中国计量科学研究院
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CCQM-K128: Measurement of Heavy Metals and Organo-Tin in Leather Powder

Final Report

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[1]NIM [2]GLHK [3]INMETRO [4]NMIJ [5]NMIM [6]NIMT [7]UME [8]UNIIM [9]VNIIFTR [10]VNIIM

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Contents

Abstract

The CCQM-K128 key comparison was organized by the Inorganic Analysis Working Group (IAWG) of CCQM to test the abilities of national metrology institutes in measuring the heavy metals and organo-tin in leather matrix material or other similar organics content materials, and a pilot study CCQM-P163 was conducted in parallel with this key comparison. The National Institute of Metrology (NIM), P. R. China, acted as the coordinating laboratory. Eleven NIMs registered in the key comparison and ten of them reported their results. Eight elements (As, Cd, Pb, Co, Cu, Hg, Ni, Sb) in leather powder with the concentrations levels (30~100) mg/kg have been studied, different measurement methods (ID-ICPMS, ICP-MS, ICP-OES) and the microwave digestion method were used in Part A; for organo-tin comparison, tributyltin in leather powder with the concentration range (150-600) nmol/g has been studied, the results by different methods (ID-LC-ICPMS, ID-GC-ICPMS and LC-ICPMS) were comparable in Part B.

In short, good overlap of results was observed, and some problem of mercury and antimony determination had been discussed and summarized; all participants have shown their capabilities and gained experience through this comparison.

Introduction

For a long time, leather products are very popular with people. And leather industry is the main part of the national economy in extremely important position in many countries. But there is one severe thing leather industry will bring a lot of environmental problems, such as it was always adding many kinds of chemical reagents in leather processing, this can bring heavy metals and other harmful substances to environment. In response to leather safety issue, the accurate measurement of the heavy metals in leather is, therefore, particularly important. NMIs from different countries should establish their chemical metrology traceability system in this area, which include both measurement methods research and certain CRMs development. It should be noted that because the matrix of many leather is complex and the contents of some elements are so high to inference other elements in measurement, it still is a challenging task to measure the analytes with high accuracy and precision.

Based on above situation, National Institute of Metrology (NIM), P. R. China, proposed a key comparison focus on the measurements of heavy metals and organo-tin in leather powder at IAWG meeting April 2014, and it was approved by CCQM as CCQM-K128 (and a parallel pilot study CCQM-P163), the comparison include two parts with two samples: part A is for heavy metals, and part B is for organo-tin-tributyltin. All samples were prepared similar to the real industrial leather with the same tanning process. For part A, there were 10 laboratories registered in CCQM-K128; for part B, there were 3 laboratories registered.

The comparison is to ensure the comparable and traceable measurement results for heavy metals and organo-tin in leather products among the NMIs and other designated measurement bodies worldwide. The consequence of CCQM-K128 comparison is relatively successful overall. Only a few of the NMI’s results were deviated due to lack of experience in this field. After technical discussion, they also found that they had some problem in the measurement process. The results of CCQM-K128 are expected to cover the measurement capability and support CMC claiming in the leather materials and similar chemical industry products.

PART A

1. LIST OF PARTICIPANTS

10 institutes registered in CCQM-K128Part A.

The lists of all the participating institutes were shown in Table 1 according to the first letter of institutes’ name.

Table 1. List of participants

Institute	***Country***	***Contact Person***	***Analyst(s)***	Pb	Cd	As	Hg	Sb	Co	Cu	Ni
BIM Bulgarian Metrology Institute	Bulgarian	Veronika Ivanova	/	√	√	√	/	/	/	√	/
GLHK Government Laboratory	Hong Kong, China	Dr. WONG Yee-lok， Mr.TANG Po-on	Dr. LEE Ho-man, Dr. SZE Kwan-lok	√	√	√	/	/	/	/	/
INMETRO National Institute of Metrology, Quality and Technology	Brazil	Dr Marcelo de AlmeidaDomiguez, Dr Thiago Araujo, DrRodrigo Caciano de Sena	Rodrigo C. de Sena, Marcelo M. de Almeida, Thiago O. Araújo	√	√	√	√	/	√	√	√

NIM National Institute of Metrology, China	China	Ma Liandi, Wang Qian, Wei Chao	Wang Qian	√	√	√	√	√	√	√	√
NMIJ National Metrology Institute of Japan	Japan	Dr. Yanbei Zhu	Dr. Yanbei Zhu	√	√	√	√	√	√	√	√
NMIM National Metrology Institute of MALAYSIA	Malaysia	HASLINA ABD KADIR, NORLIZA BAHAROM	NORLIZA BAHAROM	√	√	√	√	/	/	/	√
NIMT National Institute of Metrology, Thailand	Thailand	Miss UsanaThiengmanee	Miss UsanaThiengmanee, Dr. NattikarnKaewkhomdee, Dr. SutthinunTaebunpakul, Dr. Charun Yafa	√	√	√	/	/	/	√	√
UME National Metrology Institute TURKEY	Turkey	Suleyman Z. Can	F. GoncaCoskun	√	√	√	/	/	/	/	/

UNIIM Ural Scientific Research Institute for Metrology	Russia	EgorSobina	Tatyana Tabatchikova	√	√	√	√	√	√	√	√
VNIIFTRI Russian Metrological Institute of Technical Physics and Radio	Russia	Dr Vladimir Dobrovolskiy, Mr Aleksey Stakheev	Vladimir Dobrovolskiy, AlekseiStakheev, Tatiana Stolboushkina, Dmitry Frolov	√	√	√	√	√	√	√	√

Note: BIM did not submit results due to some technical problems. VNIIFTRI did not submit result of Sb.

2. SAMPLE

Sample Preparation

The leather samples were prepared by *China Leather and Footwear Industry Research Institute*, and technical processes were quite matched with really goods. The sheep skin were adopted as raw materials, it were cleaned, degreased, depilated, soften, tanning, dyed, smashed and sieved to 0.2 mm～0.7 mm. In dyeing process, added an amount of heavy metal elements close to the target concentration by adjusting pH, temperature, time, the reagent formula and object concentration.

The samples for heavy metals measurement were blended in a mechanical blender for 2 hours. After pre-homogeneity investigated, about 4.5g leather powders were packaged into clean brown glass bottles with plastic inner lid and screw cap. After sterilized with cobalt-60 gamma radiation to 2.5 megarads, each unit was stored in shade and dry place.

Measurands

There are 8 heavy elements in leather powder for measurement arsenic, cadmium, lead, cobalt, copper, mercury, nickel and antimony respectively. Participants are encouraged to test all elements, but there are 3 elements arsenic, cadmium and lead are mandatory analytes and others are optional analytes. The approximate levels of the concentrations are (30~100) mg/kg.

Moisture Content Correction

The sample should be heated at 80°C in an oven for 6 hours and then cooled down to room temperature in desiccators before weighting. After that drying procedure, the sample can be used for heavy metals measurement. For more information, please refer to Annex A.

Homogeneity test

The homogeneity of heavy metals in the sample was tested by ICP-MS and ICP-OES two methods after microwave digestion of samples, and the sampling weight is about 0.2g. 16 bottles were selected randomly from 500 bottles, and two replicates from one bottle. The data were treated with an analysis of variance. The obtained between-bottle homogeneity standard deviations of 8 elements were all less than 1.6% (technical protocol). No statistically significant heterogeneity was found based on F test. ANOVA technique was applied to assess the between bottle heterogeneity and the standard uncertainty originated from the between bottle heterogeneity was calculated using the formula given below in accordance with ISO Guide 35:2017 [1]. The results are summarized in Table 2.

$$u_{bb} = \sqrt{\frac{MS_{within}}{n}} \cdot \sqrt[4]{\frac{2}{\nu_{MSwithin}}} \quad (1)$$

Where:

u_{bb} standard uncertainty due to between bottles heterogeneity

MS_{within} mean square of within bottles variance

$\nu_{MSwithin}$ degree of freedom of MS_{within}

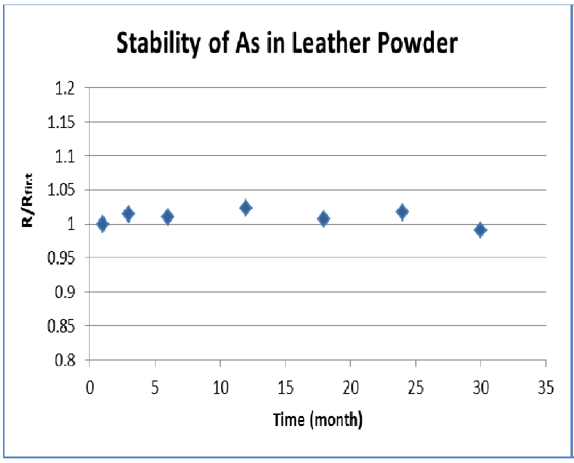
n number of subsample

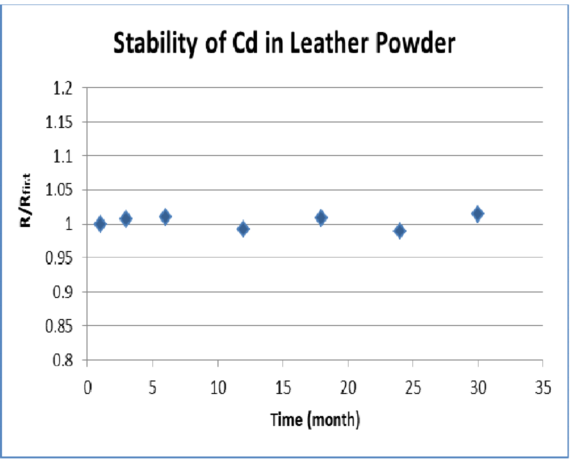
Table 2. Summary of homogeneity study results

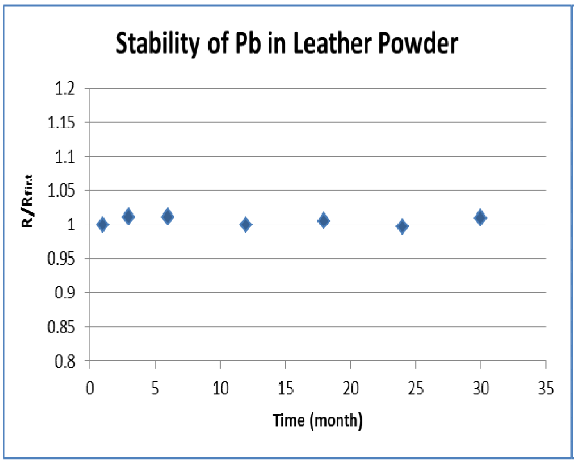
Measurand	ANOVA test on heterogeneity		Relative standard uncertainty due to between bottle heterogeneity, u_{bb}(%)
	F-statistics	Critical value	
As	0.67	2.35	0.74
Cd	1.71	2.35	0.88
Pb	1.55	2.35	0.97
Co	1.43	2.35	1.30
Cu	1.18	2.35	1.28
Hg	0.88	2.35	0.81
Ni	1.58	2.35	1.38
Sb	0.94	2.35	0.62

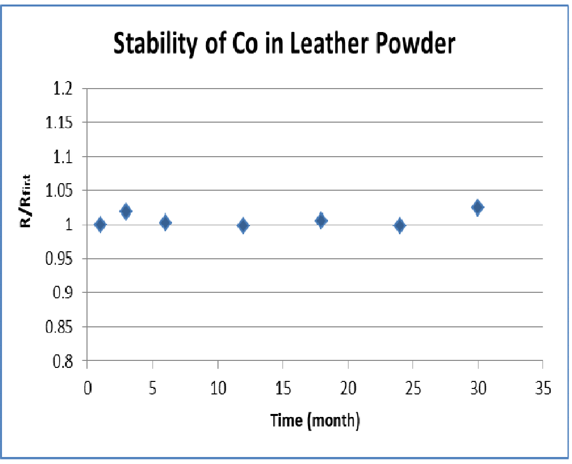
Stability monitoring

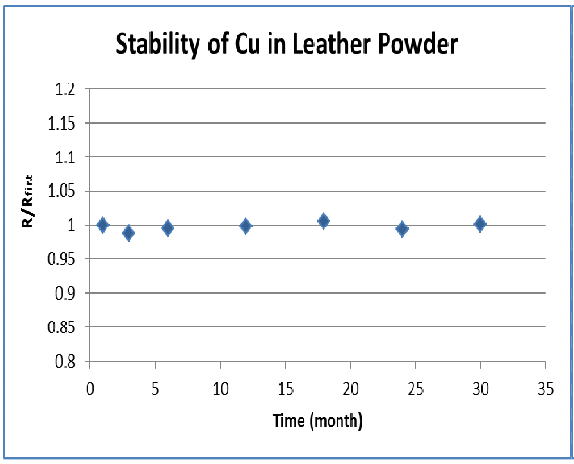
The stability of heavy metals in the sample was investigated more than 2 years by ICP-MS. The results show that the stability level of this leather material fit the objective of the comparison.

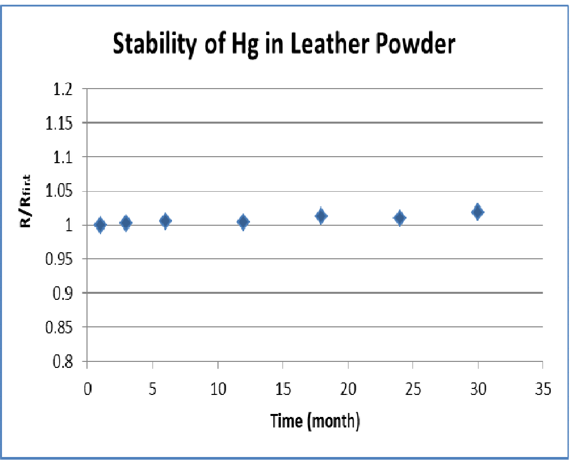

Stability of As in Leather Powder


Stability of Cd in Leather Powder


Stability of Pb in Leather Powder


Stability of Co in Leather Powder


Stability of Cu in Leather Powder


Stability of Hg in Leather Powder

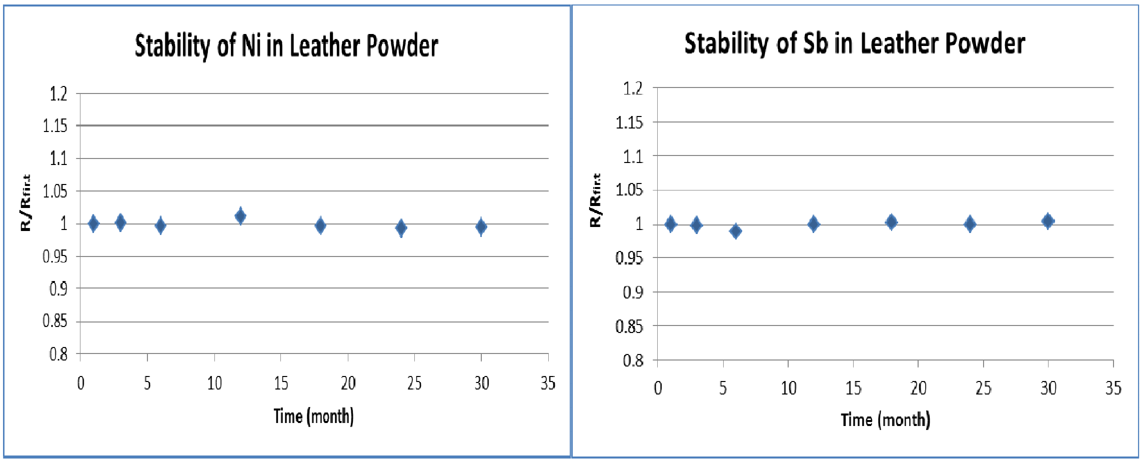


Fig.1. Stability Test

Distribution

Each participant received two numbered bottles with leather powder sample for heavy metal measurement. Participants were informed the date of samples dispatching.

3. INSTRUCTIONS TO PARTICIPANTS

The instruction relating to CCQM-K128 was sent to each participant by e-mail, which consisted of technical protocol, results report form and inorganic core capabilities tables.

To avoid any decomposition, the samples were recommended to be kept sealed until they are used. Each unit should be stored in its original bottle, capped tightly and not exposed to intense direct light and ultraviolet radiation. Before it is opened, it should be shaken for 5 min so that the material within is re-homogenized. Sample should be carefully opened for analysis in a short period of time to avoid contamination. The leather sample should be stored at room temperature (18-25) °C.

A Results Report was sent to the participants by email while the samples were dispatched. At least 6 independent determinations were requested to perform for each element. The results were reported as mass faction (mg/kg). Calculation of the uncertainty expressed as a combined standard uncertainty and an expanded uncertainty at 95% confidence. In order to allow a sufficient evaluation of the comparison, the report was required to include a detail description of the applied method of measurement, information about sample digestion and preparation, information about the reference material used for calibration.

All participants were requested to fill and submit their organic core capability tables to the coordinator. The relevant information was compiled and summarized in the Annex B.

4. METHODS OF MEASUREMENT

For this comparison, microwave assisted digestion, ICP-MS， ICP-OES and IDMS analytical techniques were adopted by the majority of participants. According to the Results Report submitted by each participant, the summary of measurement methods is shown in Table 3.

Table 3. Summary of the measurement methods

Institute	**Method**	**Microwave Digestion**	**Weight(g)**
GLHK	Gravimetric standard addition method	8mL HNO_3 +2mL 30% H_2O_2 +200uL HF	0.2
INMETRO	ICP-MS	4 mL HNO_3 + 2mL H_2O_2 + 0.05mL HF	0.3
NIM	Pb, Cd, Hg, Cu Ni, Sb (IDMS), As, Co (ICP-MS)	6mL HNO_3 + 40uL HF	0.2
NMIJ	Gravimetric standard addition ICP-QMS/QMS	3mL HNO_3 + 2mL H_2O_2 + 0.5mL HF	0.5
NMIM	Co, Ni, Hg, As (Standard Addition ICP-MS), Cd, Pb (IDMS)	5 mL 69% HNO_3 + 50uL HF	0.2
NIMT	Pb, Cd, Cu, Ni (IDMS), As(Gravimetric standard addition ICP-MS)	HNO_3+HF	0.1
TUBITAK UME	Cd,Pb (IDMS), As (ICP-MS)	HNO_3+HCl	0.1
UNIIM	Pb, Cd, Cu, Ni (IDMS), As, Hg, Sb, Co(ICPMS-addition method)	4 cm^3 HNO_3+1 cm^3 H_2O_2	0.1
VNIIFTRI	Pb, Cd, As, Hg, Co, Cu, Ni (IS+SA-ICP-OES)	4.5mL HNO_3 (65%)+ 1.5mL HCl (37%)	0.1

5. RESULTS AND DISCUSSION

5.1 General

The measurement results of 8 metals reported by each participant are summarised in Table 4~Table 11 respectively.

Table 4. Reported results of arsenic

Institute	Result (mg/kg)	n	*u* (mg/kg)	*k*	*U* (mg/kg)	Method
GLHK	**55.06**	**6**	**1.41**	**2**	**2.83**	ICP-MS（addition）

INMETRO	**50.8**	**7**	**1.35**	**2**	**2.7**	ICP-MS
NIM	**55.69**	**7**	**0.89**	**2**	**1.77**	ICP-MS
NMIJ	**54**	**4**	**1**	**2**	**2**	ICP-QMS/QMS(addition)
NMIM	**42.9208**	**5**	**4.0260**	**2**	**8.0521**	ICP-MS（addition）
NIMT	**54.4**	**8**	**1.2**	**2**	**2.5**	ICP-MS
UME	**52.4**	**8**	**1.4**	**2**	**2.9**	ICP-MS
UNIIM	**61.8**	**8**	**2.8**	**2**	**5.6**	ICP-MS（addition）
VNIIFTRI	**59.2**	**6**	**2.3**	**2**	**4.6**	ICP-OES
NIM	**56.35**	**7**	**1.19**	**2**	**2.39**	ICP-OES

Note: Blue font results are not calculated in KCRV, only be used in CMC.

