

Report of the key comparison CCQM-K33

Determination of minor elements in steel

(Final Report)

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Abstract

The CCQM-K33 key comparison was organised by the Inorganic Analysis Working Group of CCQM to test the abilities of the national metrology institutes to measure the mass fractions of minor elements in steel. Elements to be analysed were Cr, Mn, Ni and Mo in low alloy steel. National Metrology Institute of Japan (NMIJ), National Institute of Standards and Technology (NIST), and Federal Institute for Materials Research and Testing (BAM) acted as the coordinating laboratories. The participants used various measurement methods, though many of them used ICP-AES. Generally speaking, the agreement of the results was very good for each measurand.

1 Introduction

The global production and trade of metals and metal alloys is a critical component of the modern industrial infrastructure. Accurate chemical measurements are crucial not only to the production of high quality metals and metal alloys, but also for international trade in order to ensure that buyers and sellers of such materials have confidence in the quality of the traded product. The economic impact of accurate chemical measurement is substantial. The range of commercial metal and alloy materials is also very large. Thus, it has been a challenge to identify the appropriate measurement activity for the CCQM in this area. After discussions at Inorganic Analysis Working Group (IAWG) meetings, the pilot study CCQM-P25 on “Determination of minor elements in steel” was chosen as a first measurement activity, which was conducted by National Metrology Institute of Japan (NMIJ), National Institute of Standards and Technology (NIST), and Federal Institute for Materials Research and Testing (BAM) as pilot laboratories.

Following the pilot study CCQM-P25, NMIJ, NIST and BAM proposed a key comparison of “Determination of minor elements in steel” at the IAWG meeting held on April 8-9, 2003. At the CCQM meeting following the IAWG meeting, the proposal was agreed as CCQM-K33 and NMIJ, NIST and BAM were designated as coordinating laboratories. Elements to be analysed were Cr, Mn, Ni and Mo in low alloy steel at mass-fraction levels between 0.1% and 3%. This is the first key comparison within CCQM in the field of metal-and-alloy analysis.

Though two Brazilian institutes expressed an interest in participating in CCQM-K33, neither institute was the designated NMI in this field. After some discussion among the coordinating laboratories, the IAWG chairman and the CCQM president, it was decided to conduct a separate pilot study designated CCQM-P56. The same samples measured by the CCQM-K33 participants were also used for CCQM-P56.

2 List of Participants

Table 1 contains the full names of all participating NMI's.

Table 1 List of participating NMI's

| No. | Participant | Country |
|-----|--|-------------------|
| 1 | BAM Federal Institute for Materials Research and Testing | Germany |
| 2 | CENAM National Center of Metrology | Mexico |
| 3 | CSIR-NML CSIR-National Metrology Laboratory | South Africa |
| 4 | KRISS Korea Research Institute of Standards and Science | Republic of Korea |
| 5 | LGC Laboratory of the Government Chemist | UK |
| 6 | NIST National Institute of Standards and Technology | USA |
| 7 | NMIJ National Metrology Institute of Japan | Japan |
| 8 | SP SP Swedish National Testing and Research Institute | Sweden |
| 9 | VNIIM D.I. Mendeleyev Institute for Metrology | Russia |

3 Samples

The samples for CCQM-K33 were small chips of low alloy steel, that were mixed and divided into 200 bottles. The mass of each chip was approximately less than several milligram. The homogeneity test was carried out by ICP-AES using 10 bottles picked up from the 200. The results indicate that the between-bottle standard deviation and the within-bottle standard deviation are less than 0.3% (relative) and less than 0.4% (relative), respectively, for Cr, Mn, Ni, and Mo. From each of 10 bottles, ca. 0.5 g of sample was weighed, dissolved, and diluted. The 10 solutions were analysed by ICP-AES using a conventional calibration method. The whole determination process starting with sample weighing was repeated four times.

The samples were distributed to the participants from NMIJ by EMS mail on November 25, 2003. Owing to some delivery trouble, the sample for VNIIM was again sent by regular air-mail on January 15, 2004. All samples finally reached their destinations safely. The contact persons are given in Table 2.

Table 2 List of contact persons of NMI's

| Participant | Contact person |
|-----------------|------------------------------------|
| BAM | Ralf Matschat; Sebastian Recknagel |
| CENAM | Antonio Salas |
| CSIR-NML | Alex Barzev |
| KRISS | Euijin Hwang |
| LGC | Peter Evans |
| NIST | Gregory Turk |
| NMIJ | Akiharu Hioki; Masayasu Kurahashi |
| SP | Bertil Magnusson |
| VNIIM | Yury Kustikov |

4 Technical Protocol

The technical protocol attached as Annex A instructed participants concerning samples, methods of measurement, reporting and time schedule. The deadline for the result reporting was originally the end of February, 2004; it was, however, postponed to the end of March, 2004.

