

# Final report

## Key Comparison CCQM-K42

Determination of Chromium, Copper, Iron, Manganese and Zinc in Aluminium alloy

### Proposer

**Siegfried Noack (BAM) and Ralf Matschat (BAM)**



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**June 2008**

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## 1. Abstract

The CCQM-Key-Comparison K42 was organized by the inorganic analysis working group of CCQM to test the abilities of metrological institutes to measure the mass fractions of the components of an aluminium alloy.

Chosen elements were Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn) and Zinc (Zn).

The BAM Federal Institute for Materials Research and Testing (BAM Bundesanstalt für Materialforschung und –prüfung) in Berlin, Germany acted as the pilot laboratory.

CCQM-K42 demonstrates the abilities of metrological institutes to measure the mass fractions of minor and trace components (mass content about 0.05% to 0.2%) of an aluminium alloy for Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn) and Zinc (Zn).

The analytical methods used were Neutron Activation Analysis (NAA), X-Ray Fluorescence Spectrometry (XRF) using the reconstitution technique, ICP-OES and ICP-MS.

The scope of the key comparison extends to non-ferrous alloys comprising the same or similar constituents when analysed using the technique(s) applied by a participant in obtaining the results submitted for CCQM-42.

## 2. Introduction

Aluminium alloys are playing a decisive role e.g. in automotive engineering and in aircraft industry.

In this context analytical controlling of the used alloys and therefore the ability of laboratories to determine the components with sufficient precision is very important.

The uncertainty of the analytical results is especially influenced by the parameters of the sample preparation procedures (fusion procedures, solving). Thus, it has been a challenge to determine the alloy components especially with methods which are particularly different concerning the sample preparation procedure as the reconstitution technique (XRF), the Neutron Activation analysis and ICP OES/ICP – MS.

## 3. List of participants and methods

No.	Participant	Country	Method
1	<b>BAM</b> Bundesanstalt für Materialforschung und –prüfung	Germany	XRF, Reconstitution method
2	<b>NIST</b> National Institute of standards and Technology	USA	INAA and XRF, Reconstitution method
3	<b>IRMM</b> Institute for Reference Materials and Measurements	EU	INAA
4	<b>VNIIM</b> D.I. Mendeleev Institute for Metrology	Russia	ICP-OES
5	<b>CENAM</b> Centro Nacional de Metrología	Mexico	XRF, Reconstitution method
6	<b>IMGC</b> Unit of Radiochemistry and Spectroscopy c/o Dept. General Chemistry University of Pavia	Italy	INAA
7	<b>UME</b> Ulusal Metroloji Enstitüsü Kimyasal Metroloji Laboratuvarı	Turkey	ICP-MS

## 4. Proposal

<b>PROPOSED</b>	
<b>CCQM COMPARISON</b>	
<b>1. CCQM Working Group:</b> Inorganic	<b>2. Working Group Proposal Ref. No / Name:</b> CCQM-K 42
<b>3. Type of collaboration:</b> Key Comparison	<b>4. Subject field:</b> Aluminium alloy
<b>5. Proposing institute(s):</b> BAM	<b>6. Proposed Pilot Laboratory:</b> BAM
<b>7. Other interested institutes:</b> VNIIM (Russia); CENAM (Mexico); BAM (Germany); IRMM (Europe); NIST (USA).	
<b>8. Measurand and nominal value:</b> Mass fractions: Fe(0.2%), Cu(0.1%), Mn(0.1%), Cr(0,05%), Zn (0.1%), in Aluminium-alloy	
<p><b>9. Description:</b> Because Al-alloys are a very important basic material for producing several consumer goods, aluminium alloy CRMs are produced by many different CRM producers world wide. But there are significant differences between CRMs from different producers, necessitating a harmonisation. These CRMs are needed to calibrate spark optical emission spectrometers and XRF-spectrometers both widely spread for quality control in production and processing of aluminium alloys. The homogeneity of the material has to be investigated before using in the interlaboratory comparison.</p> <p><b>Remark:</b> The pilot study P34 has been completed with good results. Neutron activation analysis (INAA) and XRF combined with the reconstitution principle had been predominantly used by the participants. To document the good capability concerning these two methods it would be senseful, that the participants of the pilot study take also part in the planned key comparison using these methods again.</p> <p>The INAA is a very effective method, because sample preparation procedures are not necessary. The reconstitution method has the favourable characteristic of an accuracy controlling by the method itself: The calibration is made by gravimetrically prepared mixtures of pure substances followed by application of a fusion technique and the mass fractions of analytes in the fused calibration sample are adapted to the mass fractions of analytes in the fused analysed sample in an iterative process.</p> <p>In addition to these methods others like IDMS and ICP OES which had been also used in the pilot study by one laboratory respectively or AAS can be used naturally too.</p>	
<b>10. Additional remarks:</b> The reconstitution principle is described in the book "Qualitätssicherung in der Analytik, Die Rekonstitution, Eine Methode zur Optimierung der Richtigkeit von Analysen", 1996, Verlag Stahl-Eisen, Düsseldorf, ISBN 3-514-00581-8.	
<b>11. Proposed measurement start date and timescale:</b> Start: October 2004, Deadline for results: March 2005; Final report: October 2005	
<p><b>12. Proposer's name:</b> Dr. Siegfried Noack; Dr. Ralf Matschat  <b>Address:</b> Federal Institute for Materials Research and Testing (BAM),  Richard-Willstätter-Strasse 11, D-12489 Berlin, Germany  <b>Telephone:</b> 0049-30-8104 1113 or 1110 Fax: 0049-30-8104 1117  <b>E-Mail:</b> siegfried.noack@bam.de; ralf.matschat@bam.de</p>	
<b>13. Proposer's signature:</b> S. Noack	<b>14. Date:</b> 25 August 2004

**5. Registration form**

To Federal Institute for Materials Research and Testing (BAM),  
Division I.1, Richard-Willstaetter Str.11, 12489 Berlin, Germany



**Fax: +49 30 8104 1117**

## CCQM Key Comparison K 42

### Fe, Cu, Mn, Cr, Zn in Aluminium-alloy

## Registration Form

Measurand			Participation		Analysis method
Name/Symbol	Mass fraction*)	Yes	No		
Iron	Fe	0,2 %			
Copper	Cu	0,1 %			
Manganese	Mn	0,1 %			
Chromium	Cr	0,05 %			
Zinc	Zn	0,1 %			

\*) Nominal values

### NMI Identification (or designated laboratory)

<b>Name</b>	
<b>Institute</b>	
<b>Address</b>	
<b>Country</b>	
<b>E-Mail</b>	
<b>Tel.-Number</b>	
<b>Fax-Number</b>	
<b>Date</b>	
<b>Remark</b>	
<b>Signature</b>	

Please return this sheet by fax no later than **31st October 2004** to:

Dr. Siegfried Noack  
Bundesanstalt für Materialforschung und –prüfung (BAM)  
Projektgruppe I.1902  
**Fax: +49 30 8104 1117**

## 6. Invitation paper



Federal Institute for Materials Research and Testing (BAM), Richard-Willstaetter Str.11, 12489 Berlin, Germany

Tuesday, 15 September 2004

### To the members of CCQM inorganic working group

#### Invitation paper

#### Key comparison “CCQM-K42” and pilot study “P34.1”

Determination of alloying additions (Fe, Cu, Mn, Cr and Zn) in aluminium alloy

*(Answer is desired even if the institute or laboratory does not want to participate!)*

Dear IAWG Member,

This letter is an invitation to participate in the CCQM key comparison “K42” or in the pilot study “P34.1”.

Members of the inorganic working group, who are a national metrological institute or a designated laboratory, are invited to participate in the key comparison “K42”. These institutes or laboratories should have participated in the earlier pilot study “P34”.

IAWG members who want to repeat the pilot study “P34” or have not yet been part in this study are invited to the second pilot study “P34.1”, which comprises – just as K42 - the determination of alloying additions (Fe, Cu, Mn, Cr and Zn) in aluminium alloy.

Furthermore the NMIs are requested to nominate other laboratories in their countries as potential participants of the second pilot study “P34.1”.

Below some technical and organizational information is given:

#### Registration form

If you want to participate in the key comparison “K42” or the pilot study “P34.1” please use the accordant annexed registration sheet. Please fill in the form and specify which elements you want to analyze and which method will be used.

Please return Registration form by fax no later than **31st October 2004** to:

Dr. Siegfried Noack  
Bundesanstalt für Materialforschung und –prüfung (BAM)  
Projektgruppe I.1902  
**Fax: +49 30 8104 1117**

#### Pilot laboratory /Proposers

Federal Institute for Materials Research and Testing (BAM), Division I.1  
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Fax: +49-30-8104 1117

E-Mail: siegfried.noack@bam.de; ralf.matschat@bam.de

Proposer's name: Dr. Siegfried Noack; Dr. Ralf Matschat

**Contact persons:**

Dr. Siegfried Noack

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Dr. Ralf Matschat

E-Mail: [ralf.matschat@bam.de](mailto:ralf.matschat@bam.de)

☎ (+4930) 8104 1110

Fax: (+4930) 8104 1117

**Time schedule**

Deadline for registration of participation:	October 31 <sup>st</sup> 2004-09-14
Shipment of samples:	November 2004
Deadline for delivery of results:	March 2005
Draft report:	June 2005
Final report:	October 2005

**Participants***Key Comparison "K42":*

NMIs or designated laboratories

*Pilot Study "P34.1":*

NMIs or nominated other laboratories in their countries

NMIs can take part in one or both of the exercises**Other interested institutes / laboratories**

Until now:

- VNIIM (Russia)
- CENAM (Mexico)
- BAM (Germany)
- IRMM (Europe)
- Jozef Stefan Inst. (Slovenia)
- NIST (USA).

**Sample material**

The material to be analyzed will be send in screwed plastic bottles, each containing about 100 g of cuttings of the aluminium alloy. The material for both exercises ("K42" and "P34.1") is the same.

**Measurands**

The measurands for both exercises (K42 and P34.1) are the mass fractions of Fe, Cu, Mn, Cr and Zn in an aluminium alloy.

**Nominal values**Iron  $w(\text{Fe}) = 0,2 \%$ Copper  $w(\text{Cu}) = 0,1 \%$ Manganese  $w(\text{Mn}) = 0,1 \%$ Chromium  $w(\text{Cr}) = 0,05 \%$ Zinc  $w(\text{Zn}) = 0,1 \%$

**Description of the material**

Because Al-alloys are a very important basic material for producing several consumer goods, aluminium alloy CRMs are produced by many different CRM producers world wide. But there are significant differences between CRMs from different producers, necessitating a harmonisation. These CRMs are used to calibrate spark optical emission spectrometers and XRF-spectrometers both widely spread for quality control in production and processing of aluminium alloys. The homogeneity of the material will be investigated at BAM before using in the interlaboratory comparison.

**Analytical methods**

The earlier pilot study "P34" has been completed with good results. Instrumental Neutron activation analysis (INAA) and X-Ray-Fluorescence Analysis (XRF) combined with the reconstitution principle had been predominantly used by the participants. To document the good capability concerning these two methods it would be appropriate, that the participants of the pilot study take also part in the planned key comparison using these methods again.

The INAA is a very effective method, because sample preparation procedures are not necessary. The reconstitution method has the favourable characteristic of an accuracy controlling by the method itself: The calibration is made by gravimetrically prepared mixtures of pure substances followed by application of a fusion technique and the mass fractions of analytes in the fused calibration sample are adapted to the mass fractions of analytes in the fused analysed sample in an iterative process.

In addition to these methods others like IDMS and ICP OES which had been also used in the pilot study by one laboratory respectively or AAS can be used too.

*Remark*

The reconstitution principle is described in the book "Qualitätssicherung in der Analytik, Die Rekonstitution, Eine Methode zur Optimierung der Richtigkeit von Analysen", 1996, Verlag Stahl-Eisen, Düsseldorf, ISBN 3-514-00581-8.

**Number of results**

According to the earlier pilot study "P34" six (6) single results should be transmitted.

**Form for description of analytical procedure and results**

According to the earlier pilot study "P34" an EXCEL-sheet will be send to all participants which should be completed with the appropriate data.

**Uncertainty budget**

According to the Guide to Expression of Uncertainty in Measurement (GUM) an uncertainty budget should be calculated considering all known influencing parameters (especially contributions from calibration!) which can cause a bias of the analytical result (e.g. weighing parameters, temperatures, dispersion of measuring values, volumes etc.)

In that context it should be noted that there are two groups of influencing parameters: The parameters of the "Type A" are based on frequency distributions. The parameters of the "Type B" are based on data of former results or experiences.

With best regards

Siegfried Noack and Ralf Matschat

## 7. Instructions for participants

### Analysis

In total 6 repetitions of the analysis should be carried out. Two series should be done at different days: Each with 3 repetitions of the analysis and a new calibration.

### Calibration

Please preferably use primary substances with a definite purity for the preparation of calibration solutions or solid calibrations samples.

If this is not possible you should use at least two different commercial products which are compared. If the contents are in a good agreement, one of them can be used for the preparation of the calibration solutions or solid samples, respectively.

Alternatively you can use primary methods directly linked to SI-units.

For both series of analysis the same stock solution for the preparation of calibration solutions can be used.

### Uncertainty

According to the Guide to Expression of Uncertainty in Measurement (GUM) an uncertainty budget should be calculated considering all known influencing parameters which can cause a bias of the analytical result (e.g. weighing parameters, temperatures, dispersion of measuring values, volumes etc.)

In that context it should be noted that there are two groups of influencing parameters: The parameters of the "Type A" are based on frequency distributions. The parameters of the "Type B" are based on data of former results or experiences.

Please list the single contributions in a table.

### Reporting data

For each element one result should be reported with an uncertainty.

### Deadline for delivery of results to pilot laboratory

31 March 2005

### Confirmation

The receipt of the instructions and the samples had to be confirmed by E-Mail or by fax.

### Contact

E-Mail: siegfried.noack@bam.de

Fax: (+49) 30 8104 1117

Phone: (+49) 30 8104 1113

### CCQM K42 Aluminium

#### Declarations

The corresponding data had to be enlisted into the **green marked** cells of the excel sheet, which had been sent to each participant. If the specifications are equal for several elements, a link is sufficient!

#### Attention!

If more place for enlisting the data is needed, the table "CCQM\_K42\_Declarations (2)" can be alternatively used.

### Required information about analytical procedure

- Used primary substance for calibration
- Purity of primary substance [%]
- Uncertainty of the purity [%]
- Stock solution
  - Source
  - Preparing
  - Concentration
- Number of calibration samples (solution or solid)
- Details of calibration solutions: concentrations, if: matrix matching, addition method etc.
- Estimated limits of determination (9s-criterion)
- Kind of digestion (acid, alkaline, fusion...)

- Weighted sub-sample [mg]
- Date of digestion performance
- Details of digestion procedure
  - Reagents
  - Conditions etc.
- Wavelengths if spectrometric methods are used or other specification
- Used analytical instrument
- Instrument parameter e.g.
  - Nebulizer
  - Lines
  - Background
  - Time cycles etc.)

## 8. List of contact persons

No.	Participant	Country	Contact person
1	<b>BAM</b> Bundesanstalt für Materialforschung und –prüfung	Germany	Siegfried Noack
2	<b>NIST</b> National Institute of standards and Technology	USA	Gregory C. Turk
3	<b>IRMM</b> Institute for Reference Materials and Measurements	EU	P. Vermaerke
4	<b>VNIIM</b> D.I. Mendeleev Institute for Metrology	Russia	L.A. Konopelko
5	<b>CENAM</b> Centro Nacional de Metrología	Mexico	A.S. Téllez
6	<b>IMGC</b> Unit of Radiochemistry and Spectroscopy c/o Dept. General Chemistry University of Pavia	Italy	Mario Gallorini
7	<b>UME</b> Ulusal Metroloji Enstitüsü Kimyasal Metroloji Laboratuvarı	Turkey	Ibrahim Akdag

## 9. Measurands and nominal values

Element x	Nominal values $w(x)$ in %
Chromium	0,05
Copper	0,1
Iron	0,2
Manganese	0,1
Zinc	0,1

## 10. Sample description

The sample material was a certified reference material (aluminium alloy) of a distinguished international producer of reference materials.

The basic raw material for the pilot study consisted in 10 cylinders with a diameter of 60 mm and a height of 20 mm.

For the analysis chosen parts of the cylinders with a sufficient homogeneity were chipped by stock removal. The particle size was about 1 to 2 mm.

By chipping the chosen material and mixing the chips a homogenization of 1% or better was obtained. Every participant of the pilot study had obtained about 25 g of the chipped material.

## 11. Results, scheduler and graphical

In the following tables and graphics the results for manganese, copper, iron, chromium and zinc (analyte x) of every participant are summarized and displayed.

The uncertainties of the determined analytes x are declared by the participants (green marked) as expanded uncertainties (IRMM, CENAM), partially as relative expanded uncertainties (IMGC, UME) or as combined standard uncertainties (NIST, BAM VNIIM).

For a uniform uncertainty statement and for comparing the results the missing values have been added (yellow marked).

The reported mean values are approximately normally distributed. Therefore the mean and standard deviation of the reported means provide a justifiable basis for the KCRV and its uncertainty.