Table 5. Reported results of cadmium

Institute	Result (mg/kg)	n	*U* (mg/kg)	*k*	*U* (mg/kg)	Method
GLHK	**66.72**	**6**	**1.78**	**2**	**3.55**	ICP-MS（addition）
INMETRO	**60.1**	**7**	**1.6**	**2**	**3.2**	ICP-MS
NIM	**64.83**	**7**	**1.00**	**2**	**1.99**	IDMS
NMIJ	**64.2**	**4**	**1.3**	**2**	**2.7**	ICP-QMS/QMS(addition)
NMIM	**58.4335**	**6**	**0.9372**	**2**	**1.8745**	IDMS
NIMT	**63.2**	**5**	**0.7**	**2**	**1.5**	IDMS
UME	**65.9**	**8**	**1.0**	**2**	**2.0**	IDMS
UNIIM	**66.1**	**8**	**2.3**	**2**	**4.5**	IDMS

VNIIFTRI	63.3	6	1.1	2	2.2	ICP-OES
NIM	64.37	7	1.22	2	2.44	ICP-OES
NIM	65.00	7	1.12	2	2.24	ICP-MS
NIMT	63.2	8	2.2	2	4.5	ICP-MS

Note: Blue font results are not calculated in KCRV, only be used in CMC.

Table 6. Reported results of lead

Institute	Result (mg/kg)	n	*u* (mg/kg)	*k*	*U* (mg/kg)	Method
GLHK	66.41	6	1.62	2	3.24	ICP-MS（addition）
INMETRO	61.0	7	1.3	2	2.6	ICP-MS
NIM	65.56	7	0.67	2	1.35	IDMS
NMIJ	62.9	4	1.1	2	2.3	ICP-QMS/QMS(addition)
NMIM	60.2695	6	1.2857	2	2.5714	IDMS
NIMT	62.3	5	0.8	2	1.6	IDMS
UME	65.4	8	1.1	2	2.2	IDMS
UNIIM	64.6	8	2.2	2	4.4	IDMS
VNIIFTRI	63.5	6	1.3	2	2.6	ICP-OES
NIM	64.17	7	0.86	2	1.72	ICP-OES
NIM	64.87	7	0.88	2	1.75	ICP-MS
NIMT	62.1	8	1.9	2	3.8	ICP-MS

Note: Blue font results are not calculated in KCRV, only be used in CMC.

Table 7. Reported results of cobalt

Institute	Result (mg/kg)	n	*u* (mg/kg)	*k*	*U* (mg/kg)	Method
INMETRO	**61.5**	**7**	**1.5**	**2**	**3**	ICP-MS
NIM	**63.52**	**7**	**0.96**	**2**	**1.92**	ICP-MS
NMIJ	**63.7**	**4**	**1.2**	**2**	**2.4**	ICP-QMS/QMS(addition)
NMIM	**47.4281**	**5**	**5.1346**	**2**	**10.2692**	ICP-MS（addition）
UNIIM	**63.8**	**8**	**2.6**	**2**	**5.2**	ICP-MS（addition）
VNIIFTRI	**62.4**	**6**	**1.0**	**2**	**2.0**	ICP-OES
NIM	**64.46**	**7**	**1.19**	**2**	**2.37**	ICP-OES

Note: Blue font results are not calculated in KCRV, only be used in CMC.

Table 8. Reported results of copper

Institute	Result (mg/kg)	n	*u* (mg/kg)	*k*	*U* (mg/kg)	Method
INMETRO	**56.3**	**7**	**1.4**	**2**	**2.7**	ICP-MS
NIM	**61.37**	**7**	**0.56**	**2**	**1.12**	IDMS
NMIJ	**60.0**	**4**	**1.2**	**2**	**2.4**	ICP-QMS/QMS(addition)
NIMT	**59.8**	**5**	**0.8**	**2**	**1.6**	IDMS
UNIIM	**61.3**	**8**	**2.0**	**2**	**4.0**	IDMS
VNIIFTRI	**58.0**	**6**	**1.1**	**2**	**2.2**	ICP-OES
NIM	**60.73**	**7**	**1.18**	**2**	**2.35**	ICP-MS
NIM	**61.67**	**7**	**1.39**	**2**	**2.78**	ICP-OES

NIMT	**59.9**	**8**	**1.3**	**2**	**2.6**	ICP-MS

Note: Blue font results are not calculated in KCRV, only be used in CMC.

Table 9. Reported results of mercury

Institute	Result (mg/kg)	n	*u* (mg/kg)	*k*	*U* (mg/kg)	Method
INMETRO	**51.4**	**6**	**3**	**2**	**6**	ICP-MS
NIM	**67.37**	**7**	**1.44**	**2**	**2.88**	IDMS
NMIJ	**68.0**	**4**	**1.5**	**2**	**2.7**	ICP-QMS/QMS(addition)
NMIM	**48.6205**	**5**	**3.1208**	**2**	**6.2416**	ICP-MS（addition）
UNIIM	**70.3**	**8**	**2.7**	**2**	**5.5**	ICP-MS（addition）
VNIIFTRI	**62.1**	**6**	**1.5**	**2**	**3.0**	ICP-OES
NIM	**66.75**	**7**	**1.92**	**2**	**3.83**	ICP-OES
NIM	**66.99**	**7**	**1.99**	**2**	**3.98**	ICP-MS

Note: Blue font results are not calculated in KCRV, only be used in CMC.

Table 10.Reported results of nickel

Institute	Result (mg/kg)	n	*u* (mg/kg)	*k*	*U* (mg/kg)	Method
INMETRO	**62.1**	**7**	**1.55**	**2**	**3.1**	ICP-MS
NIM	**64.32**	**7**	**0.81**	**2**	**1.62**	IDMS
NMIJ	**63.1**	**4**	**1.5**	**2**	**2.9**	ICP-QMS/QMS(addition)
NMIM	**46.1366**	**5**	**6.2174**	**2**	**12.4348**	ICP-MS（addition）
NIMT	**62.6**	**5**	**0.7**	**2**	**1.5**	IDMS

UNIIM	**65.03**	**8**	**2.00**	**2**	**4.00**	IDMS
VNIIFTRI	**61.8**	**6**	**1.1**	**2**	**2.2**	ICP-OES
NIM	**64.63**	**7**	**1.22**	**2**	**2.44**	ICP-OES
NIM	**64.69**	**7**	**1.07**	**2**	**2.15**	ICP-MS
NIMT	**63.6**	**8**	**1.4**	**2**	**2.9**	ICP-MS

Note: Blue font results are not calculated in KCRV, only be used in CMC.

Table 11.Reported results of antimony

Institute	Result (mg/kg)	n	*u* (mg/kg)	*k*	*U* (mg/kg)	Method
NIM	**81.82**	**7**	**1.01**	**2**	**2.01**	IDMS
NMIJ	**80.4**	**4**	**1.1**	**2**	**2.2**	ICP-QMS/QMS(addition)
UNIIM	**70.5**	**8**	**2.7**	**2**	**5.3**	ICP-MS（addition）
NIM	**83.03**	**7**	**1.56**	**2**	**3.12**	ICP-MS
NIM	**84.19**	**7**	**1.60**	**2**	**3.19**	ICP-OES

Note: Blue font results are not calculated in KCRV, only be used in CMC.

Fig.2~Fig.9 shows the distribution for the results of CCQM-K128 for each measurand respectively. Error bar indicate the standard uncertainty (u) as reported. The red dot data show IDMS results, the blue dot data show ICP-MS results and the green dot data show ICP-OES results.

