

**Certification of the
mass fraction of copper
in Primary Reference Material
BAM-Y001**

CERTIFICATION REPORT

Version 2 of 2004-09-15

edited by Heinrich Kipphardt

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

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1 Issue, version and cross references

This report is replacing the reports as given in Table 1.

Table 1: Previous versions of this report.

version.	Report	major modifications
1	BAM/HKi/01-27 of 2004-06-25	After approval by BAM certification committee
2	BAM/HKi/01-27 of 2004-09-15	Editorial improvements
...

The certificates as given in Table 2 have been issued.

Table 2: Certificates issued

Certificate / date of issue	based on report version
BAM-Y001 [1] / 2004-06-25	1
BAM-Y001 [1] /2004-09-15	2
...	...

The material BAM-Y001 is also the material basis for certificate IRMM-647 [2] distributed by IRMM for the isotope amount ratios of copper in solution and also for the joint certificate [3] of IRMM and BAM for the copper amount-of-substance content in solution.

Note, that by nature a standard (which is an embodiment of something abstract) can never be perfect. With increasing effort, there will always be only an asymptotic improvement. This also holds true for the certification of BAM-Y001. We believe that BAM-Y001 is not perfect, but probably one of the best characterised copper materials available. Whenever there is new insight in form of measurement results, the certified value of BAM-Y001 will be revised (i.e. the uncertainty statement will be improved).

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3 List of abbreviations

<i>A</i>	Surface area
AAS	Atomic absorption spectrometry
CV AAS	Cold furnace atomic absorption spectrometry
<i>E</i>	Extinction or element
ET AAS	Atomic absorption spectrometry with electrothermal excitation
HE	(Carrier gas) hot extraction and combustion analysis
HR-ICP-MS	High resolution inductively coupled plasma mass spectrometry
ICP OES	Optical emission spectrometry using inductively coupled plasma
ICP-MS	Mass spectrometry using inductively coupled plasma
INAA	Instrumental neutron activation analysis
ISE	Ion selective electrode
<i>k</i>	Coverage factor or amount of substance content in mol/kg
LA-ICP-MS	Laser ablation ICP-MS
LD	Limit of detection (based on 3· <i>s</i>)
LOD	Limit of determination (based on 9· <i>s</i>)
<i>m</i>	Mass
<i>M</i>	Molar mass
<i>n</i>	Amount of substance or number of accepted data sets
NRA	Nuclear Reaction Analysis (here with ¹⁵ N)
PAA	Photon Activation Analysis
photom.	Spectrophotometry
<i>s</i>	Standard deviation
Stat. MS	Stationary gas source Mass Spectrometry (for noble gases)
SD	Standard deviation
THE	Estimated value based on theoretical considerations
<i>U</i>	expanded uncertainty
<i>u</i> or <i>u_c</i>	(Combined) uncertainty
ULV	Upper limit value based on measurements
VAL	Value (above LOD)
<i>w</i> ; <i>w</i> (A, X)	Mass fraction; mass fraction of A in material X

In line with the ISO 31-0 (1992) in this document the comma (and not the dot) is used as a decimal separator.

4 Measurand definition, certified value and boundary conditions

When applying the prescribed sample treatment as specified below, the certified quantity value is the mass fraction of copper in the bulk of material BAM-Y001.

$$w(\text{Cu}) = (0,999\ 970 \pm 0,000\ 010) \text{ kg/kg}$$

where the number following the symbol \pm is the numerical value of an expanded uncertainty $U=k\cdot u_c$ with $k=2$ estimated according the ISO/BIPM Guide to the expression of uncertainty in measurement [4].

Taking the value for the atomic weight of copper to be $(63,546 \pm 0,003)$ from the IUPAC table 'Atomic weights of the elements' [5] this corresponds to a copper amount-of-substance content in the solid material of $k(\text{Cu}, \text{BAM-Y001}) = w/M = (15,736\ 2 \pm 0,001\ 5) \text{ mol/kg}$ (expanded uncertainty $U=k\cdot u_c$ with $k=2$).

The atomic weight of copper in this specific material has been determined experimentally. Taking the value for the molar mass of copper to be $(63,54554 \pm 0,00035) \text{ g/mol}$ from the certificate of IRMM-647 [2] this corresponds to a copper amount-of-substance content in the solid material of $k(\text{Cu}, \text{BAM-Y001}) = (15,736\ 27 \pm 0,000\ 23) \text{ mol/kg}$ (expanded uncertainty $U=k\cdot u_c$ with $k=2$).

Before use, the material has to be etched in order to achieve the defined state, to which the certified quantity value applies. The etching procedure has been adopted from BCR recommendations [6]. Solvents of high purity (at least p.a. grade) must be used. The material must be processed (i.e. weighed) within 1 h after the final etching.

T1. The preparation has to be performed under clean air conditions and using high purity acids, high purity water and cleaned vessels.

T2. Sub-sample masses of $m > 0,2 \text{ g}$ and a surface to mass ratio $A/m < 6 \text{ cm}^2/\text{g}$ must be used.

T3. Etch for 3 min in HCl ($> 30 \% m/m$) at room temperature; rinsing 3× in water.

T4. Etch for 1 min in 65 % HNO₃ + 98 % CH₃COOH + 85 % H₃PO₄ (1 Vol.+ 1 Vol.+ 1 Vol.) at room temperature; rinse 3× in water.

T5. Rinse 3× in CH₃OH; expose 1 min to hair drier or 10 min in Ar-flow.

T6. At this stage, the material can be deformed by cold pressing and cut by cold cutting under clean conditions using tools with cleaned surfaces. Avoid surface contamination and re-oxidation.

T7. Final etching: as described in T3-T5.

Obey the safety instructions of the chemicals and equipment used!

5 Concept

5.1 Field of application and target group

The material described is intended to serve as a mass fraction standard of copper with an uncertainty smaller than 10^{-4} relative. By using the concept of molar mass, an amount-of-substance or an amount-of-substance content standard can be prepared gravimetrically.

Due to the limited amount of material available and the huge effort for certification and for principal reasons, the use of the material is limited to National and International Measurement Institutes (NMIs), who are listed as signatories of the MRA [7]. The distribution of the certified value to the field laboratories in Germany is planned to be via co-operation with producers of commercial calibration solutions under supervision of BAM and PTB (Physikalisch Technische Bundesanstalt).

5.2 Realisation of SI units with small uncertainty

A measurement is a numerical comparison of an unknown quantity (value) to a known quantity (value) of the same kind by an experiment. The only values known ultimately and known without uncertainty are values which are defined values such as the SI (Système International d'Unités) units. In order to have the values defined experimentally accessible for the comparison, these abstract definitions of SI units need to be realised. It is the task of the national and international metrology institutes (NMIs) to realise SI units and other units of measurement with small(est) (combined) uncertainty and to make them available to the measurement community in form of standards. In Germany BAM and PTB co-operate in the field of chemistry and are working jointly in order to establish the German National Standards for Element Analysis. These activities are not restricted to national level but also offered to the international measurement community.

5.3 Element amount-of-substance standards

For chemical measurements amount-of-substance is the quantity of relevance, however, the reasoning given here also holds true for the more convenient quantity amount-of-substance content. The unit for amount-of-substance is defined in the abstract definition of the mole [8]: „The mole is the amount of substance of a system which contains as many elementary entities

as there are atoms in 0,012 kilogram of carbon 12.“ In order to have this definition realised, it is not necessary to provide exactly 12 g of ^{12}C . A known multiple or fraction of 12 g of ^{12}C is also suitable to establish a primary amount of substance standard. Moreover, it is not even necessary to realise the mole in ^{12}C . By using the powerful concept of atomic weight (mean atomic mass relative to ^{12}C), a realisation of the mole in form of the element or compound under investigation (e.g. Cu) is also possible and even advantageous, because chemical measurements are strongly dependent on the analyte/matrix combination.

In order to establish an amount-of-substance standard with small uncertainty, gravimetry and the concept of molar mass can be used. However, for chemical measurements, gravimetry is by definition only applicable to ideal pure substances. Since ideal substances do not exist, the value of the mass fraction of the element or compound in the material needs to be known.

5.4 Prerequisite: mass fraction standard

Since there is no method of measurement available to measure directly the mass fraction of an element with a sufficient small uncertainty, the difference approach has to be followed.

This is to measure the mass fractions of all impurities in a high purity material. The sum of the mass fractions of all impurities (all elements not being the matrix element) is subtracted from the mass fraction of an ideally pure material (which is by definition unity). This includes not only the measurement of the ‘easy-to-measure’ elements but of all elements not being the main matrix element. In non-metrological practice the non-metals such as O, N, halogens and noble gases are normally simply ignored, although they might be significant impurities of the solid starting material.

Apparently, at this stage there is no way to avoid the quantity called mass fraction. The impurities can be measured in terms of amount-of-substance, of course. However, at one stage the conversion to mass fraction is unavoidable, because measuring in terms of quantity mole fraction would require to know the amount-of-substance of the matrix element, which is in fact the quantity intended to be measured.

From this, the material certified is in the first place a mass fraction standard of an element. Taking the molar mass, either from the IUPAC table ‘Atomic weights of the elements’ [5] or from an additional measurement (with probably smaller uncertainty) makes this material an element amount-of-substance content standard.

Note that this material is not certified for the mass fraction of trace elements, but only for the mass fraction of the matrix element.

5.5 Why high purity materials ?

Typically constant relative uncertainties are achieved by methods of measurement for impurities. A rather large *relative* uncertainty on a small absolute value will still result in a small *absolute* uncertainty. From this, it is advantageous to use high purity materials in order to achieve a small combined uncertainty on the certified value. Usually a compromise must be found between purity and amount of material available. Purification of a commercial material in the laboratory is one option. However, usually only small batches can be processed in a laboratory resulting in a material of probably high purity, but only in a very limited amount. This might be useful for isotopically highly enriched spikes, but for repeated batches it seems to be difficult to establish all batches having the same impurity values. We therefore decided not to purify small batches of material commercially available, but to put rather more effort in the chemical characterisation of a larger batch.

5.6 Technical requirements

When aiming at the impurity measurement of all elements not being the matrix element at trace level, access to a wide variety of methods and wide experience is required. This involves also the methods of measurement based on nuclear properties.

5.7 Values and Uncertainty

The uncertainty statement of the certified value is based on a combined uncertainty according to the 'Guide to the expression of uncertainty in measurement' (GUM) [4] and the EURACHEM/CITAC Guide on Quantifying Uncertainty in Analytical Measurement' [9]. Since in trace analysis a metrological measurement budget is far from being uncomplicated, the following worst case estimates for the uncertainty are taken:

- For values of impurities found below the limit of determination, an impurity value of half the value of the limit of determination was assumed, and the uncertainty estimated conservatively to be 100 % relative.
- For values above the limit of determination and measured with only one method of measurement, as an impurity value the measured value was assumed, estimating conservatively an uncertainty of at least 30 % relative, although the reported uncertainty is

smaller. The uncertainty is increased conservatively, when the measurement of an impurity results in an uncertainty larger than 30 % relative.

- In cases of a very detailed investigated impurity by independent methods of measurement this value can carefully be decreased. Usually this is applicable to dominating impurities, which have been measured with more than one method of measurement.

Although rather conservative, these uncertainty estimates can result in an uncertainty which is considerably smaller than the target uncertainty, if a very pure material is used.

In the frame of this project, the target uncertainty aimed at is 10^{-4} rel. for the mass fraction of the matrix element concerned. This is typically about one order of magnitude better than the uncertainty best generated by IDMS (Isotope Dilution Mass Spectrometry), a method of measurement which possibly results for many applications in the smallest achievable combined uncertainty for the measurement of an element concentration in a complex matrix.

Note that the material is not certified for the individual impurity concentrations but only for the mass fraction of the matrix element.