5 Methods of Measurement

Participants were allowed to use any suitable method(s) of measurement. Any participant that chose to use multiple methods was required to report only one composite result (e.g., an average value from different methods) for each element. Though many of the results were obtained by ICP-AES, various methods of measurement were employed: inductively coupled plasma atomic emission spectrometry (ICP-AES), isotope-dilution inductively coupled plasma mass spectrometry (ID-ICP-MS), X-ray fluorescence spectrometry (XRF), inductively coupled plasma mass spectrometry (ICP-MS), instrumental neutron activation analysis (INAA), titrimetry and spectrophotometry. The number of results by each method is summarized in Table 3.

Table 3 The number of results by each method for CCQM-K33

| | Cr | Mn | Ni | Mo |
|-------------------------|-----|-----|-----|-----|
| ICP-AES | 3 | 4 | 3 | 5 |
| ID-ICP-MS | 1.5 | --- | 2.5 | 0.5 |
| XRF | 1.5 | 1.5 | 2 | 1.5 |
| ICP-MS | 0.5 | 1 | 0.5 | 0.5 |
| INAA | 0.5 | 0.5 | 0 | 0.5 |
| titrimetry | 1 | 0 | 0 | 0 |
| spectrophotometry | 0 | 1 | 1 | 0 |
| number of data reported | 8 | 8 | 9 | 8 |

The number for each method of the participants that chose to use two methods was counted as one half.

6 Results

The results are given in Tables 4-7 including information on the measurement methods and illustrated in Figures 1-4. The half of the error bar of each data in the Figures indicates the expanded uncertainty reported. Each Figure contains a solid, horizontal line representing the median of the submitted data for the set of laboratories shown in the Figure.

After disclosure of all results from participants, NIST discovered that a bad calibration standard was inadvertently included in analysis. Recalculation of the nickel result from NIST with the bad standard removed would yield a nickel mass fraction of 2.533% with an expanded uncertainty of 0.029% mass fraction ($k=2$). The originally submitted NIST value for nickel is used for any calculation on equivalence. The result of nickel from NIST was excluded for the calculation of median and mean.

After circulation of the draft A report, CENAM reported that one of the 5 sub-samples was improperly fused, and that the nickel results for that sub-sample appeared to be statistical outliers. Recalculation of the nickel result from CENAM with the bad results removed would yield a nickel mass fraction of 2.6032% with an expanded uncertainty of 0.0656% mass fraction ($k=2.45$). The originally submitted CENAM value for nickel is used for any calculation on equivalence. The result of nickel from CENAM was excluded for the calculation of median and mean.

Table 4 Results for Chromium (CCQM-K33)

| Participant | Method | Materials used for calibration *1 | Matrix matching | Internal standard for ICP-AES or ICP-MS | Reported value / mass fraction (%) | Expanded uncertainty / mass fraction (%) | |
|-----------------|------------|---|-----------------|---|------------------------------------|--|--------|
| | | | | | | | |
| BAM | titrimetry | K ₂ Cr ₂ O ₇ | | ----- | 0.5115 | 0.0018 | k=2 |
| CENAM | XRF | steel CRMs | yes | ----- | 0.5130 | 0.0127 | k=2.2 |
| CSIR-NML | ICP-AES | CSS | | Y | 0.5114 | 0.0122 | k=2 |
| KRISS | ID-ICP-MS | std soln from Cr | | ----- | 0.5068 | 0.0067 | k=2.06 |
| LGC | ICP-AES | std soln from Cr | yes | Au | 0.5056 | 0.0065 | k=2 |
| NIST | XRF | SRM std soln | yes | ----- | 0.5060 | 0.0042 | k=2 |
| | INAA | Cr metal | | ----- | | | |
| NMIJ | ID-ICP-MS | std soln from K ₂ Cr ₂ O ₇ | | ----- | 0.5118 | 0.0021 | k=2 |
| | ICP-MS | std soln from K ₂ Cr ₂ O ₇ | yes | Y | | | |
| SP | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| VNIIM | ICP-AES | std soln from Cr | yes | ----- | 0.506 | 0.018 | k=2 |

*1 CSS: standard solutions prepared from a commercial standard solution.