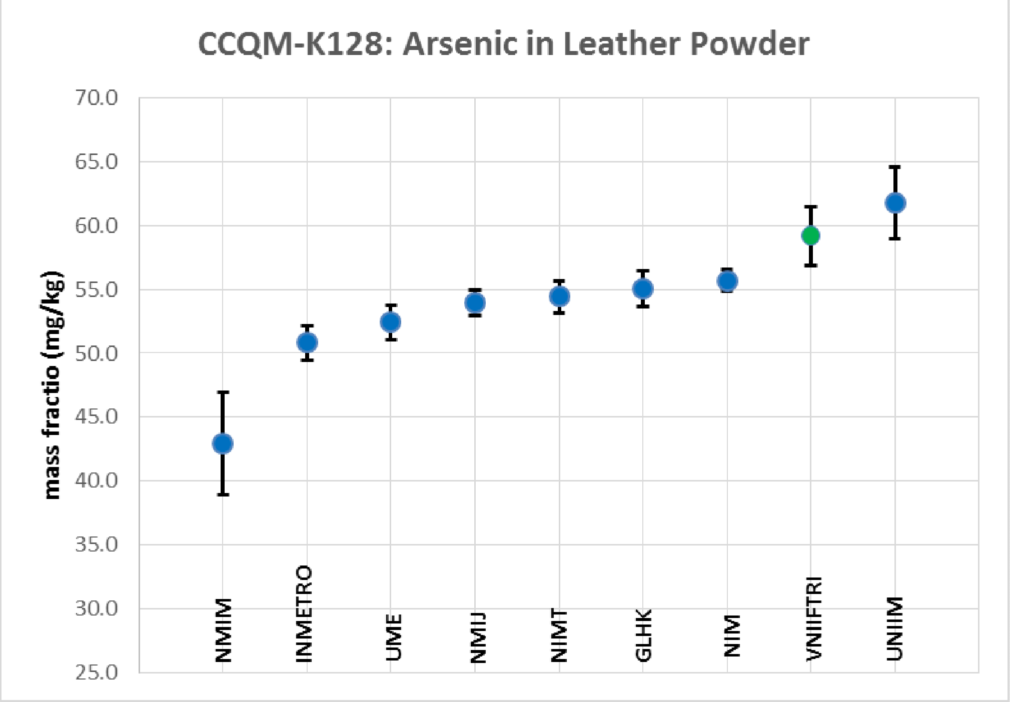


Fig.2. All results of Arsenic in Leather Powder

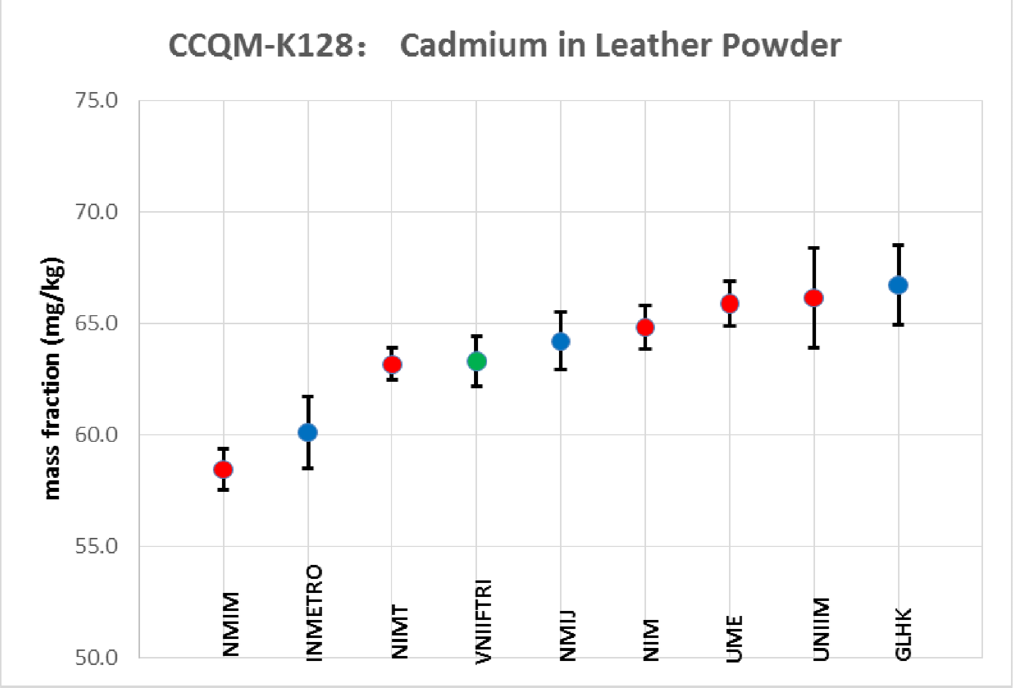


Fig.3. All results of Cadmium in Leather Powder

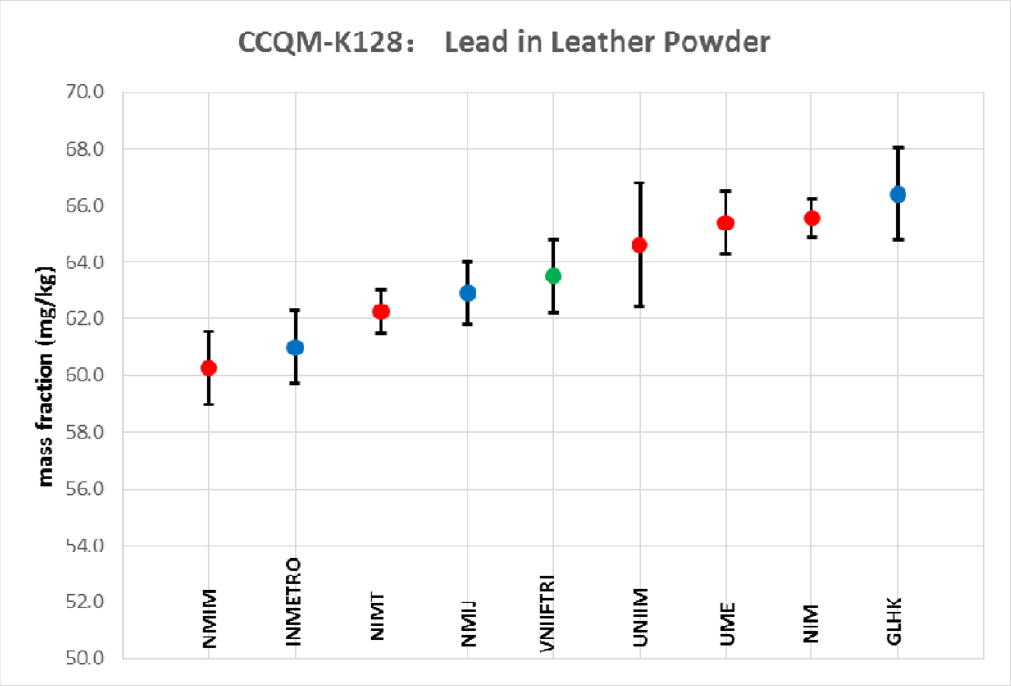


Fig.4. All results of Lead in Leather Powder

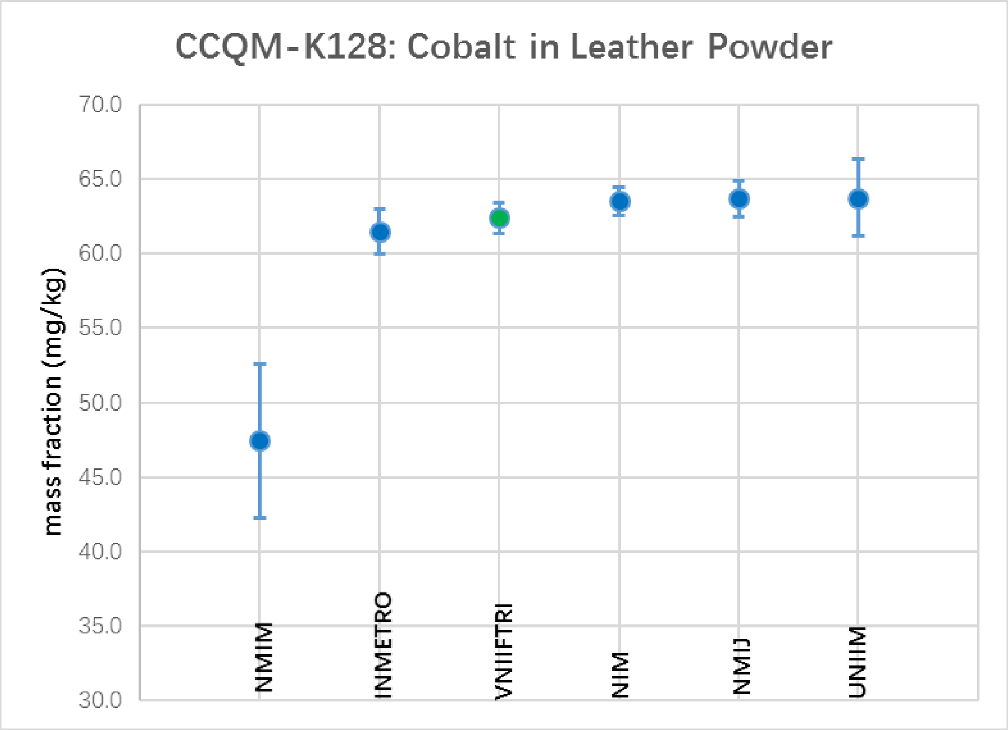


Fig.5. All results of Cobalt in Leather Powder

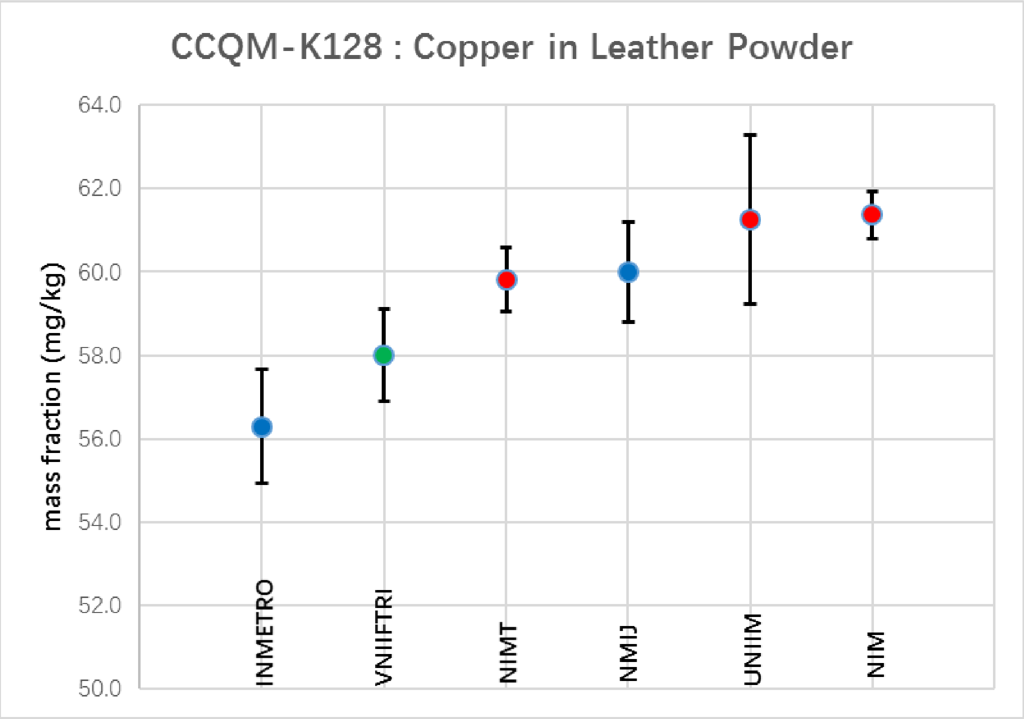


Fig.6. All results of Copper in Leather Powder

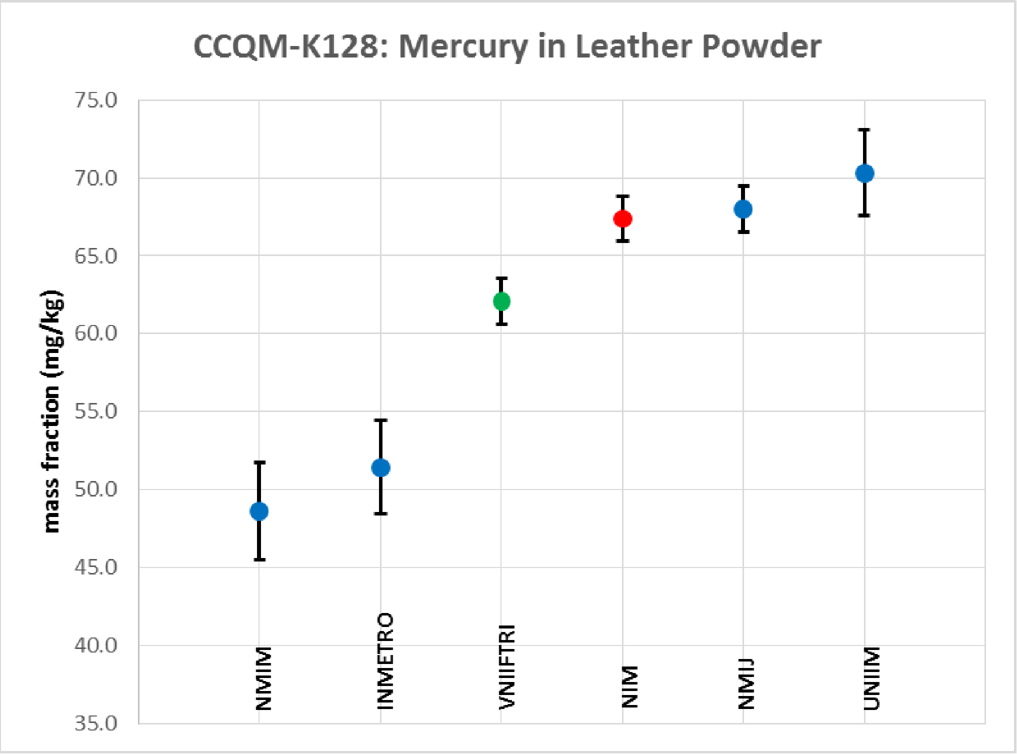


Fig.7. All results of Mercury in Leather Powder

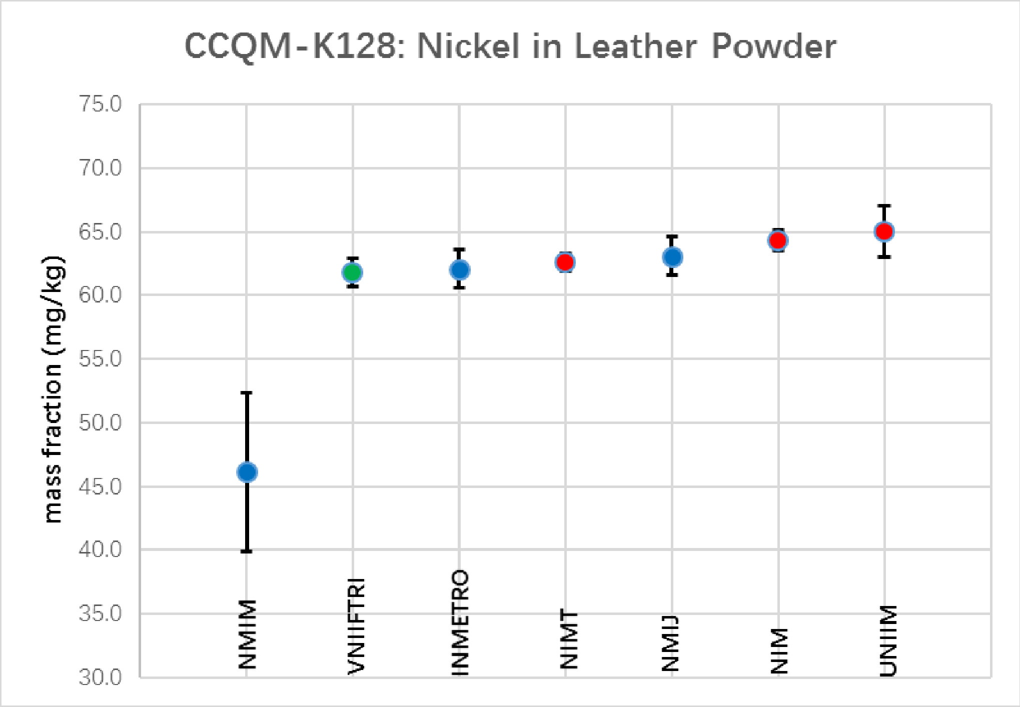


Fig.8. All results of Nickel in Leather Powder

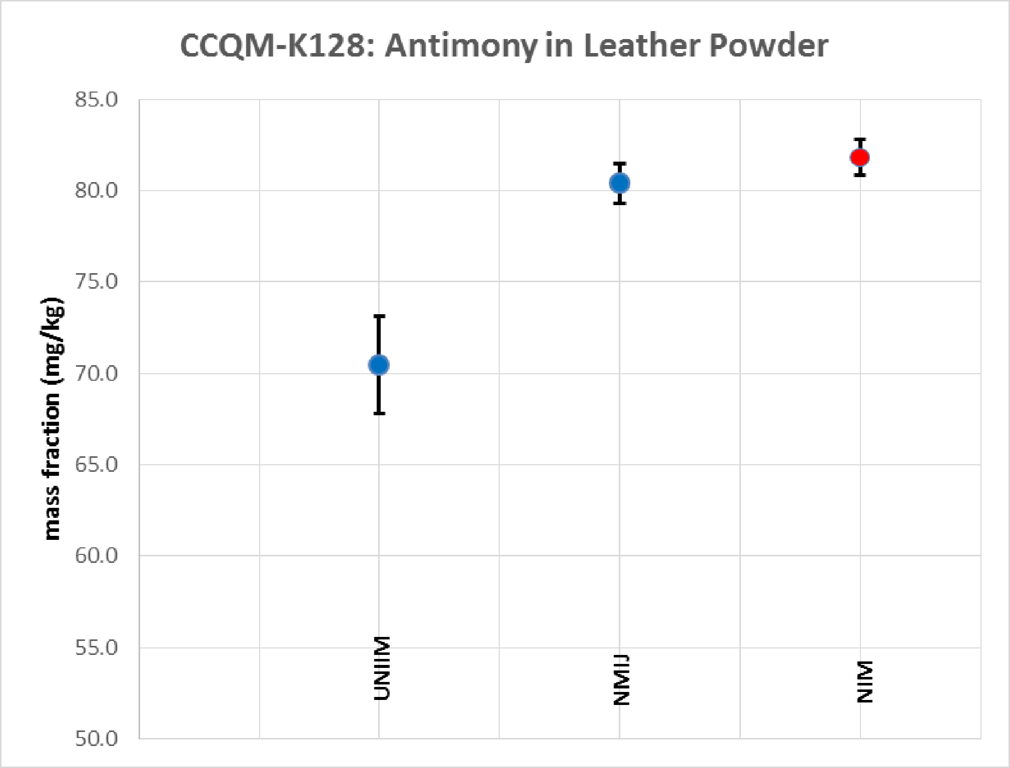


Fig.9. All results of Antimony in Leather Powder

5.2 Screening the data for consistency and anomalous values

According to the CCQM Guidance Note [2], robust estimate of location $\hat{\mu}$ and dispersion $\hat{\sigma}$, are hence used to detect possible outliers, i.e. values would be considered as extreme when outside $\hat{\mu} \pm 2\hat{\sigma}$ (corresponding to approximately 95 % confidence). The result data reported by each participant was detected by the rule, and the outlier testing results was shown in Table 12.

Table 12. Summary of outlier testing results using robust estimates

Measurand	Robust mean $\hat{\mu}$ (mg/kg)	Robust SD dispersion $\hat{\sigma}$ (mg/kg)	$\hat{\mu} - 2\hat{\sigma}$ (mg/kg)	$\hat{\mu} \pm 2\hat{\sigma}$ (mg/kg)	Institutes found with suspected extreme results
As	54.30	3.96	46.38	62.22	NMIM, VNIIFTRI, UNIIIM
Cd	62.80	2.87	57.05	68.55	NMIM, INMETRO
Pb	63.55	2.41	58.73	68.37	/
Co	62.69	1.29	60.11	65.26	NMIM
Cu	59.34	2.50	54.33	64.35	INMETRO
Hg	62.93	7.70	47.54	78.32	NMIM, INMETRO
Ni	62.74	1.51	59.71	65.77	NMIM, UNIIM
Sb	79.82	2.66	74.50	85.14	UNIIM

5.3 Discussion of the reference values and associated uncertainties

The report summarized the calculated consensus values and their respective standard deviation using different location estimators including arithmetic mean, median and robust mean with or without the suspected extreme values being included in the calculation. The calculated results are presented in Table 13 and Table 14.

Table 13. Results of calculation of consensus values and respective standard deviation (*all data included*)

Measurand	n	Arithmetic Mean (mg/kg)	SD (mg/kg)	**Median (mg/kg)**	MADe (mg/kg)	Robust mean (mg/kg)	Robust SD (mg/kg)
As	9	54.03	5.33	**54.44**	3.03	54.30	3.96
Cd	9	63.64	2.80	**64.20**	2.52	62.80	2.87
Pb	9	63.55	2.13	**63.50**	2.82	63.55	2.41
Co	6	60.38	6.41	**62.96**	1.14	62.69	1.29
Cu	6	59.46	1.97	**59.91**	2.08	59.34	2.50
Hg	6	61.30	9.19	**64.74**	6.56	62.93	7.70
Ni	7	60.73	6.54	**62.62**	1.22	62.74	1.51
Sb	3	77.56	6.19	**80.40**	2.11	79.82	2.66

Table 14. Results of calculation of consensus values and respective standard deviation (*after removal of suspected extreme values*)

Measurand	n	Arithmetic Mean (mg/kg)	SD (mg/kg)	**Median (mg/kg)**	MADe (mg/kg)	Robust mean (mg/kg)	Robust SD (mg/kg)
As	6	53.73	1.82	**54.22**	1.71	53.87	1.77
Cd	7	64.89	1.41	**64.83**	1.95	64.83	1.95
Pb	9	63.55	2.13	**63.50**	2.82	63.55	2.41
Co	5	62.98	0.99	**63.52**	0.36	63.39	0.44
Cu	5	60.09	1.37	**60.00**	1.87	60.00	1.87
Hg	4	66.95	3.47	**67.69**	2.19	67.27	3.28
Ni	5	62.79	0.99	**62.62**	0.78	62.68	0.90
Sb	2	81.11	1.01	**81.11**	1.05	81.11	1.05

It can be found that the Median values are very similar between in Table 13 and Table14 compared with other estimators (except Hg). Also other values approach to the median value after removal of suspected extreme results in Table 14. So the Median and MADe values (in Table 13) calculated are more reasonable than others for reference purposes (except Hg) from statistic. For Mercury, medians are very different between table 13 and table 14.

A preliminary report of the results had been circulated in February 2017, and the results of the CCQM-K128 and proposed KCRV and KCRU were first time discussed at the IAWG meetings held in BIPM, Paris on April 2017. After that, NIM contacted the outlier institute and asked if there had a suspected technical reason for the deviation. The responds and conclusions as follows:

1) About mercury in this comparison, technicians of INMETRO suspected that the main source of variation and losses were come from the digestion of sample after technical exchange; NMIM's technician pointed out their results below the assign value was because their digestion vessels had opened in high pressure during digestion process, there had an excess solution coming out with pressure when the vessel were opened. On the basis of technical discussion, they all agreed that calculate KCRV for Hg will be without the results from INMETRO and NMIM. So only 4 results from NMIs that go into the statistics at last and arithmetic average value was adopted as KCRV for Hg.
2) About antimony in this comparison, UNIIM's technicians had found error only with calculation after they have checked results for Sb; and the correct result of Sb is 83 mg/kg after corrected. And they agreed that calculate KCRV for Sb will be without result from UNIIM. Same to the Hg, arithmetic average value was adopted as KCRV for Sb.

Based on above discussion, the draft A report of CCQM-K128 had been prepared and circulated to participants, and no further comment feedback, then Dr. Mike Sargent helped us to circulate the draft A report to IAWG members in September 2017. After that, the results of this comparison had been discussed second time and the proposed KCRV had been approved at the IAWG meetings held in Turin, Italy on Sep. 2017. And the draft B report of CCQM-K128 had been send to participants and been discussed third time at IAWG meeting held in Paris on April, 2018, no more comments returned except format problems. In this comparison, the median for all results except Hg and Sb, and arithmetic average value for Hg (4 results) and Sb (2 results) were used as KCRV, and their associated uncertainties were used as KCRU.

5.4 KCRV and KCRU

According to the about conclusions, the median of all results and associated uncertainties were calculated as KCRV and KCRU of CCQM-K128 for As, Cd, Pb, Co, Cu, and Ni. The associated uncertainty is calculated using formulas (2) and (3) according to the CCQM Guidance Note [2].

$$u(\mathrm{KCRV}) = \frac{1.25 \times \mathrm{MADe}}{\sqrt{n}} \tag{2}$$

$$U = 2 \times u \tag{3}$$

For Hg, the arithmetic average value (without results of NMIM and INMETRO) and associated uncertainty was chosen as KCRV and KCRU. For Sb, the arithmetic average value (without result of UNIIM) and associated uncertainty was chosen as KCRV and KCRU. The associated uncertainty is calculated using formulas (4) and (5).

$$\mathrm{u} = {SD}/{\sqrt{n}} \tag{4}$$

$$U = 2 \times u \tag{5}$$

The final KCRV and KCRU of the eight measurands are listed in Table 15.

Table 15. KCRV and KCRU

Measurand	n	KCRV (mg/kg)	*u* (mg/kg)	KCRU (*k* = 2) (mg/kg)	Expended Relative Uncertainty (%)
As	9	**54.44**	1.26	2.53	4.64
Cd	9	**64.20**	1.05	2.10	3.27
Pb	9	**63.50**	1.17	2.35	3.70
Co	6	**62.96**	0.58	1.16	1.85
Cu	6	**59.91**	1.06	2.12	3.54
Hg	4	**66.95**	1.74	3.47	5.19
Ni	7	**62.62**	0.58	1.15	1.84
Sb	2	**81.11**	0.71	1.42	1.75

The results for eight elements in the CCQM-K128 are graphically displayed in Fig.10 ~Fig.17. The red straight line represents the KCRV and the red dashed lines represent the standard uncertainty of KCRV (*u*(KCRV)). The bar line of individual participant’s result covers reported result and standard uncertainty. The red dot data show IDMS results, the blue dot data show ICP-MS results and the green dot data show ICP-OES results.