### Caption of tables

Participant	Participating institute
Country	Participating country
Method	Used analytical method for determination of analyte x
w(x) %	Mass fraction of determined analyte x
$u$	Combined uncertainty of w(x)
k	Expansion factor
$U_{\text{exp}}$	Expanded uncertainty of w(x)
$U_{\text{exp}}$ rel. %	Relative expanded uncertainty of w(x) (related to w(x))
KCRV	Key comparison reference value
SD	Standard deviation of the mean values of participants
$u[\text{KCRV}]$	Combined uncertainty of KCRV
$U[\text{KCRV}]$	Expanded uncertainty of KCRV (k = 2)

### Caption of diagrams

————	Total mean of all mean results
-----	Expanded uncertainty of the KCRV (k = 2)
┌ └	Expanded uncertainty of a single mean result
●	INAA
▲	XRF (reconstitution technique)
◆	INAA /XRF
■	ICP - MS
□	ICP OES

**Manganese**

Participant	Country	Method	w(Mn) %	<i>u</i>	k	<i>U</i> <sub>exp</sub>	<i>U</i> <sub>exp</sub> rel. %
IMGC	Italy	INAA	0,1058	0,0011	2,00	0,0022	2,10
IRMM	Belgium/EU	INAA	0,1079	0,0025	2,00	0,0050	4,6
UME	Turkey	ICP -MS	0,1161	0,0010	2,00	0,0020	1,74
NIST	USA	XRF/INAA	0,10853	0,00053	2,00	0,0011	1,0
BAM	Germany	XRF	0,1106	0,0008	2,00	0,0016	1,4
CENAM	Mexico	XRF	0,1064	0,0008	2,02	0,0016	1,5
VNIIM	Russia	ICP OES	0,1033	0,0020	2,00	0,0040	3,9
<b>KCRV</b>	<b>0,1084</b>	<b>SD</b>	<b>0,0041</b>	<b><i>u</i>[KCRV]</b>	<b>0,0015</b>	<b><i>U</i>[KCRV]</b>	<b>0,0031</b>

**Copper**

Participant	Country	Method	w(Cu) %	<i>u</i>	k	<i>U</i> <sub>exp</sub>	<i>U</i> <sub>exp</sub> rel. %	
IMGC	Italy	INAA	not determined					
IRMM	Belgium/EU	INAA	0,1081	0,0026	2,00	0,0051	4,7	
UME	Turkey	ICP -MS	0,1068	0,0008	2,00	0,0017	1,56	
NIST	USA	XRF/INAA	0,1129	0,0022	2,00	0,0044	3,9	
BAM	Germany	XRF	0,1099	0,0026	2,00	0,0052	4,7	
CENAM	Mexico	XRF	0,1114	0,0007	2,05	0,0015	1,3	
VNIIM	Russia	ICP OES	0,1100	0,0025	2,00	0,0050	4,5	
<b>KCRV</b>	<b>0,1098</b>	<b>SD</b>	<b>0,0022</b>	<b><i>u</i>[KCRV]</b>	<b>0,0009</b>	<b><i>U</i>[KCRV]</b>	<b>0,0018</b>	

**Iron**

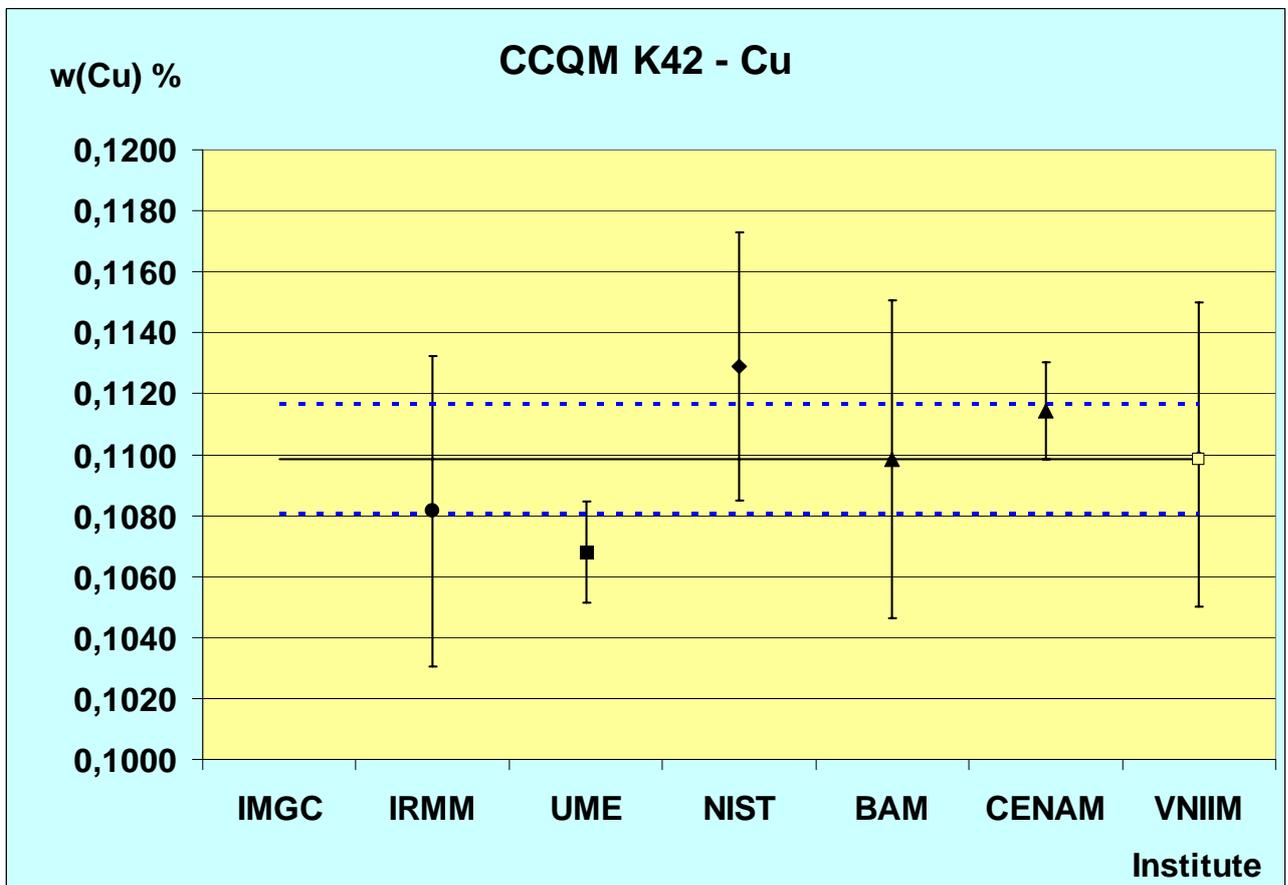
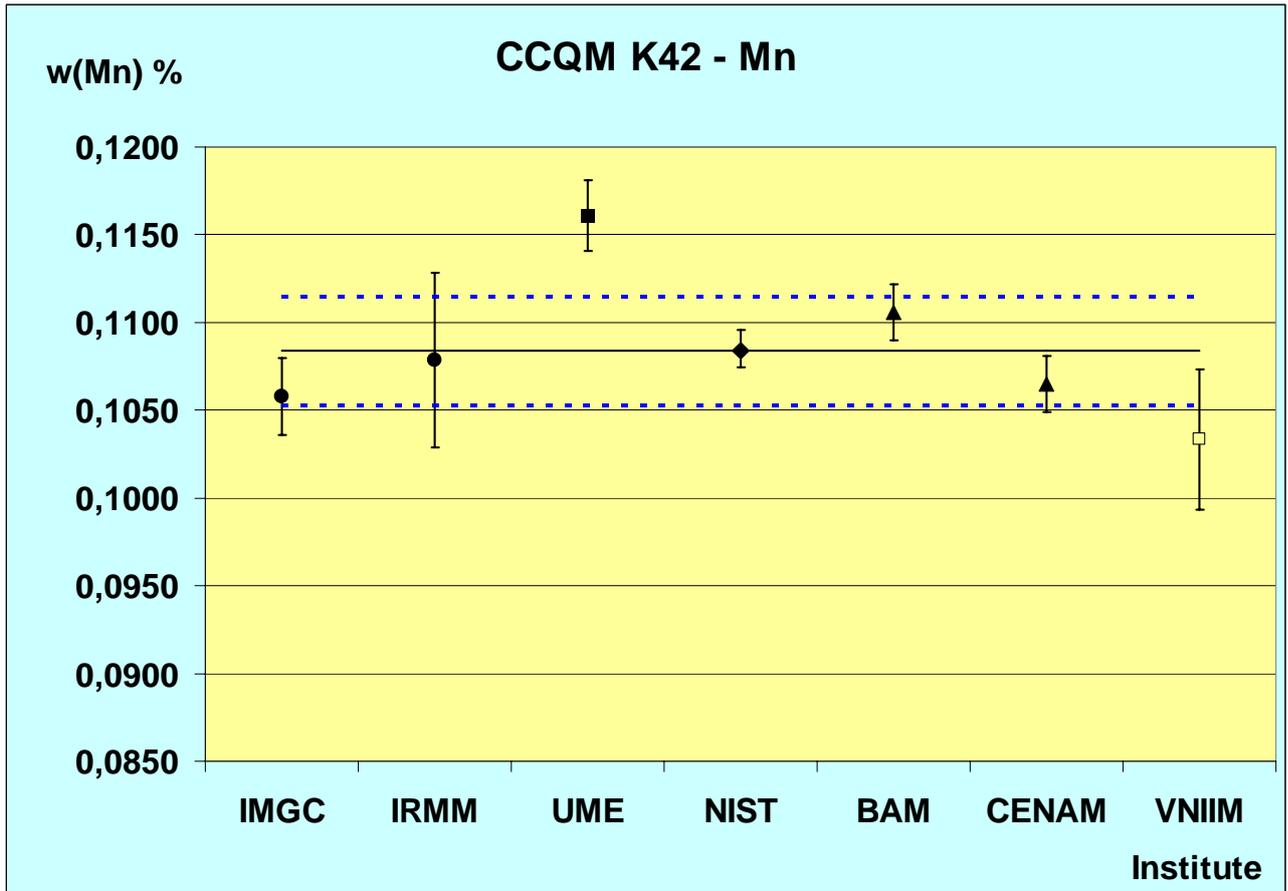
Participant	Country	Method	w(Fe) %	<i>u</i>	k	<i>U</i> <sub>exp</sub>	<i>U</i> <sub>exp</sub> rel. %
IMGC	Italy	INAA	0,1940	0,0025	2,00	0,0050	2,57
IRMM	Belgium/EU	INAA	0,1998	0,0047	2,00	0,0094	4,7
UME	Turkey	ICP -MS	0,1971	0,0015	2,00	0,0030	1,54
NIST	USA	XRF/INAA	0,2040	0,0018	2,00	0,0036	1,8
BAM	Germany	XRF	0,2031	0,0014	2,00	0,0028	1,4
CENAM	Mexico	XRF	0,2030	0,0014	2,03	0,0029	1,4
VNIIM	Russia	ICP OES	0,2013	0,0045	2,00	0,0090	4,5
<b>KCRV</b>	<b>0,2003</b>	<b>SD</b>	<b>0,0037</b>	<b><i>u</i>[KCRV]</b>	<b>0,0014</b>	<b><i>U</i>[KCRV]</b>	<b>0,0028</b>

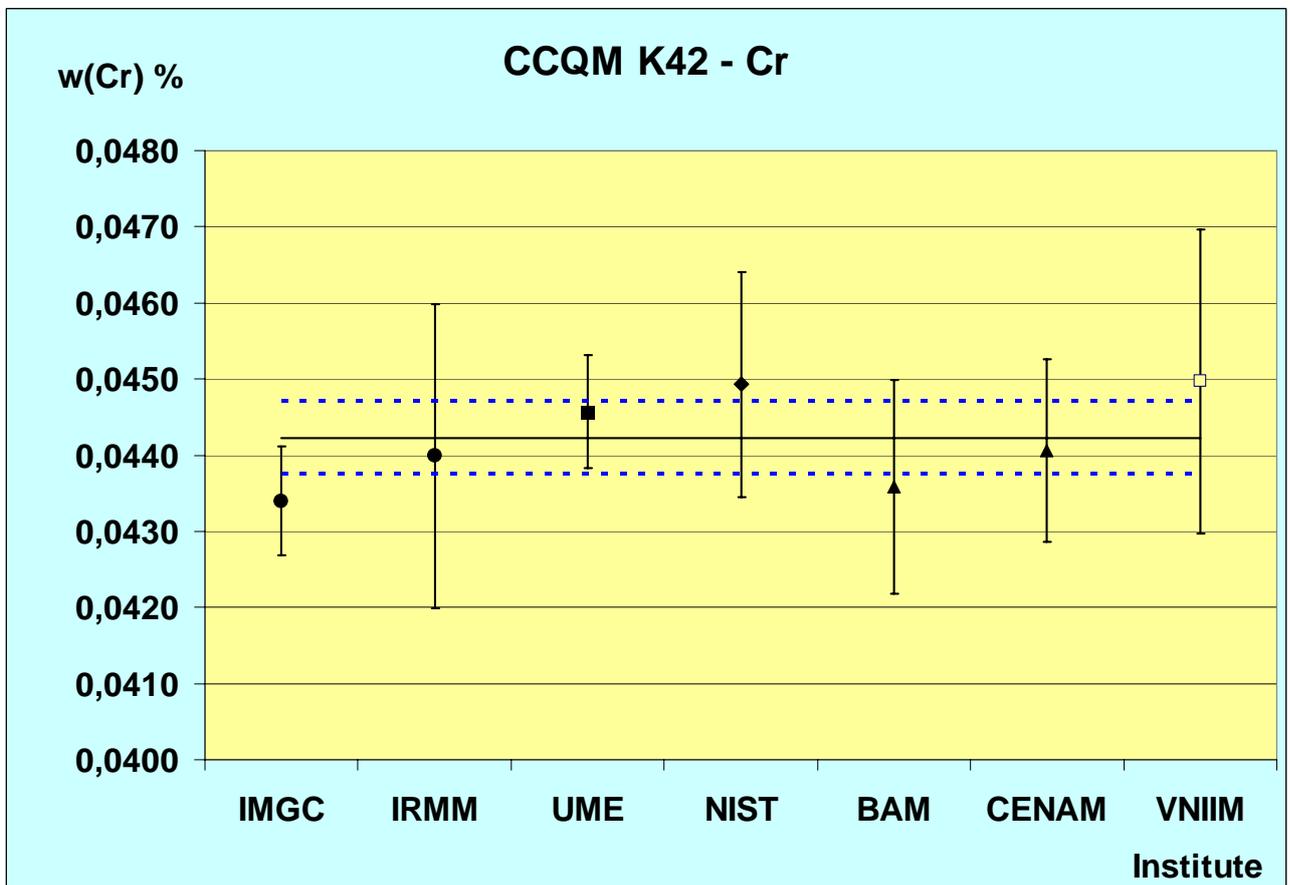
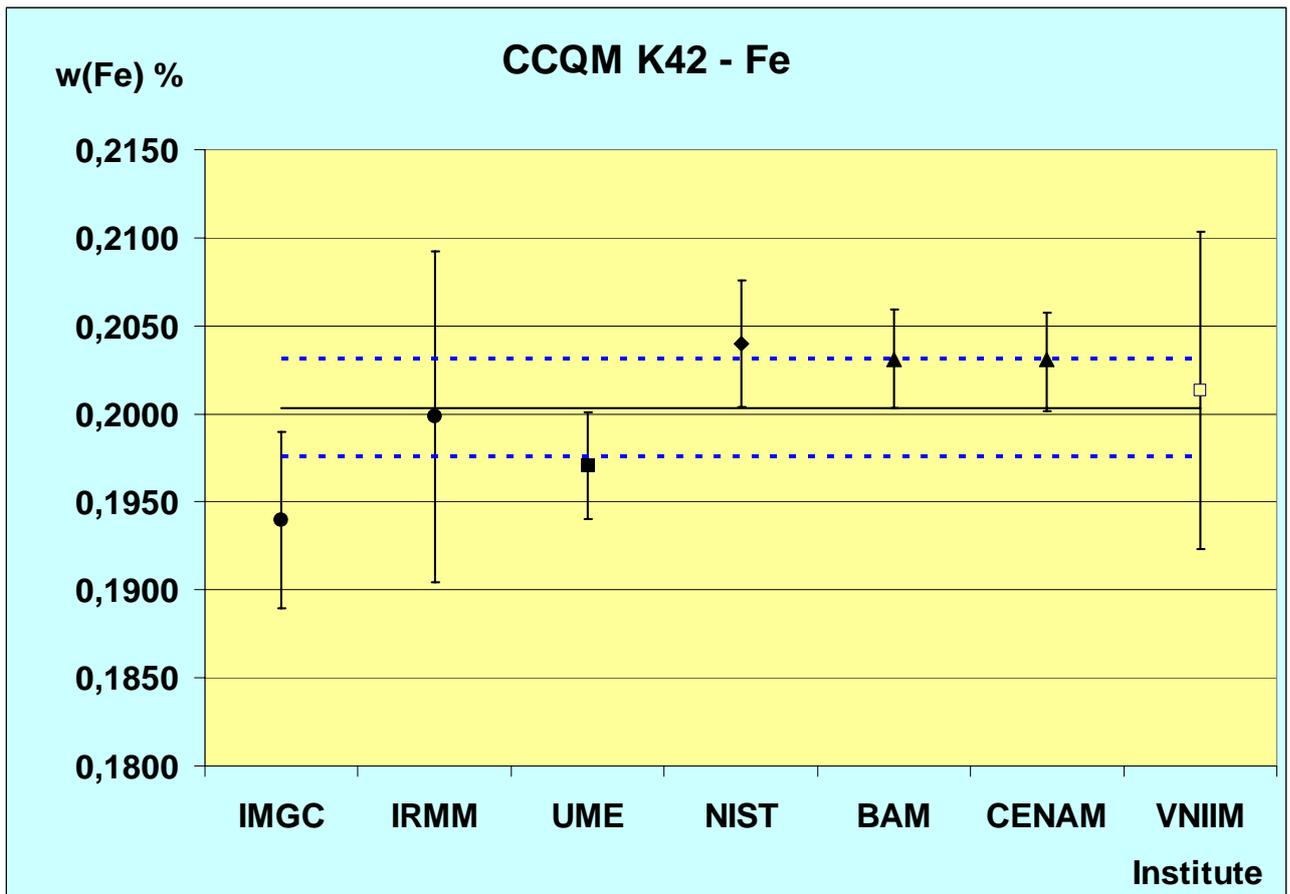
**Chromium**