Table 5 Results for Manganese (CCQM-K33)

| Participant | Method | Materials used for calibration *1 | Matrix matching | Internal standard for ICP-AES or ICP-MS | Reported value / mass fraction (%) | Expanded uncertainty / mass fraction (%) | |
|-----------------|--------------------|--------------------------------------|-----------------|---|------------------------------------|--|--------|
| | | | | | | | |
| BAM | Spectro-photometry | std soln from Mn | | ----- | 0.511 | 0.007 | k=2 |
| CENAM | XRF | steel CRMs | yes | ----- | 0.5017 | 0.0112 | k=2.11 |
| CSIR-NML | ICP-AES | CSS | | Y | 0.5067 | 0.0060 | k=2 |
| KRISS | ICP-AES | std soln from Mn | yes | ----- | 0.5072 | 0.0011 | k=2.04 |
| LGC | ICP-AES | std soln from Mn | yes | Au | 0.5058 | 0.0048 | k=2 |
| NIST | XRF | SRM std soln | yes | ----- | 0.5040 | 0.0077 | k=2 |
| | INAA | SRM std soln | | ----- | | | |
| NMIJ | ICP-MS | std soln from Mn | yes | Y | 0.5049 | 0.0043 | k=2 |
| SP | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| VNIIM | ICP-AES | std soln from Mn | yes | ----- | 0.508 | 0.018 | k=2 |

*1 CSS: standard solutions prepared from a commercial standard solution.

Table 6 Results for Nickel (CCQM-K33)

| Participant | Method | Materials used for calibration *1 | Matrix matching | Internal standard for ICP-AES or ICP-MS | Reported value / mass fraction (%) | Expanded uncertainty / mass fraction (%) | |
|-----------------|-------------------|--------------------------------------|-----------------|---|------------------------------------|--|--------|
| | | | | | | | |
| BAM | Spectrophotometry | std soln from Ni | | ----- | 2.5497 | 0.0429 | k=2 |
| CENAM | XRF | steel CRMs | yes | ----- | 2.6502 *3 | 0.1028 *3 | k=2.36 |
| CSIR-NML | ICP-AES | CSS | | Y | 2.560 | 0.058 | k=2 |
| KRISS | ID-ICP-MS | std soln from Ni | | ----- | 2.524 | 0.022 | k=1.97 |
| LGC | ICP-AES | std soln from Ni | yes | Au | 2.549 | 0.047 | k=2 |
| NIST | XRF | SRM std soln | yes | ----- | 2.479 *2 | 0.021 *2 | k=2 |
| NMIJ | ID-ICP-MS | std soln from Ni | | ----- | 2.5385 | 0.0072 | k=2 |
| | ICP-MS | std soln from Ni | yes | Y | | | |
| SP | ID-ICP-MS | std soln from Ni-62 | | ----- | 2.536 | 0.021 | k=2 |
| VNIIM | ICP-AES | std soln from Ni | yes | ----- | 2.58 | 0.09 | k=2 |

*1 CSS: standard solutions prepared from a commercial standard solution.

*2 The result from NIST is as originally submitted, which is used for any calculation on equivalence. After disclosure of all results from participants, NIST discovered a calibration error. The information of the correct result is as follows: 2.533% mass fraction, $u_c=0.014\%$ mass fraction, $U=0.029\%$ mass fraction ($k=2$).

*3 The result from CENAM is as originally submitted, which is used for any calculation on equivalence. After circulation of the draft A report, CENAM reported a problem of measurement outliers. The information of the correct result is as follows: 2.6032% mass fraction, $u_c=0.0268\%$ mass fraction, $U=0.0656\%$ mass fraction ($k=2.45$).

Table 7 Results for Molybdenum (CCQM-K33)

| Participant | Method | Materials used for calibration *1 | Matrix matching | Internal standard for ICP-AES or ICP-MS | Reported value / mass fraction (%) | Expanded uncertainty / mass fraction (%) | |
|-----------------|-----------|--------------------------------------|-----------------|---|------------------------------------|--|--------|
| | | | | | | | |
| BAM | ICP-AES | std soln from Mo | yes | Y | 1.0475 | 0.0136 | k=2 |
| CENAM | XRF | steel CRMs | yes | ----- | 1.0325 | 0.0257 | k=2.2 |
| CSIR-NML | ICP-AES | CSS | | Y | 1.052 | 0.023 | k=2 |
| KRISS | ICP-AES | std soln from Mo | yes | ----- | 1.0353 | 0.0034 | k=2.04 |
| LGC | ICP-AES | std soln from Mo | yes | Au | 1.035 | 0.014 | k=2 |
| NIST | XRF | std soln from MoO ₃ | yes | ----- | 1.0371 | 0.0056 | k=2 |
| | INAA | Mo metal | | ----- | | | |
| NMIJ | ID-ICP-MS | std soln from Mo | | ----- | 1.0415 | 0.0080 | k=2 |
| | ICP-MS | std soln from Mo | yes | Y | | | |
| SP | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| VNIIM | ICP-AES | std soln from Mo | yes | ----- | 1.05 | 0.039 | k=2 |

*1 CSS: standard solutions prepared from a commercial standard solution.