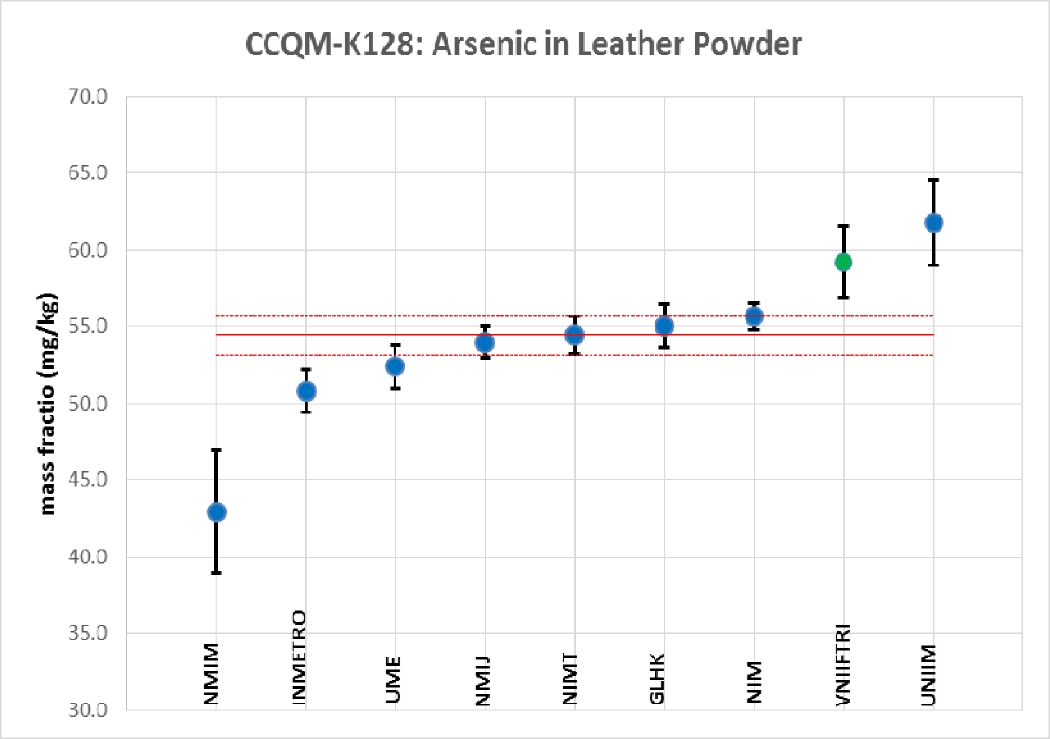


Fig.10. CCQM-K128 Results for Arsenic in leather powder

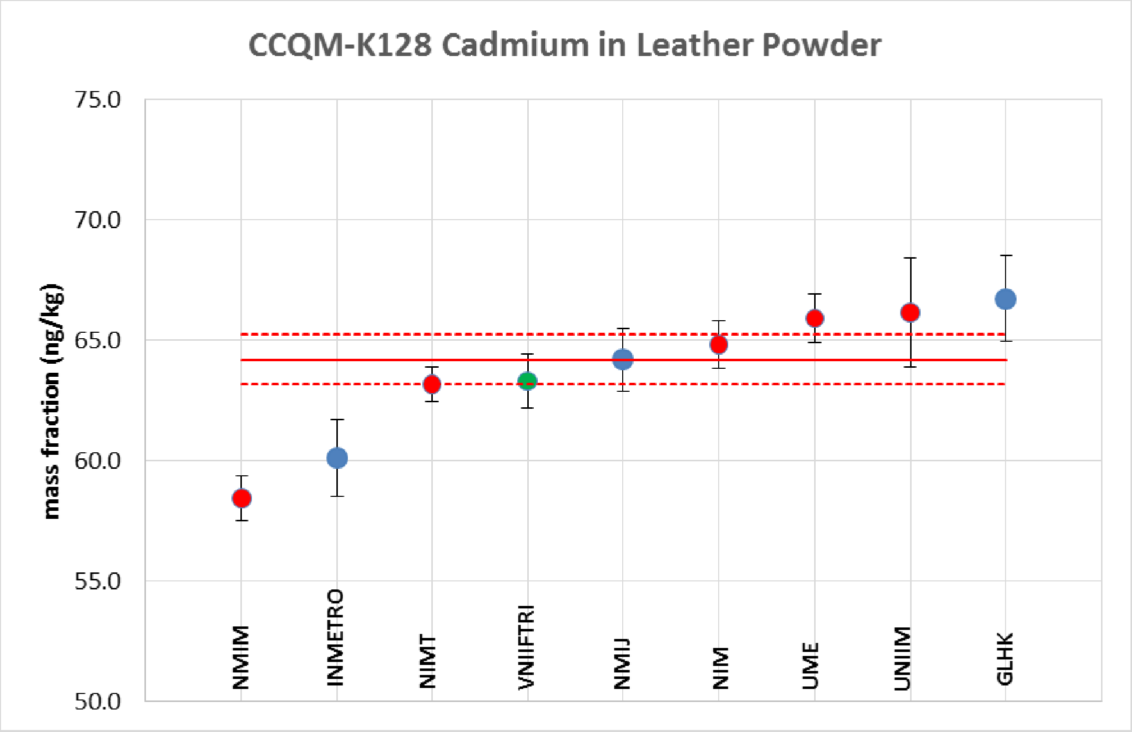


Fig.11. CCQM-K128 Results for Cadmium in leather powder

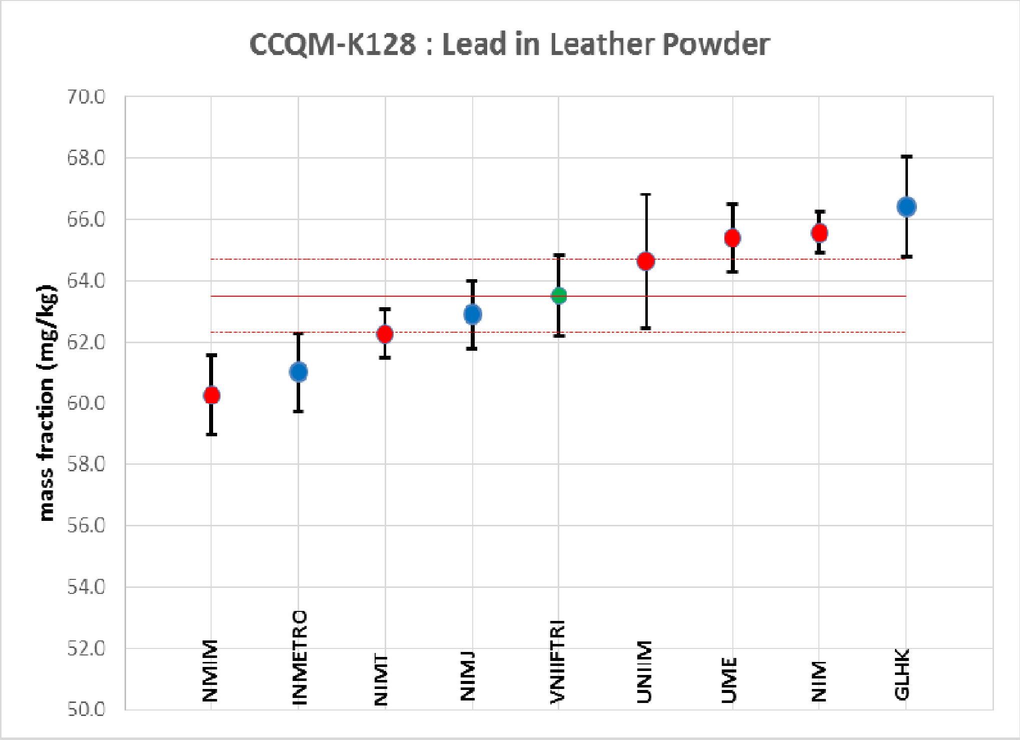


Fig.12. CCQM-K128 Results for Lead in leather powder

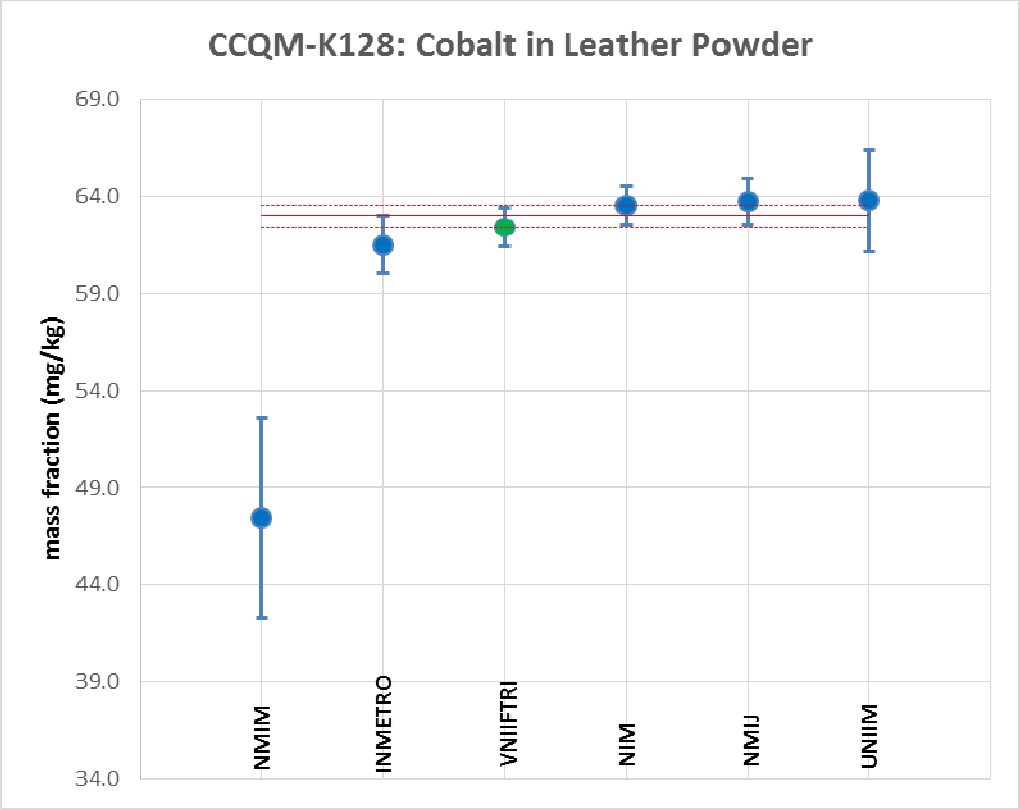


Fig.13. CCQM-K128 Results for Cobalt in leather powder

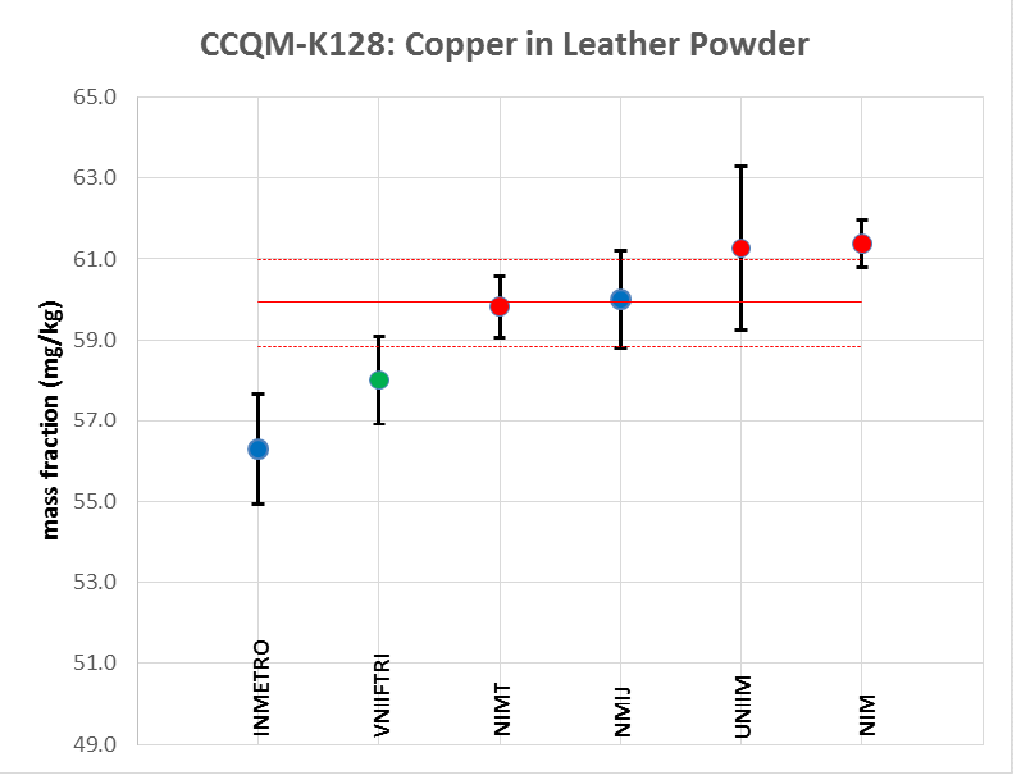


Fig.14. CCQM-K128 Results for Copper in leather powder

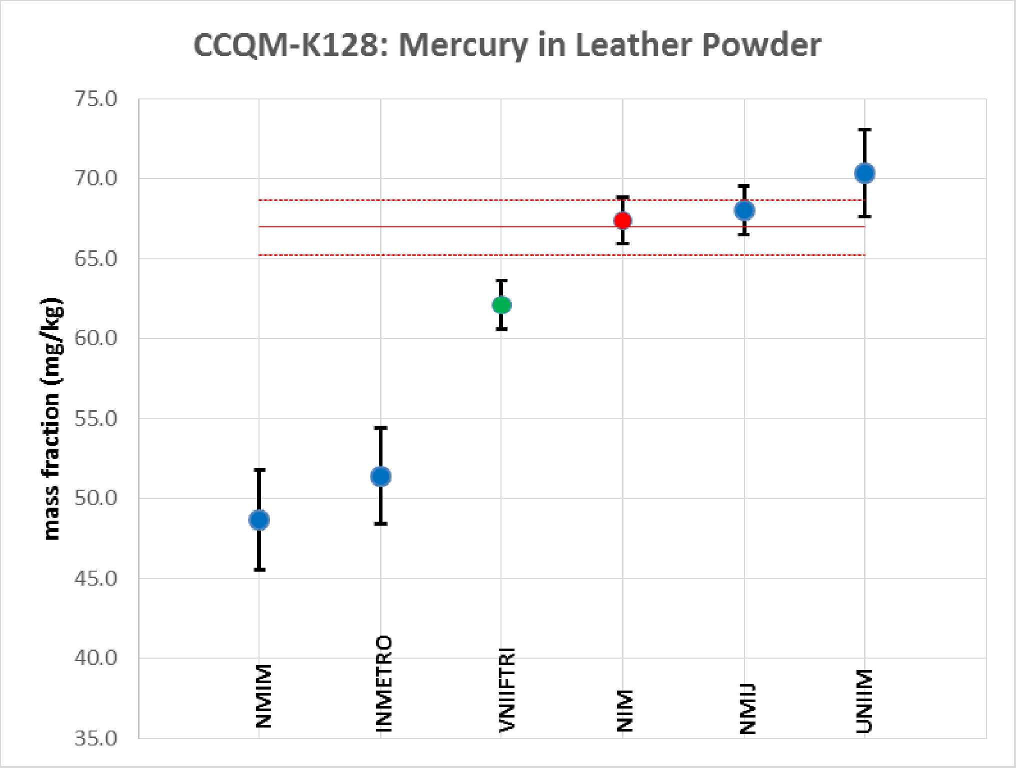


Fig.15. CCQM-K128 Results for Mercury in leather powder

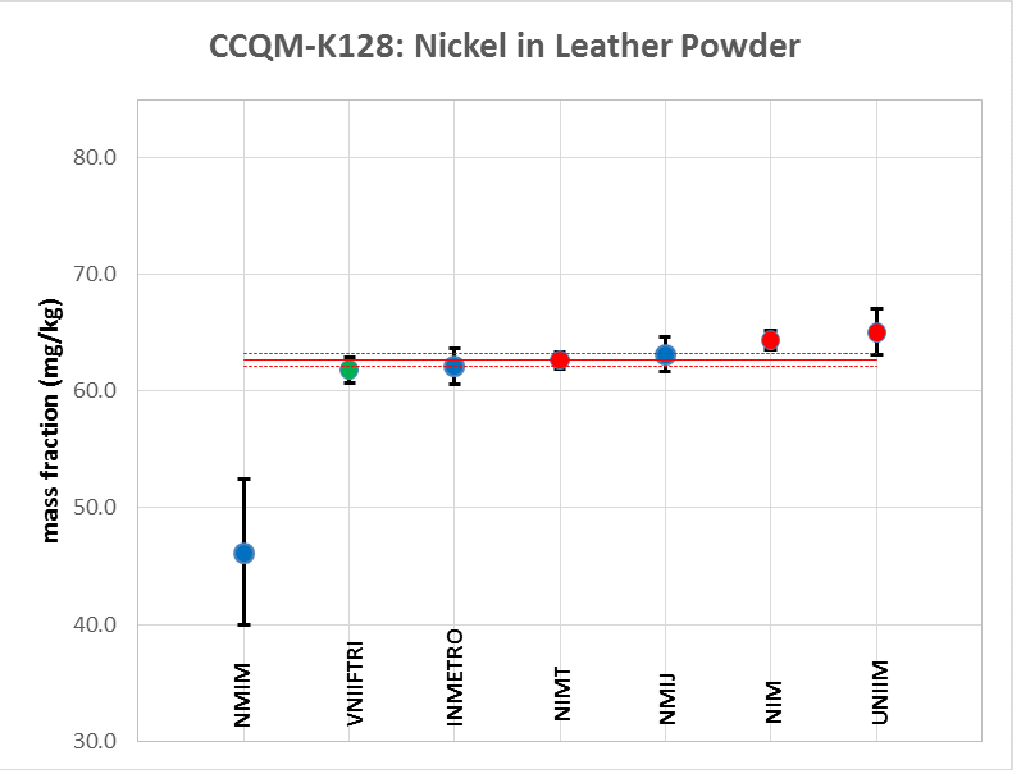


Fig.16. CCQM-K128 Results for Nickel in leather powder

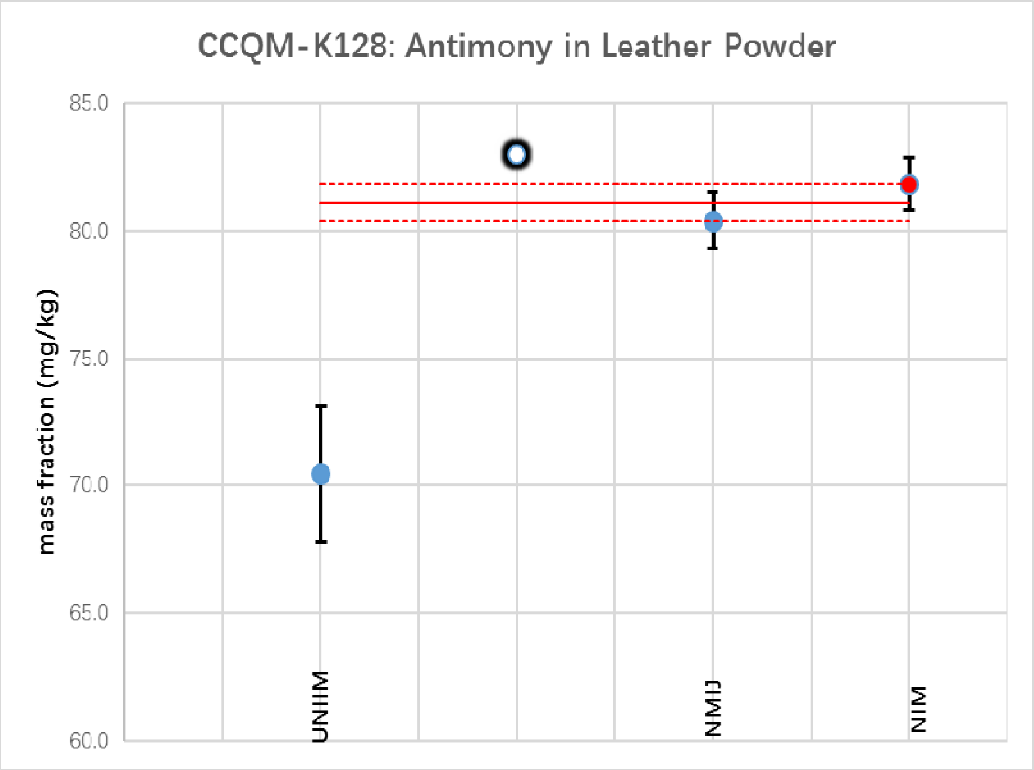


Fig.17. CCQM-K128 Results for Antimony in leather powder

Note: Black circle shows the corrected result of UNIIM after technical discussion, it’s just a information value can’t to support CMC claim.

6. EQUIVALENCE STATEMENTS

According to CCQM Guidance Note [2], the degree of equivalence of each national measurement standard is expressed quantitatively by two terms: its deviation from the key comparison reference value and the uncertainty of this deviation (at a 95 % level of confidence). The degree of equivalence or DoE (d_i, $U(d_\mathrm{i})$) are calculated using formulas (6) and (7).

$$d_i = \left(x_i - \mathrm{KCRV}\right) \qquad (6)$$

$$U\left(d_i\right) = 2 \cdot \sqrt{u(x_\mathrm{i})^2 + u(\mathrm{KCRV})^2} \qquad (7)$$

Where:

x_i : reported value submitted by participant i (i = 1, …, n)

d_i : value component x_i– KCRV of the degree of equivalence (DoE) for participant i (i = 1, …, N)

$U(d_\mathrm{i})$: uncertainty component of the DoE for participant i (i = 1, …, N), this uncertainty isexpressed at 95 %confidence.

Reported value x_i for measurand (8 elements) in the leather powder with their associated combined standard uncertainties $u(x_\mathrm{i})$, together with the d_i, and the associated expanded combined uncertainties $U(d_\mathrm{i})$, are listed for each participant in Table16~ Table23.

The equivalence statements for CCQM-K128 are shown graphically in Fig.18~Fig.25.