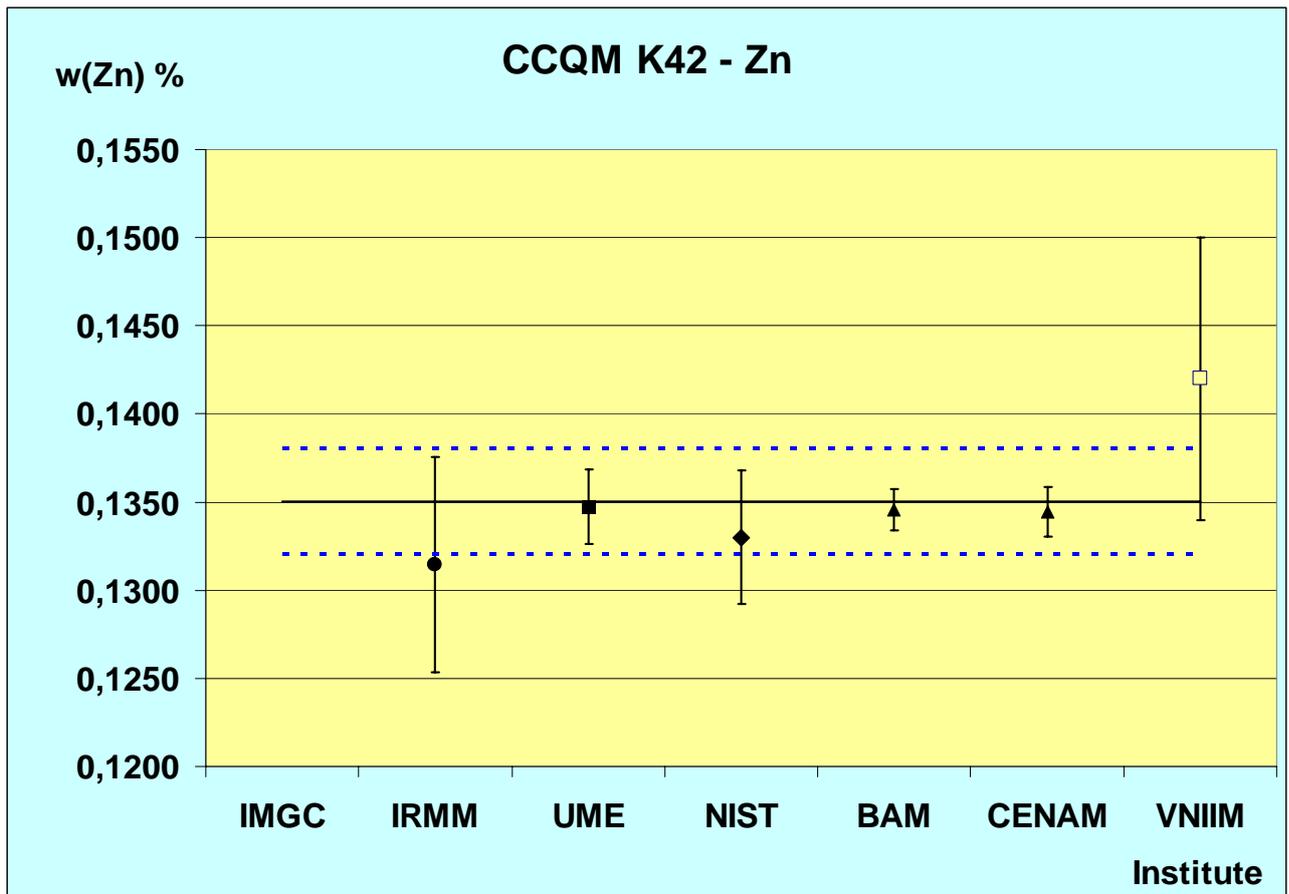
Participant	Country	Method	w(Cr) %	<i>u</i>	k	<i>U</i> <sub>exp</sub>	<i>U</i> <sub>exp</sub> rel. %
IMGC	Italy	INAA	0,0434	0,0004	2,00	0,0007	1,64
IRMM	Belgium/EU	INAA	0,0440	0,0010	2,00	0,0020	4,5
UME	Turkey	ICP -MS	0,0446	0,0004	2,00	0,0007	1,68
NIST	USA	XRF/INAA	0,04493	0,00074	2,00	0,0015	3,3
BAM	Germany	XRF	0,0436	0,0007	2,00	0,0014	3,2
CENAM	Mexico	XRF	0,0441	0,0006	2,14	0,0013	3,0
VNIIM	Russia	ICP OES	0,0450	0,0010	2,00	0,0020	4,4
<b>KCRV</b>	<b>0,0442</b>	<b>SD</b>	<b>0,0006</b>	<b><i>u</i>[KCRV]</b>	<b>0,0002</b>	<b><i>U</i>[KCRV]</b>	<b>0,0005</b>

**Zinc**

Participant	Country	Method	w(Zn) %	<i>u</i>	k	<i>U</i> <sub>exp</sub>	<i>U</i> <sub>exp</sub> rel. %	
IMGC	Italy	INAA	not determined					
IRMM	Belgium/EU	INAA	0,1314	0,0031	2,00	0,0061	4,6	
UME	Turkey	ICP -MS	0,1347	0,0011	2,00	0,0021	1,57	
NIST	USA	XRF/INAA	0,1330	0,0019	2,00	0,0038	2,9	
BAM	Germany	XRF	0,1346	0,0006	2,00	0,0012	0,9	
CENAM	Mexico	XRF	0,1344	0,0008	1,98	0,0015	1,1	
VNIIM	Russia	ICP OES	0,1420	0,0040	2,00	0,0080	5,6	
<b>KCRV</b>	<b>0,1350</b>	<b>SD</b>	<b>0,0036</b>	<b><i>u</i>[KCRV]</b>	<b>0,0015</b>	<b><i>U</i>[KCRV]</b>	<b>0,0030</b>	







## 12. Degree of equivalence

For the benchmarking of participant mean values  $w(x)$  of the determined analyte  $x$  the degree of equivalence  $D_i$  for the participant  $i$  is calculated as the absolute difference between  $w_i(x)$  of participant  $i$  and the key comparison reference value  $KCRV(x)$ . The relative degree of equivalence  $D_{i,rel}$  is corresponding to the  $KVRV(x)$ . The  $KCRV(x)$  itself is calculated as the total mean of all the participants results (mean values).

$$D_i = w_i(x) - KCRV(x) \qquad D_{i,rel} \% = \frac{100 \cdot D_i}{KCRV(x)}$$

$$KCRV(x) = \frac{1}{n} \cdot \sum_{i=1}^n w_i(x)$$

with

$w_i(x)$ : Mean value of determined mass fractions for analyte  $x$  by participant  $i$

$KCRV(x)$ : Key comparison reference value: total mean value of all participants results  $w_i(x)$

$n$ : Number of participants for the determination of the analyte  $x$

Then the combined uncertainty  $u[D_i]$  of the degree of equivalence can be calculated by

$$u_x[D_i] = \sqrt{u[w_i(x)]^2 + u[KCRV(x)]^2}$$

$u[w(x)]$ : Combined uncertainty of the value  $w(x)$  for the participant  $i$

$u[KCRV(x)]$ : Uncertainty of the key comparison reference value

The uncertainty  $u[KCRV(x)]$  of the key comparison reference value is calculated as standard deviation of the mean of means:

$$u[KCRV(x)] = \frac{SD(x)}{\sqrt{n}} \qquad SD(x) = \sqrt{\frac{\sum_{i=1}^n [w_i(x) - \bar{w}(x)]^2}{n-1}}$$

$n$ : Number of participants for the determination of the analyte  $x$

$SD(x)$  Standard deviation of participants results (mean values) for the analyte  $x$

The expanded uncertainty of the degree of equivalence is then calculated by

$$U_x[D_i] = \sqrt{k_i^2 \cdot u[w_i(x)]^2 + k_{KCRV}^2 \cdot u[KCRV(x)]^2}$$

$$U_x[D_i]_{rel\%} = 100 \cdot \frac{U_x[D_i]}{KCRV(x)}$$

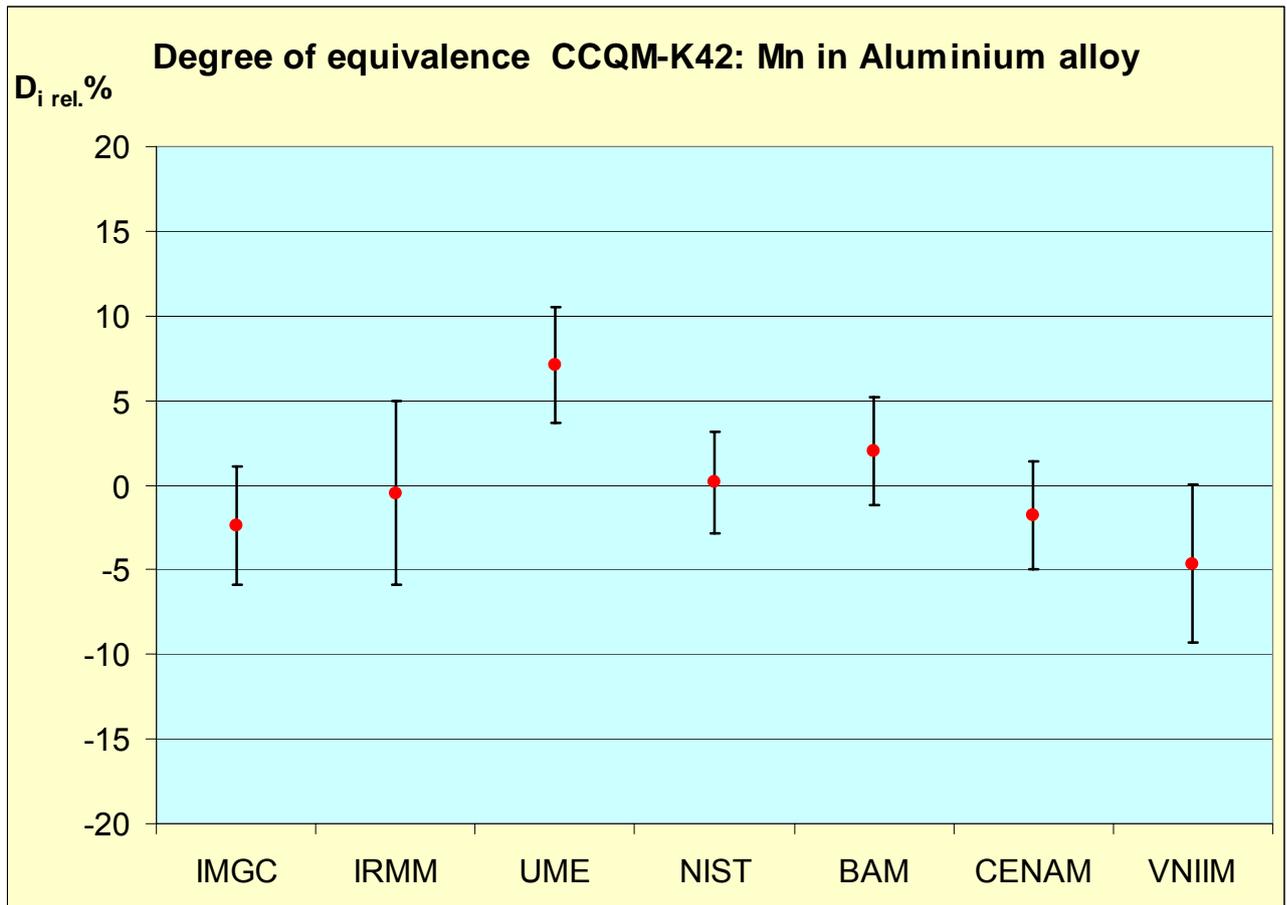
$k_{KCRV} = 2$  (corresponding to a confidence level of about 95%).

The order of magnitude for the uncertainties  $U(D_i)$  (mass content of analyte  $x$ ) of Mn, Cu, Fe, Cr and Zn is about 0,01 %.

KCRV(Mn) 0,1084  
 u[KCRV(Mn)] 0,0015  
 n 7

CCQM K42 Aluminium alloy  
 Degree of equivalence Analyte x: Mn

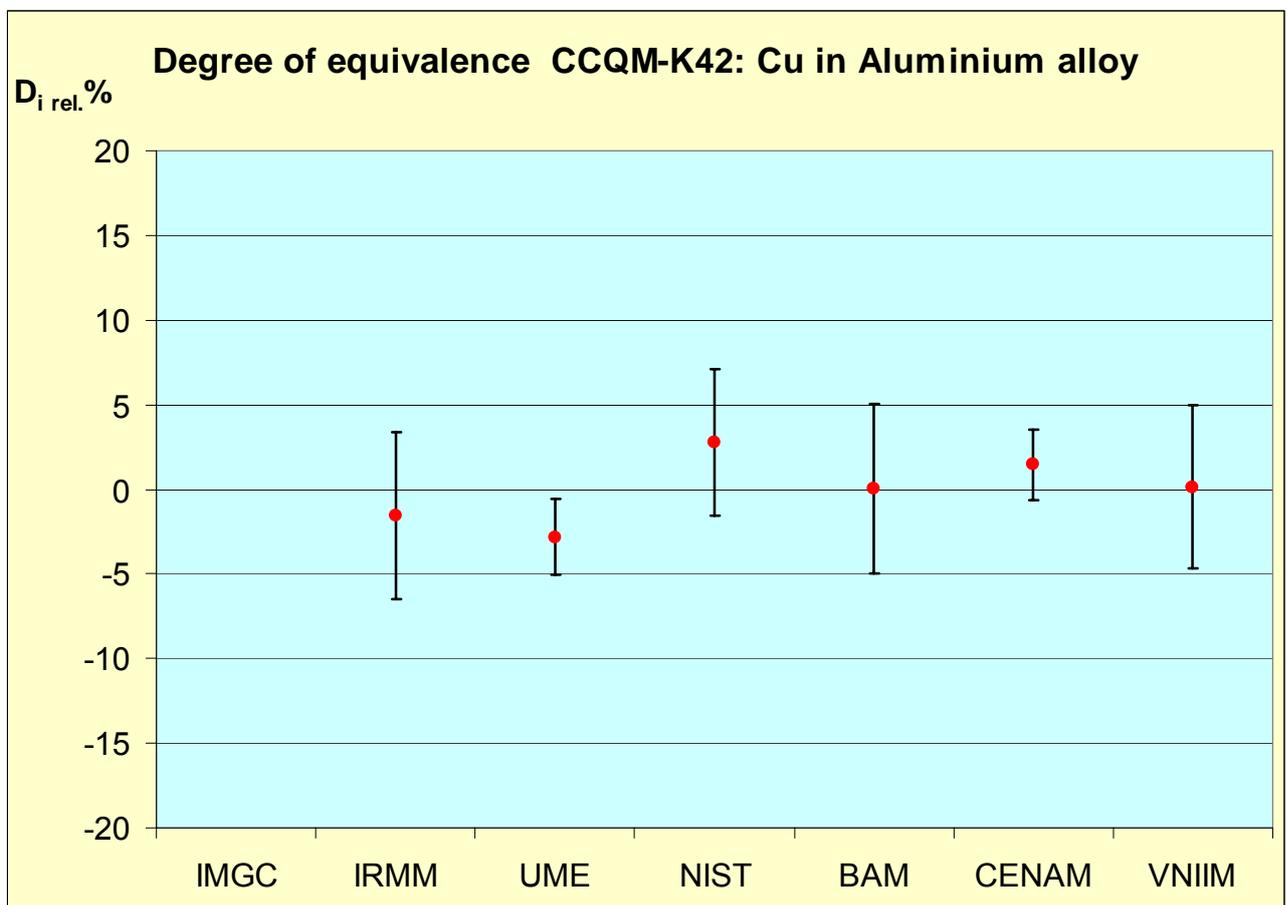
1	2	3	4	5
No.	Participant	$D = w(\text{Mn}) - \text{KCRV}(\text{Mn})$	$U_{\text{Mn}}(D)$	$U_{\text{Mn}}(D)_{\text{rel. \%}}$
1	IMGC	-0,0026	0,0038	3,5
2	IRMM	-0,0005	0,0059	5,4
3	UME	0,0077	0,0037	3,4
4	NIST	0,0002	0,0033	3,0
5	BAM	0,0022	0,0035	3,2
6	CENAM	-0,0019	0,0035	3,2
7	VNIIM	-0,0050	0,0051	4,7



**KCRV(Cu)** 0,1098  
 **$u$ [KCRV(Cu)]** 0,0009  
**n** 6

**CCQM K42 Aluminium alloy**  
**Degree of equivalence Analyte x: Cu**

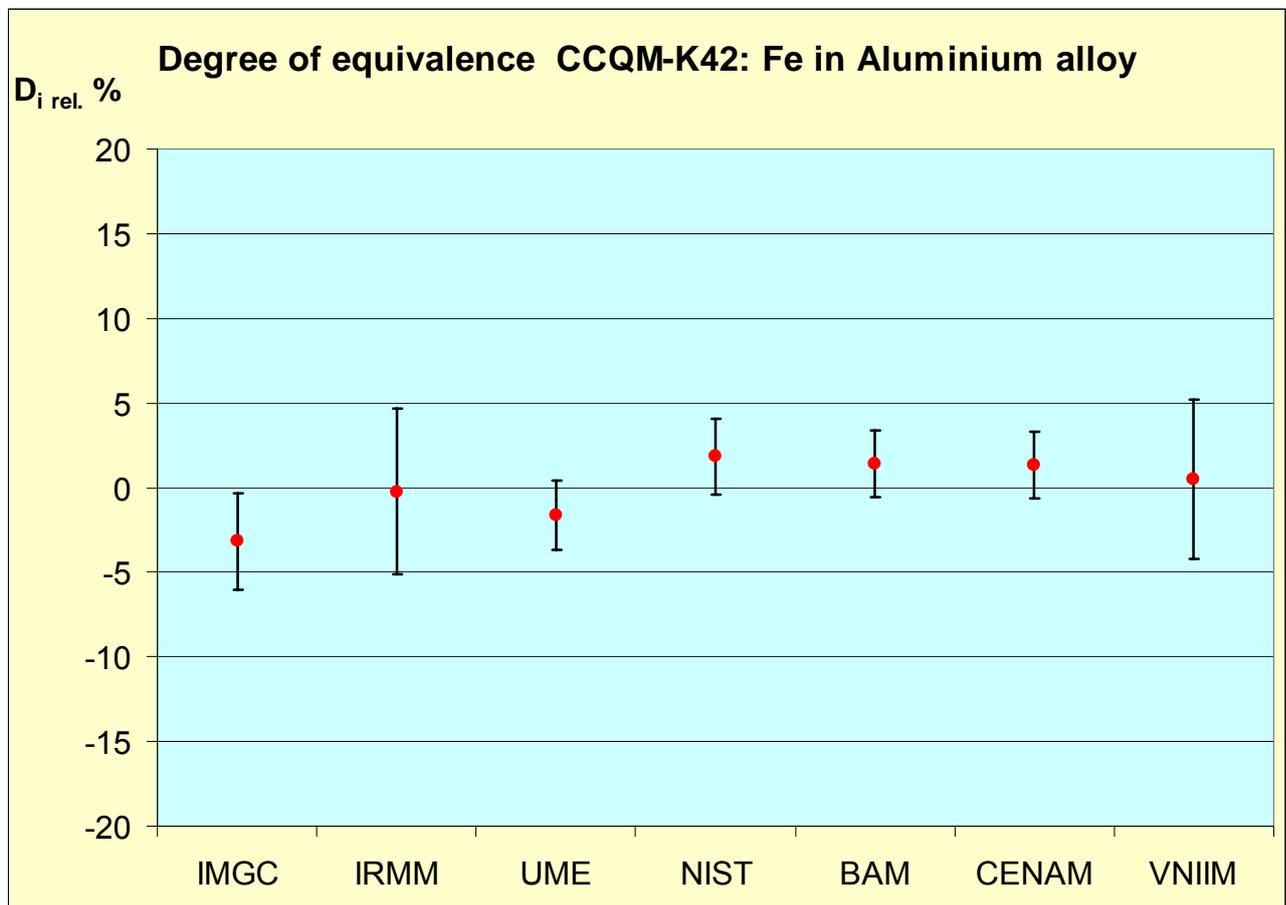
1	2	3	4	5
No.	Participant	$D = w(\text{Cu}) - \text{KCRV}(\text{Cu})$	$U_{\text{Cu}}(D)$	$U_{\text{Cu}}(D)_{\text{rel.}\%}$
1	IMGC			
2	IRMM	-0,0017	0,0054	4,9
3	UME	-0,0031	0,0025	2,2
4	NIST	0,0031	0,0048	4,3
5	BAM	0,0000	0,0055	5,0
6	CENAM	0,0016	0,0023	2,1
7	VNIIM	0,0002	0,0053	4,8