Note that in principle asymmetric uncertainties must be applied when dealing with purity statements, because a purity can not exceed 1 kg/kg. Moreover, a triangular uncertainty distribution might be more applicable when upper limit values (e.g. resulting from LOD statements) are involved. However, the concept of GUM [4] is based on standard uncertainties and there is no generally accepted concept of treating asymmetric uncertainties at limit values. Stating a lower limit for a purity is not useful, because usually a number is needed for further calculations. This is why (symmetric) standard uncertainties are kept, even if a part of the standard uncertainty range may lie out of physical reality (i.e. > 1 kg/kg).

6 Material's description, form, supplier, amount available

The material basis for BAM-Y001 are six bottles containing 500 g each of 'copper pellets 6,4 -13 mm; oxygen free; 99,99 % (metals) LOT B27F17' obtained from Alfa Johnson-Matthey, Karlsruhe, Germany. After the certification analysis there is about 2,3 kg of material left.

7 Sizing, pre-cleaning, packaging and labelling

The material was not further processed, it is available in the original geometry. It is packed in glass bottles containing one copper 'sphere' of about 12 g. Other geometries might also be supplied on agreement. The material has been etched at least once before packing, however

surface re-oxidation requires etching before use as described in chapter 8. The bottles are labelled by stickers giving the identity of the material and a running number.

8 Instructions for use

Before use, the material has to be etched in order to achieve the defined state, to which the certified quantity value applies. The etching procedure has been adopted from BCR recommendations [6]. Solvents of high purity (at least p.a. grade) must be used. The material must be processed (i.e. weighed) within 1 h after the final etching.

T1. The preparation has to be performed under clean air conditions and using high purity acids, high purity water and cleaned vessels.

T2. Sub-sample masses of $m > 0,2$ g and a surface to mass ratio $A/m < 6$ cm²/g must be used.

T3. Etch for 3 min in HCl (> 30 % m/m) at room temperature; rinsing 3× in water.

T4. Etch for 1 min in 65 % HNO₃ + 98 % CH₃COOH + 85 % H₃PO₄ (1 Vol.+ 1 Vol.+ 1 Vol.) at room temperature; rinse 3× in water.

T5. Rinse 3× in CH₃OH; expose 1 min to hair drier or 10 min in Ar-flow.

T6. At this stage, the material can be deformed by cold pressing and cut by cold cutting under clean conditions using tools with cleaned surfaces. Avoid surface contamination and re-oxidation.

T7. Final etching: as described in T3-T5.

Obey the safety instructions of the chemicals and equipment used!

9 Stability

Most compact metals are known to be stable in the bulk chemical composition at ambient temperatures for long time because the kinetics is very slow. In the case of BAM-Y001 a shelf life time of 200 year is estimated, when the material is kept in the original containers. The certificate will carry a formal expiry date of ten years. Note that the surface oxidation requires etching before use as described in chapter 8.

10 Homogeneity testing

In accordance with ISO Guide 35 [10], high purity materials (especially metals), which are certified for purity and not for impurities of individual elements, are expected to be

homogeneous on thermodynamic grounds, when all material was produced under absolutely the same conditions (i.e. same lot number). From this, a systematic homogeneity test was not carried out. In the course of the certification measurements, it was looked for possible signs of contamination. Consistent results have been obtained for different sub-samples as also indicated by the data given in Table 4.

11 Results of chemical analysis

The results from the measurement of the impurities in BAM-Y001 are summarised in Table 3 and displayed in Figure 1.

The first two columns of Table 3 show the element symbol and the method code for establishing the impurity value. Next the value derived from the measurements as described in chapter 5.7 is reported as a mass fraction in mg/kg. The next column gives the absolute uncertainty in mg/kg. It is calculated from the relative uncertainty, which is set conservatively to 30% when the impurity value is above the limit of determination ($9\cdot s$). Only in case of an impurity investigated very detailed this value might be decreased. The value is increased, when the measurement of an impurity results in a larger relative uncertainty than 30 %. For measurement values below the limit of determination the relative uncertainty was conservatively set to 100 %. Note that for values which are below the limit of determination, only the half of this value is used for the calculation as explained in chapter 5.7. The last column shows the relative uncertainty contribution to the certified value by the values for each impurity. Values that contribute to the combined uncertainty of the purity statement to more than 10 % rel. are shaded in grey. Technical details on how these values for impurities have been established from the measurement data are given in chapter 13.

Table 3: Summary of results from impurity measurement in BAM-Y001.

method	w	u(w)	unc.	method	w	u(w)	unc.	method	w	u(w)	unc.
	mg/kg	mg/kg	contr.		mg/kg	mg/kg	contr.		mg/kg	mg/kg	contr.
H NRA	< 2,1	1,1	0,05	Ge ICP-MS	< 0,12	0,06	<<0,01	Eu ICP-MS	< 0,0030	0,0015	<<0,01
He stat MS	< 0,0010	0,0005	<<0,01	As ET AAS, ICP-MS	0,50	0,15	<<0,01	Gd ICP-MS	< 0,0010	0,0005	<<0,01
Li ICP-MS	< 0,31	0,16	<<0,01	Se ET AAS	0,22	0,07	<<0,01	Tb ICP-MS	< 0,0010	0,0005	<<0,01
Be ICP OES	< 0,2	0,1	<<0,01	Br PAA	< 0,017	0,007	<<0,01	Dy ICP-MS	< 0,0010	0,0005	<<0,01
B ICP-MS	< 3,2	1,6	0,11	Kr stat MS	< 0,0010	0,0005	<<0,01	Ho ICP-MS	< 0,0010	0,0005	<<0,01
C PAA	0,040	0,012	<<0,01	Rb ICP-MS	< 0,050	0,025	<<0,01	Er ICP-MS	< 0,0010	0,0005	<<0,01
N PAA	0,2	0,1	<<0,01	Sr ICP-MS	< 0,014	0,007	<<0,01	Tm ICP-MS	< 0,0010	0,0005	<<0,01
O HE, PAA	1,0	0,5	0,01	Y ICP-MS	< 0,030	0,015	<<0,01	Yb ICP-MS	< 0,0010	0,0005	<<0,01
F Dist	< 3,0	1,5	0,10	Zr ICP-MS	< 0,015	0,008	<<0,01	Lu ICP-MS	< 0,0020	0,0010	<<0,01
Ne stat MS	< 0,0010	0,0005	<<0,01	Nb ICP-MS	< 0,020	0,010	<<0,01	Hf ICP-MS	< 0,0030	0,0015	<<0,01
Na ET AAS	0,0020	0,0006	<<0,01	Mo ICP-MS	< 0,06	0,03	<<0,01	Ta ICP-MS	< 0,0030	0,0015	<<0,01
Mg ET AAS	0,004	0,002	<<0,01	Tc THE	< 0,0010	0,0005	<<0,01	W ICP-MS	< 0,12	0,06	<<0,01
Al AAS	< 0,07	0,04	<<0,01	Ru ICP-MS	< 0,030	0,015	<<0,01	Re ICP-MS	< 0,009	0,005	<<0,01
Si ET AAS	< 0,2	0,1	<<0,01	Rh HR-ICP-MS	< 1,6	0,8	0,03	Os ICP-MS	< 0,0040	0,0020	<<0,01
P ICP-MS, Photom	< 2,0	1,0	0,04	Pd ICP-MS	< 0,014	0,007	<<0,01	Ir ICP-MS	< 0,007	0,004	<<0,01
S Photom	5,4	1,6	0,12	Ag ET AAS, INAA, ICP OES, ICP-MS	11,3	3,4	0,51	Pt ICP-MS	< 0,007	0,004	<<0,01
Cl PAA	< 0,6	0,3	<<0,01	Cd ICP-MS	< 0,015	0,008	<<0,01	Au ICP-MS	< 0,008	0,004	<<0,01
Ar stat MS	< 0,0010	0,0005	<<0,01	In ICP-MS	< 0,050	0,025	<<0,01	Hg CV AAS	< 0,030	0,015	<<0,01
K ET AAS	< 0,0020	0,0010	<<0,01	Sn ET AAS, ICP-MS	0,14	0,04	<<0,01	Tl ICP-MS	< 0,0050	0,0025	<<0,01
Ca ET AAS, ICP-MS	0,060	0,018	<<0,01	Sb ET AAS, INAA, ICP-MS	1,0	0,3	<<0,01	Pb ET AAS, ICP-MS	0,47	0,14	<<0,01
Sc ICP-MS	< 0,06	0,03	<<0,01	Te ICP-MS	< 0,22	0,11	<<0,01	Bi ET AAS, ICP-MS	0,23	0,07	<<0,01
Ti ICP OES, ICP-MS	< 0,32	0,16	<<0,01	I ICP-MS	< 0,09	0,05	<<0,01	Po THE	< 0,0010	0,0005	<<0,01
V ICP-MS	< 0,040	0,020	<<0,01	Xe stat MS	< 0,0010	0,0005	<<0,01	At THE	< 0,0010	0,0005	<<0,01
Cr ET AAS, ICP-MS	0,050	0,015	<<0,01	Cs ICP-MS	< 0,006	0,003	<<0,01	Rn THE	< 0,0010	0,0005	<<0,01
Mn ET AAS	0,010	0,003	<<0,01	Ba ICP-MS	< 0,017	0,009	<<0,01	Fr THE	< 0,0010	0,0005	<<0,01
Fe ET AAS, ICP OES, ICP-MS	< 0,8	0,4	0,01	La ICP-MS	< 0,0020	0,0010	<<0,01	Ra THE	< 0,0010	0,0005	<<0,01
Co ICP-MS	< 0,110	0,055	<<0,01	Ce ICP-MS	< 0,006	0,003	<<0,01	Ac THE	< 0,0010	0,0005	<<0,01
Ni ET AAS, ICP-MS	1,64	0,49	0,01	Pr ICP-MS	< 0,0020	0,0010	<<0,01	Th ICP-MS	< 0,02	0,01	<<0,01
Cu matrix				Nd ICP-MS	< 0,21	0,11	<<0,01	Pa THE	< 0,0010	0,0005	<<0,01
Zn ET AAS	0,057	0,068	<<0,01	Pm THE	< 0,0010	0,0005	<<0,01	U ICP-MS	< 0,0010	0,0005	<<0,01
Ga ICP-MS	< 0,11	0,06	<<0,01	Sm ICP-MS	< 0,007	0,004	<<0,01				

Value contributes > 10 % to combined uncertainty

BAM-A-primary-Cu-1
 LOT B27F17

	matrix	impurity	sum 'above'	sum/2 'below'	not relevant for measurement
	in %	in mg/kg	in mg/kg	in mg/kg	
mass fraction	99,9970	30,30	22,32	7,98	
abs. uncertainty	0,0005	4,76	3,84	2,81	

H < 2,1																	He < 0,001	
Li < 0,31	Be < 0,2											B < 3,2	C 0,04	N 0,2	O 1	F < 3	Ne < 0,001	
Na 0,002	Mg 0,004											Al < 0,07	Si < 0,2	P < 2	S 5,4	Cl < 0,6	Ar < 0,001	
K < 0,002	Ca 0,06	Sc < 0,06	Ti < 0,32	V < 0,04	Cr 0,05	Mn 0,01	Fe < 0,8	Co < 0,11	Ni 1,64	Cu matrix	Zn 0,057	Ga < 0,11	Ge < 0,12	As 0,5	Se 0,22	Br < 0,014	Kr < 0,001	
Rb < 0,05	Sr < 0,014	Y < 0,03	Zr < 0,015	Nb < 0,02	Mo < 0,06	Tc < 0,001	Ru < 0,03	Rh < 1,6	Pd < 0,014	Ag 11,3	Cd < 0,015	In < 0,05	Sn 0,14	Sb 1	Te < 0,22	I < 0,09	Xe < 0,001	
Cs < 0,006	Ba < 0,017	La < 0,002	Hf < 0,003	Ta < 0,003	W < 0,12	Re < 0,009	Os < 0,004	Ir < 0,007	Pt < 0,007	Au < 0,008	Hg < 0,03	Tl < 0,005	Pb 0,47	Bi 0,23	Po < 0,001	At < 0,001	Rn < 0,001	
Fr < 0,001	Ra < 0,001	Ac < 0,001																
			Ce < 0,006	Pr < 0,002	Nd < 0,21	Pm < 0,001	Sm < 0,007	Eu < 0,003	Gd < 0,001	Tb < 0,001	Dy < 0,001	Ho < 0,001	Er < 0,001	Tm < 0,001	Yb < 0,001	Lu < 0,002		
			Th < 0,02	Pa < 0,001	U < 0,001													

Figure 1: Summary of the results of impurity measurements of BAM-Y001. 'sum above' is the sum of all impurity values found above the respective limit of determination; 'sum below' is the half of the sum of the respective limits of determination for impurities found below the limit of determination.