Table 16. Equivalence statement of arsenic for CCQM-K128

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	d_i/ $U(d_i)$
NMIM	42.9208	4.0260	-11.52	8.44	-1.37
INMETRO	50.8	1.35	-3.64	3.69	-0.99
UME	52.4	1.4	-2.04	3.77	-0.54
NMIJ	54.0	1.0	-0.44	3.22	-0.14
NIMT	54.4	1.2	0.00	3.54	0.00

GLHK	55.06	1.41	0.62	3.78	0.16
NIM	55.69	0.89	1.25	3.08	0.41
VNIIFTRI	59.2	2.3	4.76	5.25	0.91
UNIIM	61.8	2.8	7.34	6.13	1.20

Table 17. Equivalence statement of cadmium for CCQM-K128

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i/ U(d_i)$
NMIM	58.4335	0.9372	-5.77	2.82	-2.05
INMETRO	60.1	1.6	-4.10	3.83	-1.07
NIMT	63.2	0.7	-1.03	2.55	-0.41
VNIIFTRI	63.3	1.1	-0.90	3.04	-0.30
NMIJ	64.2	1.3	0.00	3.34	0.00
NIM	64.83	1.00	0.63	2.90	0.22
UME	65.9	1.0	1.70	2.90	0.59
UNIIM	66.1	2.3	1.94	4.98	0.39
GLHK	66.72	1.78	2.52	4.13	0.61

Table 18. Equivalence statement of lead for CCQM-K128

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i/ U(d_i)$
NMIM	60.2695	1.2857	-3.23	3.48	-0.93
INMETRO	61.0	1.3	-2.50	3.50	-0.71

NIMT	62.3	0.8	-1.24	2.83	-0.44
NMIJ	62.9	1.1	-0.60	3.22	-0.19
VNIIFTRI	63.5	1.3	0.00	3.50	0.00
UNIIM	64.6	2.2	1.12	4.95	0.23
UME	65.4	1.1	1.90	3.22	0.59
NIM	65.56	0.67	2.06	2.71	0.76
GLHK	66.41	1.62	2.91	4.00	0.73

Table 19. Equivalence statement of cobalt for CCQM-K128

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i/\ U(d_i)$
NMIM	47.4281	5.1346	-15.53	10.34	-1.50
INMETRO	61.5	1.5	-1.46	3.22	-0.45
VNIIFTRI	62.4	1.0	-0.56	2.32	-0.24
NIM	63.52	0.96	0.56	2.25	0.25
NMIJ	63.7	1.2	0.74	2.67	0.28
UNIIM	63.8	2.6	0.80	5.35	0.15

Table 20. Equivalence statement of copper for CCQM-K128

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i/\ U(d_i)$
INMETRO	56.3	1.4	-3.61	3.47	-1.04
VNIIFTRI	58.0	1.1	-1.91	3.06	-0.63

NIMT	59.8	0.8	-0.09	2.62	-0.03
NMIJ	60	1.2	0.09	3.20	0.03
UNIIM	61.3	2.0	1.35	4.56	0.30
NIM	61.37	0.56	1.46	2.40	0.61

Table 21. Equivalence statement of mercury for CCQM-K128

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i/\ U(d_i)$
NMIM	48.6205	3.1208	-18.33	7.14	-2.57
INMETRO	51.4	3	-15.55	6.93	-2.24
VNIIFTRI	62.1	1.5	-4.85	4.59	-1.06
NIM	67.37	1.44	0.42	4.52	0.09
NMIJ	68	1.5	1.05	4.59	0.23
UNIIM	70.3	2.7	3.38	6.49	0.52

Table 22. Equivalence statement of nickel for CCQM-K128

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i/\ U(d_i)$
NMIM	46.1366	6.2174	-16.49	12.49	-1.32
VNIIFTRI	61.8	1.1	-0.82	2.48	-0.33
INMETRO	62.1	1.55	-0.52	3.31	-0.16
NIMT	62.6	0.7	0.00	1.85	0.00
NMIJ	63.1	1.5	0.48	3.21	0.15

NIM	64.32	0.81	1.70	1.99	0.85
UNIIM	65.03	2.00	2.41	4.16	0.58

Table 23. Equivalence statement of antimony for CCQM-K128

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i/ U(d_i)$
UNIIM	70.5	2.7	-10.65	5.52	-1.93
NMIJ	80.4	1.1	-0.71	2.62	-0.27
NIM	81.82	1.01	0.71	2.46	0.29

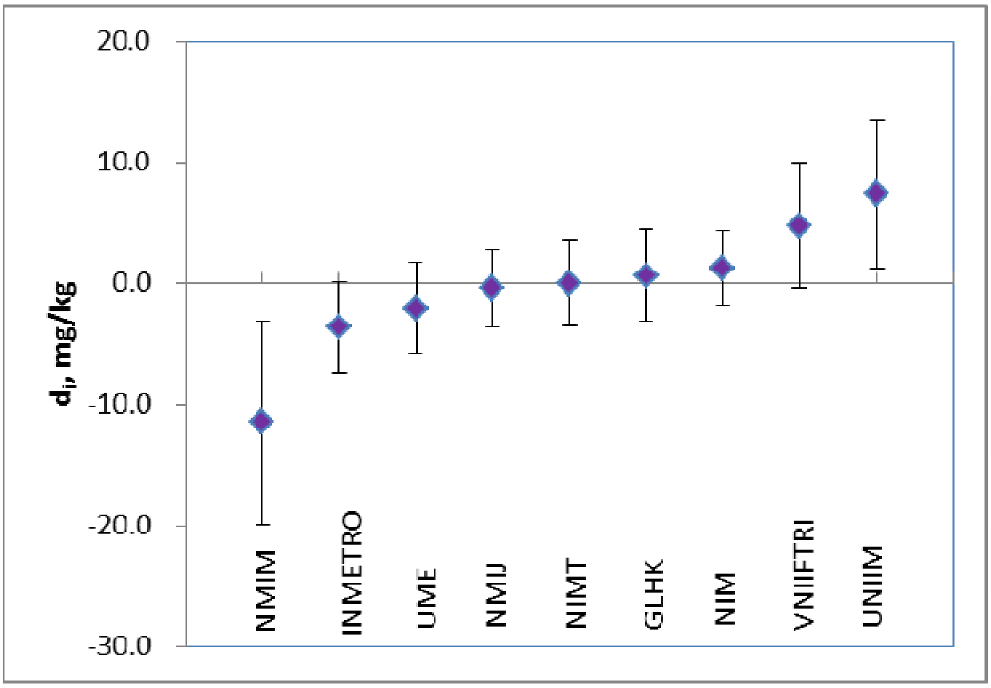


Fig.18. Equivalence statement of arsenic for CCQM-K128.

Points show the d_i, while the error bars denote the $U(d_i)$.

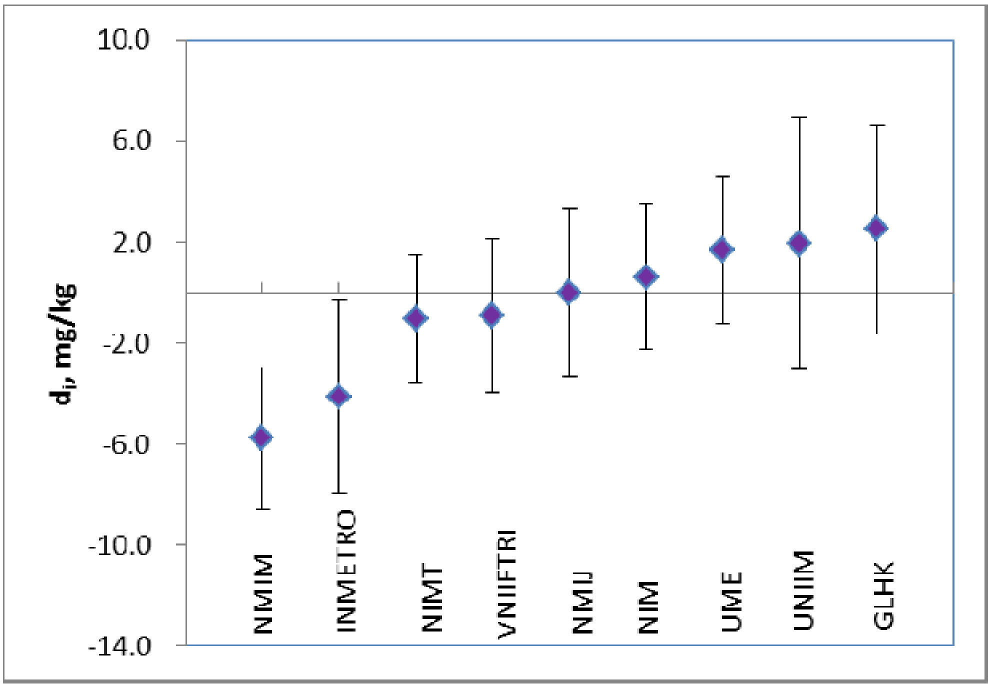


Fig.19. Equivalence statement of cadmium for CCQM-K128.

Points show the d_i, while the error bars denote the $U(d_i)$.

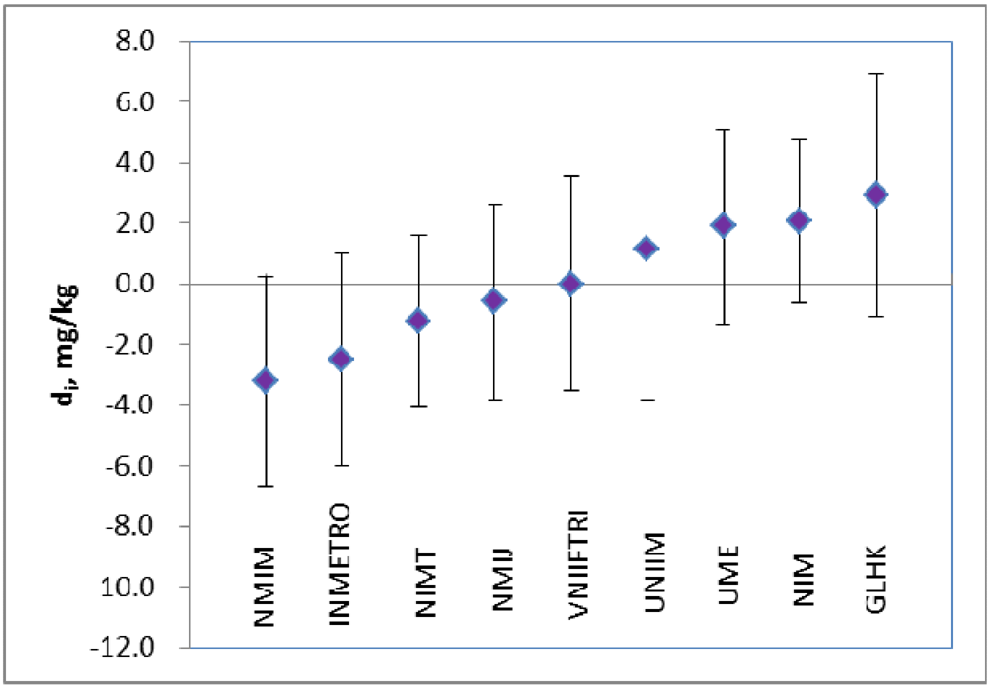


Fig.20. Equivalence statement of lead for CCQM-K128.

Points show the d_i, while the error bars denote the $U(d_i)$.

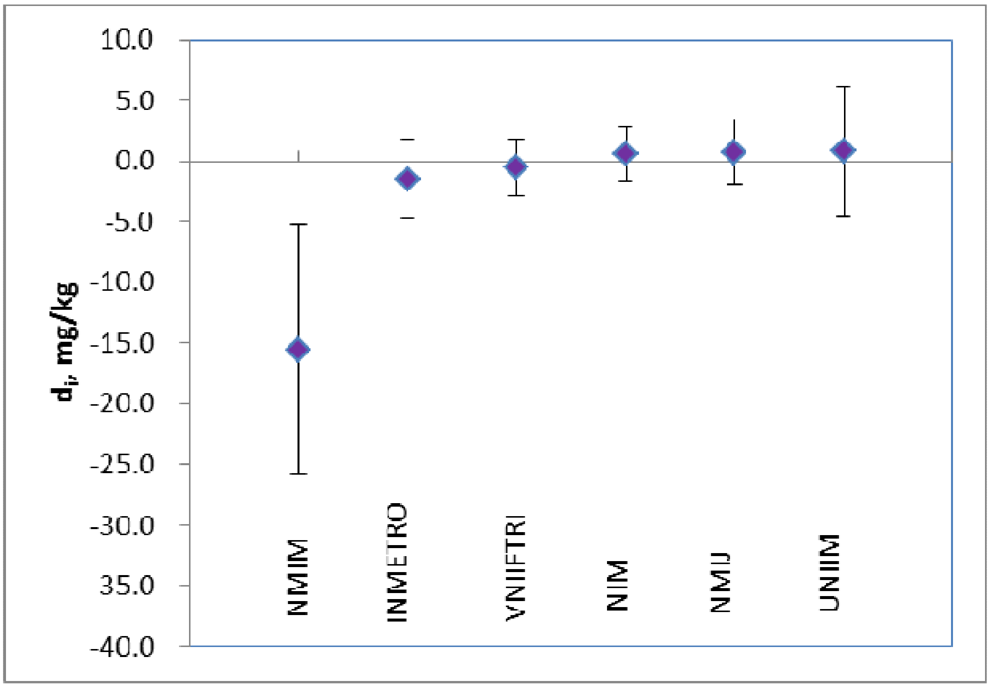


Fig.21. Equivalence statement of cobalt for CCQM-K128.

Points show the d_i, while the error bars denote the $U(d_i)$.

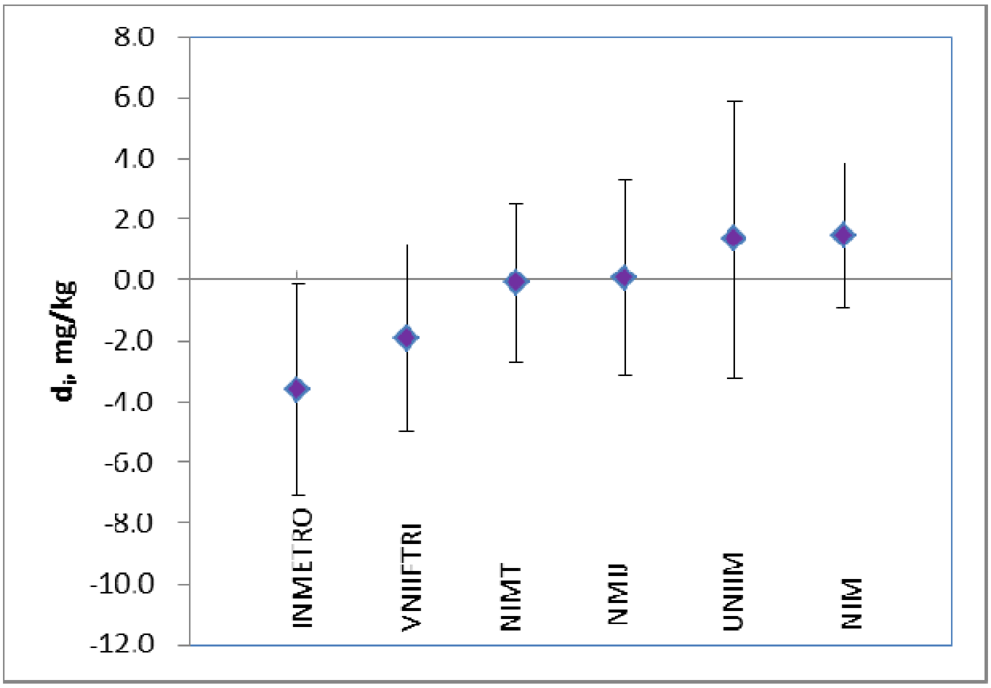


Fig.22. Equivalence statement of copper for CCQM-K128.

Points show the d_i, while the error bars denote the $U(d_i)$.

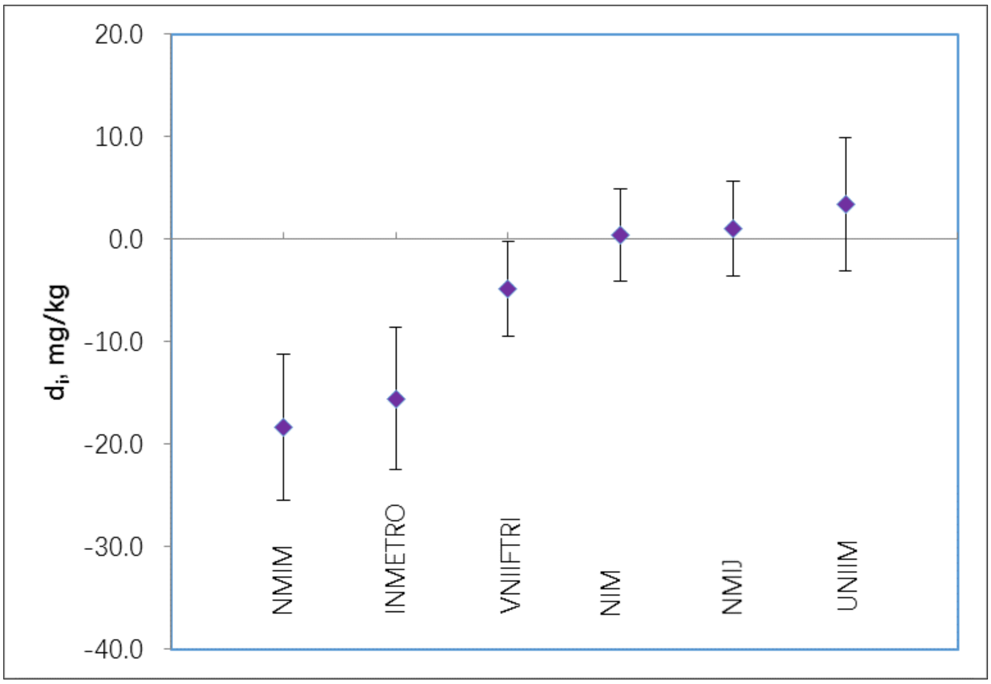


Fig.23. Equivalence statement of mercury for CCQM-K128.

Points show the d_i, while the error bars denote the $U(d_i)$.

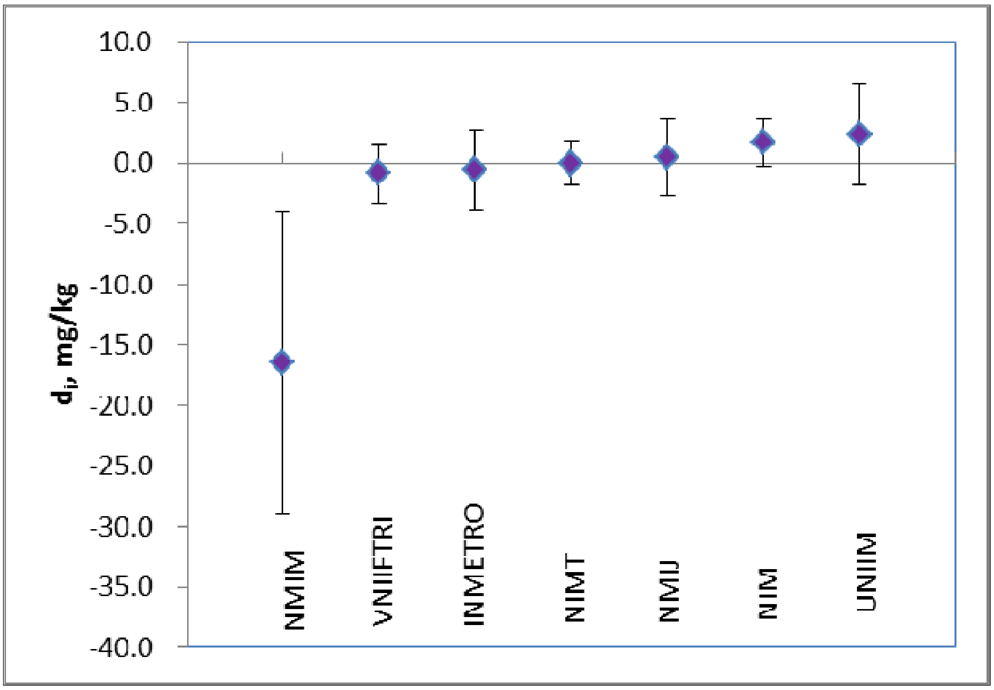


Fig.24. Equivalence statement of nickel for CCQM-K128.

Points show the d_i, while the error bars denote the $U(d_i)$.

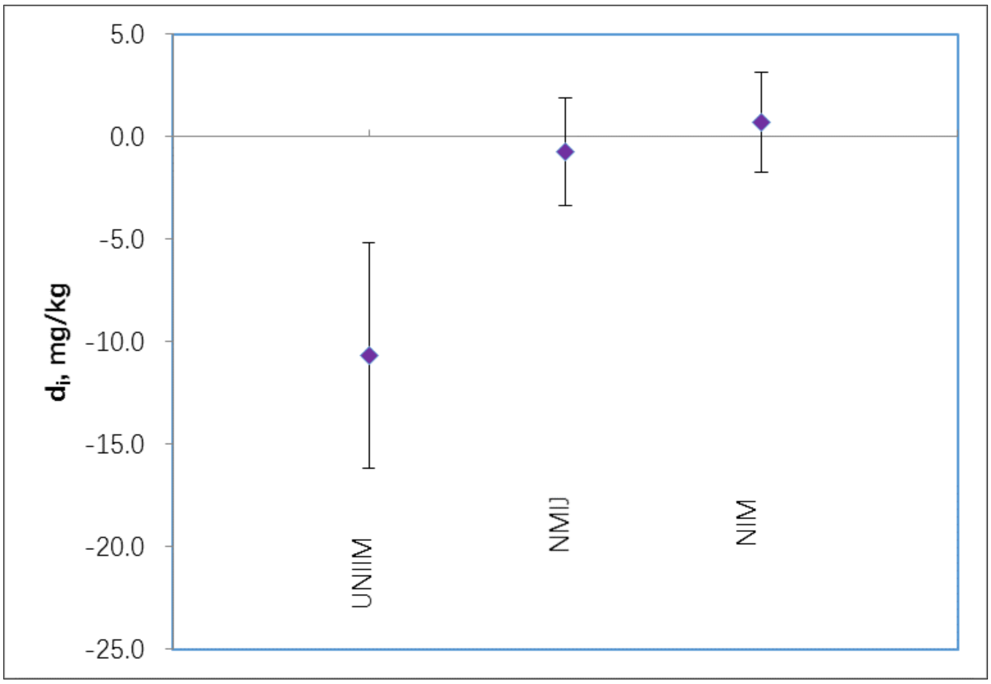


Fig.25. Equivalence statement of antimony for CCQM-K128.