KCRV(Fe) 0,2003  
 u[KCRV(Fe)] 0,0014  
 n 7

CCQM K42 Aluminium alloy  
 Degree of equivalence Analyte x: Fe

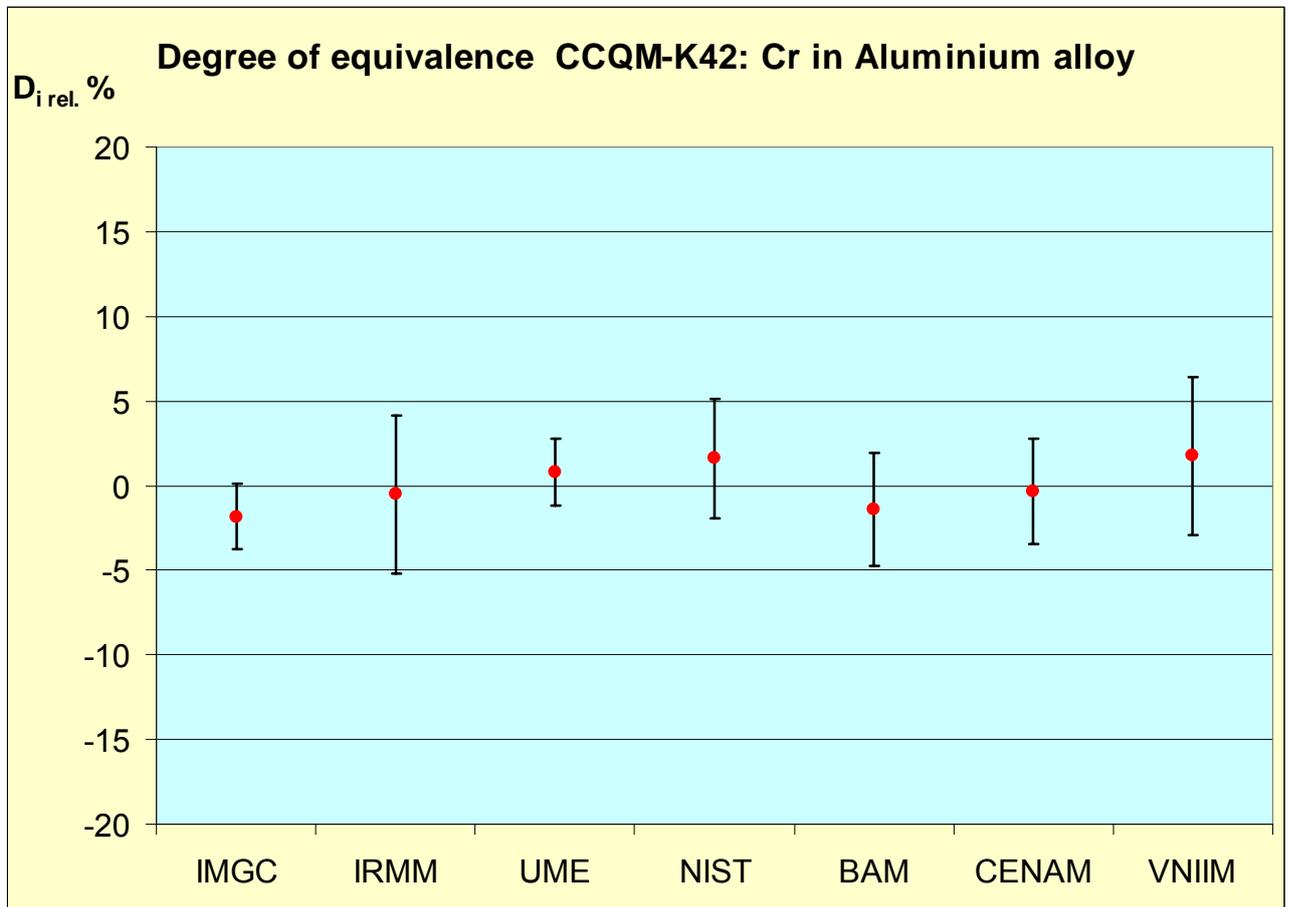
1	2	3	4	5
No.	Participant	$D = w(\text{Fe}) - \text{KCRV}(\text{Fe})$	$U_{\text{Fe}}(D)$	$U_{\text{Fe}}(D)_{\text{rel.}\%}$
1	IMGC	-0,0064	0,0057	2,9
2	IRMM	-0,0005	0,0098	4,9
3	UME	-0,0033	0,0041	2,1
4	NIST	0,0037	0,0045	2,3
5	BAM	0,0028	0,0039	2,0
6	CENAM	0,0026	0,0040	2,0
7	VNIIM	0,0010	0,0094	4,7



KCRV(Cr) 0,0442  
 u[KCRV(Cr)] 0,0002  
 n 7

CCQM K42 Aluminium alloy  
 Degree of equivalence Analyte x: Cr

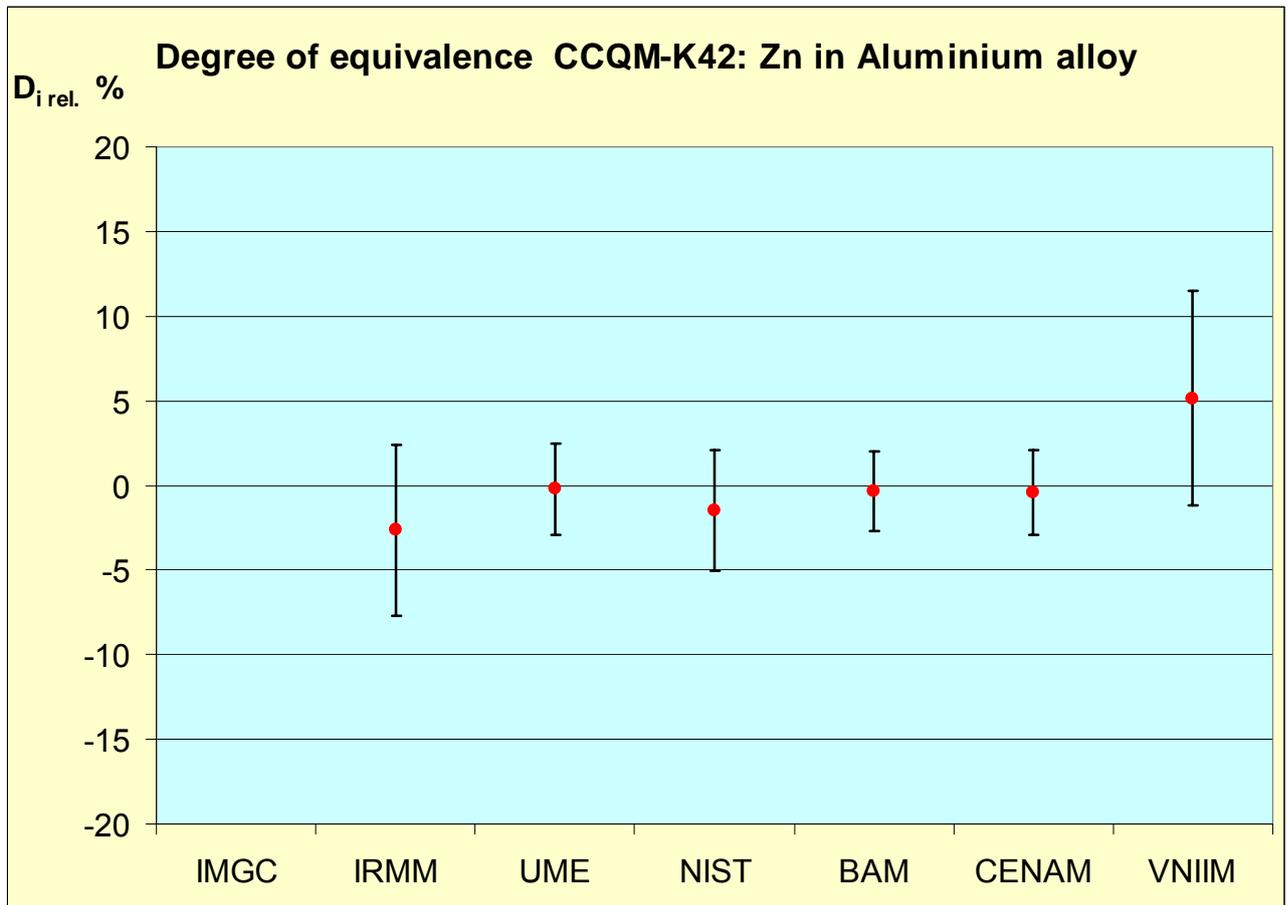
1	2	3	4	5
No.	Participant	$D = w(\text{Cr}) - \text{KCRV}(\text{Cr})$	$U_{\text{Cr}}(D)$	$U_{\text{Cr}}(D)_{\text{rel.}\%}$
1	IMGC	-0,0008	0,0009	1,9
2	IRMM	-0,0002	0,0021	4,6
3	UME	0,0004	0,0009	2,0
4	NIST	0,0007	0,0016	3,5
5	BAM	-0,0006	0,0015	3,3
6	CENAM	-0,0002	0,0014	3,1
7	VNIIM	0,0008	0,0021	4,6



**KCRV(Zn)** 0,1350  
**u[KCRV(Zn)]** 0,0015  
**n** 6

**CCQM K42 Aluminium alloy**  
**Degree of equivalence Analyte x: Zn**

1	2	3	4	5
No.	Participant	$D = w(\text{Zn}) - \text{KCRV}(\text{Zn})$	$U_{\text{Zn}}(D)$	$U_{\text{Zn}}(D)_{\text{rel.}\%}$
1	<b>IMGC</b>			
2	<b>IRMM</b>	-0,0036	0,0068	5,0
3	<b>UME</b>	-0,0003	0,0036	2,7
4	<b>NIST</b>	-0,0020	0,0048	3,6
5	<b>BAM</b>	-0,0005	0,0032	2,4
6	<b>CENAM</b>	-0,0006	0,0034	2,5
7	<b>VNIIM</b>	0,0070	0,0085	6,3



### 13. Evaluation of results

The object of K42 was the determination of Mn, Cu, Fe, Cr and Zn in aluminium alloys with a mass content of about 0,05% to 0,2%.

The participants have used the following methods

<b>Participant</b>	<b>Method</b>
<b>BAM</b>	XRF <sup>*)</sup>
<b>NIST</b>	INAA and XRF <sup>*)</sup>
<b>IRMM</b>	INAA
<b>VNIIM</b>	ICP OES
<b>CENAM</b>	XRF <sup>*)</sup>
<b>IMGC</b>	INAA
<b>UME</b>	ICP - MS

\*) Reconstitution method

The expanded relative uncertainties reported by then participants are mostly in the range of 1% to 5%. The total range is 0,9%rel to 5,6%rel.

The participant's results overlap (or nearly overlap) the KCRV within their reported uncertainties with two exceptions. The measurement uncertainties of UME for Mn and Cu seem to be underestimated.

From the rather limited set of data there can be not drawn any conclusion on the general advantage of a specific method (as well with respect to deviation from the KCRV and the reported uncertainties).

The deviation of the labs results (reported mean values) from the KCRV is in general smaller than 3% relative. Only three individual results show greater deviations: the VNIIM values (ICP-OES) for Mn and Zn (both 5% rel.) and the UME value (ICP-MS) for Mn (7% rel.).

The K42 demonstrated a satisfying level of equivalence in the measurement capabilities of the participating institutes.

The scope of the key comparison extends to non-ferrous alloys comprising the same or similar constituents when analysed using the technique(s) applied by a participant in obtaining the results submitted for CCQM-42.

## Annex A

### General description of methods

#### Neutron Activation Analysis (NAA)

The most common type of nuclear reaction used for NAA is the neutron capture or (n,gamma) reaction: When a neutron interacts with the target nucleus via a non-elastic collision, a compound nucleus forms in an excited state. The excitation energy of the compound nucleus is due to the binding energy of the neutron with the nucleus. The compound nucleus will almost instantaneously de-excite into a more stable configuration through emission of one or more characteristic prompt gamma rays. In many cases, this new configuration yields a radioactive nucleus which also de-excites (or decays) by emission of one or more characteristic delayed gamma rays, but at a much slower rate according to the unique half-life of the radioactive nucleus. Depending upon the particular radioactive species, half-lives can range from fractions of a second to several years.

Neutron activation analysis (NAA) is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements in samples from almost every conceivable field of scientific or technical interest. For many elements and applications, NAA offers sensitivities that are superior to those attainable by other methods, on the order of parts per billion or better. In addition, because of its accuracy and reliability.

NAA is generally recognized as the "referee method" of choice when new procedures are being developed or when other methods yield results that do not agree. Worldwide application of NAA is so widespread it is estimated that approximately 100,000 samples undergo analysis each year.

The basic essentials required to carry out an analysis of samples by NAA are a source of neutrons, instrumentation suitable for detecting gamma rays, and a detailed knowledge of the reactions that occur when neutrons interact with target nuclei. Brief descriptions of the NAA method, reactor neutron sources, and gamma-ray detection are given below.

With the use of automated sample handling, gamma-ray measurement with solid-state detectors, and computerized data processing it is generally possible to simultaneously measure more than thirty elements in most sample types without chemical processing. The application of purely instrumental procedures is commonly called instrumental neutron activation analysis (INAA) and is one of NAA's most important advantages over other analytical techniques.

If chemical separations are done to samples after irradiation to remove interferences or to concentrate the radioisotope of interest, the technique is called radiochemical neutron activation analysis (RNAA). The latter technique is performed infrequently due to its high labour cost.

#### Optical Emission Spectrometry with ICP (ICP OES)

The optical emission spectrometry with inductively coupled plasma (ICP OES) is a widely-used analytical spectrometric method for determination of "inorganic" elements in sample material, of which aqueous solutions can be prepared, e.g. by digestion.

Because of the world wide use of this analytical method and the wide publicity a detailed description is resigned.

A disadvantage of ICP OES is, that this method is not a primary method because of the need of calibration and the necessary sample preparation.

#### ICP – Mass Spectrometry (ICP - MS)

ICP – MS is a kind of mass spectrometry method which uses an inductively plasma as an ion source. The advantage of ICP – MS is the higher detection sensitivity compared to ICP OES.

The physical value is a mass-to-charge-ratio. The sample preparation and the calibration procedure is similar to the ICP OES-method.

Because of the world wide use of this analytical method and the wide publicity a detailed description is resigned.

#### Reconstitution technique with XRF (borate fusions)

The basic principle of the reconstitution technique is – based on a pre analysis of the analysis sample and „bracketing“ calibration samples – an iterative equalization of the composition of the calibration samples and the analysis sample itself.

The reconstitution technique is based on the use of synthetic calibration samples.

In contrast to the conventional „analytical mode“ (calibration for realization a correlation between measuring values and amounts) the amounts of elements by using the „synthetic mode“ of reconstitution can only be accepted as free of interferences and therefore as true, if an identity of analysis sample and the reference sample is obtained in a sufficient way:

The constitution of an unknown analysis sample is determined by synthesis of calibration samples which give the „same signals“ as the analysis sample.

That means: The constitution of the calibration samples is varied in an iterative way, until the differences of the signals of all samples are no longer significant.

The calibration range therefore is always adjusted to the individual case.

If XRF-analysis is applied the preparation of the calibration samples and the measuring sample of the material to be investigated is realized by the fusion technique using lithium- or sodium tetraborate.

Because of the definite manufacturing process it is possible, to use the same sample preparation procedure for the analysis sample and for the calibration samples too.

Matrix effects and a deviation from the linear calibration function are avoidable in most cases because of the iterative adjusting of the constitution of the calibration samples and the analysis sample. Therefore the accuracy of the technique is controlled by the iterative principle itself.

The advantages of applying XRF and using the reconstitution technique can be summarized to:

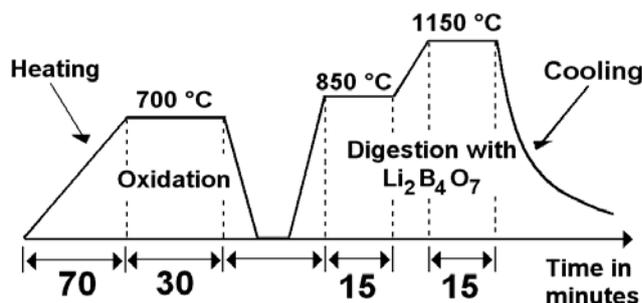
- Non destructive measuring
- High time stability of the signals
- Calculable uncertainty contributions by sample preparation procedures
- Optimal controlling of accuracy
- Elimination of matrix effects and optimization of calibration

For preparation of the synthetic calibration samples pure substances are used, which are exactly stoichiometrically defined and of which the grade of impurities is well known.

Generally oxides, carbonates or other compounds of the relevant elements are used, which can be produced in a sufficient way with a high grade of purity. Also pure elements can be used.

The analysis sample as well as the synthetic mixtures for preparation the calibration samples are prepared as glass fusions (lithium- or sodiumtetraborate) to obtain homogeneous samples for measuring e.g. for XRF- measuring.

At preparing the borate fusions reproducible operating conditions (temperature programme) must be kept, to get an optimal comparability of the calibrations samples and the analysis sample.