12 Values of impurities reviewed element by element

Table 4 shows element by element the finally concluded values used for the impurity statement from the underlying values obtained by the different measurements, which are described in chapter 13. Lines starting with the atomic number and the element symbol contain the value and uncertainty, which was used as impurity statement in order to calculate the mass fraction of copper in BAM-Y001. In case of more than one value of type 'VAL' for one analyte, the average was calculated and used to establish the impurity statement for this analyte. For values which are not of the type 'VAL' (i.e. for values 'below') the lowest value was used to establish the impurity statement for this analyte. Note, that only half of this value is used in the sum of the impurity values as described in chapter 5.5. The data of lines starting with the symbol '#' are only given as additional information, as explained in the relevant technical sections in chapter 13, they were not used for establishing the purity statement.

Table 4: Results of impurity measurement in BAM-Y001 element by element.

	Type	Result in mg/kg	Uncertainty in mg/kg	Method
89Ac	THE	0,001		THE
	1THE	0,001		THE
47Ag	VAL	11,3	3,39	ET AAS, INAA, ICP OES, ICP-MS
	1VAL	11,3	1,12	ET AAS
	2VAL	10,56	0,88	INAA
	3VAL	11,3		ICP OES
	4VAL	11,43	0,32	ICP-MS
	5VAL	11,29	0,43	ICP-MS
	# 6VAL	10	20	GDMS
13Al	LOD	0,07		AAS
	1LOD	0,6		ICP OES
	2LOD	0,3		ICP-MS
	3LOD	0,07		AAS
	# 4VAL	0,09	0,17	GDMS
18Ar	LOD	0,001		stat MS
	1LOD	0,001		stat MS
33As	VAL	0,5	0,15	ET AAS, ICP-MS
	1VAL	0,5	0,06	ET AAS
	# 2VAL	2		?
	3VAL	0,5	0,0415	ICP-MS
	# 4LD	0,39		GDMS
85At	THE	0,001		THE
	1THE	0,001		THE
79Au	LOD	0,008		ICP-MS

	Type	Result in mg/kg	Uncertainty in mg/kg	Method
	1LOD	0,0079		ICP-MS
#	2LD	0,015		GDMS
5B	LOD	3,2		ICP-MS
	1LOD	3,2		ICP-MS
#	2LD	0,0020		GDMS
56Ba	LOD	0,017		ICP-MS
	1LOD	0,017		ICP-MS
#	2LD	0,0004		GDMS
4Be	LOD	0,2		ICP OES
	1LOD	0,2		ICP OES
	2LOD	1,1		ICP-MS
#	3LD	0,0002		GDMS
83Bi	VAL	0,23	0,069	ET AAS, ICP-MS
	1VAL	0,28	0,04	ET AAS
	2VAL	0,167	0,0153	ICP-MS
#	3VAL	0,14	0,28	GDMS
35Br	LOD	0,02		PAA
	1LOD	0,02		PAA
#	2LD	0,010		GDMS
6C	VAL	0,04	0,012	PAA
	1VAL	0,04	0,01	PAA
#	2VAL	0,6	3	GDMS
20Ca	VAL	0,06	0,018	ET AAS, ICP OES
	1VAL	0,093		ICP OES
	2VAL	0,02	0,028	ET AAS
#	3LD	0,028		GDMS
48Cd	LOD	0,015		ICP-MS
	1LOD	0,015		ICP-MS
#	2LD	0,012		GDMS
58Ce	LOD	0,006		ICP-MS
	1LOD	0,0057		ICP-MS
#	2LD	0,0001		GDMS
17Cl	LOD	0,6		PAA
	1LOD	0,6		PAA
#	2VAL	0,09	0,19	GDMS
27Co	LOD	0,11		ICP-MS
	1LOD	0,11		ICP-MS
#	2VAL	0,0020	0,0040	GDMS
24Cr	VAL	0,05	0,015	ET AAS, ICP-MS
	1LOD	0,5		ICP OES
	2VAL	0,06	0,0027	ICP-MS
	3VAL	0,028	0,027	ET AAS
#	4VAL	0,06	0,11	GDMS
55Cs	LOD	0,006		ICP-MS
	1LOD	0,0057		ICP-MS
#	2LD	0,0002		GDMS
29Cu	VAL	Matrix		
#	1VAL	999870		?
	2VAL	999700	120	Coul

	Type	Result in mg/kg	Uncertainty in mg/kg	Method
	3VAL	999900	100	EI Grav
66Dy	LOD	0,001		ICP-MS
	1LOD	0,00005		ICP-MS
#	2LD	0,002		GDMS
68Er	LOD	0,001		ICP-MS
	1LOD	0,0006		ICP-MS
#	2LD	0,003		GDMS
63Eu	LOD	0,003		ICP-MS
	1LOD	0,0033		ICP-MS
#	2LD	0,001		GDMS
9F	ULV	3		Dist
	1ULV	3		Dist
#	2LD	0,010		GDMS
26Fe	LOD	0,8	0,24	ET AAS, ICP OES, ICP-MS
	1VAL	0,6	0,07	ET AAS
#	2VAL	3		?
	3VAL	0,5		ICP OES
	4VAL	0,77	0,15	ICP-MS
	5VAL	1,32	4,89	ET AAS
#	6VAL	0,48	0,96	GDMS
87Fr	THE	0,001		THE
	1THE	0,001		THE
31Ga	LOD	0,11		ICP-MS
	1LOD	0,13		ICP-MS
	2LOD	0,11		ICP-MS
#	3VAL	0,0010	0,0020	GDMS
64Gd	LOD	0,001		ICP-MS
	1LOD	0,0148		ICP-MS
	2LOD	0,0007		ICP-MS
#	3LD	0,003		GDMS
32Ge	LOD	0,12		ICP-MS
	1LOD	0,12		ICP-MS
#	2LD	0,0002		GDMS
1H	LOD	2,1		NRA
	1LOD	2,1		NRA
2He	LOD	0,001		stat MS
	1LOD	0,001		stat MS
72Hf	LOD	0,003		ICP-MS
	1LOD	0,0027		ICP-MS
	2LOD	0,055		ICP-MS
#	3LD	0,0003		GDMS
80Hg	LOD	0,03		CV AAS
	1LOD	0,03		CV AAS
#	2LD	0,005		GDMS
67Ho	LOD	0,001		ICP-MS
	1LOD	0,0012		ICP-MS
#	2LD	0,001		GDMS
53I	LOD	0,12		PAA
	1LOD	0,12		PAA

	Type	Result in mg/kg	Uncertainty in mg/kg	Method
	2LOD	0,16		ICP-MS
#	3LD	0,0020		GDMS
49In	LOD	0,05		ICP-MS
	1LOD	0,05		ICP-MS
#	2LD	0,008		GDMS
77Ir	LOD	0,007		ICP-MS
	1LOD	0,0071		ICP-MS
#	2LD	0,001		GDMS
19K	LOD	0,002		ET AAS
	1LOD	0,002		ET AAS
#	2LD	0,0030		GDMS
36Kr	LOD	0,001		stat MS
	1LOD	0,001		stat MS
57La	LOD	0,002		ICP-MS
	1LOD	0,0019		ICP-MS
#	2VAL	0,0002	0,0004	GDMS
3Li	LOD	0,31		ICP-MS
	1LOD	0,31		ICP-MS
#	2LD	0,0002		GDMS
71Lu	LOD	0,002		ICP-MS
	1LOD	0,0018		ICP-MS
#	2LD	0,001		GDMS
12Mg	VAL	0,004	0,002	ET AAS
	1LOD	0,05		ICP OES
	2LOD	0,47		ICP-MS
	3VAL	0,004	0,004	ET AAS
#	4LD	0,005		GDMS
25Mn	VAL	0,01	0,003	ET AAS
	1VAL	0,01	0,007	ET AAS
	2LOD	0,25		ICP-MS
#	3VAL	0,006	0,012	GDMS
42Mo	LOD	0,06		ICP-MS
	1LOD	0,06		ICP-MS
#	2VAL	0,003	0,006	GDMS
7N	VAL	0,2	0,1	PAA
	1VAL	0,6	0,6	HE
	2VAL	0,2	0,1	PAA
#	3VAL	0,10	0,48	GDMS
11Na	VAL	0,002	0,0006	ET AAS
	1LOD	0,5		ICP OES
	2LOD	1,2		ICP-MS
	3VAL	0,002	0,005	ET AAS
#	4LD	0,0004		GDMS
41Nb	LOD	0,02		ICP-MS
	1LOD	0,02		ICP-MS
#	2LD	0,0004		GDMS
60Nd	LOD	0,21		ICP-MS
	1LOD	0,09		ICP-MS
	2LOD	0,21		ICP-MS

	Type	Result in mg/kg	Uncertainty in mg/kg	Method
#	3LD	0,003		GDMS
10Ne	LOD	0,001		stat MS
	1LOD	0,001		stat MS
28Ni	VAL	1,64	0,492	ET AAS, ICP-MS
	1VAL	1,66	0,2	ET AAS
#	2VAL	1		?
	3LOD	2		ICP OES
	4VAL	1,55	0,053	ICP-MS
	5VAL	1,72	0,048	ICP-MS
#	6VAL	1,6	3,2	GDMS
8O	VAL	1	0,5	HE, PAA
#	1LOD	10		?
	2VAL	1	0,6	HE
	3VAL	1	0,4	PAA
#	4VAL	2,3	11,5	GDMS
76Os	LOD	0,004		ICP-MS
	1LOD	0,02		ICP-MS
	2LOD	0,004		ICP-MS
#	3LD	0,001		GDMS
15P	LOD	2		ICP-MS, Photom
#	1VAL	9		?
	2LOD	2		Photom
	3LOD	2		ICP-MS
#	4VAL	0,042	0,084	GDMS
91Pa	THE	0,001		THE
	1THE	0,001		THE
82Pb	VAL	0,47	0,141	ET AAS, ICP-MS
	1VAL	0,46	0,06	ET AAS
#	2VAL	1		?
	3VAL	0,48	0,0168	ICP-MS
	4VAL	0,5	0,018	ICP-MS
#	5VAL	0,35	0,70	GDMS
46Pd	LOD	0,014		ICP-MS
	1LOD	0,014		ICP-MS
	2LOD	0,016		ICP-MS
#	3LD	0,006		GDMS
61Pm	THE	0,001		THE
	1THE	0,001		THE
84Po	THE	0,001		THE
	1THE	0,001		THE
59Pr	LOD	0,002		ICP-MS
	1LOD	0,002		ICP-MS
#	2LD	0,001		GDMS
78Pt	LOD	0,007		ICP-MS
	1LOD	0,0068		ICP-MS
#	2VAL	0,004	0,008	GDMS
88Ra	THE	0,001		THE
	1THE	0,001		THE
37Rb	LOD	0,05		ICP-MS