Points show the d_i, while the error bars denote the $U(d_i)$.

7. DISSCUSSION

With respect to the methodology, all participants used microwave acid digestion methods for sample pre-treatment. For the instrumental determination, a variety of techniques like ICP-MS, IDMS, ICP-OES were used by the participants. For most elements, the results were not statistically different generally, but for mercury and antimony some participants shown relative big difference due to lack of experience. About matrix sample, the digestion process is very important in measurement process, how to make sure the sample were digested completely without any loss is every analyzer should think about. For leather sample, it seemed it can be digested well if add amount of hydrofluoric acid in digestion process. But in this comparison, except for Sb, no clear evidence show digestion reagents can cause different results. For Sb digestion reagent might affect the results and hydrolysis should not be ignored. For mercury measurement, it is very easy to loss in digestion process and it is easy to absorb on the walls of vessel or pipe in storage and test process, so IDMS is more suitable to measure mercury in matrix materials.

On the whole, all participants have gained some experience and established their chemical metrology traceability system to measure heavy metal in leather powder or similar samples through this comparison.

PART B

1. LIST OF PARTICIPANTS

3 institutes registered in CCQM-K128 Part B. The list of all the participating institutes is shown in Table 24 according to the first letter of institutes' name.

Table 24. List of participants

Institute	**Country**	**Contact Person**	***Analyst(s)***
NIM National Institute of Metrology, China	China	Ma Liandi, Wang Qian, Wei Chao	Wei Chao
UME National Metrology Institute TURKEY	Turkey	Suleyman Z. Can	Murat Tunc
VNIIM Mendeleyev Institute for Metrology	Russia	Krylov Anatolij Ivanovich, Belyakov Mikhail Vladimirovich, Smirnov Vadim Vladimirovich	Belyakov Mikhail Vladimirovich (GC-MS), Smirnov Vadim Vladimirovich (HPLC-ICP-MS)

2. SAMPLE

The leather samples were prepared by *China Leather and Footwear Industry Research Institute*, and technical processes were quite matched with real goods. Raw materials were adopted the sheep skin, it were cleaned, degreased, depilated, soften, tanning, dyed, smashed and sieved to 0.2 mm～0.7 mm. In dyeing process, added an amount of organo-tin (tri-n-butyltin chloride) close to the target concentration by adjusting pH, temperature, time, the reagent formula and object concentration.

The samples for tributyltin measurement were blended in a mechanical blender for 2 hours. After pre-homogeneity investigated, about 8g leather powders were packaged into a PE plastic bag (inner) and an aluminium foil bag (outside) as one unit. Each unit was stored in -18℃ freezer.

Measurand

TBT (tributyltin) in leather powder for measurement: The approximate levels of the concentrations were (150-600) nmol/g. About this part, NIM provided CRM GBW08710 Tributyltin in methanol as calibrate solution. And participates were free to choose if they use the NIM standard or their own.

Moisture content correction

The sample for TBT measurement were not recommended to be heated before analyzing, because TBT could be vaporized and lost in high temperature. The samples for the moisture content correction should be other separate aliquots samples. At least two separate aliquots of leather sample (0.2g-0.3g/aliquot) should be heated at 80°C in an oven for 6 hours, then be cooled down to room temperature in desiccators and weighed. The average moisture content of the samples will be used for TBT content correction based on dry mass.

Homogeneity test

The homogeneity of tributyltin in the sample was tested by HPLC-ICPMS after extraction separation, and the sampling weight is about 0.2g. 12 units were selected randomly from 500 units, and two replicates from one unit. The data were treated with an analysis of variance. The obtained between-bottle homogeneity standard deviation was 1.4%. No statistically significant heterogeneity was found based on F test. The stability of TBT in the sample was investigated about one year. The results show that the stability level of this leather material fit the objective of the comparison.

Stability monitoring

The stability of TBT in the sample was investigated more than 16 months by HPLC-ICP-MS. The results show that the stability level of this leather material fit the objective of the comparison.

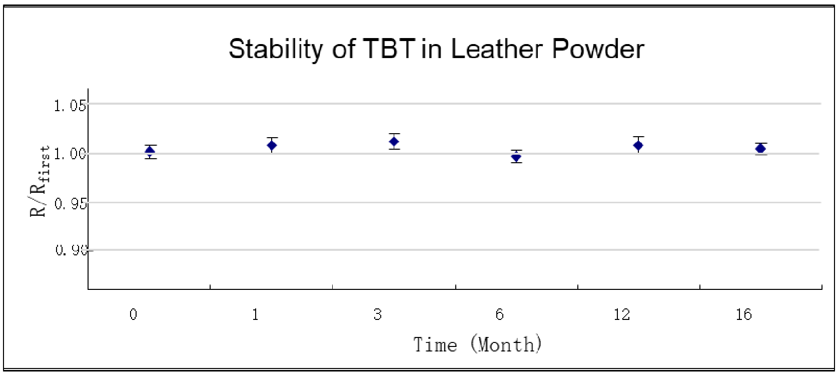


Fig.26. Stability of TBT in Leather Powder

Distribution

Each participant received two numbered bags leather powder for TBT measurement, one bottle of TBT calibration solution, and one CERTAN capillary bottle for dilution.

Participants were required to confirm the receipt of the sealed samples, to fill in the return receipt table and sent it to the coordinator by e-mail.

NMI/DI	Country	Date of Shipment	Date of Delivered	Situation
NIM	China	/	/	OK
UME	Turkey	2016-07-27	2016-07-29	OK
VNIIM	Russia	2016-07-27	2016-08-01	OK

3. INSTRUCTIONS TO PARTICIPANTS

The instruction relating to CCQM-K128 Part B was sent to each participant by e-mail, which consisted of technical protocol, results report form and core capabilities tables.

To avoid any decomposition, the samples should be kept sealed until they are used. Sample should be carefully opened for analysis in a short period of time to avoid contamination. The short term (2~3 weeks) stability of leather sample is no problem in room temperature, but we advise that the sample should be stored at -18°C for long-term preservation.

A Results Report was sent to the participants by email while the samples were dispatched. At least 6 independent determinations should be performed for each measurement. For PART B -

TBT, the results will be reported as molar mass faction (nmol/g as TBT). Calculation of the uncertainty expressed as a combined standard uncertainty and an expanded uncertainty at 95% confidence. In order to allow a sufficient evaluation of the comparison, the report was required to include a detail description of the applied method of measurement, information about sample preparation and determination, information about the reference material used for calibration.

All participants were requested to fill and submit the core capability tables to the coordinator. The potentially interferes resulting from the complicated matrix make it a tough job even for the determination of the common organo-tin in the leather. The core capabilities demonstrated in this comparison focus on the following aspects. Firstly, the complex components matrices in the leather sample should be considered carefully in the sample pre-treatment procedure. Secondly, methodologies established would focus on the different aspects during measurement. For example, more attentions should be paid for spike equilibration with the sample, matrix influence, separation of tin species and accurate measurement of isotopic ratios for the ID-HPLC-ICPMS or ID-GC-MS method. The relevant methodology information were compiled and summarized in the Annex B.

Participants were free to use any suitable method but please include a full description of the method of analysis when reporting the results.

4. METHODE OF MEASUREMENT

According to the results report submitted by each participant, the summary of measurement methods is shown in Table 25.

Table 25 Summary of the measurement methods

Institute	**Preparation Method**	**Analytical Method**	**Calibrant**
NIM	Ultrasonic Extraction	ID-LC-ICPMS	GBW08710 Tributyltin solution CRM
UME	Liquid Liquid Extraction and Derivatization	ID-GC-ICPMS	GBW08710 Tributyltin solution CRM
VNIIM	Ultrasonic Extraction, Derivatization and Second Extraction	GC-MS LC-ICP-MS (Additional method for confirmation of GC-MS result)	GBW08710 Tributyltin solution CRM

5. RESULTS AND DISCUSSION

5.1 General

The measurement results of TBT reported by each participant are summarised in Table 26.

Table 26. Reported results of TBT

Institute	Result *(nmol/g as tributyltin)*	n	*u* *(nmol/g as tributyltin)*	*k*	*U* *(nmol/g as tributyltin)*	Method
VNIIM	313.8	17	8.5	2	17	GC-MS
UME	334.2	6	8.1	2	16.2	ID-GC-ICPMS
NIM	335.3	8	7.9	2	15.8	ID-LC-ICPMS
VNIIM	312.3	6	14.3	2	28.5	HPLC-ICPMS(addition)

Note: Blue font results are not calculated in KCRV, only be used in CMC.

Figure.27 shows the distribution for the results of CCQM-K128 for TBT measurement. Error bar indicates the standard uncertainty (u), as reported. The blue dot data show GC-MS results, the red dot data show ID-GC-ICPMS result, the purple dot data show ID-LC-ICPMS result and the green dot data show LC-ICP-MS result.

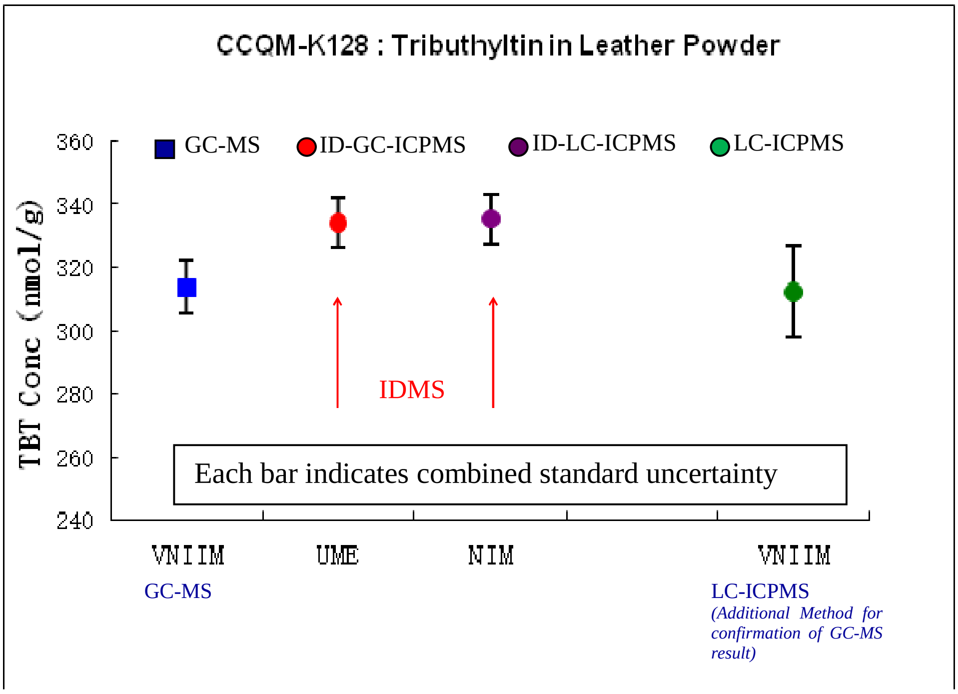


Fig.27. CCQM-K128 all results for TBT in leather powder

5.2 Calculation of the reference value and associated uncertainty

The effective results of CCQM-K128 were chosen and summarized in Table 27. Several approaches to estimate the key comparison reference value (KCRV) were considered. The differences among the arithmetic mean, the median and the weighted mean are compared in Table 28.

Table 27 Effective CCQM-K128 results of TBT in leather powder

	Institute	**Result (nmol/g as tributyltin)**	**U (nmol/g as tributyltin)**	***k***
1	VNIIM	313.8	17.0	2
2	UME	334.2	16.2	2
3	NIM	335.3	15.8	2

Table 28 KCRV and KCRU of CCQM-K128 for TBT in leather powder

	Value (nmol/g as tributyltin)	**Expanded uncertainty (*k* = 2, nmol/g as tributyltin)**
Arithmetic Mean (*1)	327.8	14.0
Median (*2)	334.2	2.4
Weighted mean (*3)	328.3	9.4

*1: The uncertainty was based on the standard deviation of the mean.

*2: The uncertainty of the median was $1.25 \times \mathrm{MADe}/\sqrt{n}$

*3: The square of reciprocal of reported uncertainty was used as a weight.

The results of the CCQM-K128 Part B were discussed at the IAWG meetings held at Paris on April 2017. NIM reported the TBT data results and proposed the arithmetic mean as the KCRV of CCQM-K128, the standard deviation of the arithmetic mean ($u = s / \sqrt{n}$) as the standard uncertainty of the KCRV. All participants agree to the proposed KCRV and KCRU. The KCRV of the TBT in leather powder is 327.8nmol/g and the associated expanded uncertainty is 14.0nmol/g as KCRU.

The results for TBT in the CCQM-K128 are graphically displayed in Fig.28. The red straight line represents the KCRV (arithmetic average) and the red dashed lines represent the standard uncertainty (u (KCRV)). The bar line of individual participant’s result covers reported result and standard uncertainty.

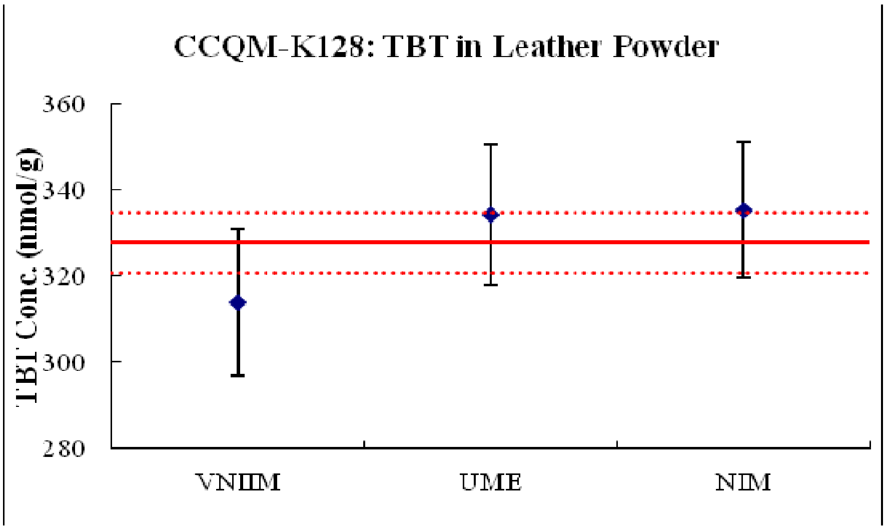


Fig.28. The results for TBT in the CCQM-K128

6.EQUIVALENCE STATEMENTS

The equivalence statements have been calculated according to the BIPM guidelines. The degree of equivalence (and its uncertainty) between a NMI result and the KCRV is calculated according to the following equations:

$$d_i = (x_i - x_{ref}) \quad U(d_i) = 2 \cdot \sqrt{(u(x_i))^2 + u(x_{ref})^2}$$

Reported value x_i for measurand TBT in the leather powder with their associated combined standard uncertainties $u(x_i)$, together with the d_i, and the associated expanded combined uncertainties $U(d_i)$, are listed for each participant in Table 30.

The equivalence statements for CCQM-K128 Part B are shown graphically in Fig.29.

Table 29. Equivalence statement of TBT for CCQM-K128 Part B

Institute	x_i (nmol/g)	$u(x_i)$ (nmol/g)	d_i (nmol/g)	$U(d_i)$ (nmol/g)	$d_i/U(d_i)$
VNIIM	313.8	8.5	-14.0	22.0	-0.64
UME	334.2	8.1	6.4	21.4	0.30
NIM	335.3	7.9	7.5	21.1	0.36

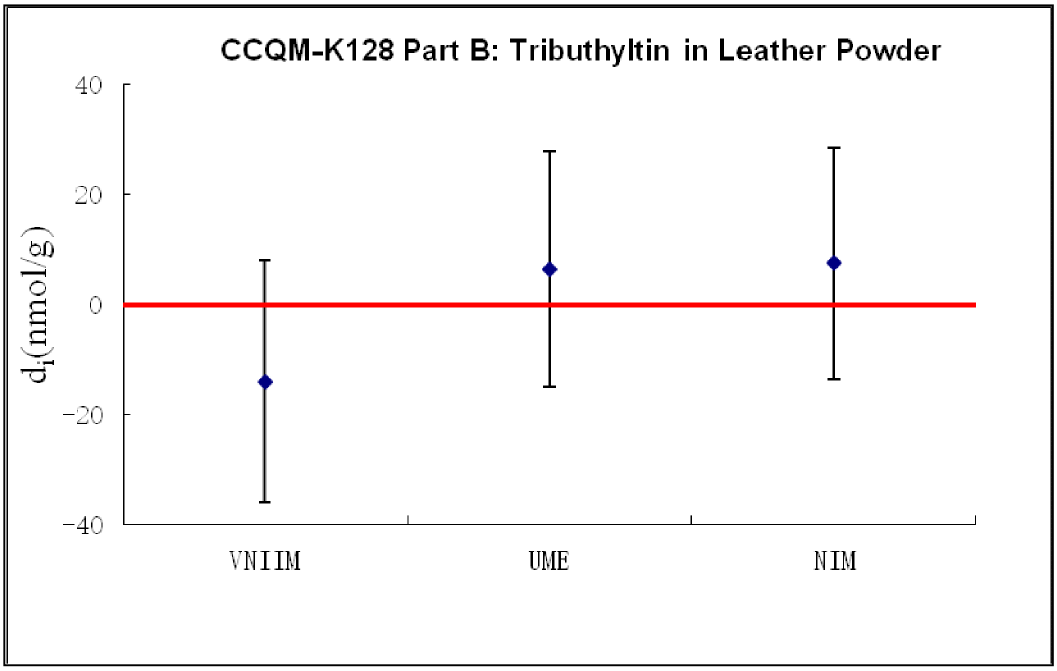


Fig.29. Equivalence statement of TBT for CCQM-K128.
Points show the d_i, while the error bars denote the $U(d_i)$.

7.DISSCUSSION

The key comparison CCQM-K128 was successfully organized. The participating NMIs demonstrated a high level of measurement capabilities and technical competence in analyzing organo-tin in consumer goods such as leather powder. The results by different methods (ID-LC-ICPMS, ID-GC-ICPMS and GC-MS) were comparable. The between-laboratories reproducibility standard deviation was 3.0%, which reflects an excellent agreement of between-laboratories measurement results. Based on this result, the measurement capability of the NMIs which participated in CCQM-K128 has been demonstrated in determining TBT in leather.

Demonstration of Core Capabilities

The six tables of demonstrated core capabilities are attached as Annex B.
The simplified core capabilities table is attached as Annex C.

Acknowledgement

Thank Dr. Mike Sargent, chairman of IAWG/CCQM for his valuable suggestions and many helps, especially for the KCRV evaluation. Thanks all of the analysts from the participant institutes for their efforts and contributions for CCQM-K128 as well as the contact persons.

References

[1] International Standards Organization, ISO Guide 35: Reference materials – Guidance for characterization and assessment of homogeneity and stability, 2017.

[2] CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, Version: 10, 2013-04-12.