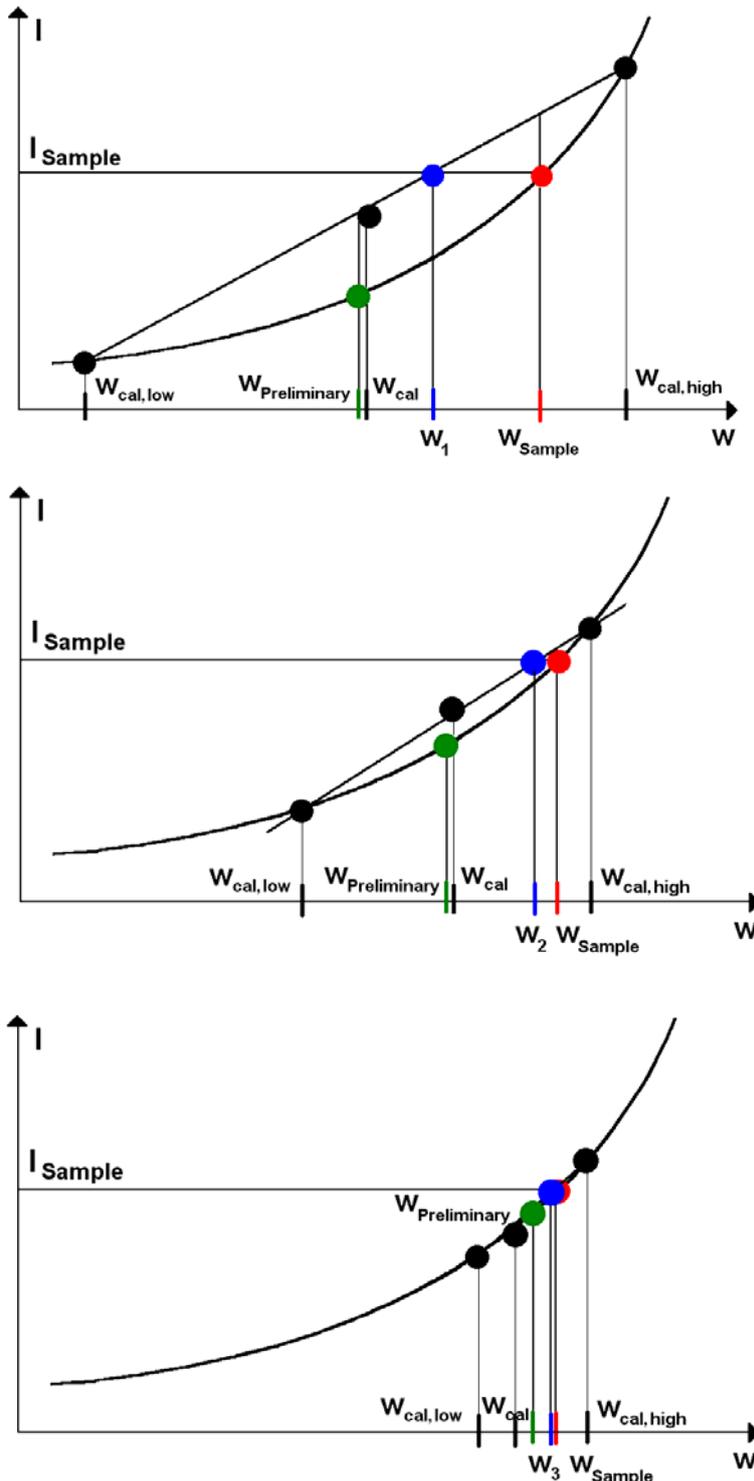
### Example for temperature programme

#### Literature

Gotthard Staats und Siegfried Noack, Qualitätssicherung in der Analytik;  
Die Rekonstitution – Eine Methode zur Optimierung der Richtigkeit von Analysen  
Verlag Stahleisen GmbH, Düsseldorf 1996 ISBN 3-514-00581-8

**Single steps of a reconstitution analysis**  
 Preanalysis of the sample material: Initial value for the calibration range  
 Calculating the composition of calibration samples using the preanalysis values: Wide bracketing range  
 Preparing calibration samples and analysis sample as borate fusions using the same preparation technique  
 Measuring the analysis and the calibration samples  
 Calculating the composition of the analysis sample using linear calibration  
 Defining the calculated mass content as initial value for the next iteration step  
 Repeating the steps 1 to 6 with decreasing the bracketing range until calibration and analysis sample do not differ significantly

**Iterative principle of reconstitution analysis**



## Annex B

## Analytical procedures

## BAM

CCQM P34.1/K42 Aluminium							
Declarations							
Please enlist the corresponding data into the <b>green marked</b> cells of the table! If the specifications are equal for several elements, a link is sufficient! <b>Attention!</b> If you need more place for enlisting your data you can use alternatively the table "CCQM_P34.1/K42_Declarations (2)" Use the horizontal scroll bar for displaying the cells for the desired element!							
Participant	BAM Berlin Germany						
							Comment
		Fe	Cu	Mn	Cr	Zn	
Used primary substance for calibration		Fe <sub>2</sub> O <sub>3</sub>	Cu <sub>2</sub> O	MnO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	ZnO	Pure substances by Alpha Johnson Matthey
Purity of primary substance [%]		>99,99%					Purity: Metals basis
Uncertainty of the purity [%]		<0,1%					
Number of calibration samples (solution or solid)		4	4	4	4	4	
Details of calibration solutions: concentrations, if: matrix matching, addition method...)		Reconstitution Method with XRF					
Estimated limits [%] of determination (9s-criterion)		0,0100					
Kind of digestion (acid, alkaline, fusion...)		Fusion with lithium tetraborate Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>					
Weighted sub-sample [mg]	1	300 mg					
	2						
	3						
	4						
	5						
	6						
Date of digestion performance	1	March 15 <sup>th</sup> 2005					
	2						
	3						
	4	March 30 <sup>th</sup> 2005					
	5						
	6						
Details of digestion procedure (reagents, conditions etc.)	1	Dissolving of 300 mg Sample with conc. HNO <sub>3</sub> . Fusion of the dried solution with 6g Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>					
	2						
	3						
	4						
	5						
	6						
Used analytical instrument		Magix ProPANalytical					
Intrument parameter (e.g. nebulizer, lines, background, time cycles etc.)							

**NIST**

Declarations for INAA

<b>CCQM P34.1/K42 Aluminium</b>
<b>Declarations</b>
Please enlist the corresponding data into the <b>green marked</b> cells of the table! If the specifications are equal for several elements, a link is sufficient! <b>Attention!</b> If you need more place for enlisting your data you can use alternatively the table "CCQM_P34.1/K42_Declarations (2)" Use the horizontal scroll bar for displaying the cells for the desired element!

Participant							
		Fe	Cu	Mn	Cr	Zn	Comment
Used primary substance for calibration		Yes	Yes	Yes	Yes	Yes	
Purity of primary substance [%]		99,9950	99,9990	99,9500	99,9960	99,9500	
Uncertainty of the purity [%]		0,0012	0,0012	0,0115	0,0012	0,0115	
Stock solution (source, preparing, concentration...)				Yes			Prepared from same Mn source, 0.05% Mn; 0.1 g pipetted on filter paper and dried
Number of calibration samples (solution or solid)		6,0000	4,0000	4 + 4	4,0000	8,0000	
Details of calibration solutions: concentrations, if: matrix matching, addition method...)							
Estimated limits of determination (9s-criterion)							
Kind of digestion (acid, alkaline, fusion...)							
Weighted sub-sample [mg]	1	104,360					
	2	102,780					
	3	107,140					
	4	104,480					
	5	105,450					
	6	110,510					additional sample 100.14
Date of digestion performance	1						
	2						
	3						
	4						
	5						
	6						
Details of digestion procedure (reagents, conditions etc.)	1						
	2						
	3						
	4						
	5						
	6						
Wavelengths if spectrometric methods are used or other specification	25 + 1291.60 (c	1345,840	846,810	320,080	1115,5500		gamma-ray energy in keV
Used analytical instrument		Linda	Tracy	Tracy	Linda	Linda	gamma-ray detection system
Instrument parameter (e.g. nebulizer, lines, background, time cycles etc.)		5,000	10,000	20,000	5,000	5,0000	Counting geometry (cm)

Declarations for XRF

CCQM P34.1/K42 Aluminium						
Declarations						
<p>Please enlist the corresponding data into the <b>green marked</b> cells of the table!                  If the specifications are equal for several elements, a link is sufficient!  <b>Attention!</b>                  If you need more place for enlisting your data you can use alternatively the table "CCQM_P34.1/K42_Declarations (2)"                  Use the horizontal scroll bar for displaying the cells for the desired element!</p>						

Participant							
						<b>Comment</b>	
		<b>Fe</b>	<b>Cu</b>	<b>Mn</b>	<b>Cr</b>	<b>Zn</b>	
Used primary substance for calibration		SRM 3126a	SRM 3114	SRM 3132	SRM 3112a	SRM 3168a	
Mass Fraction of primary substance [mg/g]		10,00	9,99	10,01	9,96	10,01	
Uncertainty of the Mass Fraction of primary substance [mg/g]		0,015	0,008	0,015	0,015	0,010	
Stock solution (source, preparing, concentration...)							
Number of calibration samples (solution or solid)		5	5	5	5	5	
Details of calibration solutions: concentrations, if: matrix matching, addition method...)		Matrix Matching	Matrix Matching	Matrix Matching	Matrix Matching	Matrix Matching	
Estimated limits of determination (9s-criterion)							
Kind of digestion (acid, alkaline, fusion...)		HBr digestion and fuming with HNO3 in Teflon beaker followed by borate fusion					
Weighted sub-sample [mg]	1	Approximately 500 mg each					
	2						
	3						
	4						
	5						
	6						
Date of digestion performance	1						
	2						
	3						
	4						
	5						
	6						
Details of digestion procedure (reagents, conditions etc.)	1						
	2						
	3						
	4						
	5						
	6						
Wavelengths if spectrometric methods are used or other specification		K-L2,3					
Used analytical instrument		Philips model PW2402 WDXRF					
Intrument parameter (e.g. nebulizer, lines, background, time cycles etc.)							

## IRMM

CCQM P34.1/K42 Aluminium						
Declarations						
<p>Please enlist the corresponding data into the <b>green marked</b> cells of the table!            If the specifications are equal for several elements, a link is sufficient!</p> <p style="text-align: center;"><b>Attention!</b></p> <p>If you need more place for enlisting your data you can use alternatively the table "CCQM_P34.1/K42_Declarations (2)"</p> <p style="text-align: center;">Use the horizontal scroll bar for displaying the cells for the desired element!</p>						
Participant	IRMM_SCK, IRMM - Dr. P. Robouch, Retieseweg, B-2440 Geel, Belgium, SCK - ir. P. Vermaercke, Boeretang, 200, B-2400 Mol, Belgium					
						Comment
	Fe	Cu	Mn	Cr	Zn	
Used primary substance for calibration	Alfa - Johnson Fe ICP standard	Alfa - Johnson Cu ICP standard	Alfa - Johnson Mn ICP standard	Alfa - Johnson Cr ICP standard	Alfa - Johnson Zn ICP standard	
Purity of primary substance [%]	not used					
Uncertainty of the purity [%]	0,3%	0,3%	0,3%	0,3%	0,3%	
Stock solution (source, preparing, concentration...)	1000 ± 3	1000 ± 3	1000 ± 3	1000 ± 3	1000 ± 3	µg/mL
Number of calibration samples (solution or solid)	3	3	3	3	3	
Details of calibration solutions: concentrations, if: matrix matching, addition method...)	No calibration performed as INAA was used					
Estimated limits of determination (9s-criterion)	72	2	3	2	3	[mg/kg]
Kind of digestion (acid, alkaline, fusion...)	Not needed					
Weighted sub-sample [mg]	1	246	246	246	246	246
	2	245	245	245	245	245
	3	121	121	121	121	121
	4	128	128	128	128	128
	5	127	127	127	127	127
	6	127	127	127	127	127
Date of digestion performance	1	nr				
	2					
	3					
	4					
	5					
	6					
Details of digestion procedure (reagents, conditions etc.)	1	nr				
	2					
	3					
	4					
	5					
	6					
Wavelengths if spectrometric methods are used or other specification	nr					
Used analytical instrument	HP Ge for INAA					
Instrument parameter (e.g. nebulizer, lines, background, time cycles etc.)	1099;1292 keV	1346 keV	847;1811 keV	320 keV	1115 keV	

## VNIIM

## CCQM P34.1/K42 Aluminium

## Declarations

Please enlist the corresponding data into the **green marked** cells of the table!  
If the specifications are equal for several elements, a link is sufficient!

**Attention!**

If you need more place for enlisting your data you can use alternatively the table "CCQM\_P34.1/K42\_Declarations (2)"

Use the horizontal scroll bar for displaying the cells for the desired element!

Participant						
	Fe	Cu	Mn	Cr	Zn	Comment
Used primary substance for calibration	Pure metal Fe	Pure metal Cu	Pure metal Mn	Pure metal Cr	Pure metal Zn	
Purity of primary substance [%]	99.9	99.99	99.9	99.9	99.9	
Uncertainty of the purity [%]					0,02	
Stock solution (source, preparing, concentration...)	Preparation of the main calibration solution with the mass concentration 1.0 mg/ml					
Number of calibration samples (solution or solid)	5 solutions	5 solutions	5 solutions	5 solutions	5 solutions	
Details of calibration solutions: concentrations, if: matrix matching, addition method...)	Matrix – aluminium content at 0,5 g per 250 ml of solution, Solutions – (0,02-1,0 mg/l)					
Estimated limits of determination (9s-criterion)	1,1 µg/l	2,6 µg/l				
Kind of digestion (acid, alkaline, fusion...)	Acid + fusion	Acid + fusion	Acid + fusion	Acid + fusion	Acid + fusion	
Weighted sub-sample [mg]	1	500,000	500,000	500,000	500,000	500,000
	2	500,000	500,000	500,000	500,000	500,000
	3	500,000	500,000	500,000	500,000	500,000
	4	500,000	500,000	500,000	500,000	500,000
	5	500,000	500,000	500,000	500,000	500,000
	6	500,000	500,000	500,000	500,000	500,000
Date of digestion performance	1	14 March	14 March	14 March	14 March	14 March
	2	16 March	16 March	16 March	16 March	16 March
	3	18 March	18 March	18 March	18 March	18 March
	4	22 March	22 March	22 March	22 March	22 March
	5	23 March	23 March	23 March	23 March	23 March
	6	25 March	25 March	25 March	25 March	25 March
Details of digestion procedure (reagents, conditions etc.)	1	HCl (1:1), H <sub>2</sub> O <sub>2</sub>				
	2					
	3					
	4	HCl :HNO <sub>3</sub> (3:1), fusion sodium + borax				
	5					
	6					
Wavelengths if spectrometric methods are used or other specification	238,204; 239,562; 259,837; 259,940	324,754; 327,396	257,610; 260,610	205,552 267,716 283,563	206,200; 213,856	
Used analytical instrument	ICP Atomic Emission Spectrometer IRIS Advantage and Flame Atomic Absorption Spectrometer SOLAAR 6M					
Intrument parameter (e.g. nebulizer, lines, background, time cycles etc.)	Integration time: 10 c	20 c	10 c	20 c	10c	

		Fe	Cu	Mn	Cr	Zn
Used primary substance for calibration		Pure metal Fe	Pure metal Cu	Pure metal Mn	Pure metal Cr	Pure metal Zn
Purity of primary substance [%]		99.9	99.99	99.9	99.9	99.9
Uncertainty of the purity [%]						
Stock solution (source, preparing, concentration...)		Preparation of the main calibration solution with the mass concentration 1.0 mg/ml				
Number of calibration samples (solution or solid)		5 solutions				
Details of calibration solutions: concentrations, if: matrix matching, addition method...)		Matrix – aluminium content at 0,5 g per 250 ml of solution, Solutions – (0,02-1,0 mg/l)				
Limits of determination: Values and calculating procedure (formula!)		1,1 µg/l				
Kind of digestion (acid, alkaline...)		Acid + fusion				
Weighted sample	1	500,000				
	2					
	3					
	4					
	5					
	6					
Date of digestion performance	1	14 March				
	2	16 March				
	3	18 March				
	4	22 March				
	5	23 March				
	6	25 March				
Details of digestion procedure (sub-sample weight, reagents, conditions etc.)	1	HCl (1:1), oxidation H <sub>2</sub> O <sub>2</sub>				
	2					
	3					
	4	HCl :HNO <sub>3</sub> (3:1),fusion sodium + borax				
	5					
	6					
Wavelengths if spectrometric methods are used		238,204; 239,562; 259,837; 259,940	324,754; 327,396	257,610; 260,610	205,552; 267,716; 283,563	206,200; 213,856
Used analyzer		ICP Atomic Emission Spectrometer IRIS Advantage and Flame Atomic Absorption Spectrometer SOLAAR 6M				
Instrument parameter (e.g. nebulizer, lines, background, time cycles etc.)		Integration time: 10 c				

## CENAM

CCQM P34.1/K42 Aluminium						
Declarations						
<p>Please enlist the corresponding data into the <b>green marked</b> cells of the table!            If the specifications are equal for several elements, a link is sufficient!</p> <p style="text-align: center;"><b>Attention!</b></p> <p>If you need more place for enlisting your data you can use alternatively the table "CCQM_P34.1/K42_Declarations (2)"</p> <p style="text-align: center;">Use the horizontal scroll bar for displaying the cells for the desired element!</p>						
Participant						
						<b>Comment</b>
	<b>Fe</b>	<b>Cu</b>	<b>Mn</b>	<b>Cr</b>	<b>Zn</b>	
Used primary substance for calibration	DMR 86b	DMR 17e	SRM 3132	DMR 94b	DMR 61c	Spectrometric solutions
Concentration of primary substance [mg/L]	997,4	992,6	10010,0	500,9	1001,2	None
Uncertainty [mg/L]	6,2	8,9	30,0	3,0	7,4	None
Stock solution (source, preparing, concentration...)	None	None	None	None	None	Independent preparation of each calibration sample.
Number of calibration samples (solution or solid)	5	5	5	5	6	Choosing the calibration samples suitable for each analyte calibration.
Details of calibration solutions: concentrations, if: matrix matching, addition method...)	Matrix matching	Matrix matching	Matrix matching	Matrix matching	Matrix matching	Solid solution.
Estimated limits of determination (9s-criterion)	0,9996	0,9999	0,9997	0,9996	0,9997	None
Kind of digestion (acid, alkaline, fusion...)	HNO <sub>3</sub> After fusion with Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	HNO <sub>3</sub> After fusion with Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	HNO <sub>3</sub> After fusion with Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	HNO <sub>3</sub> After fusion with Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	HNO <sub>3</sub> After fusion with Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	None
Weighted sub-sample [mg]	1	50,00				9,5 g of flux
	2	50,00				9,5 g of flux
	3	50,00				9,5 g of flux
	4	50,00				9,5 g of flux
	5	50,00				9,5 g of flux
	6	50,00				9,5 g of flux
Date of digestion performance	1					None
	2	February 22th				
	3					
	4					None
	5	March 10th				
	6					
Details of digestion procedure (reagents, conditions etc.)	1					Same procedure for each subsample and CRM.
	2					
	3	Digestion with HNO <sub>3</sub> ultrex in teflon beakers, transfer to platinum crucibles and evaporation until dryness at 50°C.				
	4					
	5					
	6					
Wavelengths if spectrometric methods are used or other specification	Fe Kα 1,2	Cu Kα 1,2	Mn Kα 1,2	Cr Kα 1,2	Zn Kα 1,2	None
Used analytical instrument	Spectrometer SIEMENS SRS 3000 (XRF)					Rhodium tube, operated at 45 kV, 45 mA at vacuum. No filter used.
Instrument parameter (e.g. nebulizer, lines, background, time cycles etc.)	80 s	80 s	80 s	120 s	80 s	Time of measurement for peak and background.