	Type	Result in mg/kg	Uncertainty in mg/kg	Method
	1LOD	0,05		ICP-MS
#	2LD	0,0001		GDMS
75Re	LOD	0,009		ICP-MS
	1LOD	0,0089		ICP-MS
#	2LD	0,001		GDMS
45Rh	LOD	1,6		HR-ICP-MS
	1LOD	1,6		ICP-MS
#	2LD	3,0		GDMS
86Rn	THE	0,001		THE
	1THE	0,001		THE
44Ru	LOD	0,03		ICP-MS
	1LOD	0,19		ICP-MS
	2LOD	0,03		ICP-MS
#	3LD	0,008		GDMS
16S	VAL	5,4	1,62	Photom
	1VAL	5,4	0,4	Photom
#	2VAL	3		?
#	3VAL	4,8	9,6	GDMS
51Sb	VAL	1	0,3	ET AAS, INAA, ICP-MS
	1VAL	0,99	0,13	ET AAS
	2VAL	0,839	0,009	INAA
	3VAL	1,02	0,0714	ICP-MS
	4VAL	1,03	0,0714	ICP-MS
#	5VAL	0,9	1,8	GDMS
21Sc	LOD	0,06		ICP-MS
	1LOD	0,06		ICP-MS
#	2LD	0,0002		GDMS
34Se	VAL	0,22	0,066	ET AAS
	1VAL	0,22	0,09	ET AAS
	2VAL	0,141	0,019	INAA
#	3VAL	0,13	0,26	GDMS
14Si	LOD	0,2		ET AAS
	1LOD	0,2		ET AAS
#	2VAL	0,24	0,48	GDMS
62Sm	LOD	0,007		ICP-MS
	1LOD	0,007		ICP-MS
#	2LD	0,003		GDMS
50Sn	VAL	0,14	0,042	ET AAS, ICP-MS
	1VAL	0,14	0,03	ET AAS
#	2VAL	2		?
	3VAL	0,15	0,0021	ICP-MS
	4VAL	0,147	0,00515	ICP-MS
#	5VAL	0,14	0,28	GDMS
38Sr	LOD	0,014		ICP-MS
	1LOD	0,014		ICP-MS
#	2LD	0,0002		GDMS
73Ta	LOD	0,003		ICP-MS
	1LOD	0,0032		ICP-MS
65Tb	LOD	0,001		ICP-MS

	Type	Result in mg/kg	Uncertainty in mg/kg	Method
	1LOD	0,0005		ICP-MS
#	2LD	0,001		GDMS
43Tc	THE	0,001		THE
	1THE	0,001		THE
52Te	LOD	0,22		ICP-MS
	1LOD	0,22		ICP-MS
	2LOD	0,49		ICP-MS
#	3VAL	0,021	0,042	GDMS
90Th	LOD	0,02		ICP-MS
	1LOD	0,02		ICP-MS
#	2LD	0,0002		GDMS
22Ti	LOD	0,32		ICP OES, ICP-MS
	1LOD	0,3		ICP OES
	2LOD	0,33		ICP-MS
#	3VAL	0,007	0,014	GDMS
81Ti	LOD	0,005		ICP-MS
	1LOD	0,0048		ICP-MS
#	2LD	0,0010		GDMS
69Tm	LOD	0,001		ICP-MS
	1LOD	0,001		ICP-MS
#	2LD	0,001		GDMS
92U	LOD	0,001		ICP-MS
	1LOD	0,0012		ICP-MS
#	2LD	0,0002		GDMS
23V	LOD	0,04		ICP-MS
	1LOD	0,04		ICP-MS
#	2VAL	0,33	0,66	GDMS
74W	LOD	0,12		ICP-MS
	1LOD	0,12		ICP-MS
#	2VAL	0,0020	0,0040	GDMS
54Xe	LOD	0,001		stat MS
	1LOD	0,001		stat MS
39Y	LOD	0,03		ICP-MS
	1LOD	0,03		ICP-MS
#	2LD	0,0002		GDMS
70Yb	LOD	0,001		ICP-MS
	1LOD	0,0005		ICP-MS
#	2LD	0,002		GDMS
30Zn	VAL	0,057	0,068	ET AAS
#	1VAL	9		?
	2LOD	2,6		ICP-MS
	3VAL	0,057	0,136	ET AAS
#	4LD	0,031		GDMS
40Zr	LOD	0,015		ICP-MS
	1LOD	0,015		ICP-MS
#	2LD	0,0003		GDMS

13 Technical details of Chemical Analysis

The measurements of most of the impurities (all by ICP-MS) in BAM-Y001 are described to very detail in the dissertation of S. Pattberg [11] and in [12, 13].

The direct measurements of $w(\text{Cu}, \text{BAM-Y001})$ have been performed using electrogravimetry. The metallic impurities have been measured using atomic spectrometry, namely HR-ICP-MS supported by ICP OES and AAS. LA-ICP-MS has been used to check for possible losses of elements (esp. noble metals) in the dissolution step. For non-metals, specific techniques such as spectrophotometry, CG-HE, PAA and beam analysis have been applied. Estimates have been made for impurities with radioactive elements.

The limit of determination has been measured using the blank value method according to [14], which is:

$$LOD = \frac{9 \cdot s(\text{BV})}{b}$$

LOD: limit of determination

s(BV): standard deviation of the blank

b: slope of the calibration curve

The blank here includes the reagents as well as the matrix (Cu). For the blank in most cases a second material (BAM-B-primary-Cu-1) was used, which was of higher purity with respect to ‘metallic’ impurities (but less pure with respect to non-metallic impurities). In principle, BAM-Y001 could have been used here as well, provided that the concentration of the analyte in the material is small compared to the analyte portion added by standard addition. The slope of the calibration curve was typically established by standard-addition or interpolation using the response curve.

13.1 Direct measurement of copper using electrogravimetry

The mass fraction of copper in BAM-Y001 was measured directly using electrogravimetry according to [15,16] by H. Reichelt under the responsibility of K.A. Meier in 1996. The data are reported in [17]. In summary, the sample was weighed and dissolved in nitric acid and electrolytically deposited on a Pt-net. The Pt-electrode was weighed for the mass increase, the remaining copper in the electrolyte was measured by AAS. Ag was also deposited

electrolytically under these conditions. The material BAM-Y001 was etched as prescribed. Three samples of about 5 g have been measured, resulting in a mean value of $w(\text{Cu, BAM-Y001})=0,9999$, the uncertainty is estimated to be below 0,0001. The individual values are given in Table 5. The silver mass fraction of about 10 $\mu\text{g/g}$ does not significantly influence this result.

Table 5: Individual values for $w(\text{Cu, BAM-Y001})$.

$m(\text{BAM-Y001}) / \text{g}$	m / g as electrolytically deposited	$m(\text{Cu}) / \text{g}$ as found by AAS	$m_{\text{total}}(\text{'Cu'}) / \text{g}$	$w(\text{Cu, BAM-Y001}) / \%$
5,02670	5,02588	0,00017	5,02605	99,99
5,01877	5,01832	0,00020	5,01852	100,00
5,02105	5,02020	0,00018	5,02038	99,99

Additionally, the copper mass fraction of one ball BAM-Y001 was measured externally by a co-operation partner of PTB using constant potential coulometry. Nine repeated measurements were performed. A type A standard uncertainty as the experimental standard deviation of means ($s/n^{1/2}$) of 0,00006 was reported, and a Type B standard uncertainty of 0,00012. The value was reported to be $w(\text{Cu, BAM-Y001})=(0,9997\pm 0,0003)$ kg/kg with a level of confidence of 95 % [18].

13.2 Measurements of 'metallic' impurities by HR-ICP-MS

13.2.1 Values below limit of determination using standard addition

The measurement by HR-ICP-MS have been performed by S. Pattberg and M. Czerwensky using 'Element' spectrometer Finnigan MAT. The general parameter settings are given in Table 6. Resolution was set typically to 300 (LR) or 3000 (MR). The measurement of the limit of determination has been performed as described in paragraph 13. (Although determined using individual isotopes, the limits of determination given apply to the element and not to the individual isotopes used.) The copper concentration of the sub-sample solution used was about 1 g/L. The normal solution and the solution spiked with the analytes of 1 ng/L were measured. The results are given in Table 7. The spikes have been prepared from commercially available standards, which have been checked against solutions prepared from pure compounds. Linearity of the calibration curve has been checked for ^{75}As , ^{115}In , ^{133}Cs , ^{138}Ba , ^{129}La , ^{140}Ce , ^{141}Pr , ^{152}Sm , ^{153}Eu , ^{165}Ho , ^{166}Er , ^{174}Yb , ^{175}Lu , ^{187}Re and ^{205}Tl .

Table 6: Instrument and method settings for HR-ICP-MS measurements.

Instrument Settings		Method settings	
flow rate cooling gas / L·min ⁻¹	13	scans /measurement (resolution)	15 (LR); 20 (MR)
flow rate auxiliary gas / L·min ⁻¹	0,8-1,4	sample-time	0,01 s
HF power / kW	1,3	settling time	max. 0,3 s; depending on the mass difference to previous isotope
HF frequency / MHz	27,4	mass window	150 %
		integration window	80 % (LR); 60 % (MR)
		samples / peak	15 (LR); 20 (MR)

Table 7: Limits of determination by standard-addition with reference to the elements in the solid material BAM-Y001.

Isotope	LOD of the element / µg/kg	Isotope	LOD of the element / µg/kg	Isotope	LOD of the element / µg/kg
⁷ Li	310	⁹⁹ Ru	190	¹⁵⁹ Tb	0,5
⁹ Be	1100	¹⁰² Ru	30	¹⁶⁴ Dy	0,05
¹¹ B	3200	¹⁰³ Rh (HR)	1600	¹⁶⁵ Ho	1,2
²³ Na	1200	¹⁰⁶ Pd	14	¹⁶⁶ Er	0,6
²⁴ Mg	470	¹⁰⁸ Pd	16	¹⁷⁴ Yb	0,5
²⁷ Al	500	¹¹⁴ Cd	15	¹⁷⁵ Lu	1,8
³¹ P (MR)	2000	¹¹⁵ In	50	¹⁷⁸ Hf	55
⁴⁵ Sc	60	¹²⁶ Te	490	¹⁸⁷ Re	8,9
⁴⁸ Ti	330	¹³³ Cs	5,7	¹⁹⁰ Os	4,0
⁵⁵ Mn	250	¹³⁸ Ba	17	¹⁹³ Ir	7,1
⁵⁹ Co	110	¹³⁹ La	1,9	¹⁹⁵ Pt	6,8
⁶⁸ Zn	2600	¹⁴⁰ Ce	5,7	¹⁹⁷ Au	7,9
⁶⁹ Ga	130	¹⁴¹ Pr	2,0	²⁰⁵ Tl	4,8
⁷¹ Ga	110	¹⁴² Nd	210	²³⁸ U	1,2
⁸⁵ Rb	50	¹⁵³ Eu	3,3		
⁸⁸ Sr	14	¹⁵⁸ Gd	0,7		

The large values for ¹⁰³Rh, ¹²⁶Te and ¹⁴²Nd are due to the interferences of ⁶³Cu⁴⁰Ar, ⁶³Cu⁶³Cu and ⁶³Cu⁶³Cu¹⁶O respectively. The large value for ²⁷Al is due to memory effects caused by the history of the instrument.

13.2.2 Values below limit of determination using response curve

The response curve was established by measuring the sensitivity of 15 isotopes spread over the mass range of interest. To measure the limits of determination of isotopes, where no standard-addition has been applied, the spread of blanks was measured and a sensitivity interpolated from experimental values was used. The validity of this approach was tested by comparing values for the limits of determination obtained by standard-addition and by the response curve. The comparison is given in Table 8. More values for the limit of determination using the response curve are given in Table 9. The large value of ^{184}W is due to the previous history of the instrument.

Table 8: Comparison of the limits of determination obtained by standard-addition and response curve with reference to the elements in the solid material BAM-Y001.

Isotope	limit of determ. / $\mu\text{g}/\text{kg}$	limit of determ. / $\mu\text{g}/\text{kg}$
	by standard-addition	by response curve
^{48}Ti	330	200
^{55}Mn	250	280
^{59}Co	110	110
^{102}Ru	30	18
^{195}Pt	6,8	8,2
^{197}Au	7,9	8,7

Table 9: Limits of determination from response curve with reference to the elements in the solid material BAM-Y001.