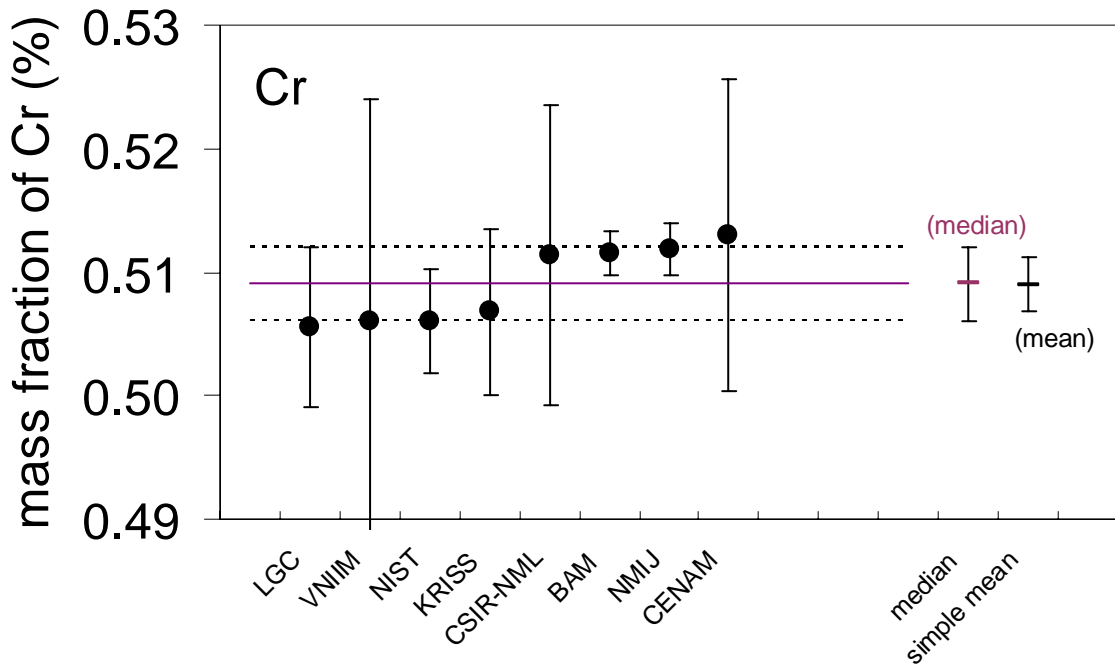


Fig. 1 Results for Cr of CCQM-K33

The half of each bar indicates the expanded uncertainty ($k=2$).
 The results of CENAM and KRISS are followed by the expanded uncertainties with coverage factors $k=2.2$ and 2.06 , respectively.