**IMGC****CCQM P34.1/K42 Aluminium****Declarations**

Please enlist the corresponding data into the **green marked** cells of the table!  
If the specifications are equal for several elements, a link is sufficient!

**Attention!**

If you need more place for enlisting your data you can use alternatively the table "CCQM\_P34.1/K42\_Declarations (2)"

Use the horizontal scroll bar for displaying the cells for the desired element!

Participant	IMGC-Italy						
							Comment
		Fe	Cu	Mn	Cr	Zn	Determination by INAA
Used primary substance for calibration		solution		solution	solution		see declaration (2) and progress report
Number of calibration samples (solution or solid)		4,0000		4,0000	4,0000		4 independent aliquots of solution samples
Weighted sub-sample [mg]	1	316,850		288,940	316,850		
	2	326,690		333,110	326,690		
	3	288,950		290,330	288,950		
	4	301,940		295,450	301,940		
	5	299,380		319,690	299,380		
	6	306,310		306,050	306,310		
Date of digestion performance	1						Direct instrumental analysis (INAA)
	2						
	3						
	4						
	5						
	6						
Used analytical instrument		INAA		INAA	INAA		

**Used primary substances for calibration "**

**Fe:** Standard solution (Aldrich) certificate states 10,126 mg/L with expanded uncertainty of 50,6mg/L (0,5%)

**Mn:** Standard solution (BDH) certificate states 1,001mg/L with expanded uncertainty of 5mg/L (0,5%)

**Cr:** Standard solution (BDH) certificate states 990mg/L with expanded uncertainty of 4.9 mg/L (0,5%)

## UME

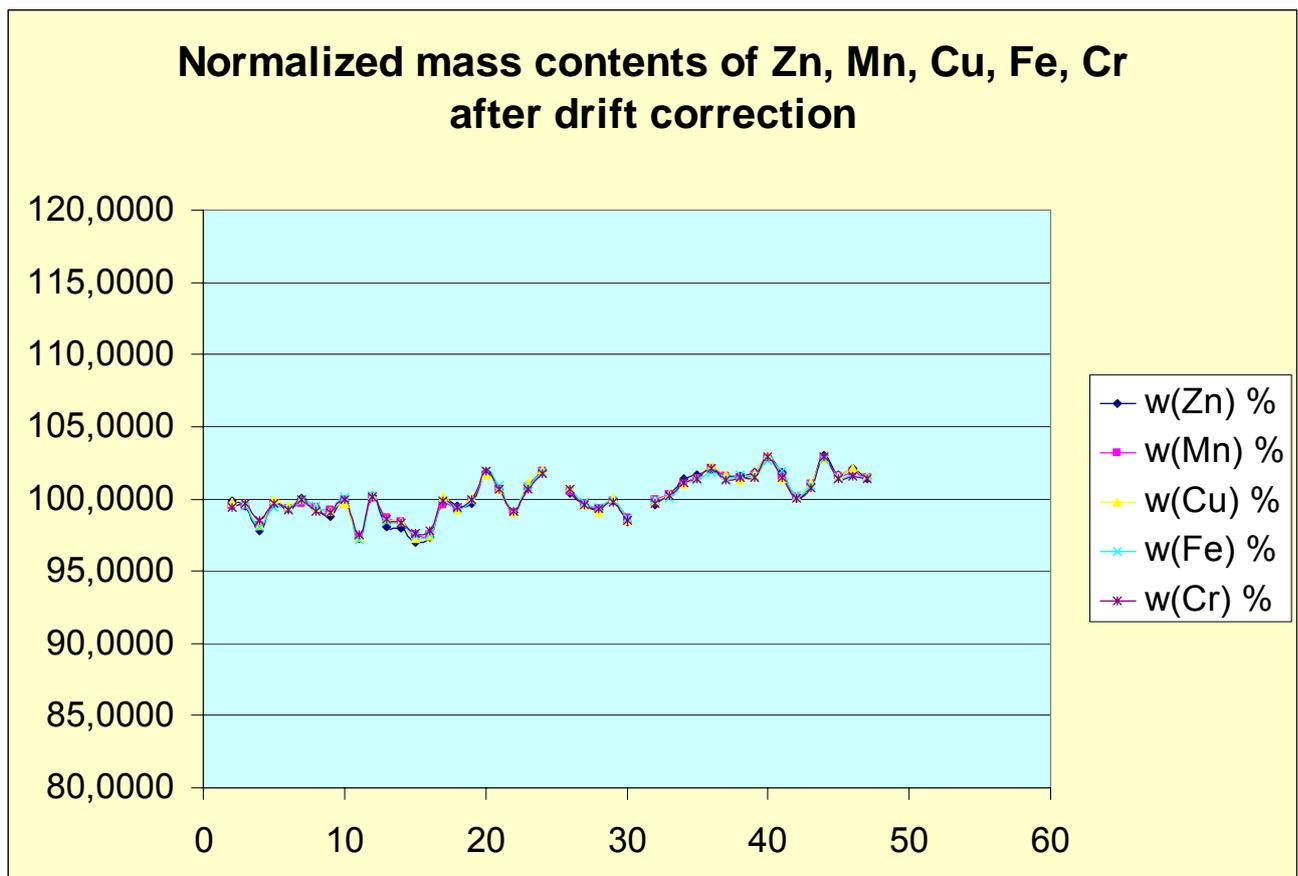
<b>CCQM P34.1/K42 Aluminium</b>						
<b>Declarations</b>						
Please enlist the corresponding data into the green marked cells of the table! If the specifications are equal for several elements, a link is sufficient! Attention! If you need more place for enlisting your data you can use alternatively the table "CCQM_P34.1/K42_Declarations (2)" Use the horizontal scroll bar for displaying the cells for the desired element!						
Participant						
UME NATIONAL METROLOGY INSTITUTE CHEMICAL METROLOGY LABORATORY İBRAHİM AKDAĞ						
						Comment
		Fe	Cu	Mn	Cr	Zn
Used primary substance for call		Primary Solution	Primary Solution	Primary Solution	Primary Solution	Primary Solution
Purity of primary substance [%]		99,99850	99,9999			99,999
Uncertainty of the purity [%]		0,0008	0,0001			0,0005
Stock solution (source, preparing, concentration...)		From primary substance	From primary substance	1000 mg/L	1000 mg/L	From primary substance
Number of calibration samples (solution or solid)		3	3	3	3	3
Details of calibration solutions: concentrations, if: matrix matching, addition method...)		External Calibration	External Calibration	External Calibration	External Calibration	External Calibration
Estimated limits of determination (9s-criterion)	ng/g	0,05	0,05	0,08	0,06	0,04
Kind of digestion (acid, alkaline, fusion...)		Acid digestion				
Weighted sub-sample [mg]	1	309,850	Same			
	2	310,830	Same			
	3	301,860	Same			
	4	308,880	Same			
	5	300,600	Same			
	6	303,360	Same			
Date of digestion performance	1	March 14 2005				
	2					
	3					
	4					
	5					
	6					
Details of digestion procedure (reagents, conditions etc.)	1	8 ml Merck Suprapure acid microwave digestion				
	2					
	3					
	4					
	5					
	6					
Wavelengths if spectrometric methods are used or other specification						
Used analytical instrument		Perkin Elmer DRC-e ICP-MS				
Intrument parameter (e.g. nebulizer, lines, background, time cycles etc.)		Scott Spray Chamber and Nebuliser, sweep/readings 60, replicate 5, integration time per reading 3000 ns, RF power: 1100 W, argon flow rate: 15 L min-1, auxiliary flow rate: 1 L min-1, nebulizer flow rate: 1 L min-1. Fe is measured in DRC mode with methane cell gas, other metals are measured in standard mode.				

## Annex C

### Homogeneity testing

In addition to the tests described in the draft report a new test series was analyzed because of the results of the previous homogeneity tests it could be assumed that the dissolution procedure of the sample material in hydrochloric acid is not complete:

- For the correction of drift effects the previous homogeneity testing was done by alternating measuring of sample solutions and one and the same calibration solution.
- The deviation of the results for the sample solutions was significantly higher than the deviation of the results for the calibration solution.
- The relative deviation of the analyzed mass contents was nearly the same for all the analyzed elements like Fe, Cu, Mn, Cr and Zn:



Normalized mass contents after drift correction during homogeneity testing

### New homogeneity testing

Therefore the analytical procedure for preparing sample solutions for the test of homogeneity was repeated in the following way:

- Weighed portion: 300 mg
- Additional digestion of the residue after filtering the acidic sample solution
- Consideration of the mass fractions of Fe, Cu, Mn, Cr and Zn in the residue
- Measuring of sample solutions with ICP OES.

The homogeneity testing was done with 5 bottles by analyzing 2 samples of each bottle respectively. (totally 10 samples). The sample solutions had been measured two times. The mean value was used for data evaluation.

Because of an intensive milling of the raw grinded material (about 1 kg) a differentiation of “between” and “within” bottle effects is only of low interest. However both effects have been considered.

The relative deviations of mass contents for the analyzed samples is pointed up by the fig. x to y.

For calculating the maximum deviation of the results of participants caused by inhomogeneity the deviation of the analytical procedure has to be considered.

The contribution of inhomogeneities to the deviation of mass contents in different samples can be calculated by:

$$s(x)_{\text{inhom}} = \sqrt{s(x)_{\text{between}}^2 + s(x)_{\text{within}}^2}$$

$$s(x)_{\text{between}} = \sqrt{s(x)_{\text{between,measured}}^2 - s(x)_{\text{Procedure}}^2}$$

$$s(x)_{\text{within}} = \sqrt{s(x)_{\text{within,measured}}^2 - s(x)_{\text{Procedure}}^2}$$

- x: Element (Fe, Cu, Mn, Cr, Zn)  
 $s(x)_{\text{Procedure}}$ : Deviation of the analytical procedure  
 $s(x)_{\text{between}}$ : Deviation between bottles  
 $s(x)_{\text{within}}$ : Deviation within bottles

Because of the uncertainty of a standard deviation it is possible that the measured standard deviation caused by an inhomogeneity is smaller than the standard deviation of the analytical procedure by chance.

In this case according to **ISO Guide 35** the following term is a criterion for an undetected inhomogeneity:

$$u(x)_{\text{bb}} = \sqrt{\frac{s(x)_{\text{Procedure}}^2}{p}} \cdot \sqrt[4]{\frac{2}{v_{s(x)_{\text{Procedure}}^2}}}$$

- p: Number of measurements for calculating  $s(x)_{\text{Procedure}}$

The correct mathematical condition is:

$$s(x)_{\text{inhom}} \geq u(x)_{\text{bb}} \quad \Rightarrow \quad u_{\text{inhom}} = s(x)_{\text{inhom}}$$

$$s(x)_{\text{inhom}} < u(x)_{\text{bb}} \quad \Rightarrow \quad u_{\text{inhom}} = u(x)_{\text{bb}}$$

**Results of homogeneity testing; Tolerance limits for results of round robin test**

		Element	Fe	Cu	Mn	Cr	Zn
		w(x) [%]	0,2003	0,1098	0,1084	0,0442	0,1350
		STD <sub>procedure</sub>	9,46E-04	2,59E-04	4,98E-04	2,68E-04	6,39E-04
		RSD <sub>Procedure</sub> %	0,47	0,24	0,46	0,61	0,47
		u <sup>2</sup> <sub>bb</sub>	4,22E-08	3,16E-09	1,17E-08	3,39E-09	1,93E-08
		STD <sup>2</sup> <sub>inhom</sub>	-2,57E-07	1,46E-06	-4,42E-08	-2,41E-04	1,81E-09
Inhomogeneity	experimental	STD <sub>between,exp</sub>	8,72E-04	1,01E-03	4,18E-04	1,35E-04	9,86E-04
		STD <sub>within,exp</sub>	8,79E-04	7,56E-04	5,28E-04	1,60E-04	4,25E-05
	effective	STD <sub>between,eff</sub>	A	9,77E-04	A	A	7,50E-04
		STD <sub>within,eff</sub>	B	7,10E-04	1,73E-04	B	B
		u <sub>inhom</sub> abs.	2,05E-04	1,21E-03	1,08E-04	5,82E-05	1,39E-04
		u <sub>inhom</sub> rel. %	0,10	1,10	0,10	0,13	0,10
Tolerance limits for results of round robin test		lower limit	0,2001	0,1086	0,1083	0,0441	0,1349
		upper limit	0,2005	0,1110	0,1085	0,0443	0,1351

STD<sub>between,exp</sub>  
<STD<sub>procedure</sub>

**A**

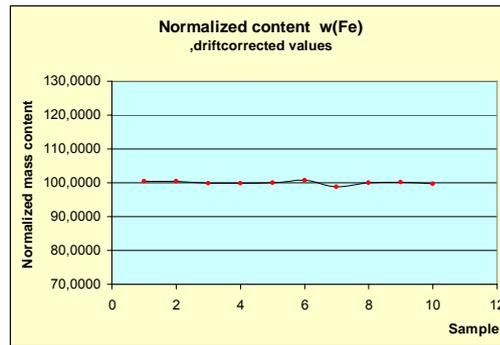
STD<sub>within,exp</sub>  
<STD<sub>procedure</sub>

**B**

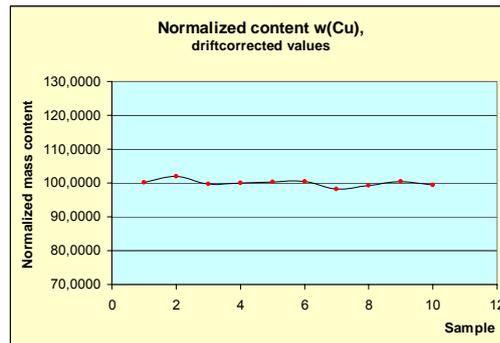
The maximum contribution of inhomogeneities to the uncertainty of the mean value of the round robin test is about 0,1 % other than copper. The maximum contribution of inhomogeneities for copper is about 1%.

Normalized mass contents of Fe, Cu, Mn, Cr, Zn in sample material

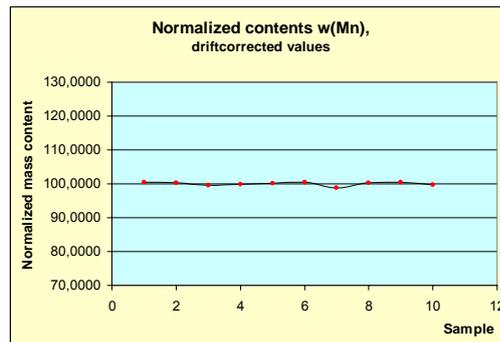
$w(\text{Fe}) \approx 0,2\%$



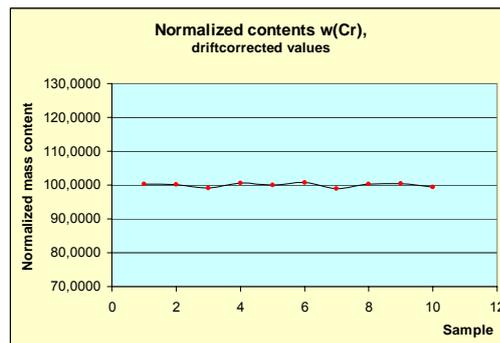
$w(\text{Cu}) \approx 0,1\%$



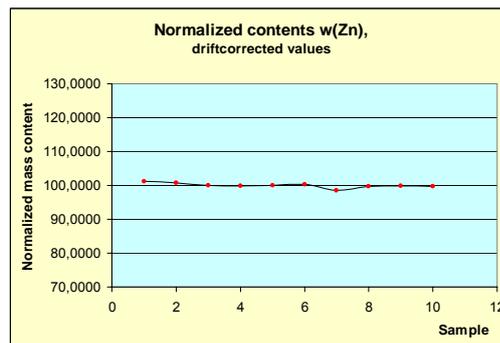
$w(\text{Mn}) \approx 0,1\%$



$w(\text{Cr}) \approx 0,05\%$



$w(\text{Zn}) \approx 0,1\%$



## Annex D

### Uncertainty budgets

#### Uncertainty budget of participant 1 “BAM”

The Uncertainty budget was calculated according to GUM and EURACHEM/CITAC GUIDE, 2000 (Quantifying Uncertainty in Analytical Measurement, Second edition).

#### **Uncertainty sources**

The following uncertainty sources (standard uncertainties  $u$ ) are influencing the result of a reconstitution analysis accomplished by XRF:

1.	Calibration function	$U_{\text{cal}}$
2.	Purity of primary standards for preparation of synthetic calibration samples; error of insufficient stoichiometry	$U_{\text{pur}}$
3.	Counting rates	$U_{\text{count}}$
4.	Matrix effects (secondary excitation, absorption)	$U_{\text{matrix}}$
5.	Contamination	$U_{\text{cont}}$
6.	Loss of volatile components during the borate fusion procedure	$U_{\text{loss}}$
7.	Error of weighing	$U_{\text{weigh}}$
8.	Reproducibility	$U_{\text{rep}}$

The resulting combined uncertainty  $u_{\text{comb}}$  can be calculated by combining the following uncertainty contributions:

#### **1. Uncertainty contribution by calibration $U_{\text{cal}}$**

Caused by the principle of reconstitution technique (bracketing technique for mass contents of elements) the calibration function can be estimated by a linear function (Counts as function of mass content).

The uncertainty contribution can be calculated by the inverse analysis function and the following formulas:

Calibration function  $y = a \cdot x + b$

Slope  $a = Q_{xy} / Q_{xx}$

Intercept  $b = \bar{y} - a \cdot \bar{x}$

Residual standard deviation 
$$s_{y,x} = \sqrt{\frac{\sum_{i=1}^n y_i^2 - b \cdot \sum_{i=1}^n y_i - a \cdot \sum_{i=1}^n x_i y_i}{n-2}}$$

Correlation coefficient 
$$r = \frac{\sum_{i=1}^n x_i y_i - \frac{1}{n} \sum_{i=1}^n x_i \cdot \sum_{i=1}^n y_i}{\sqrt{\left[ \sum_{i=1}^n x_i^2 - \frac{1}{n} \left( \sum_{i=1}^n x_i \right)^2 \right] \cdot \left[ \sum_{i=1}^n y_i^2 - \frac{1}{n} \left( \sum_{i=1}^n y_i \right)^2 \right]}}$$

Analysis function 
$$x_{\text{sample}} = \frac{\bar{y}_{\text{sample}} - b}{a}$$

Uncertainty contribution  
by calibration

$$u_{\text{cal}} = \sqrt{\frac{1}{a^2} \left\{ s_{yx}^2 \left[ \frac{1}{N} + \frac{(x_{\text{sample}} - \bar{x})^2}{\sum (x_i - \bar{x})^2} \right] \right\}}$$

Number of measured values  
for calibration

N

Mean values and auxiliary values

$$\bar{x} = \sum_{i=1}^n x_i / n \quad Q_{xx} = \sum_{i=1}^n (x_i - \bar{x})^2$$

$$\bar{y} = \sum_{i=1}^n y_i / n \quad Q_{xy} = \sum_{i=1}^n [(x_i - \bar{x}) \cdot (y_i - \bar{y})]$$

The uncertainty contributions caused by the calibration procedure are listed in table 1.