Isotope	limit of determ. / $\mu\text{g}/\text{kg}$	Isotope	limit of determ. / $\mu\text{g}/\text{kg}$	Isotope	limit of determ. / $\mu\text{g}/\text{kg}$
^{51}V	40	^{127}I	160	^{180}Hf	2,7
^{74}Ge	120	^{130}Te	220	^{181}Ta	3,2
^{89}Y	30	^{142}Nd	90	^{184}W	120
^{90}Zr	15	^{152}Sm	7,1	^{192}Os	20
^{93}Nb	20	^{158}Gd	14,8	^{232}Th	20
^{98}Mo	60	^{169}Tm	0,05		

13.2.3 Values above limit of determination using standard addition

Mass fraction values of Ag, As, Bi, Cr, Fe, Ni, Pb, Sb and Sn have been found to be above the limit of determination. The values have been measured with a resolution of 300 using ^{89}Y ,

and above mass 207 ^{232}Th , as an internal standard. Additionally Fe and Cr have been measured with a resolution of 3000 using ^{59}Co as an internal standard. An aqueous solution, the sample (1 g/L) and the sample spiked with the analyte adapted to concentration known from test measurements were prepared. In total three sample solutions have been prepared. About 12 g BAM-Y001 each have been dissolved in 50 % (*m/m*) HNO_3 in a PFA container under an Ar flow in a class 10 environment, which took up to four days. The results of the measurements are summarised in Table 10. In parallel five independently prepared solutions from CRM BCR 074 (of about 2 g each) have been measured as a consistency check. The results are compared with the certified values in Table 11. Very good agreement was found.

Table 10: Values for mass fraction of impurities in BAM-Y001 found above the limit of determination using standard addition.

Isotope	mean of $w(E, \text{BAM-Y001}) / \text{mg/kg}$	RSD / %	n	C.I. 95 % / mg/kg
^{107}Ag	11,43	2,8	9	1,4
^{109}Ag	11,29	3,8	9	1,8
^{75}As	0,50	8,3	22	0,13
^{209}Bi	0,167	9,2	24	0,049
^{52}Cr (MR)	0,06	4,5	24	0,01
^{56}Fe (MR)	0,77	19,4	19	0,48
^{58}Ni	1,55	3,4	24	0,17
^{60}Ni	1,72	2,8	23	0,15
^{207}Pb	0,48	3,5	24	0,05
^{208}Pb	0,50	3,6	22	0,06
^{121}Sb	1,02	7,0	24	0,23
^{123}Sb	1,03	7,0	24	0,23
^{118}Sn	0,150	1,4	24	0,007
^{120}Sn	0,147	3,5	24	0,016

Table 11: Comparison of measured and certified values of the element impurities E in BCR CRM 074.

measured Isotope	mean of $w(E, \text{BCR CRM 074}) / \text{mg/kg}$	RSD / %	n	C.I. 95 % / mg/kg	certified value [19] $w_{\text{cert.}}(E, \text{BCR CRM 074}) / \text{mg/kg}$	C.I. 95 %	p
^{107}Ag	12,85	2,3	29	0,8	12,8	0,7	5

¹⁰⁹ Ag	12,87	1,6	29	0,6	12,8	0,7	5
⁷⁵ As	0,78	0,8	29	0,02	0,78	0,14	3
²⁰⁹ Bi	0,098	0,6	28	0,002	0,10 indicative	0,03	
⁵² Cr (MR)	0,05	12	28	0,02	<0,1		
⁵⁶ Fe (MR)	1,14	4,9	26	0,16	1,14	0,06	
⁵⁸ Ni	0,98	3,7	29	0,10	1,04	0,11	4
⁶⁰ Ni	1,14	0,7	28	0,02	1,04	0,11	4
²⁰⁷ Pb	0,96	2,7	29	0,07	0,97	0,05	6
²⁰⁸ Pb	0,96	2,6	28	0,07	0,97	0,05	6
¹²¹ Sb	0,60	0,8	26	0,01	0,58	0,03	7
¹²³ Sb	0,60	0,8	29	0,01	0,58	0,03	7
¹¹⁸ Sn	0,033	12,4	28	0,011	<0,07		6
¹²⁰ Sn	0,033	16,7	27	0,015	<0,07		6

13.3 Measurements by LA-ICP-MS

Additionally to the wet chemical analysis, laser ablation high resolution ICP mass spectrometry [13] was used as a solid sampling method, to check for losses of impurities in the dissolution step. In this context, the platinum group elements were of special interest. The calibration was performed by doping a high purity copper powder (BAM-B-primary-Cu-1, which had less metallic impurities than BAM-Y001) with aqueous calibration solutions and pressing the powder to a pellet. Internal standardisation was applied using the signal from ⁶⁵Cu⁴⁰Ar. In the frame of [11] imaging techniques such as SIMS (secondary ion mass spectrometry) and REM (scanning electron microscopy) were used to check for micro local distribution of the calibration samples. For the analysis of BAM-Y001 a UV Laser Probe (Finnigan MAT) coupled to the Element spectrometer also used for the HR-ICP-MS on aqueous samples were used. The laser energy of the Nd:YAG laser was 25 mJ at a wavelength of 266 nm and the beam diameter of 200 µm. Measurements have been performed shootings along a trace. Within the stated uncertainty of about 30 %, agreement between the results from wet chemical analysis and the results from laser ablation measurements were found.

13.4 Measurements by AAS

The measurements using AAS were performed by H.-J. Heinrich and A. Dette under the responsibility of R. Matschat and S. Noack in 1997 - 2001.

13.4.1 Measurement of Mercury using flow injection cold vapour AAS (FI-CV AAS)

More technical details on the measurement described in this paragraph can be found in [20]. Mercury has been measured using flow injection cold vapour AAS. After etching with HNO₃, about 12 g of the material have been dissolved in HNO₃ (1+1) and diluted. A Perkin-Elmer Zeeman 5100 PC equipped with FIAS-200/AS-90 and an electrically heated quartz cell (up to 200 °C) was used. The peak height at a wave length of 253,7 nm with a spectral band width of 0,7 nm was measured. For stabilisation of the mercury in solution, K₂Cr₂O₇ was used. A carrier solution of 3 % HCl and a reduction solution of 6 % SnCl₂ in 3 % HCl were applied. The sample volume was 500 µL. Calibration was performed by standard addition (10 µg/L Hg). The blank was found to be below 0,1 µg/L. The concentration was calculated by the instrument software. The value for Hg was found to be below the limit of determination: $w(\text{Hg, BAM-Y001}) < 0,03 \mu\text{g/g}$.

13.4.2 Measurement using ET AAS for Ag, As, Bi, Fe, Mn, Ni, Pb, Sb, Se and Sn

More technical details on the measurement described in this paragraph can be found in [21]. For the measurement of Ag, As, Bi, Fe, Mn, Ni, Pb, Sb, Se and Sn electrothermal atomic absorption spectrometry was applied. After etching with HNO₃, 6 solutions containing about 12 g of the material each (dissolved in HNO₃ (1+1) and diluted) have been prepared. A Perkin-Elmer Zeeman 5100 PC equipped with HGA-600/AS-60 (instrument A) and a Perkin-Elmer SIMAA-6000/AS-72 (instrument B) were used. The parameter settings are given in Table 12. The sample volume was 10 µL + 5 µL modifier. Calibration was performed by external calibration using BAM-B-primary-Cu-1, which is more pure with respect to metallic impurities. In some cases standard addition was used, too. BCR 074 and BCR 075 have been measured in the same series as a consistency check, the results are given in Table 13. The results for the impurity measurement of BAM-Y001 are given in Table 14. The uncertainty is calculated from measurement statistics and additionally applying a multiplicative factor of two to account type B uncertainties according to $U = b \cdot \frac{s}{\sqrt{N}} \cdot t$, where s is the standard

deviation, N is the number of replicates, t is the student factor (95 %) and the factor b accounts for type B uncertainties.

Table 12: Instrument settings for ET AAS.

	Instrument	lamp		wave length		atomiser	modifyer	pyrolysis	atomisation
		type	current / mA	/ nm				/ °C	/ °C
Ag	A	HKL	10	328,1	Py+GK	-	600	1800	
Ag	B	HKL	15	328,1	THGA	-	400	1700	
As	A	EDL	380	193,7	Py+GK	10 µg Pd	1200	2500	
Bi	A	EDL	300	223,1	Py+GK	10 µg Pd	1000	2000	
Fe	A	HKL	30	248,3	Py+GK	-	1000	2500	
Mn	A	HKL	20	279,5	Py+GK	-	900	2300	
Ni	A	HKL	30	232,0	Py+GK	-	1200	2600	
Ni	B	HKL	30	232,0	THGA	-	1100	2300	
Pb	A	HKL	10	283,3	Py+GK	10 µg Pd	700	2000	
Sb	A	EDL	380	217,6	Py+GK	10 µg Pd	1200	2500	
Se	A	EDL	230	196,0	Py+GK	10 µg Pd	1000	2300	
Sn	A	EDL	280	286,3	Py+GK	10 µg Pd	1200	2500	

Py: Pyrocarbon coated graphite tube (Perkin-Elmer, Elektrokohle Lichtenberg)

GK: Glassy carbon platform

THGA: Standard THGA graphite tube with integrated platform (pyro-coated)

Table 13: Measurement of BCR 074 and BCR 075 as a consistency check.

	$w(E, \text{BCR 074}) / \text{mg/kg}$ [19]		$w(E, \text{BCR 075}) / \text{mg/kg}$ [22]	
	certified	measured	certified	measured
Ag	12,8±0,7	12,3	12,2±0,4	11,9
As	0,78±0,14	0,71	3,74±0,19	3,58
Bi	(0,10)	0,21	1,44±0,07	1,64
Fe	1,14±0,06	1,20	9,0±0,4	9,6
Mn	1,27±0,05	1,26	3,23±0,19	3,08
Ni	1,04±0,11	0,98	1,45±0,10	1,52
Pb	0,97±0,05	0,94	3,27±0,10	3,28
Sb	0,58±0,13	0,59	2,56±0,15	2,65
Se	0,37±0,04	0,39	1,26±0,07	1,30

Sn < 0,07 < 0,05 1,09±0,06 1,09

Table 14: Results of $w(E, \text{BAM-Y001}) / \text{mg/kg}$ obtained from different sub-samples (Hr; De; Pa 0; Pa 1; Pa 2; Pa 3).

	Hr	De	Pa 0	Pa 1	Pa 2	Pa 3	mean value	<i>s</i>	<i>U</i>
Ag	10,40			11,80	11,15	11,94	11,3	0,7	2,24
As	0,41	0,56	0,53	0,49	0,46	0,55	0,50	0,06	0,12
Bi	0,28	0,26			0,29		0,28	0,02	0,08
Fe	0,60	0,59	0,55		0,66		0,60	0,04	0,14
Mn	0,007	0,013			0,009		0,010	0,003	0,014
Ni	1,79	1,52	1,59		1,75		1,66	0,13	0,40
Pb	0,41	0,48	0,49		0,46		0,46	0,04	0,12
Sb	0,80	0,97	1,07	1,08	0,90	1,13	0,99	0,13	0,26
Se	0,20	0,20			0,26		0,22	0,04	0,18
Sn	0,14			0,15	0,12	0,16	0,14	0,02	0,06

Additional measurements for iron using ET AAS are reported in chapter 13.4.3.

13.4.3 Measurement using ET AAS for Al, Ca, Cr, Fe, K, Mg, Na, Si and Zn

More technical details on the measurement described in this paragraph can be found in [23]. For the measurement of Al, Ca, Cr, Fe, K, Mg, Na, Si and Zn electrothermal atomic absorption spectrometry was applied. After etching with HNO_3 (1+2) about 12 g of the material have been dissolved in HNO_3 (1+1) at 80-90 °C and diluted. A Perkin-Elmer Zeeman 5100 PC equipped with HGA-600/AS-60 was used. The parameter settings are given in Table 15. The sample volume was 20 μL . Calibration was performed by external calibration using BAM-B-primary-Cu-1. In some cases standard addition was used, too. The results for the impurity measurements of BAM-Y001 are given in Table 16. Solution PHrAAS210 seemed to have been contaminated with Fe and Zn. The uncertainty is calculated from measurement statistics and additionally applying a multiplicative factor of two to account type B uncertainties according to $U = b \cdot \frac{s}{\sqrt{N}} \cdot t$, where *s* is the standard deviation, *N* is the number of replicates, *t* is the student factor (95 %) and the factor *b* accounts for type B uncertainties.

