

**Certification of the  
mass fraction of sodium chloride  
in Primary Reference Material  
BAM-Y009**

**CERTIFICATION REPORT**

**Version 1 of 2004-09-15**

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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/2004-08 of 2004-09-15	after approval by BAM certification committee
	...	

The certificates as given in Table 2 have been issued.

Table 2: Certificates issued

Certificate / date of issue	based on report version
BAM-Y009 [1] / 2004-09-15	1
...	
...	

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-Y009. We believe that BAM-Y009 is not perfect, but probably one of the best characterised sodium chloride materials available. Whenever there is new insight in form of measurement results, the certified value of BAM-Y009 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
<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-MS	Mass spectrometry using inductively coupled plasma
<i>k</i>	Coverage factor or amount of substance content in mol/kg
LD	Limit of detection (based on $3 \cdot s$ )
LOD	Limit of determination (based on $9 \cdot s$ )
<i>m</i>	Mass
<i>M</i>	Molar mass
<i>n</i>	Amount of substance or number of accepted data sets
<i>s</i>	Standard deviation
SD	Standard deviation
THE	Estimate based on theoretical considerations
<i>U</i>	Expanded uncertainty
<i>u</i> or <i>u<sub>c</sub></i>	(Combined) uncertainty
ULV	Upper limit value (based on measurements)
ULV-EST	Upper limit value based on estimate (not measured yet)
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 sodium chloride in the bulk of material BAM-Y009.

$$w(\text{NaCl}) = (0,999\ 84 \pm 0,000\ 09) \text{ kg/kg}$$

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 [2].

Taking the value for the atomic weight of sodium chloride to be  $(58,442\ 5 \pm 0,000\ 9)$  as calculated from the IUPAC table 'Atomic weights of the elements' [3] this corresponds to a sodium chloride amount-of-substance content in the solid material of  $k(\text{NaCl, BAM-Y009}) = w/M = (17,108\ 1 \pm 0,001\ 6) \text{ mol/kg}$  (expanded uncertainty  $U=k\cdot u_c$  with  $k=2$ ).

Before use, the material has to be pre-treated in order to achieve the defined state, to which the certified quantity value applies.

T1. Heat material for 5 h at 500 °C in order to remove trapped mother solution. Avoid contamination.

T2. Sub-sample masses of  $m > 0,1 \text{ g}$  must be used.

T3. The material must be stored in a desiccator to avoid contamination and moisture take-up.

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 sodium chloride 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 [4]. 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 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 [5]:

„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  $^{12}\text{C}$ . A known multiple or fraction of 12 g of  $^{12}\text{C}$  is also suitable to establish a primary amount of substance standard. Moreover, it is not even necessary to realise the mole in  $^{12}\text{C}$ . By using the powerful concept of atomic weight (mean atomic mass relative to  $^{12}\text{C}$ ), a realisation of the mole in form of the element or compound under investigation (e.g. NaCl) 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’ [3] 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) [2] and the EURACHEM/CITAC Guide on Quantifying Uncertainty in Analytical Measurement’ [6]. 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 or where an upper limit value is reported, 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 [2] 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).

For impurities which have not been measured yet, upper limit values are conservatively estimated and treated in the same way as LOD values. The purer (and better characterised) the material, the bigger is the relative contribution of these estimates to the certified value and its uncertainty. Admittedly, there is some degree of freedom in these estimates and these estimates are certainly an imperfection in the certification of the material, however, we believe that BAM-Y009 is still one of the best characterised sodium chloride materials available. Whenever there is new insight in form of measurement results, the certified value of BAM-Y009 will be revised (i.e. the uncertainty statement will be improved).

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

The material basis for BAM-Y009 are ten bottles of about 25 g each of sodium chloride 99,999 % (metals) LOT 22080 obtained from Alfa Johnson-Matthey, Karlsruhe, Germany. After the certification analysis there is about 250 g of material left.

## **7 Sizing, pre-cleaning, packaging and labelling**

The material was not further processed, it is available in glass bottles containing about 0,5 g of material. 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 pre-treated in order to achieve the defined state, to which the certified quantity value applies.

T1. Heat material for 5 h at 500 °C in order to remove trapped mother solution. Avoid contamination.

T2. Sub-sample masses of  $m > 0,1$  g must be used.

T3. The material must be stored in a desiccator to avoid contamination and moisture take-up.