**Table 1:** Uncertainty contributions by calibration

Element	Calibration 1 (sample 1 to 3)		Calibration 2 (sample 4 to 6)	
	$u_{\text{cal}}$ [%]	$u_{\text{cal}}$ [rel %]	$u_{\text{cal}}$ [mg/g]	$u_{\text{cal}}$ [rel %]
Manganese	0,0004	0,3	0,0001	0,1
Copper	0,0019	1,7	0,0080	6,4
Iron	0,0007	0,4	0,0030	1,5
Chromium	0,0011	2,5	0,0011	2,7
Zinc	0,0006	0,4	0,0001	0,1

## 2. Purity of primary standards

$u_{\text{pur}}$

For preparation of the synthetic calibration samples pure substances (oxides, industrial products) with a purity of >99,99% (TMI = Total Metal Impurity) are used: Fe<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, ZnO, CuO.

**Tab. 2:** Used primary substances for preparation of synthetic calibration samples

Element	Primary substance	Purity [%]	Uncertainty of purity [%]
Manganese	MnO <sub>2</sub>	> 99,99	≈0,005
Copper	CuO	> 99,99	≈0,005
Iron	Fe <sub>2</sub> O <sub>3</sub>	> 99,99	≈0,005
Chromium	Cr <sub>2</sub> O <sub>3</sub>	> 99,99	≈0,005
Zinc	ZnO	> 99,99	≈0,005

## 3. Counting statistic

$u_{\text{count}}$

Every counting number Z of the borate fusions by XRF has an uncertainty  $u(Z)$  which is equal to the square root of the total counting number:

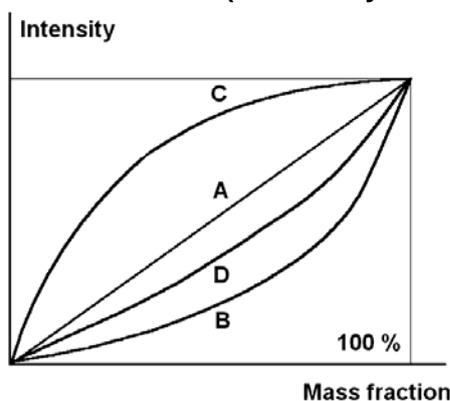
$$u(Z) = \sqrt{Z}$$

This contribution has to be added to the repeatability standard deviation if a sample is measured n times.

**Table 3:** Uncertainty contributions by counting statistics

Element	Medial number of Counts				Mean	U <sub>count</sub> rel%
	Calibration 1		Calibration 2			
	Calibration	Sample	Calibration	Sample		
Manganese	476673	503588	477240	495390	488223	0,14
Copper	1645943	1769768	1645148	1703408	1691067	0,08
Iron	1159815	1170383	1150890	1146885	1156993	0,09
Chromium	275685	260693	276090	260828	268324	0,19
Zinc	1393765	1645210	1396130	1321800	1439226	0,08

#### 4. Matrix effects (secondary excitation, absorption) U<sub>matrix</sub>

**Fig.3:** Types of XRF calibration functions

The basic principle of the reconstitution technique is – based on a pre analysis of the analysis sample and „bracketing” calibration samples – an iterative equalization of the composition of the calibration samples and the analysis sample itself.

But the equalization is limited by the counting rate statistics: The pulse numbers of the calibration samples must be discriminable and definitely assigned to the analyte mass fractions of the calibration samples. Otherwise the calibration function is not reliably defined.

Because of this the intrinsic advantage of negligible deviations from a linear calibration function and negligible matrix effects is theoretically decreased.

Therefore it should be realized, that the absorption coefficients for the synthetic calibration samples are nearly constant by mixing the composition concerning the mass absorption of the whole sample in an appropriate way.

Further on the calibration range is very close.

If these aspects are taken into account a deviation of the calibration function from linearity (and that means the matrix effects) can be neglected in spite of the mentioned restriction (Fig. 1, calibration function “A”).

Because of the principle of the reconstitution technique matrix effects are existing for the calibration sample and the analyse sample but they are nearly equal.

#### 5. Contamination U<sub>cont</sub>

Because using primary substances of high purity (see 2. “Purity of primary standards”) for the preparation procedures and working in an environment with high air quality contamination effects can be neglected.

#### 6. Loss of volatile components during the borate fusion procedure U<sub>loss</sub>

Elements which are highly volatile like halogens and other are not analysed..

## 7. Error of weighing $u_{\text{weigh}}$

The minimum weighted sample mass (oxide for preparation of calibration standard was about 750  $\mu\text{g}$ . The maximum error is about 0,1%. Therefore it is calculated:  
 $u_{\text{weigh}} < 0,1\%$

## 8. Reproducibility

The reproducibility for all 6 sample analyses was:

Element	RSD%
<b>Manganese</b>	1,72
<b>Copper</b>	5,38
<b>Iron</b>	1,65
<b>Chromium</b>	2,31
<b>Zinc</b>	0,92

## Calculation of combined uncertainty

Tab 4a: Uncertainty contributions

No.	Type	Kind of uncertainty contribution to the mass content of analyte (oxide)		$u_{\text{rel}}$
1	A	Calibration procedure (rel. %)	$U_{\text{cal}}$	Mn: 0,3/0,1 % Cu: 1,7/6,4 % Fe: 0,4/1,5 % Cr: 2,5/2,7 % Zn: 0,4/0,1 %
2	B	Purity of primary standards for preparation of synthetic calibration samples; error of insufficient stoichiometry	$U_{\text{pur}}$	< 0,05%
3	B	Counting rates	$U_{\text{count}}$	<0,2%
4	B	Matrix effects (secondary excitation, absorption)	$U_{\text{matrix}}$	negligible
5	B	Contamination	$U_{\text{cont}}$	negligible
6	B	Loss of volatile components during the fusion procedure	$U_{\text{loss}}$	negligible
7	B	Error of weighing	$U_{\text{weigh}}$	<0,1%
8	A	Reproducibility (rel%)	$U_{\text{rep}}$	Mn: 1,7 % Cu: 5,4 % Fe: 1,7 % Cr: 2,3 % Zn: 0,9 %

Tab.4b: Combined uncertainty contributions and expanded uncertainty

Analyte	w(x) [%]	A	A	A	B	B	$U_{\text{comb}}$	$U_{\text{exp}}$	$U_{\text{exp}}$ rel.%
		$u_{\text{rep}}$	$U_{\text{cal}}$		$u_{\text{mess}}$	$u_{\text{prep}}$			
			Cal 1	Cal 2					
<b>Mn</b>	0,1106	0,0019	0,0004	0,0001	0,0002	0,0001	0,0008	0,0016	1,4
<b>Cu</b>	0,1099	0,0059	0,0019	0,008	0,0001	0,0001	0,0026	0,0052	4,7
<b>Fe</b>	0,2031	0,0034	0,0007	0,003	0,0002	0,0002	0,0014	0,0029	1,4
<b>Cr</b>	0,0436	0,0010	0,0011	0,0011	0,0001	0,0001	0,0007	0,0014	3,2
<b>Zn</b>	0,1346	0,0012	0,0006	0,0001	0,0001	0,0002	0,0006	0,0012	0,9

**Uncertainty budget of participant 2 “NIST”**

March 31, 2005

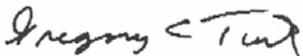
Dr. Siegfried Noack  
 Projektgruppe I.1902  
 Bundesanstalt für Materialforschung und -prüfung  
 Richard-Willstätter-Straße 11  
 12200 Berlin

Dear Dr. Noack:

The NIST results for CCQM Key Comparison K42 Minor Elements in Aluminum Alloy are summarized in the table below. Two methods of analysis, XRF and INAA, were used for all five analytes. For these elements, we are reporting the average result and have estimated the uncertainty using the approach described by Levenson, et al.<sup>1</sup> The NIST Reports of Analysis for the two methods will be forwarded under separate cover.

PERCENT MASS FRACTIONS IN K42 ALUMINUM ALLOY SAMPLE					
	Cr	Mn	Fe	Cu	Zn
XRF Determined Value	0.04494	0.10895	0.2033	0.1162	0.1317
XRF Combined Standard Uncertainty	0.00086	0.00089	0.0034	0.0023	0.0034
INAA Determined Value	0.0449	0.10812	0.20463	0.10968	0.13428
INAA Combined Standard Uncertainty	0.0012	0.00032	0.00085	0.00054	0.00026
Average Determined Value	0.04493	0.10853	0.2040	0.1129	0.1330
Combined Within-Method Standard Uncertainty	0.00074	0.00047	0.0018	0.0012	0.0017
Between-Method Standard Uncertainty (Type B)	0.000006	0.00024	0.0004	0.0019	0.00076
Combined Standard Uncertainty	0.00074	0.00053	0.0018	0.0022	0.0019
Expanded Uncertainty (k=2)	0.0015	0.0011	0.0036	0.0044	0.0038

Sincerely,



Gregory C. Turk, Ph.D.  
 Spectrochemical Methods Group  
 Analytical Chemistry Division

Copies to: S.A.Wise, R.R.Greenberg, J.R. Sieber, A.F. Marlow, R.L. Zeisler

<sup>1</sup> Levenson, M.S., Banks, D.L., Eberhart, K.R., Gill, L.M., Guthrie, W.F., Liu, H.K., Vangel, M.G., Yen, J.H., Zhang, N.F., "An Approach to Combining Results From Multiple Methods Motivated by the ISO Guide" J. Res. Natl. Inst. Stand., 105, 521 (2000).



Uncertainty budgets for INAA and XRF see appendix

**Uncertainty budget of participant 3 “IRMM”**

The expanded uncertainty is calculated by:

$$U_i = 2 * \sqrt{\frac{u_i^2(Np_{\text{sample}})}{n} + \frac{u_i^2(Np_{\text{Standard}})}{n} + u_m^2}$$

Np: Peak area (counting statistics)

n: Number of subsamples;

$u_m$ : B-type uncertainty (Efficiency of detector, coincidence corrections,)  
 $u_m = 2,3 \%$  for long lived radio-isotopes and  $u_m = 2,6 \%$  for short lived radio-isotopes;

**Uncertainty budget of participant 4 “VNIMM”**  
**Evaluation of uncertainty of measurements in CCQM-K42**

**Iron**

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$ , (mass fraction, %)	Coefficient of sensitivity	Contribution $U_i(y)$ , (mass fraction, %)
Calibration (including preparation of calibration standards)	A, B	0,0038	1	0,0038
Standard deviation of measurement result	A	0,0024	1	0,0024
<b>Total standard uncertainty</b>				<b>0,0045</b>
<b>Expanded uncertainty (<math>k=2</math>)</b>				<b>0,0090</b>

**Copper**

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$ , (mass fraction, %)	Coefficient of sensitivity	Contribution $U_i(y)$ , (mass fraction, %)
Calibration (including preparation of calibration standards)	A, B	0,0021	1	0,0021
Standard deviation of measurement result	A	0,0014	1	0,0014
<b>Total standard uncertainty</b>				<b>0,0025</b>
<b>Expanded uncertainty (<math>k=2</math>)</b>				<b>0,0050</b>

**Manganese**

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$ , (mass fraction, %)	Coefficient of sensitivity	Contribution $U_i(y)$ , (mass fraction, %)
Calibration (including preparation of calibration standards)	A, B	0,0017	1	0,0017
Standard deviation of measurement result	A	0,0010	1	0,0010
<b>Total standard uncertainty</b>				<b>0,0020</b>
<b>Expanded uncertainty (<math>k=2</math>)</b>				<b>0,0040</b>

**Chromium**

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$ , (mass fraction, %)	Coefficient of sensitivity	Contribution $U_i(y)$ , (mass fraction, %)
Calibration (including preparation of calibration standards)	A, B	0,0008	1	0,0008

Standard deviation of measurement result	A	0,0006	1	0,0006
<b>Total standard uncertainty</b>				<b>0,0010</b>
<b>Expanded uncertainty (<math>k=2</math>)</b>				<b>0,0020</b>

**Zinc**

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$ , (mass fraction, %)	Coefficient of sensitivity	Contribution $U_i(y)$ , (mass fraction, %)
Calibration (including preparation of calibration standards)	A, B	0,0027	1	0,0027
Standard deviation of measurement result	A	0,0029	1	0,0029
<b>Total standard uncertainty</b>				<b>0,0040</b>
<b>Expanded uncertainty (<math>k=2</math>)</b>				<b>0,0080</b>

**Uncertainty budget of participant 5 “CENAM”****UNCERTAINTY BUDGET CCQM-K42****CENAM (Bottle number 20)**

				Concentration (mass fraction %)									
				Zn		Cu		Fe		Mn		Cr	
				0,1344		0,1114		0,2030		0,1064		0,0441	
SOURCE	DESCRIPTION OF STANDARD UNCERTAINTY	UNIT	EVALUATION TYPE										
REPRODUCIBILITY	Mean standard deviation of independent measurements.	mass fraction %	A	0,00014		0,00012		0,00025		0,00035		0,00024	
CALIBRATION	Calibration of analytical balance	g	B	0,00005		0,00005		0,00005		0,00005		0,00005	
	Primary standard solution	mg/L	B	3,00		8,90		6,20		30,00		7,40	
	CRM calibrants	mass fraction %	B	Synthetic	u standard	CRM No.	u standard						
				1	0,0004	1	0,0005	1	0,0006	1	0,0003	1	0,0002
				2	0,0006	2	0,0007	2	0,0008	2	0,0004	2	0,0002
				3	0,0003	3	0,0003	3	0,0005	3	0,0003	3	0,0001
				4	0,0002	4	0,0001	4	0,0004	4	0,0003	4	0,00003
				5	0,0005	5	0,0004	5	0,0005	5	0,0004	5	0,0001
				6	0,0006	6	0,0002	6	0,0007	6	0,0003	6	0,0002
				7	0,0005	7	0,0006	7	0,0007	7	0,0003	7	0,00004
				8	0,0003	8	0,0010	8	0,0006	8	0,0003	8	0,00003
				9	0,0002	9	0,0011	9	0,0008	9	0,0003	9	0,00004
	CRM No.	u standard	CRM No.	u standard	CRM No.	u standard	CRM No.	u standard	CRM No.	u standard			
	1	0,0010	1	0,0050	1	0,0050	1	0,0010	1	0,00050			
2	0,0100	2	0,0050	2	0,0015	2	0,0050	2	0,00010				
3	0,0200	3	0,0050	3	0,0035	3	0,0010	3	0,00400				
	Repeability of weights	g	A	0,0001		0,0001		0,0001		0,0001		0,0001	
	Repeatability of spectrometer	kcps	A	0,0135		0,0211		0,0057		0,0059		0,0013	
	CALIBRATION	mass fraction %	A	0,0004		0,0006		0,0010		0,0005		0,0005	
VARIATIONS OF PREPARATION	Variation observed	mass fraction %	B	0,0006		0,0005		0,0010		0,0005		0,0002	
<b>COMBINED STANDARD UNCERTAINTY</b>				<b>0,0007</b>		<b>0,0008</b>		<b>0,0014</b>		<b>0,0008</b>		<b>0,0006</b>	
DEGREES OF FREEDOM	REPRODUCIBILITY			5		4		4		5		5	
	CALIBRATION			10		8		8		8		8	
	PREPARATION			1000		1000		1000		1000		1000	
EFFECTIVE DEGREES OF FREEDOM				98		27		34		38		14	
COVERAGE FACTOR				1,98		2,05		2,03		2,02		2,14	
<b>EXPANDED UNCERTAINTY</b>				<b>0,0015</b>		<b>0,0015</b>		<b>0,0029</b>		<b>0,0016</b>		<b>0,0013</b>	

## Uncertainty budget of participant 6 “IMGC”

### Report on the determination by Instrumental Neutron Activation Analysis (INAA) of Chromium and Iron in Aluminium alloy in the frame of the CCQM-K42

Pavia: 15 March, 2005

Dr. Mario Gallorini

and

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## 1. RECEIPT OF SAMPLE

The aluminium alloy sample was received at the Unit of Pavia from BAM in good order at 12/12/04.

## 2. ANALYSIS

2.1 The total Cr content was determined by Instrumental Neutron Activation Analysis (INAA) via the nuclear reaction  $^{50}\text{Cr} (n,\gamma) \rightarrow ^{51}\text{Cr}$  ( $t_{1/2}$  27.8 days) and by counting the corresponding gamma peak at 320.0 keV.

2.2 The total Fe content was determined by Instrumental Neutron Activation Analysis (INAA) via the nuclear reaction  $^{58}\text{Fe} (n,\gamma) \rightarrow ^{59}\text{Fe}$  ( $t_{1/2}$  45.1 days) and by counting the corresponding gamma peaks at 1098.6 keV and at 1291.5 keV.

## 3. STANDARD

### 3.1 Traceability of Standard

Standard Solution. Certificate (Aldrich, USA Cat. No 40410-1) specifies the Cr concentration of 990 mg/L with an expanded uncertainty of 4.9 mg/L .

Standard Solution. Certificate (Aldrich, USA Cat. No 35630-1) specifies the Fe concentration of 10,126 mg/L with an expanded uncertainty of 50.6 mg/L.

### 3.2 Standard preparation

All weighing was done using a balance, calibrated by a certified calibration body, thus maintaining traceability to the kg. The balance was checked weekly for its performance and there are no indications for deviation from the calibrated status.

The Cr and Fe standards were prepared gravimetrically by pipetting aliquots of the above standard solutions onto a filter paper rolled up as a cylinder and inserted in the a polyethylene capsule. The same capsules were also used for sealing the aluminium samples and the certified reference mate-

rials. The pipetted aliquots were evaporated to dryness in a fume hood under ambient conditions. The standards, obtained in this way, and samples (about 300 mg) have the same geometry i.e. 15 mm high and 6 mm diameter. Two blanks consisting of polyethylene capsule with filter paper inside have been also prepared.

An additional aliquot of the Cr and Fe standard solution (about 0.5 mL each) were sealed in two different quartz vials (Suprasil, Heraeus - Germany) and neutron irradiated together with the samples and standards (see the Fig.n.1). After irradiation, aliquots of the irradiated standard solution were gravimetrically pipetted onto not irradiated aluminium samples (about 300 mg) obtaining a very close counting geometry to those of the samples and the standards.

Samples of the certified reference materials SRM Coal 1632b and SRM Buffalo River Sediment 8704 from NIST (Gaithersburg, MD, USA) were also analyzed as comparator standards.