Annex A

CCQM-K128/-P163

Measurement of Heavy Metals and Organo-Tin in Leather Powder

Technical Protocol

Introduction

Almost all over the world famous luxury brands is to rely on leather, some of the best leather has been far beyond its basic functions, beyond its original value, from the top to show aesthetic feeling and modern civilization. Nowadays, the leather goods (e.g. fur clothing, wallet, leather accessory etc.) are very popular in worlds. And it is acknowledged that a large amount of hazardous chemicals are used in the leather production process e.g. heavy metals, hexavalent chromium, organo-tin, azo dyes, formaldehyde, and so on. Now limited of harmful materials mainly from several aspects, there are ISO/TC216 footwear, EU directives such as91/338/EEC, 2009/425/EC, 2002/62/EC, 2002/61/EC etc. and national standards.

Recently a number of international regulations have been applied to leather products which require accurate methods with certain trace ability for this complex matrix analysis.To face on this situation, NMIs from different countries are establishing their chemical metrology traceability systems in this area which include both measurement methods research and certain CRMs development; it needs an international comparison for MRA. It should be noted that because the matrix of leather samples are complex and the contents of some elements are so high to inference other elements in measurement, it is a challenging task to measure analytes with high accuracy and precision.

The key comparison CCQM-K128 and the parallel pilot study CCQM-P163, measurement of heavy metals and tributyltin in Leather Powder, will be carried out in 2016.In this comparison, the test materialsare two parts, part A is for heavy metals, and part B is for organo-tin. All samples are similar to the real leather powder. The comparison is to ensure the comparable and traceable measurement results for heavy metals and organo-tin in leather products among the NMIs and other designated measurement bodies worldwide. The results of CCQM-K128 are expected to cover the measurement capability and support CMC claiming in the similar leather materials and chemical industry products.

PART A

1. Samples

The leather samples were prepared by *China Leather and Footwear Industry Research Institute*, and technical processes were quite matched with real goods. Raw materials were adopted the sheep skin, it were cleaned, degreased, depilated, soften, tanning, dyed, smashed and sieved to 0.2 mm～0.7 mm. In dyeing process, added an amount of heavy metal elements close to the target concentration by adjusting pH, temperature, time, the reagent formula and object concentration.

The samples for heavy metals measurement were blended in a mechanical blender for 2 hours. After pre-homogeneity investigated, about 4.5g leather powders were packaged into clean brown glass bottles with plastic inner lid and screw cap. After sterilized with cobalt-60 gamma radiation to 2.5 megarads, each unit was stored in shade and dry place.

The homogeneity of heavy metals in the sample was tested by ICP-MS and ICP-OES two methods after microwave digestion of samples, and the sampling weight is about 0.2g. 15 bottles were selected randomly from 500 bottles, and two replicates from one bottle. The data were treated with an analysis of variance.The obtained between-bottle homogeneity standard deviations of 8 elements were all less than 1.6%, results details were shown in table 1. No statistically significant heterogeneity was found based on F test.

Table 1 Homogeneity Test Results

Element	**ICP-OES** RSD_{bb} **(%)**	**ICP-MS** RSD_{bb} **(%)**
As	**1.40**	**0.74**
Cd	**1.22**	**0.88**
Co	**1.56**	**1.30**
Cu	**1.17**	**1.28**
Hg	**1.49**	**0.81**

Ni	**1.29**	**1.38**
Pb	**1.25**	**0.97**
Sb	**1.45**	**0.62**

The stability of heavy metals in the sample was investigated more than 2 years by ICP-MS. The results show that the stability level of this leather material fit the objective of the comparison.

2. Measurands

There are 8 heavy elements in leather powder for measurement, lead, cadmium, mercury, arsenic, antimony, cobalt, copper and nickel respectively. Participants are encouraged to test all elements, but there are 3 elements lead, cadmium, arsenicare mandatory analytes and others are optional analytes. The approximate levels of the concentrations are (30~100) mg/kg.

3. Measurement method

Participants are free to use any suitable method but please include a full description of the method of analysis when reporting the results.

Core capability

The potentially interferes resulting from the complicated matrix make it a tough job even for the determination of the common heavy metal elements in the leather. The core capabilities demonstrated in this comparison focus on the following aspects. Firstly, the complex components matrices in the leather sample should be considered carefully in the sample pre-treatment procedure. Secondly, methodologies established would focus on the different aspects during measurement. For example, more attentions should be paid for spike equilibration with the sample, matrix influence and accurate measurement of isotopic ratios for the IDMS method. For external standard calibration method, the standard (working) curves and the selection of the internal standard should be key steps. If the AAS and ICP-OES methods are used, the matrix interference procedure should be taken into consideration. Thirdly, for methods validation, it is the best choice to be conducted it through the analysis of a certified reference material. However, there are few available leather matrix CRMs. The last resort is an attempt to establish accuracy through spike recovery experiments and/or the use of standard additions.

4. Distribution

Each participant will receive one numbered bottle for heavy metalmeasurement. Participants will be informed the date of samples dispatching.

Participants are required to confirm the receipt of the sealed samples, to fill in the return receipt table and send it to the coordinator by e-mail. If there is any damage, please contact us immediately and NIM will mail out another one.

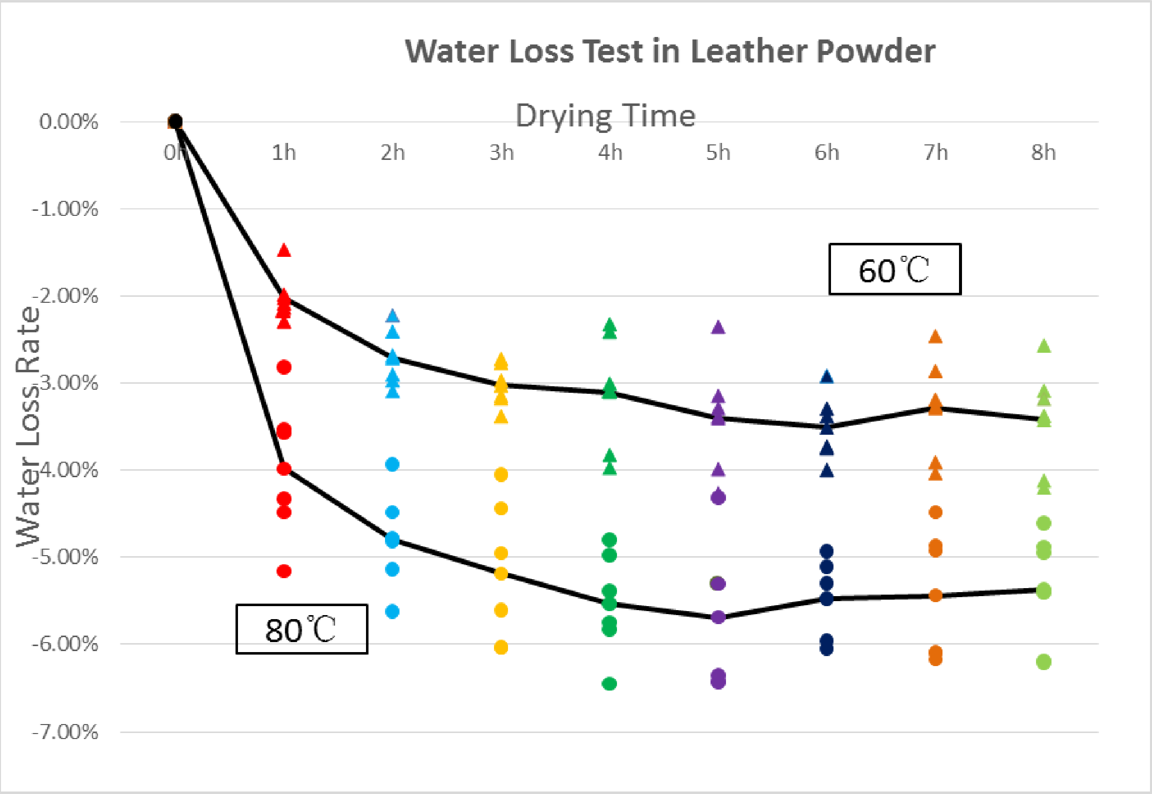
5. Instructionsfor use and storage

To avoid any decomposition, the samples should be kept sealed until they are used. Each unit should be stored in its original bottle, capped tightly and not exposed to intense direct light and ultraviolet radiation. Before it is opened, it should be shaken for 5 min so that the material within is re-homogenised. Sample should be carefully opened for analysis in a short period of time to avoid contamination. The leather sample should be stored at room temperature (18-25)°C.

6. Moisture content correction

Water loss experiments had been done at 60°C and 80°Cseparately. The data were recorded after the aliquot heating for 1h, 2h, 3h, 4h, 5h, 6h, 7h and 8h respectively. 6 parallel samples were test at every point every time. The results were shown in graph1.

The samples were also test by head space gas chromatography (HSGC) to prove whether there were some organic ingredients were losing in drying process. And the results of HSGC showed that the loss of organic ingredients can be ignored at 60°C and 80°C.



Graph 1 Water Loss Test

From the results, there are very different water loss ratio between 60°C and 80°C. And the rate is remaining unchanged when the samples were drying more than 4 hours. So the drying condition was adopted at 80°C 6 hours.

The sample should be heated at 80°Cin an oven for 6 hours and then cooled down to room temperature in desiccators before weighting. After that drying procedure, the sample can be used for heavy metals measurement.

PARTB

1. Samples

The leather samples were prepared by *China Leather and Footwear Industry Research Institute*, and technical processes were quite matched with real goods. Raw materials were adopted the sheep skin, it were cleaned, degreased, depilated, soften, tanning, dyed, smashed and sieved to 0.2 mm～0.7 mm. In dyeing process, added an amount of organo-tin (tri-n-butyltin chloride) close to the target concentration by adjusting pH, temperature, time, the reagent formula and object concentration.

The samples for tributyltin measurement were blended in a mechanical blender for 2 hours. After pre-homogeneity investigated, about 8g leather powders were packaged into a PE plastic bag (inner) and an aluminium foil bag (outside) as one unit. Each unit was stored in -18℃ freezer.

The homogeneity of tributyltin in the sample was tested by HPLC/ICP-MS after extraction separation, and the sampling weight is about 0.2g.12units were selected randomly from 500 units, and two replicates from one unit. The data were treated with an analysis of variance. The obtained between-bottle homogeneity standard deviation was 1.4%. No statistically significant heterogeneity was found based on F test. The stability of TBT in the sample was investigated about one year. The results show that the stability level of this leather material fit the objective of the comparison.

2. Measurand

Tributyltin in leather powder for measurement: the approximate levels of the concentrations are (150-600) nmol/g. About this part, NIM will provide CRM GBW08710 Tributyltin in methanol as calibrate solution. And participates are free to choose if they use the NIM standard or their own. Also an enriched TBT spike is available from a Spanish company (http://www.isc-science.com/key/organic-compounds/tributyltin-quantid_168_20_315_0_1_pros.html).

3. Measurement method

Participants are free to use any suitable method but please include a full description of the method of analysis when reporting the results.

Core capability

The potentially interferes resulting from the complicated matrix make it a tough job even for the determination of the common organo-tin in the leather. The core capabilities demonstrated in this comparison focus on the following aspects. Firstly, the complex components matrices in the leather sample should be considered carefully in the sample pre-treatment procedure. Secondly, methodologies established would focus on the different aspects during measurement. For example, more attentions should be paid for spike equilibration with the sample, matrix influence, separation of tin species and accurate measurement of isotopic ratios for the ID-HPLC-ICPMS or ID-GC-MS method.

4. Distribution

Each participant will receive one numbered bag leather powder for TBT measurement, one bottle of TBT calibrate solution, and one CERTAN capillary bottle for dilution.

Participants are required to confirm the receipt of the sealed samples, to fill in the return receipt table and send it to the coordinator by e-mail. If there is any damage, please contact us immediately and NIM will mail out another one.

5. Instructionsfor use and storage

To avoid any decomposition, the samples should be kept sealed until they are used. Sample should be carefully opened for analysis in a short period of time to avoid contamination. The short term (2~3 weeks) stability of leather sample is no problem in room temperature, but we advise that the sample should be stored at -18°C for long-term preservation.

6. Moisture content correction

The sample for TBT measurement should not be heated before analysing, because TBT could be vaporized and lost in high temperature. The samples for the moisture content correction should be other separate aliquots samples. At least two separate aliquots of leather sample (0.2g-0.3g/aliquot) should be heated at 80°C in an oven for 6hours, then be cooled down to room temperature in desiccators and weighed. The average moisture content of the samples will be used forTBT content correction based on dry mass.

Time schedule

Call for Participation: March 2015

Deadline for registration: June 10, 2016

Dispatch of the samples: Before the end of June 2016

Deadline for receipt of the result report: February28, 2017

Discussing of the result: CCQM/ IAWG Paris meeting of 2017

Registration

Please complete the registration form and return it to wangq@nim.ac.cn & weichao@nim.ac.cn

Please register no later than June 10, 2016.

Reporting

A suggestion for a summary report table will be sent to the participants by email while the samples are dispatched. The report should be submitted before 28 February 2016. NIM will confirm the receipt of each report. The report should include the following aspects:

- A final result and uncertainty evaluation. At least 6 independent determinations should be performed for each measurement. For PART A - heavy metals, the results will be reported as mass faction [mg/kg]; for PART B - TBT, the results will be reported as molar mass faction [nmol/g].
- Please note that only one result from each institute will be considered for calculation of the KCRV of each element.
- A detail description of the applied method of measurement. If more than one method were applied, a detail description must be given for each method.
- Information about sample digestion and preparation, including reagent, temperature, produce and blank etc.
- Information about the reference material used for calibration (origin, standard value, standard uncertainty and isotopic ratio if necessary) or other materials used in the analytical procedure.
- Information about the uncertainty of measurement. The uncertainty should be evaluated

according to the ISO Guide to the Expression of Uncertainty in Measurement, 1993. It should include:

-The complete specification of the measurement equation including corrections e.g. for blanks and interferences.

- The identification and quantification of all uncertainty sources.

- The combined standard uncertainty.

- The value for the coverage factor and the expanded uncertainty.

✧ Filled Core capability tables related to the measurement methods used by participants.

Participation

National metrological institutes (NMIs), or an appropriate designated institute in accordance with the CIPM MRA, are welcome to participate in the key comparison CCQM-K128 or the pilot study CCQM-P163. Other expert institutes from countries that are members of the Metre Convention are also invited to participate in the pilot study.

Coordinating laboratory and contact person

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Annex B

Inorganic Core Capabilities

Report from Participating Institute (Part A)

CCQM Study: **☑ CCQM-K128□ CCQM-P163**

Institute: TÜBİTAK UME, NIMT, UNIIM, NIM，NMIM

Method: ID-ICP-MS

Analyte(s): Cd, Cu, Ni, Pb, Sb, Hg

Instructions:

List element symbols for analytes in the appropriate column ('Not tested' or 'Tested') for all capabilities relevant to your measurements. Provide a brief explanation of the challenges you encountered in the final column, highlighting any aspects where you believe this measurement presented an unusually high degree of difficulty. Please add rows for any other capabilities which you used but which have not been included in this table.

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
Contamination control and correction *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.*	NIMT(Cd, Cu, Ni, Pb)	UME(Cd, Pb), UNIIM(Cd, Cu, Ni, Pb), NIM(Cd, Cu, Ni, Pb, Sb, Hg), NMIM(Cd, Pb)	In order to minimize the possible contamination of sample, ultrapure reagents and pre-cleaned unused PFA labwares were used during the analysis. (UME) Using of software of mass spectrometer NexION 300D (blank). (UNIIM) Adopt concentrated distill HNO$_3$and high purity reagent to reduce blank, at the same time to carry on the blank correction.(NIM) For each digestion, a separate blank sample was included. The blank samples containing all acids, without the sample itself, went through all analytical procedure stages and measured. Microwave vessels were cleaned and rinsed thoroughly between digestions. Blanks were also run through the entire procedure to identify if contamination occurred. (NMIM)
Digestion/dissolution of organic matrices	NIMT(Cd, Cu, Ni, Pb)	UME(Cd, Pb), UNIIM(Cd,	Closed vessel microwave assisted sample digestion was used to decompose the

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.		Cu, Ni, Pb), NIM(Cd, Cu, Ni, Pb, Sb, Hg), NMIM(Cd, Pb)	sample matrix, and to bring the analyte into solution. (UME) Add HF acid in microwave digestion procedure.(NIM) 0.2 g of samples, add 5 ml HNO3+50uL HF+spike 0.4g of Pb206+0.2 g Cd 111 pre digest for 3 hours and digest using microwave digestion, diluted with DI water for 100ml sample was completed digest.(NMIM)
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.*	UME(Cd, Pb), NIM(Cd, Cu, Ni, Pb, Sb, Hg), NMIM(Cd, Pb)	NIMT(Cd, Cu, Ni, Pb), UNIIM(Cd, Cu, Ni, Pb)	Not only nitric acid, but also hydrofluoric acid was employed for achieving clear digest, under microwave condition used. (NIMT)
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	UME(Cd, Pb), NIMT(Cd, Cu, Ni, Pb), UNIIM(Cd, Cu, Ni, Pb), NIM(Cd, Cu, Ni, Pb, Sb, Hg)	NMIM(Cd, Pb)	Close vessel digestion. Cooling to room temperature. (NMIM)
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	UME(Cd, Pb), NIMT(Cd, Cu, Ni, Pb), UNIIM(Cd, Cu, Ni, Pb), NIM(Cd, Cu, Ni, Pb, Sb, Hg), NMIM(Cd, Pb)		
Vapor generation *Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.*	UME(Cd, Pb), NIMT(Cd, Cu, Ni, Pb), UNIIM(Cd, Cu, Ni, Pb), NIM(Cd, Cu, Ni, Pb, Sb, Hg), NMIM(Cd, Pb)		
Matrix separation	UME(Cd, Pb), NIMT(Cd, Cu, Ni, Pb),		

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	UNIIM(Cd, Cu, Ni, Pb), NIM(Cd, Cu, Ni, Pb, Sb, Hg), NMIM(Cd, Pb)		
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample.*	NIMT(Cd, Cu, Ni, Pb), NIM(Cd, Cu, Ni, Pb, Sb, Hg)	UME(Cd, Pb), UNIIM(Cd, Cu, Ni, Pb), NMIM(Cd, Pb)	Measurements of blend solutions were performed at least 16 hours after preparation for isotopic equilibration. (UME) It is essential for accurate IDMS and needed to mix well. (NIMT) Prepared the calibration blend mixture of 50 mg/kg of Pb and Cd. Spike with Pb 206 and Cd 111. Then run for analysis using ICPMS. (NMIM)
Signal detection *The detection and recording of the analyte isotope signals. The degree of difficulty increases for analytes present at low concentrations, of low isotopic abundance, or that are poorly ionized.*	UME(Cd, Pb), NIMT(Cd, Cu, Ni, Pb), NMIM(Cd, Pb)	UNIIM(Cd, Cu, Ni, Pb), NIM(Cd, Cu, Ni,Pb, Sb, Hg)	In the process of measuring, adjust the signal of different mass number in a same mode.(NIM)
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	NIMT(Cd, Cu, Ni, Pb)	UME(Cd, Pb), UNIIM(Cd, Cu, Ni, Pb), NIM(Cd, Cu, Ni, Pb, Sb, Hg), NMIM(Cd, Pb)	The lines were throughly rinsed to get rid of any memory effects between the samples and standards. Background measurements performed before each measurement. (UME) Enough washing procedures were inserted between every sample measurements.(NIM) Washing procedures: before and after each measurement, 2 % HNO3. (NMIM)
Correction or removal of isobaric/polyatomic interferences	NIMT(Cd, Cu, Ni, Pb), UNIIM(Cd, Cu,	UME(Cd, Pb)	For Cd, measurements were performed at medium resolution mode of HR-ICP-MS to avoid possible isobaric interferences.