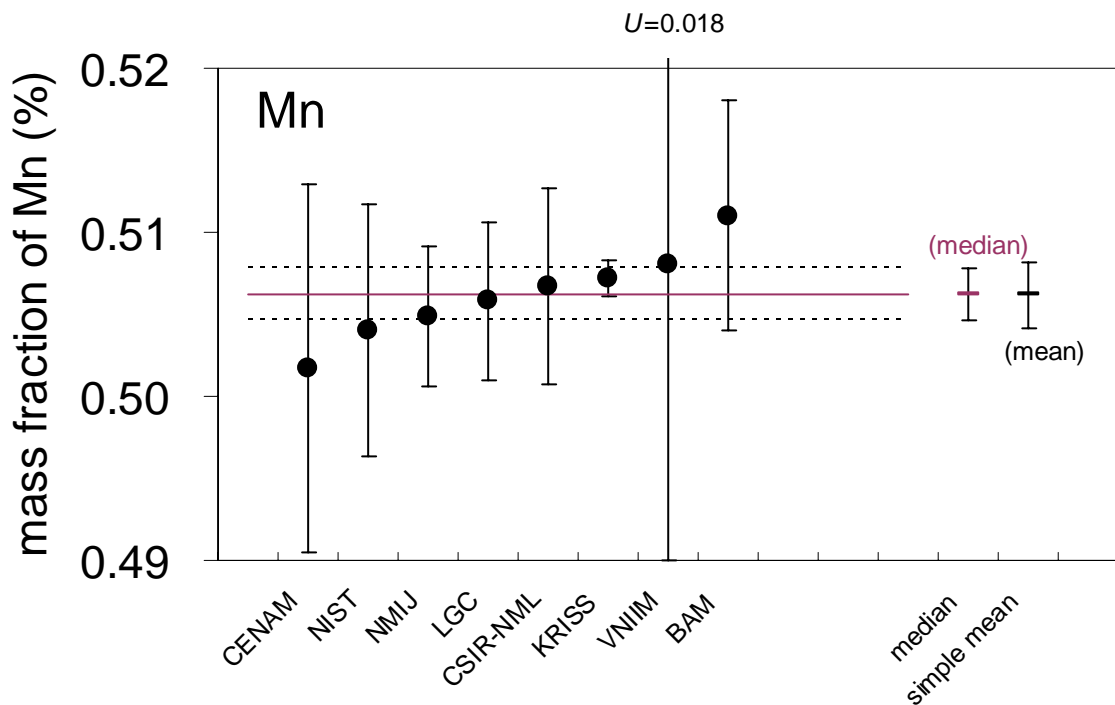


Fig. 2 Results for Mn of CCQM-K33

The half of each bar indicates the expanded uncertainty ($k=2$).
 The results of CENAM and KRISS are followed by the expanded uncertainties with coverage factors $k=2.11$ and 2.04 , respectively.

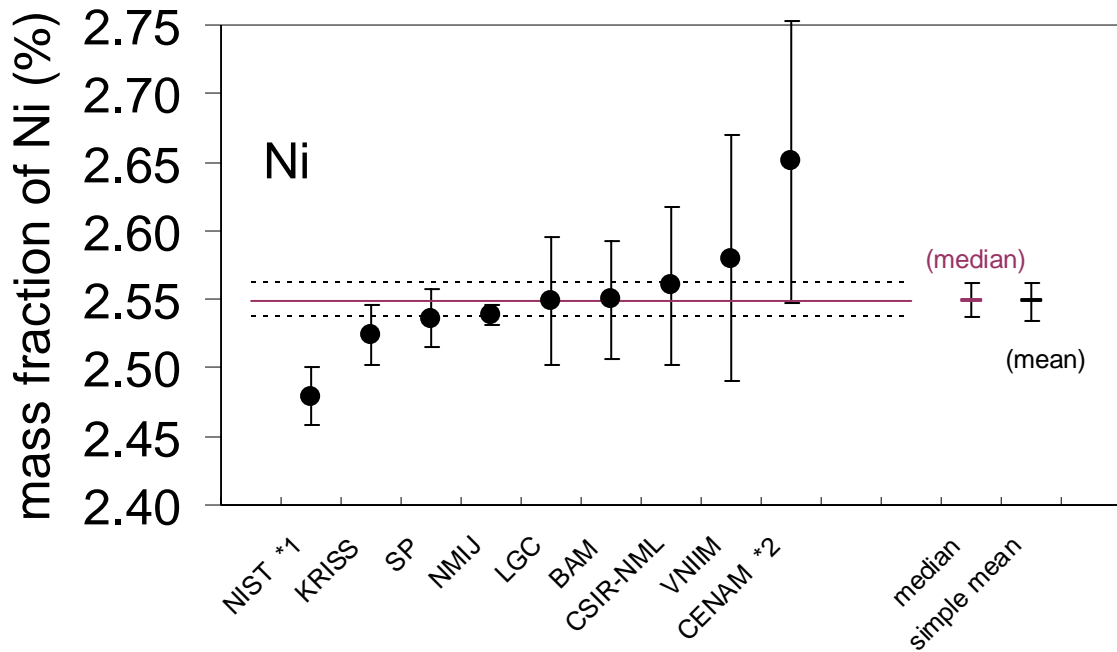


Fig. 3 Results for Ni of CCQM-K33

The half of each bar indicates the expanded uncertainty ($k=2$).

The results of CENAM and KRISS are followed by the expanded uncertainties with coverage factors $k=2.36$ and 1.97 , respectively.

*1 The result of NIST was excluded for the calculation of median and mean.

*2 The result of CENAM was excluded for the calculation of median and mean.