Table 15: Instrument settings for ET AAS

	lamp		wave length / nm	atomiser	pyrolysis / °C		atomisation / °C
	type	current / mA			blank	sample	
Al	HKL	25	309,3;396,2	Py+GL	800	1000	2500
Ca	HKL	20	422,7	Py	1000	1300	2600
Cr	HKL	25	357,9	Py		1200	2300
Fe	HKL	30	248,3	Py	700	1100	2200
K	HKL	18	766,5	Py	800	900	1500
Mg	HKL	8	285,2	Py+GL	600	900	2000
Na	HKL	8	589,0	Py	800	800	1500
Si	HKL	40	251,63	Py+GL	800	1000	2500
Zn	EDL	250	213,9	Py+GL	400	400	1500

Py: Pyrocarbon coated graphite tube (Perkin-Elmer, Elektrokohle Lichtenberg)

PL: integrated platform (pyro-coated)

Table 16: Results of $w(E, \text{BAM-Y001})$ / mg/kg obtained on different sub-samples (PHRAAS210-PHrAAS213)).

	Al	Ca	Cr	Fe	K	Mg	Na	Si	Zn
PHrAAS210	<0,07	0,031	0,015	3,62	0,002	0,004	<0,002	<0,2	0,121
PHrAAS211	<0,07	0,015	0,031	0,46	<0,002	0,004	0,002	<0,2	0,034
PHrAAS212	<0,07	0,012	0,033	0,51	<0,002	0,004	0,002	<0,2	0,031
PHrAAS213	<0,07	0,022	0,032	0,69	<0,002	0,006	0,002	<0,2	0,043
Mean	<0,07	0,020	0,028	1,32	<0,002	0,004	0,002	<0,2	0,057
SD		0,009	0,008	1,54		0,001	0,0002		0,043
<i>U</i>		0,028	0,027	4,89		0,004	0,0005		0,136

13.5 Measurements by ICP OES

The three solutions prepared from BAM-Y001 as described in paragraph 13.2.3 were measured by N. Langhammer under the responsibility of R. Matschat for Ag, Al, Be, Ca, Cr, Fe, Mg, Na, Ni and Ti by high resolution ICP OES in 1997/1998. The data are reported in [24]. The original solutions have been diluted to about 1 mass % of copper and measured over a time of 7 months. On each solution repeated measurements have been performed. A high

resolution ICP OES (5 pm) from Jobin Yvon equipped with an ultrasonic nebuliser (Transducer 0-201) was used. The results are given in Table 17. For Ag, Ca and Fe the six individual results given in Table 17 represent mean values of measurement series performed on the three solutions with two series performed at one day. Al, Be, Cr, Mg, Na and Ni have only been measured in one series each. Calibration was established by doping BAM-B-primary-Cu-1, with the analytes, taking the blanks into account. The values for nickel are only of qualitative nature due to a spectral interference from copper.

Table 17: Measurement results for impurities in BAM-Y001 using ICP OES.

Element <i>E</i>	λ /nm	$w(E, \text{BAM-Y001})$ / mg/kg	mean $w(E, \text{BAM-Y001})$ / mg/kg
Al	396,152	<0,59	<0,60
		<0,63	
		<0,65	
Be	313,042	<0,18	<0,20
		<0,17	
		<0,17	
Cr	206,149	<0,95	<0,50
		<0,53	
		<0,31	
Mg	279,553	<0,01	<0,05
		<0,01	
		<0,05	
Na	589,592	<0,33	<0,50
		<0,31	
		<0,42	
Ni*	352,454	1,65	<2,0
		1,63	
		1,23	
Ti	336,121	<0,24	<0,30
		<0,24	
		<0,28	
Ag	338,289	11,0	11,3
		11,7	
		11,9	
		10,3	
		11,2	
		11,4	
Ca	393,366	0,050	0,093

Element E	λ /nm	$w(E, \text{BAM-Y001})$ / mg/kg	mean $w(E, \text{BAM-Y001})$ / mg/kg
		0,082	
		0,080	
		0,074	
		0,132	
		0,142	
Fe	238,204	0,42	0,50
		0,47	
		0,71	
		0,65	
		0,32	
		0,40	

13.6 Measurements by spectrophotometry

13.6.1 Sulphur

Sulphur was measured in 1996 by H. Reichelt under the responsibility of K.A. Meier using the methylene blue distillation as described in [25,26,27], the data are reported in [28]. The method is critically reviewed in [29]. In summary, the sample is dissolved in the presence of hypophosphorous acid to form hydrogen sulphide, which is swept by a gas stream into zinc acetate solution. Methylene-blue is formed with N,N-Dimethyl-p-phenylendiamine in the presence of Fe(III). The method is considered to require special experience and special skills. (However the persons involved have partly developed this method.) The material BAM-Y001 was pre-treated as prescribed. The extinction E was measured at 665 nm using cuvettes with an optical path length of 10 mm. Using K_2SO_4 , the calibration curve was established to be $m(\text{S}) / \mu\text{g} = 52,4612 \cdot E - 0,4389$, the blank value was taken into account. Eight individual samples of about 1 g have been measured, resulting in a mean value of $w(\text{S}, \text{BAM-Y001}) = (5,4 \pm 0,4) \mu\text{g/g}$ (standard deviation only). The individual values are given in Table 18. As a consistency check, 10 μg of sulphur in form of K_2SO_4 were processed, giving a result of 10,8 μg . In an analogous measurement three days later on BCR CRM 017 a value of $w(\text{S}, \text{BCR CRM 017}) = 10,4 \pm 0,6 \mu\text{g/g}$ (standard deviation only) was found, which is identical with the certified value of $w_{\text{cert}}(\text{S}, \text{BCR CRM 017}) = (10,4 \pm 0,6) \mu\text{g/g}$ (uncertainty being here the half width of 95 % confidence interval) [30]. Here the consistency check on 10 μg S gave a result of 10,3 μg .

For the calculation of the mass fraction of copper a value of $w(\text{S, BAM-Y001}) = 5,4 \mu\text{g/g}$ is used. The uncertainty is conservatively taken to be 30 % relative.

Table 18: Individual values for $w(\text{S, BAM-Y001})$.

$m(\text{BAM-Y001}) / \text{g}$	E	$m(\text{S, BAM-Y001}) / \mu\text{g}$
1,04701	0,130-0,018=0,112	5,2
1,01317	0,127-0,019=0,108	5,2
1,01864	0,128-0,018=0,110	5,2
1,0329	0,124-0,018=0,106	5,0
1,00195	0,137-0,018=0,119	5,8
1,06850	0,138-0,029=0,109	4,9
1,0673	0,154-0,029=0,125	5,7
1,11277	0,162-0,028=0,134	5,9

13.6.2 Phosphorus

Phosphorus was measured in 1996 by H. Reichelt under the responsibility of K.A. Meier using the molybdovanadate spectrophotometric method as described in [31], the data are reported in [32]. In summary, the sample is dissolved in nitric acid, disturbing elements are fumed off using HF and HBr. By adding ammonium vanadate and ammonium molybdate, the molybdovanadate phosphate is formed and extracted using MIBK. The extinction E was measured at 400 nm using cuvettes with an optical path length of 50 mm. Using KH_2PO_4 , the calibration curve was established to be $m(\text{P}) / \mu\text{g} = 96,3894 \cdot E - 0,2054$. The blank value was taken into account. Eight individual samples of about 1 g have been measured, resulting in a mean value of $w(\text{P, BAM-Y001}) < 2 \mu\text{g/g}$. The individual values are given in Table 19. In an analogous measurement three days earlier on BCR CRM 017 a value of $w(\text{P, BCR CRM 017}) = (5,9 \pm 0,6) \mu\text{g/g}$ (standard deviation only) was found, which seems to be slightly different from the certified value of $w_{\text{cert}}(\text{P, BCR CRM 017}) = (6,9 \pm 0,3) \mu\text{g/g}$ (half width of 95 % confidence interval) [30].

Table 19: Individual values for $w(\text{P, BAM-Y001})$.

$m(\text{BAM-Y001}) / \text{g}$	E	$w(\text{P, BAM-Y001}) / \mu\text{g/g}$
1,06009	0,101-0,115= -	< 2
1,03037	0,108-0,115= -	< 2

1,04332	0,120-0,115=0,005	< 2
1,00026	0,111-0,105=0,006	< 2
1,00083	0,098-0,105= -	< 2
1,02266	0,142-0,105=0,037	3,4
1,01743	0,062-0,059=0,003	< 2
1,03154	0,059-0,059= -	< 2

13.7 Measurements by CG-HE

Oxygen and Nitrogen were measured in 1997 by H. Strehlau and A. Meckelburg under the responsibility of K.A. Meier and R. Oberhauser using classical carrier gas hot extraction. The sample was melted in a carbon crucible. The CO/CO₂ produced was swept to an infra-red detector by a He flow and measured. N₂ was measured after removal of CO/CO₂ by thermal conductivity. Measurements of oxygen in copper are well investigated; often it has been used for systematic studies.

An instrument Ströhlein ON-mat 8500 was used. The calibration was performed using CO and N₂. The calibration was additionally checked against KNO₃ for nitrogen and Fe₂O₃ for oxygen. 10 samples with masses of about 1 g were prepared as described in section 8 and etched according to [6], the data are reported in [33,34]. From 10 individual measurements a mean value of $w(\text{O}, \text{BAM-Y001}) = (1,0 \pm 0,6) \mu\text{g/g}$ was found, the individual values measured are given in Table 20. As a consistency check for oxygen sample RN5 was used, which has been measured by 10 laboratories from copper producing industry in a round robin campaign organised by GDMB (Gesellschaft für Bergbau, Metallurgie Rohstoff- und Umwelttechnik). At BAM a value of $w(\text{O}, \text{RN5}) = (3,6 \pm 0,6) \mu\text{g/g}$ (standard deviation) was found, which is not inconsistent with the mean value of $w(\text{O}, \text{RN5}) = (4,4 \pm 0,7) \mu\text{g/g}$ (standard deviation) obtained from the 10 laboratories participating. Additionally, material 501-644 supplied from an instrument manufacturer was measured as a consistency check. From six individual measurements a value of $w(\text{O}, 501-644) = (65 \pm 2) \mu\text{g/g}$ (standard deviation) was found, the manufacturer gave a value of $w(\text{O}, 501-644) = (64 \pm 3) \mu\text{g/g}$ (standard deviation).

The values for nitrogen were found not to be different from the blank.

Table 20: Individual values for $w(\text{O}, \text{BAM-Y001})$ and $w(\text{N}, \text{BAM-Y001})$ measured by HE.

$w(\text{O}, \text{BAM-Y001}) / \mu\text{g/g}$	$w(\text{N}, \text{BAM-Y001}) / \mu\text{g/g}$
1,0	0,0

1,5	0,9
1,8	0,1
0,6	0,9
1,9	0,0
1,0	1,4
0,2	
1,6	
0,4	
0,4	

13.8 Measurements by PAA

13.8.1 Oxygen, Nitrogen and Carbon

Oxygen, nitrogen and carbon have been measured by Th. Dudzus under the responsibility of M. Hedrich using photon activation with successive radiochemical separation by carrier gas hot extraction (determination of O and N) or by combustion (determination of C). Due to the effort these RPAA techniques are only applied by a few laboratories in the world. The technical set-up is described in [35], the data are reported in [36]. In RPAA the samples are irradiated together with a standard (BeO, BN or pure carbon) with bremsstrahlung of the linear accelerator BAM 35 MeV LINAC for < 8 min. Under these conditions the nuclear reactions $^{16}\text{O}(\gamma,n)^{15}\text{O}$, $^{14}\text{N}(\gamma,n)^{13}\text{N}$ and $^{12}\text{C}(\gamma,n)^{11}\text{C}$ are induced. The nuclides formed decay by positron emission according to $^{15}\text{O}(\beta^+)^{15}\text{N}$, $^{13}\text{N}(\beta^+)^{13}\text{C}$ and $^{11}\text{C}(\beta^+)^{11}\text{B}$, with half lives of about 2, 10 and 20 min respectively. At an energy of 511 keV the two γ -quants produced by the annihilation of the positrons can be detected in coincidence geometry. Since the signals from oxygen, nitrogen and carbon occur in the energy spectrum at the same position, and also the matrix is usually activated, a separation of the analytes is necessary. The experimental set-up is described in detail in [37, 38].