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
Any techniques used to remove, reduce, or mathematically correct for interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	Ni, Pb), NIM(Cd, Cu, Ni, Pb, Sb, Hg), NMIM(Cd, Pb)		Mathematical corrections were applied for Pd, Sn and In isobaric interferences. (UME)
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	NIMT(Cd, Cu, Ni, Pb), UNIIM(Cd, Cu, Ni, Pb), NIM(Cd, Cu, Ni,Pb, Sb, Hg), NMIM(Cd, Pb)	UME(Cd, Pb)	Dead time correction was measured before measurements. (UME)
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	UNIIM(Cd, Cu, Ni, Pb)	UME(Cd, Pb), NIMT(Cd, Cu, Ni, Pb), NIM(Cd, Cu, Ni,Pb, Sb, Hg), NMIM(Cd, Pb)	Mass bias correction factors were determined between runs and included in the calculations. (UME) Use standard solution to monitor mass bias. (NIMT) Mass bias/fractionation was corrected for by bracketing correction using an isotope ratio standard.(NIM) Run the SRM 981 for mass bias correction.(NMIM)
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*		UME(Cd, Pb), NIMT(Cd, Cu, Ni, Pb), UNIIM(Cd, Cu, Ni, Pb), NIM(Cd, Cu, Ni,Pb, Sb, Hg)	Double (or reverse) IDMS method were applied for Pb to determine the concentration in SRM 991 enriched spike solution. (UME) Reverse IDMS to calibrate the isotopic spike. (NIMT) Using procedure of preparation. (UNIIM) Double isotope dilution technique was used.(NIM)

Inorganic Core Capabilities

Report from Participating Institute (Part A)

CCQM Study: ■ CCQM-K128 □ CCQM-P163

Institute: GLHK, NMIJ, UNIIM, INMETRO, UME, NIM, NIMT

Method: ICPMS

Analyte(s): As, Cd, Pb, Hg, Sb, Co, Cu, Ni

Instructions:

List element symbols for analytes in the appropriate column ('Not tested' or 'Tested') for all capabilities relevant to your measurements. Provide a brief explanation of the challenges you encountered in the final column, highlighting any aspects where you believe this measurement presented an unusually high degree of difficulty. Please add rows for any other capabilities which you used but which have not been included in this table.

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
Contamination control and correction *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.*	NIMT(As, Cd, Cu, Ni, Pb)	GLHK(As, Cd, Pb), UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb), UME(As), NIM(Co, As)	Blank correction for calibration.(UNIIM) Adopted procedures to avoid contamination included: in-house distilled acid for purification and blank control. (INMETRO) In order to minimize the possible contamination of sample, ultrapure reagents and pre-cleaned unused PFA labwares were used during the analysis.(UME) Adopt concentrated distill $HNO_3$and high purity reagent to reduce blank, at the same time to carry on the blank correction.(NIM)
Digestion/dissolution of organic matrices *All techniques and procedures used to bring a sample*	NIMT(As, Cd, Cu, Ni, Pb)	GLHK(As, Cd, Pb), NMIJ(Pb, Cd, As, Hg, Sb, Co,	A mix acid of HNO_3:H_2O_2:HF is required to digest the sample completely. Partly digestion of the

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.		Cu, Ni), UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb), UME(As), NIM(Co, As)	sample resulted in an apparent lower result for Sb.(NMIJ) Closed vessel microwave assisted sample digestion was used to decompose the sample matrix, and to bring the analyte into solution.(UME) Add HF acid in microwave digestion procedure.(NIM)
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.*	UME(As), NIM(Co, As)	UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb), NIMT(As, Cd, Cu, Ni, Pb)	HF acid was added in the microwave digestion procedure. The amount of HF was optimized in order to minimize the dilutions. (INMETRO) Not only nitric acid, but also hydrofluoric acid was employed for achieving clear digest, under microwave condition used.(NIMT)
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	UME(As), NIM(Co, As), NIMT(As, Cd, Cu, Ni, Pb)	UNIIM(Co, Sb, Hg, As), INMETRO(Hg)	Recovery tests were performed in order to monitory Hg loss. (INMETRO)
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb), UME(As), NIM(Co, As), NIMT(As, Cd, Cu, Ni, Pb)		
Vapor generation *Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.*	UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb), UME(As), NIM(Co, As), NIMT(As, Cd, Cu, Ni, Pb)		
Matrix separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce*	UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg,	NIMT(As)	To avoid $^{40}Ar^{35}Cl^+$ polyatomic interferences, oxygen gas acting as a DRC gas makes it possible to shift analytical m/z 75($^{75}As^+$) to m/z 91^+

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	Ni, Pb), UME(As), NIM(Co, As), NIMT(Cd, Cu, Ni, Pb)		(^{75}As^{16}O). (NIMT)
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*	NIMT(As, Cd, Cu, Ni, Pb)	GLHK(As, Cd, Pb), NMIJ(Pb, Cd, As, Hg, Sb, Co, Cu, Ni), UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb), UME(As), NIM(Co, As)	Standard addition was applied to all of the analytes.(NMIJ) Gravimetric standard addition method was used for the calibration. In order to monitor and minimize the drift on the signal, internal standard was used.(UME) Standard solution and internal standard were used in all of the analytes. (NIM)
Signal detection *The detection and recording of the analyte isotope signals. The degree of difficulty increases for analytes present at low concentrations, of low isotopic abundance, or that are poorly ionized.*	UNIIM(Co, Sb, Hg, As), UME(As), NIMT(As, Cd, Cu, Ni, Pb)	GLHK(As, Cd, Pb), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb), NIM(Co, As)	In the process of measuring, adjust the signal of standard curve in a mode of the sample.(NIM)
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	UME(As), NIMT(As, Cd, Cu, Ni, Pb)	GLHK(As, Cd, Pb), UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb), NIM(Co, As)	Memory effect of Hg was evaluated and we optimized the washing time. (INMETRO) Enough washing procedures were inserted between every sample measurements.(NIM)
Correction or removal of isobaric/polyatomic interferences *Any techniques used to remove, reduce, or mathematically correct for interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering*	UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb)	GLHK(As, Cd, Pb), NMIJ(Pb, Cd, As, Hg, Sb, Co, Cu, Ni), UME(As), NIM(Co, As)	The measurement was carried out with an ICP-QMS/QMS instrument. The results obtained with H_2 and O_2 as the reaction gas were in agreement with each other, indicating that the measurement were not affected by spectral interference. (NMIJ) HR-ICP-MS was operated at high resolution mode for the measurements of As to avoid ^{40}Ar^{35}Cl interferences.(UME) This experiment was performed with

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
species will affect the degree of difficulty.			oxygen gas used to avoid the effect of $^{40}Ar^{35}Cl^+$ polyatomic interferences. (NIMT)
Correction or removal of matrix-induced signal suppression or enhancement *Chemical or instrumental procedures used to avoid or correct for matrix-induced signal suppression or enhancement.*	NIMT(Cd, Cu, Ni, Pb)	UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb), UME(As), NIM(Co, As), NIMT(As)	Gravimetric standard additions method was applied during the measurements. (UME)
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb), UME(As), NIM(Co, As), NIMT(As, Cd, Cu, Ni, Pb)		
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	UNIIM(Co, Sb, Hg, As), INMETRO(As, Co, Cd, Cu, Hg, Ni, Pb), UME(As), NIM(Co, As), NIMT(As, Cd, Cu, Ni, Pb)	GLHK(As, Cd, Pb)	

Inorganic Core Capabilities

Report from Participating Institute (Part A)

CCQM Study: ■ **CCQM-K128** □ **CCQM-P163**

Institute: VNIIFTRI

Method: IS+SA-ICP-OES

Analyte(s): As, Cd, Co, Cu, Hg, Ni, Pb

Instructions:

List element symbols for analytes in the appropriate column (‘Not tested’ or ‘Tested’) for all capabilities relevant to your measurements. Provide a brief explanation of the challenges you encountered in the final column, highlighting any aspects where you believe this measurement presented an unusually high degree of difficulty. Please add rows for any other capabilities which you used but which have not been included in this table.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.*		VNIIFTRI (As, Cd, Co, Cu, Hg, Ni, Pb)	Sub-boiled acids and DI water were used to minimize blank.(VNIIFTRI)
Digestion/dissolution of organic matrices *All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.*		VNIIFTRI (As, Cd, Co, Cu, Hg, Ni, Pb)	Method with a mixture of nitric and hydrochloric acids was used. Leather is digested in an acid solution. 100 mg of sample was taken into the digestion vessels, then 4.5 ml of sub-boiled HNO_3 (65%) and 1.5 ml of HCl (37%) were added. Heated in microwave system in 3 steps: 1 step: T = 160 oC, p = 40 bar, power 80%, time 5 min (ramp 5 min); 2 step: T = 190 oC, p = 40 bar, power 90%, time 15 min (ramp 5 min); 3 step: T = 100 oC, p = 40 bar, power

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
			90%, time 10 min (ramp 1 min); After digestion the PTFE vessels was cooled to room temperature and then opened. (VNIIFTRI)
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.*		VNIIFTRI (As, Cd, Co, Cu, Hg, Ni, Pb)	Challenge not encountered or challenge not applicable. (VNIIFTRI)
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	VNIIFTRI (As, Cd, Co, Cu, Hg, Ni, Pb)		No procedures has been used to prevent the loss of Hg. (VNIIFTRI)
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	VNIIFTRI(As, Cd, Co, Cu, Hg, Ni, Pb)		
Vapor generation *Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.*	VNIIFTRI(As, Cd, Co, Cu, Hg, Ni, Pb)		
Matrix separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the*	VNIIFTRI(As, Cd, Co, Cu, Hg, Ni, Pb)		

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.			
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		VNIIFTRI(As, Cd, Co, Cu, Hg, Ni, Pb)	Internal standard with 4 points standard additions were used. (VNIIFTRI)
Signal detection *The detection and recording of the analyte signals. The degree of difficulty increases for analytes present at low concentrations, or that are have weak emission lines..*		VNIIFTRI(As, Cd, Co, Cu, Hg, Ni, Pb)	Measurements were performed in Axial mode. Background reduction / quieting procedures applied. (VNIIFTRI)
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		VNIIFTRI(As, Cd, Co, Cu, Hg, Ni, Pb)	No significant effect. (VNIIFTRI)
Complex spectral backgrounds *Any techniques used to remove, reduce, or mathematically correct for interferences caused by the overlap of analyte emission lines with atomic, ionic, or molecular emission from matrix components. The relative concentrations and sensitivities of the analyte and the interfering species will affect the degree of difficulty. Samples*		VNIIFTRI(As, Cd, Co, Cu, Hg, Ni, Pb)	Choose wave lines without significant interferences, IS correction was applied. (VNIIFTRI)

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
containing high concentration matrix components with large numbers of emission lines or molecular bands may increase the measurement challenge.			
Correction or removal of matrix-induced signal suppression or enhancement *Chemical or instrumental procedures used to avoid or correct for matrix-induced signal suppression or enhancement. High concentrations of acids, dissolved solids, or easily ionized elements will increase the degree of difficulty.*		VNIIFTRI(As, Cd, Co, Cu, Hg, Ni, Pb)	Standard additions calibrations were used. (VNIIFTRI)

Inorganic Core Capabilities

Report from Participating Institute (Part B)

CCQM Study: ■ **CCQM-K128** □ **CCQM-P163**

Institute: **NIM**

Method: **ID-LC-ICP-MS**

Analyte: TriButylTin (TBT) in Leather Powder

Instructions:

List element symbols for analytes in the appropriate column ('Not tested' or 'Tested') for all capabilities relevant to your measurements. Provide a brief explanation of the challenges you encountered in the final column, highlighting any aspects where you believe this measurement presented an unusually high degree of difficulty. Please add rows for any other capabilities which you used but which have not been included in this table.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Extraction of species from the sample matrix *Single- or multi-steps procedures used to efficiently extract the analyte(s) of interest from the sample matrix with preservation of the analyte (s) integrity*		NIM	Check the isotope ratios of TBT extraction by 1stextraction procedure and 2nd extraction procedure
Species pre-concentration *Techniques and procedures used to increase the concentration of the species to be analysed by HPLC-ICP-IDMS. Includes solvent evaporation, freeze-drying, etc.*	NIM		
Achieving compatibility of LC conditions with ICP-MS *Selected chromatographic conditions (e.g mobile phase composition and flow rate) selected to be compatible with conventional nebulisation ICP-MS*		NIM	ICP-MS Narrow ID torch Option gas (20% O_2/Ar) – 20% S/C Temp – -5℃

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
Selectivity of LC separation *Development of separation systems to separate the target species from other species of the same element and/or to minimise matrix interferences from other compounds that co-elute with the target species and may affect its detection by ICP-MS (e.g high C-compound interference on the detection of Se and As species)*	NIM		
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample*		NIM	Check the isotope ratios of TBT extraction by 1st extraction procedure and 2nd extraction procedure
Characterisation of the natural species standard, including purity *All techniques used to know the exact concentration of the natural species standard used as a calibrant*	NIM		
Transient isotope ratio precision *Any techniques used for improved isotope ratio precision in transient signal analysis (e.g. adequate peak area integration, isotope integration time/number of points per peak, signal intensity, etc).*	NIM		
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.*	NIM		
Control of procedural blank *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for species that are environmentally ubiquitous and also present at very low concentrations in the sample.*	NIM		

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
Correction or removal of isobaric/polyatomic interferences *Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species , which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.*	NIM		
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	NIM		
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	NIM		
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*	NIM		

Inorganic Core Capabilities

Report from Participating Institute (Part B)

CCQM Study: ■ **CCQM-K128** □ **CCQM-P163**

Institute: **VNIIM**

Method: **LC-ICP-MS**

Analyte: TriButylTin (TBT) in Leather Powder

Instructions:

List element symbols for analytes in the appropriate column ('Not tested' or 'Tested') for all capabilities relevant to your measurements. Provide a brief explanation of the challenges you encountered in the final column, highlighting any aspects where you believe this measurement presented an unusually high degree of difficulty. Please add rows for any other capabilities which you used but which have not been included in this table.

Capabilities/Challenges	***Not Tested***	***Tested***	**Specific Challenges Encountered**
Extraction of species from the sample matrix *Single- or multi-steps procedures used to efficiently extract the analyte(s) of interest from the sample matrix with preservation of the analyte (s) integrity*		VNIIM	Aliquots with an internal standart in a solvent mixture of methanol:ethanol (80:20 v/v) with tropolone was sonicated for 60 min in an ultrasonic bath. Centrifuge separation of leather powder. (Check the completeness of TBT extraction by 2nd extraction procedure)
Species pre-concentration *Techniques and procedures used to increase the concentration of the species to be analysed by HPLC-ICP-MS. Includes solvent evaporation, freeze-drying, etc.*	VNIIM		
Achieving compatibility of LC conditions with ICP-MS *Selected chromatographic conditions (e.g mobile phase composition and flow rate) selected to be compatible with conventional nebulisation ICP-MS*		VNIIM	Column: ZORBAX Eclipse Plus C18 (4.6x100 mm, 3.5 micron) Mobile phase: Acetonitrile – 65 Water – 23

			Acetic acid – 12 TEA – 0.05 Flow rate – 1 ml/min, Temperature: 30 C ICP-MS: Platinum cones RF Power – 1550 W Smpl Depth – 7.0 mm Carrier Gas – 0.6 l/min Option gas (20% O_2/Ar) – 20% S/C Temp – 2 C
Selectivity of LC separation *Development of separation systems to separate the target species from other species of the same element and/or to minimise matrix interferences from other compounds that co-elute with the target species and may affect its detection by ICP-MS (e.g high C-compound interference on the detection of Se and As species)*	VNIIM		
Characterisation of the natural species standard, including purity *All techniques used to know the exact concentration of the natural species standard used as a calibrant*	VNIIM		
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.*		VNIIM	Control by blank
Control of procedural blank *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for species that are environmentally ubiquitous and also present at*		VNIIM	Syringe washing, blank between every 3 probes

very low concentrations in the sample.			
Correction or removal of isobaric/polyatomic interferences *Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species , which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.*	VNIIM		
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*			Monitorig masses: 116, 117, 118, 119, 120. Calculation result by 120 mass
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	VNIIM		

Inorganic Core Capabilities

Report from Participating Institute (Part B)

CCQM Study: ■ **CCQM-K128** □ **CCQM-P163**

Institute: **TUBITAK UME**

Method: **ID-GC-ICP-MS**

Analyte: TriButylTin (TBT) in Leather Powder

Instructions:

List element symbols for analytes in the appropriate column (‘Not tested’ or ‘Tested’) for all capabilities relevant to your measurements. Provide a brief explanation of the challenges you encountered in the final column, highlighting any aspects where you believe this measurement presented an unusually high degree of difficulty. Please add rows for any other capabilities which you used but which have not been included in this table.

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
Extraction of species from the sample matrix *Single- or multi-steps procedures used to efficiently extract the analyte(s) of interest from the sample matrix with preservation of the analyte (s) integrity*		TUBITAK UME	Different organic solvents, acids, acid concentrations were tested.
Species pre-concentration *Techniques and procedures used to increase the concentration of the species to be analysed by GC-ICP-IDMS. Includes solvent evaporation, freeze-drying, etc.*	TUBITAK UME		
Achieving compatibility of GC conditions with ICP-MS *Selected chromatographic conditions (e.g mobile phase and flow rate) selected to be compatible with conventional nebulisation ICP-MS*		TUBITAK UME	Transfer line temperature was optimized. The plasma position and gas flows were tuned using $[^{32}O_2]^+$ signal.
Selectivity of GC separation		TUBITAK	Column oven temperature was

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Development of separation systems to separate the target species from other species of the same element and/or to minimise matrix interferences from other compounds that co-elute with the target species and may affect its detection by ICP-MS (e.g high C-compound interference on the detection of Se and As species)		UME	optimized.
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample*	TUBITAK UME		
Characterisation of the natural species standard, including purity *All techniques used to know the exact concentration of the natural species standard used as a calibrant*	TUBITAK UME		
Transient isotope ratio precision *Any techniques used for improved isotope ratio precision in transient signal analysis (e.g. adequate peak area integration, isotope integration time/number of points per peak, signal intensity, etc).*	TUBITAK UME		
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.*		TUBITAK UME	Injections of rinse solutions were performed between the samples and standards.
Control of procedural blank *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for species that are environmentally ubiquitous and also present at very low concentrations in the sample.*		TUBITAK UME	No TBT signal was detected in procedural blank.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Correction or removal of isobaric/polyatomic interferences *Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species , which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.*	TUBITAK UME		
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*		TUBITAK UME	Mass bias correction was applied with GBW08710 TBT standard solution using bracketing approch.
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	TUBITAK UME		
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*	TUBITAK UME		

Annex C.The simplified core capabilities table

CCQM-K128 Measurement of Heavy Metals and Organo-Tin in Leather Powder

(As, Cd, Pb, Co, Cu, Hg, Ni, Sb within the concentrations levels are (30~100) mg/kg.)

Analyte groups	**Matrix challenges**					
	Water	**High Silica content (e.g. Soils, sediments, plants, …)**	**High salts content (e.g. Seawater, urine, …)**	**High organics content (e.g. high carbon) (e.g. Food, blood/serum, cosmetics, …)**	**Difficult to dissolve metals (Autocatalysts, …)**	**High volatile matrices (e.g. solvents, fuels, ...)**
Group I and II: Alkali and Alkaline earth (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba)						
Transition elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ag, Cd, Ta, W, Au, Hg, Al, Ga, In, Tl, Pb, Po)						
				Co, Ni, Cu,Cd, Hg, Pb		
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)						

Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)						
				As, Sb		
Non-metals (P, S, C, N, O)						
Halogens (F, Cl, Br, I)						
Rare Earth Elements (Lanthanides, Actinides)						

Low level (e.g. ng/kg to low µg/kg)
High level (e.g. High µg/kg to mg/kg)