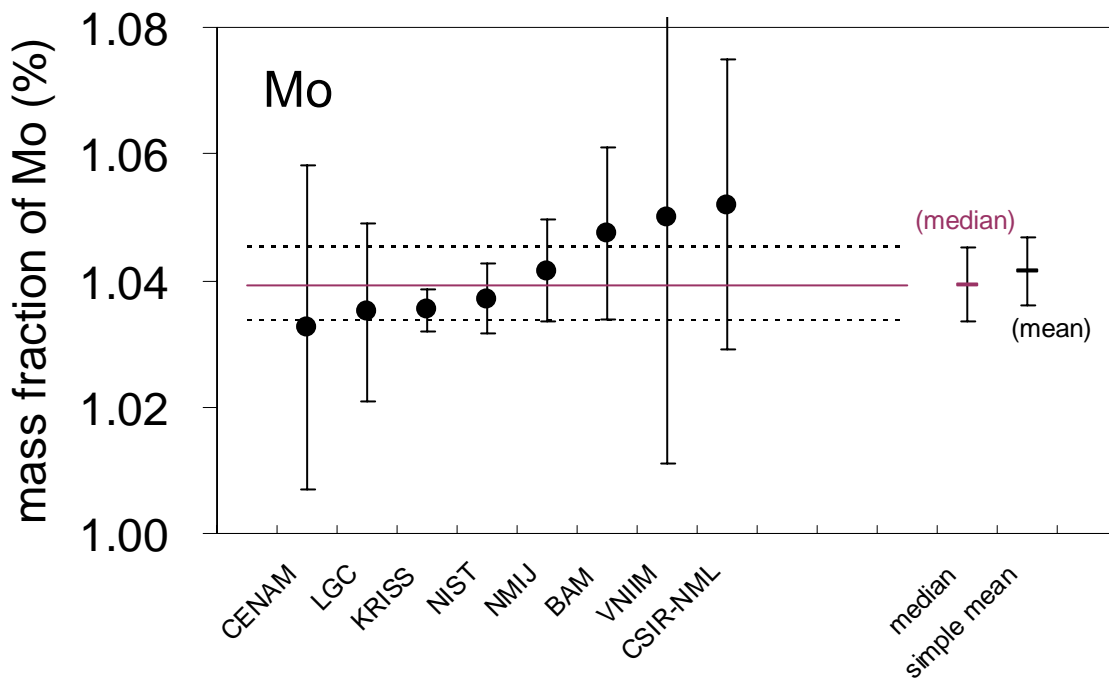


Fig. 4 Results for Mo of CCQM-K33

The half of each bar indicates the expanded uncertainty ($k=2$).

The results of CENAM and KRISS are followed by the expanded uncertainties with coverage factors $k=2.2$ and 2.04 , respectively.

7 Estimation of KCRV

Some candidates for the key comparison reference value (KCRV) for each measurand are in Tables 8-11. At the IAWG meeting held on April, 2004 (BIPM), the median for each measurand excluding NIST for nickel was chosen as the KCRV for CCQM-K33. Later the CENAM result for nickel was also excluded from the calculation of the KCRV.

Table 8. Candidates of KCRV of Cr for CCQM-K33

| | | Value mass fraction (%) | Expanded uncertainty ($k=2$) mass fraction (%) |
|---------------------------------|----|-------------------------------|--|
| Mean | *1 | 0.5090 | 0.0022 |
| Median | *2 | 0.5091 | 0.0030 |
| Weighted mean (usual weight) | *3 | 0.5107 | 0.0012 |
| Weighted mean (mild weight) | *4 | 0.5098 | 0.0016 |
| Robust mean | *5 | 0.5090 | 0.0025 |

Table 9. Candidates of KCRV of Mn for CCQM-K33

| | | Value mass fraction (%) | Expanded uncertainty ($k=2$) mass fraction (%) |
|---------------------------------|----|-------------------------------|--|
| Mean | *1 | 0.5062 | 0.0020 |
| Median | *2 | 0.5063 | 0.0016 |
| Weighted mean (usual weight) | *3 | 0.5070 | 0.0010 |
| Weighted mean (mild weight) | *4 | 0.5066 | 0.0015 |
| Robust mean | *5 | 0.5061 | 0.0022 |

Table 10. Candidates of KCRV of Ni for CCQM-K33 (*6)

| | | Value mass fraction (%) | Expanded uncertainty ($k=2$) mass fraction (%) |
|---------------------------------|----|-------------------------------|--|
| Mean | *1 | 2.5518 | 0.0308 |
| Mean (excl. NIST&CENAM) | | 2.5482 | 0.0137 |
| Median | *2 | 2.5490 | 0.0128 |
| Median (excl. NIST&CENAM) | | 2.5490 | 0.0123 |
| Weighted mean (usual weight) | *3 | 2.5335 | 0.0060 |
| Weighted mean (mild weight) | *4 | 2.5352 | 0.0083 |
| Robust mean | *5 | 2.5482 | 0.0226 |

Table 11. Candidates of KCRV of Mo for CCQM-K33

| | | Value mass fraction (%) | Expanded uncertainty ($k=2$) mass fraction (%) |
|---------------------------------|----|-------------------------------|--|
| Mean | *1 | 1.0414 | 0.0053 |
| Median | *2 | 1.0393 | 0.0058 |
| Weighted mean (usual weight) | *3 | 1.0370 | 0.0026 |
| Weighted mean (mild weight) | *4 | 1.0388 | 0.0033 |
| Robust mean | *5 | 1.0414 | 0.0061 |

- *1 The expanded uncertainty was based on the standard deviation of the mean.
 *2 The uncertainty of the median was based on the estimate from $\text{median}(|x_i - \text{median}|)/0.6745$, where x_i is each reported value.
 *3 The square of reciprocal of reported uncertainty was used as a weight.
 *4 The reciprocal of reported uncertainty was used as a weight.
 *5 Huber estimate (H15) from Analytical Methods Committee, *Analyst*, **114**, 1693-1697 (1989).
 *6 Calculated from the results as submitted.