### 3.3 Preparation for Irradiation

The aluminium alloy samples (about 300 mg), the NIST SRM samples, the blanks and standards were sealed in polyethylene capsules (Kartell<sup>®</sup>, Milan, Italy) 18 mm high and 6 mm internal diameter. Capsules and quartz vials were previously cleaned by diluted nitric acid (high purity nitric acid by Romil<sup>®</sup>, U.K.) in ultrasonic bath at 60°C, washed with MilliQ water and dried at 105°C. In addition, two samples of about 1mg of high purity iron wire (0.25 mm diam., 99.999% from Sigma Aldrich, Italy) inserted into a polyethylene capsules were also irradiated as neutron flux monitor and to test possible nuclear interferences by (n, $\alpha$ ) reaction onto <sup>54</sup>Fe (see below).

Samples and standards were then loaded in the irradiation vial in alternative sequence while the quartz vials containing the standard solution were inserted sideways as reported in Fig.1. Two sets of irradiation container each containing three alloy samples were prepared.

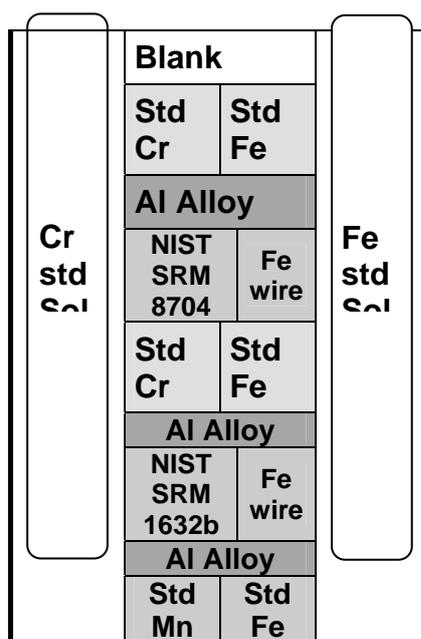


Fig.1 Loading of samples, monitors in the irradiation vial

standards, blanks and flux

## 4. IRRADIATION

The irradiation was performed for 6 hours in the central thimble irradiation facility channel of the research nuclear reactor TRIGA Mark II of the University of Pavia at the nominal neutron flux of  $9 \cdot 10^{12} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ . Two sets of irradiation were performed.

## 5. MEASUREMENTS

After 15 days of cooling time, the irradiated samples, blanks and standards have been submitted to gamma counting for the evaluation of the resulting gamma peak of <sup>51</sup>Cr ( $t_{1/2}$  27.8 d) at 320.0 keV and of <sup>59</sup>Fe ( $t_{1/2}$  45.1 d) at 1098.6 keV and at 1291.5 keV. The counting facility was consisting of an HPGe detector coupled to a multichannel computerized system (DSPEC from ORTEC-USA). The

relative efficiency of the detector was of about 45% with resolution of 1.73 at the 1332.4 keV of the  $^{60}\text{Co}$ .

Two series of gamma counting of 25,000 s each were performed during a period of 15 days following the cooling time.

The counting facility was equipped for dead-time and pile-up correction losses. All the spectrometry parameters (energy calibration, peak shape, counting geometry and counting room background) were assessed against pre-defined criteria.

## 6. SPECTRUM INTERPRETATION

The gamma-spectra were analyzed and interpreted with the Gammavision (ORTEC-USA) software.

## 7. ADDITIONAL CORRECTIONS

**7.1 Blank.** No Cr and Fe were detected in the blanks (plastic containers, filter paper, MilliQ water). The detection limit of Cr has been evaluated as twice the background counts in the region of the 320 keV gamma peak i.e. 65 counts. Samples gave approximately 850,000 counts and the corresponding detection limit (at 95% confidence) can be evaluated as 0.01% of the samples. The relative standard uncertainty estimated as half of the detection limit ( $2\sigma$ ) 0.005% was considered negligible.

The detection limit of Fe has been evaluated as twice the background counts in the region of the 1098.6 keV gamma peak i.e. 35 counts. Samples gave approximately 32,000 counts and the corresponding detection limit (at 95% confidence) can be evaluated as 0.11% of the samples. The relative standard uncertainty was estimated as half of the detection limit ( $2\sigma$ ) 0.05%.

**7.2 Cr nuclear reaction interference.** Chromium was determined through the  $^{51}\text{Cr}$ . If iron is present in the sample, the  $^{51}\text{Cr}$  can be also produced by the following nuclear side reactions i.e.  $^{54}\text{Fe}(\text{n},\alpha)\rightarrow ^{51}\text{Cr}$ . In the aluminum sample iron was present as impurity at level of 0.2% and a possible  $^{51}\text{Cr}$  could have been produced. This was experimentally verified by irradiating among the samples and standards a high purity iron wire of 1 mg (1.090 mg) The irradiated Fe wire was submitted to  $\gamma$  spectroscopy in the same way of the aluminum alloy samples to check the presence of  $^{51}\text{Cr}$ . After 25,000 s counting time a net area of 615 ( $\pm 50$ ) counts (320.0 keV) was obtained. The correction of 0.56 Cr counts/ $\mu\text{g}_{(\text{Fe})}$  applied on the basis of the iron amount found in each aluminum sample was of the order of 0.04% and considered negligible since much lower than counting statistics (0.2%).

## 8. MEASUREMENT EQUATION

The measurement equation used for determination of the amount of substance of Cr and Fe in aluminum alloy is:

$$C_x = \frac{m_s}{m_x M_s} \frac{A_x}{A_s} R_\theta R_\phi R_\sigma R_\varepsilon$$

in which the subscripts x refers to the sample and s to the standard, and

C = concentration of measurand ( $\text{mole}\cdot\text{g}^{-1}$ )

m = mass of sample (g)

M = atomic mass ( $\text{g}\cdot\text{mole}^{-1}$ )

A = peak area of the radionuclide of interest

R = ratio of sample and standard

$\theta$  = isotopic abundance (value between 0 and 1)

$\phi$  = neutron fluence rate ( $\text{m}^{-2}\text{s}^{-1}$ )

$\sigma$  = effective absorption cross section ( $\text{m}^{-2}$ )

$\varepsilon$  = absolute photopeak efficiency of the detector (value between 0 and 1)

Additional correction factors (not shown in the equation) are:

- neutron self-shielding (neutron fluence rate)
- neutron scattering (neutron fluence rate)
- dead-time and pile-up correction (counting efficiency)
- nuclear reaction interferences (correction to peak area)
- gamma-ray self-shielding and interferences (counting efficiency)
- peak integration method (correction to peak area)

## 9. UNCERTAINTY EVALUATION

Source of uncertainty	Type of evaluation	Contribution (%)	
		Cr	Fe
Counting statistics for samples	A	0.25	0.90
Counting statistics for standards	A	0.15	0.65
Blanks	A	Neglected	0.05
Isotopic abundances	B	Neglected	Neglected
Neutron fluence and irradiation geometry	B	0.5	0.5
Neutron self-shielding	B	Neglected	Neglected
Neutron scattering	B	Neglected	Neglected
Counting geometry	B	0.5	0.3
Gamma-ray self-absorption	B	0.1	0.08
Effect of half life	B	Neglected	Neglected
Pulse pileup and live time correction	B	0.1	0.1
Interfering nuclear reaction	B	Neglected	Neglected
Gamma-ray interferences	B	Neglected	Neglected
Sample Mass	B	0.03	0.03
Standards mass	B	0.25	0.25
<b>Total combined uncertainty</b>		<b>0.82</b>	<b>1.29</b>
<b>EXPANDED UNCERTAINTY</b>	<b>C.F. K=2</b>	<b>1.64</b>	<b>2.57</b>

## 10. RESULTS

Al alloy	Cr %	Fe %
1	0.0412	0.1936
2	0.0429	0.1913
3	0.0417	0.1953
4	0.0407	0.1920
5	0.0419	0.1986
6	0.0424	0.1930
<b>Mean</b>	<b>0.0418</b>	<b>0.1940</b>
<b>STD</b>	<b>0.0008</b>	<b>0.0027</b>
<b>RSD%</b>	<b>1.90</b>	<b>1.37</b>

NIST SRM	Cr found (mg/kg)	Cr certified (mg/kg)	Fe found (%)	Fe certified (%)
Buffalo River Sediment 8704	121.3 ± 2.7	121.9 ± 3.8	3.99 ± 0.05	3.97 ± 0.10
Coal 1632b	10.8 ± 0.5	11 (suggested value)	0.751 ± 0.024	0.759 ± 0.045

**Report on the determination by Instrumental Neutron Activation Analysis (INAA) of Manganese in Aluminium alloy in the frame of the CCQM-K42**

Pavia: 15 March, 2005

Dr. Mario Gallorini



and

Dr. Enrico Rizzio



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e-mail [gallorin@unipv.it](mailto:gallorin@unipv.it)[rizzio@unipv.it](mailto:rizzio@unipv.it)**1. RECEIPT OF SAMPLE**

The aluminium alloy sample was received at the Unit of Pavia from BAM in good order at 12/12/04.

**2. ANALYSIS**

The total manganese content was determined by Instrumental Neutron Activation Analysis (INAA) via the nuclear reaction  $^{55}\text{Mn}_{(\text{nat.})} (n,\gamma) \rightarrow ^{56}\text{Mn} (t_{1/2} 2.58\text{h})$  and by counting the corresponding gamma peak at 1810.7 keV.

**3. STANDARD****3.1 Traceability of Standard**

Standard Solution. Certificate (BDH, U.K. Cat. No 455642F) specifies the Mn concentration of 1001 mg/L with an expanded uncertainty of 5mg/L.

**3.2 Standard preparation**

All weighing was done using a balance, calibrated by a certified calibration body, thus maintaining traceability to the kg. The balance was checked weekly for its performance and there are no indications for deviation from the calibrated status.

The Mn standards were prepared gravimetrically by pipetting aliquots of the above standard solution onto a filter paper rolled up as a cylinder and inserted in the a polyethylene capsule. The same capsules were also used for sealing the aluminium samples and the certified reference materials. The pipetted aliquots were evaporated to dryness in a fume hood under ambient conditions. The standards, obtained in this way, and samples (about 300mg) have the same geometry i.e. 15 mm high and 6 mm diameter. Two blanks consisting of polyethylene capsule with filter paper inside have been also prepared.

An additional aliquot of the Mn standard solution (about 0.5 mL) was sealed in quartz vial (Suprasil, Heraeus - Germany) and neutron irradiated together with the samples and standards (see the Fig.n.1). After irradiation, aliquots of the irradiated standard solution were gravimetrically pipetted

onto not irradiated aluminium samples (about 300 mg) obtaining a very close counting geometry to those of the samples and the standards.

Samples of certified reference materials SRM Buffalo River Sediment 8704 from NIST (Gaithersburg, MD, USA) were also analyzed as comparator standards.

### 3.3 Preparation for Irradiation

- The aluminium alloy samples (about 300mg), the NIST SRM samples, the blanks and standards were sealed in polyethylene capsules (Kartell®, Milan, Italy) 18 mm high and 6 mm internal diameter. Capsules and quartz vials were previously cleaned by diluted nitric acid (high purity nitric acid by Romil®, U.K.) in ultrasonic bath at 60°C, washed with MilliQ water and dried at 105°C. In addition, about 1mg of high purity iron wire (0.25 mm diam., 99.999% from Sigma Aldrich, Italy) inserted into a polyethylene capsule was also irradiated to test possible nuclear interferences (by n,p reaction onto  $^{56}\text{Fe}$  and  $^{57}\text{Fe}$  leading to  $^{56}\text{Mn}$ ).
- Samples and standards were then loaded in the irradiation vial in alternative sequence while the quartz vial containing the standard solution was inserted sideways as reported in Fig.1. Two sets of irradiation container each containing three alloy samples were prepared.

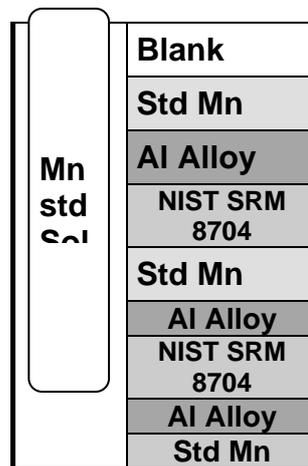


Fig.1 Loading of samples, stan-  
dards and blanks in the irradiation  
vial

dards and blanks in the irradiation

## 4. IRRADIATION

The irradiation was performed for 5 minutes in the irradiation channel "Lazy Susan" of the research nuclear reactor TRIGA Mark II of the University of Pavia at the nominal thermal neutron flux of  $1.2 \cdot 10^{12} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ . Two sets of irradiation were performed .

## 5. MEASUREMENTS

After 1 h of cooling time, the irradiated samples, blanks and standards have been submitted to gamma counting for the evaluation of the resulting gamma peak of  $^{56}\text{Mn}$  ( $t_{1/2}$  2.58 h) at 1810.7 keV. The counting facility was consisting of an HPGe detector coupled to a multichannel computerized system (DSPEC from ORTEC-USA). The relative efficiency of the detector was of about 45% with resolution of 1.73 at the 1332.4 keV of the  $^{60}\text{Co}$ .

Two series of gamma counting of 1000 s each were performed during a period of 4 hours following the cooling time.

The counting facility was equipped for dead-time and pile-up correction losses. All the spectrometry parameters (energy calibration, peak shape, counting geometry and counting room background) were assessed against pre-defined criteria.

## 6. SPECTRUM INTERPRETATION

The gamma-spectra were analyzed and interpreted with the Gammavision (ORTEC-USA) software.

## 7. ADDITIONAL CORRECTIONS

### 7.1 Blank.

No manganese was detected in the blanks (plastic containers, filter paper, MilliQ water). In this case, the detection limit of manganese has been evaluated as twice the background counts in the region of the 1810.7 keV gamma peak i.e. 25 counts. Samples gave approximately 16000 counts and the corresponding detection limit (at 95% confidence) can be evaluated as 0.15 % of the samples. The relative standard uncertainty was estimated as half of the detection limit ( $2\sigma$ ) **0.07%**.

### 7.2 Nuclear reaction interferences.

Manganese was determined through the nuclear reaction  $^{55}\text{Mn}(n,\gamma) \rightarrow ^{56}\text{Mn}$ . If iron is present in the sample, the  $^{56}\text{Mn}$  can be also produced by the following nuclear side reactions i.e.  $^{56}\text{Fe}(n,p) \rightarrow ^{56}\text{Mn}$  and  $^{57}\text{Fe}(n,pn) \rightarrow ^{56}\text{Mn}$ . Since in the sample iron was present as impurity at level of 0.2% a possible  $^{56}\text{Mn}$  could have been produced. This was experimentally verified by irradiating among the samples and standards a high purity iron wire of 2 mg. The irradiated Fe wire was submitted to  $\gamma$  spectroscopy in the same way of the aluminum alloy samples to check the presence of  $^{56}\text{Mn}$ . After 1000 s counting time a net area of 10 ( $\pm 4$ ) counts (1810.7 keV) was obtained. Samples gave about 16000  $\pm$  130 counts (0.8%); the resulting correction of about 0.06% was found negligible.

## 8. MEASUREMENT EQUATION

The measurement equation used for determination of the amount of substance of Mn in aluminum alloy is:

$$C_x = \frac{m_s}{m_x M_s} \frac{A_x}{A_s} R_\theta R_\phi R_\sigma R_\varepsilon$$

in which the subscripts x refers to the sample and s to the standard, and

C = concentration of measurand ( $\text{mole}\cdot\text{g}^{-1}$ )

m = mass of sample (g)

M = atomic mass ( $\text{g}\cdot\text{mole}^{-1}$ )

A = peak area of the radionuclide of interest

R = ratio of sample and standard

$\theta$  = isotopic abundance (value between 0 and 1)

$\phi$  = neutron fluence rate ( $\text{m}^{-2}\text{s}^{-1}$ )

$\sigma$  = effective absorption cross section ( $\text{m}^{-2}$ )

$\varepsilon$  = absolute photopeak efficiency of the detector (value between 0 and 1)

Additional correction factors (not shown in the equation) are:

- neutron self-shielding (neutron fluence rate)
- neutron scattering (neutron fluence rate)
- dead-time and pile-up correction (counting efficiency)
- nuclear reaction interferences (correction to peak area)
- gamma-ray self-shielding and interferences (counting efficiency)
- peak integration method (correction to peak area)

## 9. UNCERTAINTY EVALUATION

Source of uncertainty	Type of evaluation	Contribution (%)
Counting statistics for samples	A	0.8
Counting statistics for standards	A	0.5
Blanks	A	0.07
Isotopic abundances	B	Neglected
Neutron fluence and irradiation geometry	B	0.2
Neutron self-shielding	B	Neglected
Neutron scattering	B	Neglected
Counting geometry	B	0.3
Gamma-ray self-absorption	B	0.05
Effect of half life	B	0.05
Pulse pileup and live time correction	B	0.1
Interfering nuclear reaction	B	Negligible
Gamma-ray interferences	B	Neglected
Sample Mass	B	0.03
Standards mass	B	0.26
<b>Total combined uncertainty</b>		<b>1.05</b>
<b>EXPANDED UNCERTAINTY</b>	<b>COVERAGE FACTOR K=2</b>	<b>2.10</b>

**10. RESULTS**

<b>Al alloy</b>	<b>Mn%</b>
<b>1</b>	0.1039
<b>2</b>	0.1069
<b>3</b>	0.1015
<b>4</b>	0.1083
<b>5</b>	0.1064
<b>6</b>	0.1077
<b>Mean</b>	<b>0.1058</b>
<b>STD</b>	<b>0.0026</b>
<b>RSD%</b>	<b>1.90</b>

<b>NIST SRM</b>	<b>Mn found (mg/kg)</b>	<b>Mn certified (mg/kg)</b>
Buffalo River Sediment 8704	548 ± 12	544 ± 21

**Uncertainty budget of participant 7 “UME”**

Uncertainty Component	Uncertainty Type	Relative Uncertainty(%)				
		Cu	Zn	Mn	Fe	Cr
Standard Solution	B	6,30E-05	8,24E-05	1,50E-03	6,59E-05	1,50E-03
Metal Weight	B	1,84E-05	1,84E-05	1,84E-05	1,84E-05	1,84E-05
Solution Weight	B	1,46E-05	1,46E-05	1,46E-05	1,46E-05	1,46E-05
Dilution	B	4,47E-03	4,47E-03	4,47E-03	4,47E-03	4,47E-03
Method repeatability precision	A	6,41E-03	6,43E-03	7,30E-03	6,26E-03	6,92E-03
Combined relative standard uncertainty		0,0078	0,0078	0,0087	0,0077	0,0084
Coverage factor		2	2	2	2	2
Combined relative expanded uncertainty(%)		1,56	1,57	1,74	1,54	1,68

Method repeatability precision uncertainty is calculated by square root of method precision SD.