.182	2.096	-4.9§	unsatisfied	P14b	3.668	3.548	3.608	-3.7§	unsatisfied
I15			P15a	6.46	6.07	6.27	0.0	satisfied	P15b	7.10	7.84	7.47	-0.1	satisfied
I16			P16a	0.2455	0.2589	0.25195	-7.1§	unsatisfied	P16b	0.4955	0.5045	0.5000	-6.5§	unsatisfied
I17		ICP	P17a	5.875	5.905	5.890	-0.4	satisfied	P17b	7.605	7.665	7.635	0.1	satisfied
I18		AAS	P18a	0.865	0.936	0.901	-6.3§	unsatisfied	P18b	0.874	0.882	0.878	-6.2§	unsatisfied
Notes	Pb(a)Testing：assingned vale =6.23，standard deviation =0.841；Pb(a)Testing：assingned vale =7.55，standard deviation =1.079 $\|Z\| \leq 2.0$ means a satisfiedresult; $2.0 < \|Z\| < 3.0$ 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.													

Appendix 2 Presentation of results for Nitrite (N)

Lab code	Item	Testing method	Sample code	Conc 1 (mg/L)	Conc 2 (mg/L)	Mean values (mg/L)	z-score	Conclusion	Sample code	Conc 1 (mg/L)	Conc 2 (mg/L)	Mean values (mg/L)	z-score	Conclusion
I02	NO_2-N	Spectrophotometry	N02a	/	/	4.77	0.2	satisfied	N02b	/	/	6.75	0.2	satisfied
I03			N03a	19.78	19.51	19.65	10.5§	unsatisfied	N03b	20.05	20.05	20.05	7.7§	unsatisfied
I04		Ion Chromatography	N04a	4.5170	4.5216	4.5193	0.0	satisfied	N04b	6.5697	6.5773	6.5735	0.1	satisfied
I06		Spectrophotometry	N06a	4.10	4.30	4.20	-0.2	satisfied	N06b	6.04	5.91	5.98	-0.3	satisfied
I08			N08a	4.56	4.56	4.56	0.1	satisfied	N08b	7.30	7.30	7.30	0.5	satisfied
I10			N10a	4.433	4.6	4.517	0.0	satisfied	N10b	6.389	6.549	6.469	0.0	satisfied
I11			N11a	5.71	/	5.71	0.9	satisfied	N11b	8.13	/	8.13	0.9	satisfied
I12			N12a	4.87	4.87	4.87	0.3	satisfied	N12b	7.30	7.30	7.30	0.5	satisfied
I14			N14a	4.876	4.881	4.8785	0.3	satisfied	N14b	4.098	4.096	4.097	-1.3	satisfied
I15			N15a	8.52	8.68	8.60	2.9*	problematic	N15b	9.06	9.03	9.04	1.4	satisfied
I16			N16a	7.955	7.779	7.867	2.4*	problematic	N16b	11.422	11.202	11.312	2.7*	problematic
I17		Ion Chromatography	N17a	14.029	14.081	14.055	6.6§	unsatisfied	N17b	20.382	20.589	20.486	7.9§	unsatisfied
I18		Spectrophotometry	N18a	15.54	15.50	15.45	7.6§	unsatisfied	N18b	15.90	15.50	15.70	5.2§	unsatisfied
I19			N19a	4.0	4.0	4.0	-0.3	satisfied	N19b	6.5	6.0	6.25	-0.1	satisfied
Notes	NO_2-N(a)Testing：assingned vale=4.46，standard deviation =1.445；NO_2-N(b)Testing：assingned vale =6.48，standard deviation =1.767 $\|Z\| \leq 2.0$ 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. Lab N11 presented the testing results of nitrite not nitrite-N according to their original Report form, so we calculated nitrite into nitrite-N and then entered the database for statistical analysis.													

Appendix A Document from CNCA

国家认证认可监督管理委员会文件

国认监〔2019〕12号

认监委关于开展“玉米粉中玉米赤霉烯酮检测”和“水中铅和亚硝酸盐检测”能力验证活动的通知

中国计量科学研究院、中国科学院生态环境研究中心，各相关检验检测机构：

为充分发挥检验检测对“一带一路”倡议的技术支撑作用，提升“一带一路”沿线国家粮食、食品和水质安全检验技术保障能力，经研究，认监委决定开展“玉米粉中玉米赤霉烯酮检测”和“水中铅和亚硝酸盐检测”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”沿线国家检验检测技术机构共同参与，提升相关国家和地区检验检测机构的技术水平，为后续双边多边合作、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：

— 1 —

一、项目承担单位

本次能力验证计划由认监委组织，委托中国计量科学研究院承担“玉米粉中玉米赤霉烯酮检测”项目实施，委托中国科学院生态环境研究中心承担“水中铅和亚硝酸盐检测”项目实施。

二、检测标准和参加要求

玉米粉中玉米赤霉烯酮的检测标准为《食品中玉米赤霉烯酮的测定》（GB 5009.209—2016）；水中铅和亚硝酸盐的检测标准为《生活饮用水标准检验方法》（GB/T 5750—2006），《水质 65种元素的测定 电感耦合等离子体质谱法》（HJ 700—2014）或《水和废水监测分析方法》（第四版）。

已取得认监委颁发的检验检测机构资质认定证书，且具备食品中玉米赤霉烯酮、水中铅和亚硝酸盐检测项目资质认定的国家产品质检中心和相关食品复检机构应当报名参加本次能力验证；因故不能报名参加的，须向项目承担单位提交书面说明；认监委和项目承担单位将从报名单位中各选取 10 家国内检验检测机构参与本次能力验证。

项目承担单位负责联系和邀请“一带一路”沿线国家和其他发展中国家的检验检测机构参加本次能力验证。

三、能力验证样品信息

“玉米粉中玉米赤霉烯酮检测”能力验证项目测试样品为玉米全粉，样品规格 90 克/包，每个检验检测机构发 2 包，合计 180 克。

“水中铅和亚硝酸盐检测”能力验证项目测试样品为水溶液，样品规格 20 毫升（装于洁净安瓿瓶中），每个检验检测机构随机发 2 个浓度水平样品，每个浓度水平各 1 瓶。

四、时间安排

（一）报名：2019 年 7 月 25 日—8 月 30 日；

（二）样品发放：2019 年 9 月 1 日—9 月 5 日；

（三）检测结果反馈：2019 年 9 月 15 日前；

（四）初步技术分析报告：2019 年 10 月 30 日前；

（五）结果发布：2019 年 12 月前。

五、其他事宜

（一）本次能力验证计划不收取费用。

（二）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。

（三）联系方式

1.“玉米粉中玉米赤霉烯酮检测”能力验证项目

中国计量科学研究院

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2.“水中铅和亚硝酸盐检测”能力验证项目

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附件：1. 玉米粉中玉米赤霉烯酮检测能力验证报名表

2. 水中铅和亚硝酸盐检测能力验证报名表

国家认证认可监督管理委员会

认监委

2019 年 7 月 24 日

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