8 Equivalence statements

The degree of equivalence and its uncertainty between an NMI result and the KCRV is calculated according to the following equations:

$$D_i = (x_i - x_R)$$

$$U_i^2 = (k^2 u_i^2 + 2^2 u_R^2)$$

where D_i is the degree of equivalence between the NMI result x_i and the KCRV x_R , and U_i is the expanded uncertainty (coverage factor: $k = 2$; declared ones of some participants were not used.) of D_i calculated by both the combined standard uncertainty u_i of x_i and the standard uncertainty u_R of x_R . The calculation results are shown in Tables 12-15.

Table 12 Results for Chromium (CCQM-K33)

| Participant | Reported value / mass fraction (%) | Expanded uncertainty / mass fraction (%) | | D_i / mass fraction (%) | U_i / mass fraction (%) |
|-----------------|------------------------------------|--|----------|---------------------------|---------------------------|
| KCRV | 0.5091 | 0.0030 | $k=2$ | | |
| BAM | 0.5115 | 0.0018 | $k=2$ | 0.0024 | 0.0035 |
| CENAM | 0.5130 | 0.0127 | $k=2.2$ | 0.0039 | 0.0119 |
| CSIR-NML | 0.5114 | 0.0122 | $k=2$ | 0.0023 | 0.0126 |
| KRISS | 0.5068 | 0.0067 | $k=2.06$ | -0.0023 | 0.0072 |
| LGC | 0.5056 | 0.0065 | $k=2$ | -0.0035 | 0.0072 |
| NIST | 0.5060 | 0.0042 | $k=2$ | -0.0031 | 0.0052 |
| NMIJ | 0.5118 | 0.0021 | $k=2$ | 0.0027 | 0.0037 |
| SP | ----- | ----- | ----- | | |
| VNIIM | 0.506 | 0.018 | $k=2$ | -0.0031 | 0.0182 |

Table 13 Results for Manganese (CCQM-K33)

| Participant | Reported value / mass fraction (%) | Expanded uncertainty / mass fraction (%) | | D_i / mass fraction (%) | U_i / mass fraction (%) |
|-----------------|------------------------------------|--|----------|---------------------------|---------------------------|
| KCRV | 0.5063 | 0.0016 | $k=2$ | | |
| BAM | 0.511 | 0.007 | $k=2$ | 0.0047 | 0.0072 |
| CENAM | 0.5017 | 0.0112 | $k=2.11$ | -0.0046 | 0.0107 |
| CSIR-NML | 0.5067 | 0.0060 | $k=2$ | 0.0004 | 0.0062 |
| KRISS | 0.5072 | 0.0011 | $k=2.04$ | 0.0009 | 0.0019 |
| LGC | 0.5058 | 0.0048 | $k=2$ | -0.0005 | 0.0051 |
| NIST | 0.5040 | 0.0077 | $k=2$ | -0.0023 | 0.0079 |
| NMIJ | 0.5049 | 0.0043 | $k=2$ | -0.0014 | 0.0046 |
| SP | ----- | ----- | ----- | ----- | ----- |

| | | | | | |
|--------------|-------|-------|-------|--------|--------|
| VNIIM | 0.508 | 0.018 | $k=2$ | 0.0017 | 0.0181 |
|--------------|-------|-------|-------|--------|--------|

Table 14 Results for Nickel (CCQM-K33)

| Participant | Reported value / mass fraction (%) | Expanded uncertainty / mass fraction (%) | | D_i / mass fraction (%) | U_i / mass fraction (%) |
|-----------------|------------------------------------|--|----------|---------------------------|---------------------------|
| KCRV | 2.5490 | 0.0123 | $k=2$ | | |
| BAM | 2.5497 | 0.0429 | $k=2$ | 0.0007 | 0.0446 |
| CENAM | 2.6502 | 0.1028 | $k=2.36$ | 0.1012 | 0.0880 |
| CSIR-NML | 2.560 | 0.058 | $k=2$ | 0.0110 | 0.0593 |
| KRISS | 2.524 | 0.022 | $k=1.97$ | -0.0250 | 0.0255 |
| LGC | 2.549 | 0.047 | $k=2$ | 0.0000 | 0.0486 |
| NIST | 2.479 | 0.021 | $k=2$ | -0.0700 | 0.0243 |
| NMIJ | 2.5385 | 0.0072 | $k=2$ | -0.0105 | 0.0143 |
| SP | 2.536 | 0.021 | $k=2$ | -0.0130 | 0.0243 |
| VNIIM | 2.58 | 0.09 | $k=2$ | 0.0310 | 0.0908 |