A big advantage of the RPAA is, that after activation the measurement is insensitive to a contamination with inactive oxygen from air or reagents. This avoids many problems related to the procedure blank and helps to avoid artefacts [39]. During irradiation, oxygen from air is activated. Induced by the recoil of the nucleus, this oxygen reacts with the sample surface. Thus the surface of the sample is enriched with additional activated oxygen originating from air. Etching is therefore necessary and performed vigorously usually using HNO_3 (1+1), because re-oxidation with inactive oxygen is not disturbing the final determination. Due to the

short half lives and different intensities (1:1000), sample and standard have to be measured at the same time, and in different geometry. The individual values measured for O, N and C are given in Table 21. As a consistency check for carbon BAM-367 was measured in three repeated measurements. The measured value of $w(\text{C}, \text{BAM-367}) = (29,6 \pm 2,2) \mu\text{g/g}$ (standard deviation) was found which is consistent with the certified value of $w_{\text{cert.}}(\text{C}, \text{BAM-367}) = (28,7 \pm 0,6) \mu\text{g/g}$ [40].

Table 21: Individual values for $w(\text{O}, \text{BAM-Y001})$ and $w(\text{N}, \text{BAM-Y001})$ measured by PAA-HE.

$w(\text{O}, \text{BAM-Y001}) / \mu\text{g/g}$	$w(\text{N}, \text{BAM-Y001}) / \mu\text{g/g}$	$w(\text{C}, \text{BAM-Y001}) / \mu\text{g/g}$
0,6	0,1	0,06±0,03
1,0	0,3	0,04±0,02
0,5	0,1	0,05±0,03
1,1	0,3	0,03±0,02
1,2	0,1	0,03±0,02
1,6	0,1	0,05±0,03

13.8.2 Chlorine, Bromine and Iodine

Chlorine, bromine and iodine have been measured in 2002 by Chr. Segebade under the responsibility of M. Hedrich using photon activation analysis followed by chemical separation (RPAA). The samples and calibration materials (NaCl, NaBr and NaI) were irradiated together with 30 MeV in bremsstrahlung of the BAM 35 MeV LINAC at an electron current of 100 μA to induce the nuclear reactions $^{35}\text{Cl}(\gamma, n)^{34\text{m}}\text{Cl}$, $^{81}\text{Br}(\gamma, n)^{80}\text{Br}$ and $^{127}\text{I}(\gamma, n)^{126}\text{I}$. After activation, the sample was etched for 20 s in conc. nitric acid and then dissolved in 15 mL nitric acid. After adding 20 mg NaCl as carrier the solution was diluted to 30 mL. Precipitation of the silver halogenides was achieved using 5 % (*m/m*) AgNO_3 solution. After 8 minutes the solution was filtered and the residue was pressed to a tablet of 20×1 mm, using cellulose powder as a binding material.

After a total decay time of 45 min, the materials were measured using a coaxial germanium spectrometer. The measurement time for the samples was about 40 min for chlorine and 4000 min for the measurement of bromine and iodine. The calibration samples were measured for 4 min. The signals at the characteristic energies of 145 keV for $^{34\text{m}}\text{Cl}$, of 617 keV for ^{80}Br and of 388 keV for ^{126}I were used for quantification. The limits of determination in absolute

mass were found to be 1,4 µg for chlorine, 0,03 µg for bromine and 0,2 µg for iodine respectively. The typical sample mass was 2,4 g. The results for chlorine, which could be detected but were below the limit of determination are given in Table 22, signals for bromine and iodine were not detected.

Table 22: Individual values for $w(\text{Cl}, \text{BAM-Y001})$ using RPAA.

$m(\text{BAM-Y001}) / \text{g}$	$w(\text{Cl}, \text{BAM-Y001}) / \mu\text{g/g}$	LOD / $\mu\text{g/g}$
2,3514	0,25	0,6
2,2997	0,46	0,6
2,3900	0,39	0,6
2,4113	0,37	0,6

From 4 individual measurements the mean values $w(\text{Cl}, \text{BAM-Y001}) < 0,6 \mu\text{g/g}$, $w(\text{Br}, \text{BAM-Y001}) < 0,014 \mu\text{g/g}$ and $w(\text{I}, \text{BAM-Y001}) < 0,09 \mu\text{g/g}$ were found.

13.9 Measurements by beam analysis

The hydrogen measurement by ion beam analysis were performed by U. Reinholz under the responsibility of H.-P. Weise, the data are reported in [41]. The measurement principle is based on the nuclear reaction ${}^1\text{H}({}^{15}\text{N}, \alpha\gamma){}^{12}\text{C}$ and described in detail in [42]. Calibration was performed using Captone ($\text{C}_{22}\text{H}_{10}\text{N}_2\text{O}_5$). The sample was cut and metallographically polished to a typical roughness $< 10 \text{ nm}$ and brought into the 20° beam line of the 2 MV Tandetrot. In total, 12 measurements were performed in two series. The hydrogen signal from the BAM-Y001 material could not be distinguished from the blank signal. According to [43] the detection limit was calculated to be $0,7 \mu\text{g/g}$, for hydrogen in BAM-Y001 a value of $1,0 \mu\text{g/g}$ was found which is below the limit of determination (9·s) of $2,1 \mu\text{g/g}$.

13.10 Measurement of fluoride by ion sensitive electrode

Total fluoride in copper material BAM-Y001 was determined by use of the ion selective electrode (ISE) after separation of fluoride from the matrix by steam distillation. Steam distillation for the separation of fluoride from different matrices has been described for many years. The sample is dissolved in diluted H_2SO_4 , H_3PO_4 or a mixture of both in a silica vessel. Fluoride is distilled as hydrofluorosilicic acid which can be determined by spectrophotometry,

ion chromatography or ion selective electrode [44,45,46,47,48,49,50]. The measurements of fluoride in BAM-Y001 has been carried out by B. Lange in 2002-2003.

Since copper does not totally dissolve in the described dissolution mixture, the conditions were changed and optimised. It was found that a mass of up to 2 g of copper can be totally dissolved in boiling sulphuric acid (40 ml conc. H₂SO₄ + 10 ml H₂O) in one hour. As a consistency check, 10 µg of fluoride were added to a blank solution and distilled, giving a result of 10,9 µg F⁻.

Since spectrophotometry and ion chromatography are severely interfered by sulphur species in the distillate we used ISE for the final determination of fluoride. A Total Ionic Strength adjustment buffer (TISAB) of 60 g of NaCl, 22 g of CDTA (trans-1,2-cyclohexyldinitrilotetraaceticacid) and 300 g of sodium citrate was mixed with blank solutions, samples and standard solutions and measured alternately. 15 blank measurements (7 individual blank solutions) and 7 sample measurements (3 individual samples) were performed as given in Table 23.

Table 23: Individual values for the mass fraction of fluoride in BAM-Y001.

Date	$m(\text{BAM-Y001}) / \text{g}$	$w(\text{F, BAM-Y001}) / \mu\text{g/g}$
16.12.2002	1,648	0,93
17.12.2002	1,648	1,81
18.12.2002	1,648	0,66
18.12.2002	1,733	0,70
23.01.2003	1,548	1,27
23.01.2003	1,548	1,13
30.01.2003	1,548	1,30
mean		1,1±0,4 (stdev)

The high sulphuric acid content of the distillate made it difficult to adjust the pH to the very same value in all solutions. Additionally, the very low fluoride content of the samples resulted in a potential drift during the measurements. The limit of determination corresponding to 5 µg/l for the solution is calculated to be 1,2 µg F⁻ absolute (9·s) for a sample mass of 2 g. From the measurement results obtained, a value of $w(\text{F, BAM-Y001}) < 3 \mu\text{g/g}$ was concluded.

13.11 Measurements of noble gases by static mass spectrometry

The values for the mass fraction of the noble gases were measured in 2002 at MPI for Chemistry, Mainz, Germany under the responsibility of U. Ott using static gas mass spectrometry as described in detail in [51]. If at all, the noble gases most expected in BAM-Y001 is argon, especially when considering a possible production and treatment of the copper in inert gas environment.

Three samples of about 100 mg have been used. The signals observed for Ar were corresponding to a maximum mass fraction of 0,32 ng/g. This value is seen as an upper limit, since it includes adsorbed air. The value for He is about 1000-fold less, for the other noble gases even considerably smaller. From this the values for the noble gases in BAM-Y001 were conservatively taken to be < 0,001 mg/kg. Although these measurement results have not been obtained under direct control of BAM, the values are used for the certification of BAM-Y001, because their influence is rather marginal and the MPI laboratory has a high reputation in this field of measurements.

13.12 Measurements by Instrumental Neutron Activation Analysis

Measurements using INAA have been performed in 1999 by A. Berger under the responsibility of M. Hedrich, the data are reported in [52]. About 75 mg of material were drilled from the sample using a ceramic coated drill, additionally 173 mg E-Cu1 (internally used material) in form of chips were prepared. Calibration samples for the elements measured were prepared from commercial calibration solutions. The samples were irradiated for 7 days in DBVK (rotatable irradiation position inside the core of reactor BER II, Hahn-Meitner-Institute, Berlin) at a neutron flux of $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$, and left for decay for about 24 days. Due to the production of ^{60}Co by fast neutrons, the radiation facility available was not optimal for the measurements in copper matrix. The measurement time on the activated samples was 2 h each. Results, where self absorption was not taken into account, are given in Table 24. The uncertainties given were based on counting statistics only.

Table 24: Measurement results of BAM-Y001 obtained by INAA.

$w(E, \text{Material}) / \text{ng/g}$	Sb	Se	Ag
BAM-Y001	839±9	141±19	10560±880
E-Cu1	334±4	150±12	7334±610

E-Cu1 as certified	420±200	210±100	9000±500
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13.13 Estimates for radioactive elements

Based on theoretical considerations, estimates have been made for the artificial and radioactive elements: Technetium, Promethium, Polonium, Astatine, Radon, Francium, Radium, Actinium and Protactinium:

The mass fractions of the radioactive elements in the earth's crust according to [53] are given in Table 25. There is no indication seen to assume significant amounts of the artificial and radioactive elements in BAM-Y001. For the calculation of the mass fraction of copper the values of the mass fractions of the artificial and radioactive elements have been estimated to be < 0,001 mg/kg as given in Table 26. These values are treated in the same way as the values which are found to be below the limit of determination.

Table 25: Mass fractions of radioactive elements in the earth's crust according to [53].

Element E	Tc	Po	At	Rn	Fr	Ra	Ac	Pm	Pa
$w(E) / \%$	n.a.	10^{-4}	$3 \cdot 10^{-24}$	$5 \cdot 10^{-17}$	$2 \cdot 10^{-21}$	$3 \cdot 10^{-10}$	10^{-3}	10^{-19}	$3 \cdot 10^{-7}$
		$w(\text{Ra})$				$w(\text{U})$	$w(\text{Ra})$		$w(\text{U})$

Table 26: Values for the artificial and radioactive elements.