Table 15 Results for Molybdenum (CCQM-K33)

| Participant | Reported value / mass fraction (%) | Expanded uncertainty / mass fraction (%) | | D_i / mass fraction (%) | U_i / mass fraction (%) |
|-----------------|------------------------------------|--|----------|---------------------------|---------------------------|
| KCRV | 1.0393 | 0.0058 | $k=2$ | | |
| BAM | 1.0475 | 0.0136 | $k=2$ | 0.0082 | 0.0148 |
| CENAM | 1.0325 | 0.0257 | $k=2.2$ | -0.0068 | 0.0241 |
| CSIR-NML | 1.052 | 0.023 | $k=2$ | 0.0127 | 0.0237 |
| KRISS | 1.0353 | 0.0034 | $k=2.04$ | -0.0040 | 0.0067 |
| LGC | 1.035 | 0.014 | $k=2$ | -0.0043 | 0.0152 |
| NIST | 1.0371 | 0.0056 | $k=2$ | -0.0022 | 0.0081 |
| NMIJ | 1.0415 | 0.0080 | $k=2$ | 0.0022 | 0.0099 |
| SP | ----- | ----- | ----- | ----- | ----- |
| VNIIM | 1.05 | 0.039 | $k=2$ | 0.0107 | 0.0394 |

9 Discussion

For every element, there are no observed differences among the measurement methods employed. For every element except for nickel, most of the reported data are within ± 1 % relative to the mean, which is improved in comparison with CCQM-P25. Though there are apparently two separated clusters of data for Cr, this seems to be coincidental judging from the uncertainties of the reported data, the result of the homogeneity test and the order of the sample bottling.

10 Acknowledgement

The work of the key comparison was done by the contributions from many scientists as well as the contact persons: Antonio Salas (CENAM); Alex Barzev (CSIR-NML); Euijin Hwang (KRISS); Peter Evans and Mike Sargent (LGC); Robert Greenberg and John Sieber (NIST); Naoko

Nonose (NMIJ); Bertil Magnusson (SP); Yury Kustikov (VNIIM).

Annex A - Technical protocol**CCQM-K33 on determination of minor elements in steel****Technical protocol**
(revised in Nov. 21, 2003)**1. Introduction**

In the pilot study CCQM-P25, Cr, Ni, Mn and Mo in low alloy steel were analyzed. Generally speaking, the agreement of the results was very good for each element. A key comparison CCQM-K33 was accepted by the CCQM in 2003 as a follow-up to CCQM-P25. National Metrology Institute of Japan (NMIJ), National Institute of Standards and Technology (NIST), and Bundesanstalt für Materialforschung und -prüfung (BAM) were designated as the coordinating laboratories.

2. Samples

Each participant will receive one bottle containing a minimum of 30 g of small chips of low alloy steel. The homogeneity of the material was checked before distribution based on determination using a sample size of about 0.5 g.

The elements to be determined are Cr, Ni, Mn and Mo in low alloy steel. The mass-fraction levels are in the range 0.1 to 1 % for Cr, 0.5 to 1.5 % for Mo, 0.5 to 3 % for Ni, and 0.1 to 1 % for Mn. All of these elements are related to characteristics of steel. The mass-fraction of carbon in the steel is about 0.7 %.

3. Methods of Measurement

Each participant may use any suitable method(s) of measurement. Any NMI that chooses to use multiple methods shall report only one composite result (e.g., an average value from different methods) for each element.

4. Reference values

The key comparison reference value (KCRV) for each element will be probably the median of all results from the participants. It will be suitably decided later.

5. Reporting

Each participant shall report only one result for each element. The results should be reported in mass-fractions of each element, accompanied by a full uncertainty statement including a combined standard uncertainty and an expanded uncertainty and the coverage factor applied. In addition the report should include details of the procedure, traceability links, the uncertainty budget and the instrument(s) used.

6. Time schedule

Deadline for registration of participation: October 31, 2003
Dispatch of the samples: November, 2003
Deadline for receiving the report: March 31, 2004

7. Participants

Criteria for participation in Key Comparisons are given in paragraph 6.1 of the CIPM-MRA.

8. Coordinating laboratories

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