Element E	$w(E, \text{BAM-Y001}) / \text{mg/kg}$
Tc	< 0,001
Pm	< 0,001
Po	< 0,001
At	< 0,001
Rn	< 0,001
Fr	< 0,001
Ra	< 0,001
Ac	< 0,001
Pa	< 0,001

13.14 Measurements using Glow Discharge Mass Spectrometry

GDMS has the big advantage of being a method of measurement directly on the solid material, hence avoiding a decomposition step. The drawback is, that matrix reference materials are needed for calibration, because the sputtering behaviour and ionisation depend very much on the analyte and the matrix. An a priori calculation for the signal generation of the sample, based on sufficiently high purity standards (of known stoichiometry) is too complex. From this, the values obtained using this method of measurement were not used for the certification of BAM-Y001, but given as additional data. The measurements have been performed by A. Mykyiuk and B. Methven under the responsibility of R. Sturgeon at National Research Council (NRC), Canada in December 2003. From material BAM-Y001 a block of 3×3×13 mm was prepared and sent to NRC. The data are taken from [54].

There the material was measured as a routine sample on a VG 9000 instrument. Calibration was performed using not further specified (matrix) reference materials. The results reported are summarised in Table 27. The uncertainties are stated to be based on experience and stated to be multiplicative factors, i.e. to be typically a factor of two except for C, N, and O, where the factor is five. ‘Lower as values’ are reported to be based on 3·s of the blank. For incorporating in Table 3, these values have been multiplied by 3 in order to have comparable data based on 9·s.

Table 27: Values for the mass fraction $w(E, \text{BAM-Y001})$ of impurities in BAM-Y001 measured by GDMS.

	$w(E, \text{BAM-Y001}) /$ $\mu\text{g/kg}$		$w(E, \text{BAM-Y001}) /$ $\mu\text{g/kg}$		$w(E, \text{BAM-Y001}) /$ $\mu\text{g/kg}$
Li	< 0,2	Zn	31	Pr	<1
Be	< 0,2	Ga	1	Nd	<3
B	2	Ge	<2	Sm	<3
C	600	As	390	Eu	<1
N	95	Se	130	Gd	<3
O	2300	Br	<10	Tb	<1
H	-	Rb	<0,08	Dy	<2
F	<1	Sr	<0,2	Ho	<1
Na	<0,4	Y	<0,2	Er	<3
Mg	5	Zr	<0,3	Tm	<1
Al	86	Nb	<0,4	Yb	<2

Si	240	Mo	3	Lu	<1
P	42	Ru	<8	Hf	<0,3
S	4800	Rh	<3000	Ta	-
Cl	94	Pd	<16	W	2
K	<3	Ag	10000	Re	<0,9
Ca	28	Cd	12	Os	<1
Sc	<0,2	In	8	Ir	<1
Ti	7	Sn	140	Pt	4
V	330	Sb	910	Au	<15
Cr	56	Te	21	Hg	<5
Mn	6	I	<2	Tl	<1
Fe	480	Cs	<0,2	Pb	350
Co	2	Ba	<0,4	Bi	140
Ni	1600	La	<0,2	Th	<0,2
Cu	Matrix	Ce	<0,1	U	<0,2

13.15 Information from manufacturer

The data provided by the supplier concerning batch B27F17 are given in Table 28 as taken from [55]. These data were not used to establish the purity statement.

Table 28: Data provided by the supplier for batch B27F17.

O	S	P	Ni	Sn	Zn	Pb	Fe	As	total Cu
<10ppm	,0003%	,0009%	,0001%	,0002%	,0009%	,0001%	,0003%	,0002%	99,987%

14 Acknowledgements

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15 References

1 Certificate BAM-Y001, BAM(2004).

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- 2 Certificate IRMM-647, IRMM (2002).
 - 3 Not available yet.
 - 4 Guide to the Expression of Uncertainty in measurement, ISO, Geneve, (1993).
 - 5 IUPAC: 'Atomic weights of the elements 1995' Pure & Appl. Chem. 68 (1996), 2339-2359.
 - 6 L. Quaglia, G. Weber, D. David, J. Triffaux, J. Geerts, J. van Audenhove and J. Pauwels: 'Surface treatment of non-ferrous metals for the purpose of gas analysis', CEC, BCR Information, EUR 6602 (1979).
 - 7 <http://www.bipm.fr/en/convention/mra/> (2004).
 - 8 BIPM Comptes-rendus 14th Conférence Générale des Poids et Mesures 1971, Resolution 3, (1972), 78.
 - 9 Quantifying Uncertainty in Analytical Measurement, 2nd edition, EURACHEM, (2000).
 - 10 ISO Guide 35: Certification of reference materials – General and statistical principles, draft (2003).
 - 11 S. Pattberg: 'Multielement-Spurenbestimmung in Reinstkupfer mit HR-ICP-MS', Dissertation, Humboldt-University, Berlin (1999).
 - 12 R. Matschat, M. Czerwensky, M. Hamester, S. Pattberg: 'Investigations concerning the analysis of high purity metals (Cd, Cu, Ga and Zn) by high resolution inductively coupled plasma mass spectrometry', Fresenius J. Anal. Chem. 359 (1997), 418-423.
 - 13 S. Pattberg, R. Matschat: 'Determination of trace impurities in high purity copper using sector-field ICP-MS: continuous nebulization, flow injection analysis and laser ablation', Fresenius J. Anal. Chem. 364 (1999), 410-416.
 - 14 DIN 32645: 'Chemical analysis; decision limit; detection limit and determination limit; estimation in case of repeatability; terms, methods, evaluation', (1994).
 - 15 DIN 50502: 'Chemical analysis of copper and copper alloys - Determination of copper in unalloyed copper containing not less than 99,90 % of copper', (1973).
 - 16 ISO 1553: 'Unalloyed copper containing not less than 99,90 % of copper; determination of copper content; Electrolytic method', (1976).
 - 17 H. Reichelt: ',Versuchsheft 9' Internal Report, BAM (96-09-09).
 - 18 Private communication via PTB 97-07-17.
 - 19 BCR CRM 074 certificate, BCR, (1991).
 - 20 H.-J. Heinrich: 'Messung von Hg in Cu 99,99% Alfa Johnson-Matthey, Lot B27F17 Kandidat für primäres Kalibriernormal', Internal Report, BAM (02-02-12).
 - 21 H.-J. Heinrich: 'Messung von Ag, As, Bi, Fe, Mn, Ni, Pb, Sb, Se und Sn in in Cu 99,99% Alfa Johnson-Matthey, Lot B27F17 Kandidat für primäres Kalibriernormal', Internal Report, BAM (02-02-12).
 - 22 BCR CRM 075 certificate, BCR, (1991).
 - 23 H.-J. Heinrich: 'Messung von Al, Ca, Cr, Fe, K, Mg, Na, Si und Zn in Cu 99,99% Alfa Johnson-Matthey, Lot B27F17 Kandidat für primäres Kalibriernormal', Internal Report, BAM (2002-07-31).
 - 24 N. Langhammer: ',Zusammenstellung der Ergebnisse der ICP-OES-Analytik von Cu pellets 99,99%, LOT B27F17 (Alfa JM)', Internal Report, BAM (98-10-28).
 - 25 K. Wandelburg: 'Zum Problem der Schwefelbestimmung in Kupfer und Kupferlegierungen', in 'Analysis of Non-Metals in Metals' G. Kraft (Ed.), (1981), de Gruyter, New York, 499-508.

-
- 26 ISO 10701: 'Steel and iron; determination of sulphur content; methylene blue spectrophotometric method', (1994).
- 27 A. Watson, E. Grallath, G. Kaiser, G. Tölg: 'Microtitrimetric and photometric determination of sulphur in metals in the low $\mu\text{g g}^{-1}$ range after wet or dry evolution of hydrogen sulphide', *Anal. Chim. Acta* **100** (1978), 413-428.
- 28 H. Reichelt, 'Versuchsheft 9', Internal Report, BAM (96-11-22).
- 29 'Modern Methods for the Determination of Non-Metals in Non-Ferrous Metals' C. Engelmann, G. Kraft, J. Pauwels, C. Vandecasteele (1985) de Gruyter, New York, 386-390.
- 30 BCR CRM 017 certificate, BCR, (1989).
- 31 DIN 50511: 'Copper and copper alloys; determination of phosphor content; molybdenum blue and molybdovanadate spectrophotometric method' (1994).
- 32 H. Reichelt: 'Versuchsheft 9' Internal Report, BAM (96-09-10).
- 33 R. Oberhauser: 'O/N-Analysen an zwei Kupferproben', Internal Report, BAM (96-11-21).
- 34 K.A. Meier: 'Sauerstoffbestimmung in Kupfer', Internal Report, BAM (97-12-04).
- 35 C. Engelmann, G. Kraft, J. Pauwels and C. Vandecasteele: 'Modern methods for the determination of non-metals in non ferrous metals', de Gruyter, New York (1985), 64-94.
- 36 M. Hedrich: 'Sauerstoff- und Stickstoffbestimmung in Cu m4N und Cu m6N', Internal Report, BAM (97-03-05).
- 37 B.F. Schmitt and H.-U. Fusban: 'Analysis of carbon, nitrogen and oxygen in refractory-metals with the aid of photon-activation', *Metall* **33** (1979), 1265-1269.
- 38 H.J. Rath, P. Stallhofer, D. Huber and B.F. Schmitt: 'Determination of oxygen in silicon by photon-activation analysis for calibration of the infrared adsorption', *J. Electrochem. Soc.* **131** (1984), 1920-1922.
- 39 H. Kipphardt, T. Dudzus, K.A. Meier, S. Recknagel, M. Hedrich and R. Matschat: 'Measurement of oxygen and nitrogen in high purity metals used as national standards for elemental analysis in Germany by classical carrier gas hot extraction (HE) and HE after activation with photons', *Mat. Transactions (JIM)* **43** (2002), 98-100.
- 40 BAM-367 certificate, BAM, (1995).
- 41 H. P. Weise: 'Ionenstrahlanalyse - Wasserstoffbestimmung mittels NRA', Internal Report (02-08-03).
- 42 W.A. Lanford: 'Nuclear reactions for hydrogen analysis', in: J.R. Tesmer, M. Nastasi (Eds.): 'Handbook of modern ion beam materials analysis', Chapter 8: Materials Research Society (1995), 193 - 204.
- 43 DIN 25482-1: 'Limit of detection for nuclear radiation measurements; counting measurements neglecting the influence of sample treatment' (1989).
- 44 ISO 10359-1: 'Water Quality – Determination of Fluoride – Part 1: Electrochemical probe method for potable and lightly polluted water' (1992).
- 45 DIN 38045 Teil 4: 'Untersuchung von Lebensmitteln – Bestimmung von Fluorid in natürlichem Mineralwasser' (1985).
- 46 DIN 51 723: 'Prüfung fester Brennstoffe – Bestimmung des Gehaltes an Fluor' (1988).
- 47 ASTM 1179-99 D: 'Standard Test Methods for Fluoride Ion in Water' (1999).

-
- 48 DIN 51 084: ‚Prüfung von oxidischen Roh- und Werkstoffen für Keramik, Glas und Glasuren - Bestimmung des Gehaltes an Fluorid‘ (1990).
- 49 E. Kissa: ‚Determination of Fluoride at low concentrations with the ion-selective electrode‘, *Anal. Chem.* 55 (1983), 1445 – 1448.
- 50 I.V. Kuznetsova, S.S. Khmelev: ‚Electrode response and detection limits of a Fluoride Selective electrode in Anionic Buffer Solutions‘, *J. Anal. Chem.* 57 (2002), 270 – 275.
- 51 N. Schelhaas, U. Ott, F. Begemann: ‚Trapped noble gas in unequilibrated ordinary chondrites‘, *Geo. Cosmochim. Acta* 54 (1990), 2869-2882.
- 52 A. Berger: ‚zwischen Analysenbericht 6N und 4N Kupfer‘, Internal Report, BAM (99-05-10).
- 53 Hollemann-Wiberg: ‚Lehrbuch der Anorganischen Chemie‘, 91-100 Aufl. (1985), De Gruyter, Berlin.
- 54 R. Sturgeon: ‚Glow Discharge Mass Spectrometric Report‘, Internal Report, NRC (03-12-22).
- 55 Certificate ‚copper pellets, 6,4-13 mm [0,25-0,51in],99,99% oxygen free‘, Alfa Aesar.