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-Y009 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 [7], 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-Y009 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 a limit value the relative uncertainty was conservatively set to 100 %. Note that for values which are below a limit value, only the half of this limit 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-Y009.

method					method				method											
			w	u(w)	unc.		w	u(w)	unc.		w	u(w)	unc.							
			mg/kg	mg/kg	contr.		mg/kg	mg/kg	contr.		mg/kg	mg/kg	contr.							
H	ULV-EST	<	50	25	0,30	Ge	ICP-MS	<	0,007	0,0035	<<	0,01	Eu	ICP-MS	<	0,001	0,0005	<<	0,01	
He	THE	<	0,001	0,0005	<<	0,01	As	ICP-MS	<	5	2,5	<<	0,01	Gd	ICP-MS	<	0,004	0,002	<<	0,01
Li	ICP-MS	<	4	2	<<	0,01	Se	ICP-MS	<	0,25	0,125	<<	0,01	Tb	ICP-MS	<	0,004	0,002	<<	0,01
Be	ICP-MS	<	1	0,5	<<	0,01	Br	ICP-MS	<	15	7,5	0,03	Dy	ICP-MS	<	0,001	0,0005	<<	0,01	
B	ICP-MS	<	1,3	0,65	<<	0,01	Kr	THE	<	0,001	0,0005	<<	0,01	Ho	ICP-MS	<	0,004	0,002	<<	0,01
C	HE	<	20	10	0,05	Rb	ICP-MS	<	0,02	0,01	<<	0,01	Er	ICP-MS	<	0,001	0,0005	<<	0,01	
N	HE	<	50	25	0,30	Sr	ICP-MS	<	0,5	0,25	<<	0,01	Tm	ICP-MS	<	0,001	0,0005	<<	0,01	
O	HE	<	47	17	0,14	Y	ICP-MS	<	0,05	0,025	<<	0,01	Yb	ICP-MS	<	0,001	0,0005	<<	0,01	
F	ULV-EST	<	15	7,5	0,01	Zr	ICP-MS	<	0,05	0,025	<<	0,01	Lu	ICP-MS	<	0,001	0,0005	<<	0,01	
Ne	THE	<	0,001	0,0005	<<	0,01	Nb	ICP-MS	<	0,001	0,0005	<<	0,01	Hf	ICP-MS	<	0,001	0,0005	<<	0,01
Na	matrix					Mo	ICP-MS	<	0,001	0,0005	<<	0,01	Ta	ICP-MS	<	0,001	0,0005	<<	0,01	
Mg	ICP-MS	<	0,4	0,2	<<	0,01	Tc	THE	<	0,001	0,0005	<<	0,01	W	ICP-MS	<	0,004	0,002	<<	0,01
Al	ICP-MS	<	0,04	0,02	<<	0,01	Ru	ICP-MS	<	0,001	0,0005	<<	0,01	Re	ICP-MS	<	0,001	0,0005	<<	0,01
Si	ULV-EST	<	10	5	0,01	Rh	ICP-MS	<	0,001	0,0005	<<	0,01	Os	ICP-MS	<	0,001	0,0005	<<	0,01	
P	ICP-MS	<	0,011	0,0055	<<	0,01	Pd	ICP-MS	<	0,001	0,0005	<<	0,01	Ir	ICP-MS	<	0,004	0,002	<<	0,01
S	ULV-EST	<	30	15	0,11	Ag	ICP-MS	<	0,2	0,1	<<	0,01	Pt	ICP-MS	<	0,001	0,0005	<<	0,01	
Cl	matrix					Cd	ICP-MS	<	0,003	0,0015	<<	0,01	Au	ICP-MS	<	0,005	0,0025	<<	0,01	
Ar	THE	<	0,5	0,25	<<	0,01	In	ICP-MS	<	0,004	0,002	<<	0,01	Hg	ICP-MS	<	0,005	0,0025	<<	0,01
K	ULV-EST	<	10	5	0,01	Sn	ICP-MS	<	0,005	0,0025	<<	0,01	Tl	ICP-MS	<	0,01	0,005	<<	0,01	
Ca	ICP-MS	<	5	2,5	<<	0,01	Sb	ICP-MS	<	0,005	0,0025	<<	0,01	Pb	ICP-MS	<	0,5	0,25	<<	0,01
Sc	ICP-MS	<	0,09	0,045	<<	0,01	Te	ICP-MS	<	0,005	0,0025	<<	0,01	Bi	ICP-MS	<	0,5	0,25	<<	0,01
Ti	ICP-MS	<	0,04	0,02	<<	0,01	I	ICP-MS	<	1	0,5	<<	0,01	Po	THE	<	0,001	0,0005	<<	0,01
V	ICP-MS	<	0,1	0,05	<<	0,01	Xe	THE	<	0,001	0,0005	<<	0,01	At	THE	<	0,001	0,0005	<<	0,01
Cr	ICP-MS	<	0,4	0,2	<<	0,01	Cs	ICP-MS	<	0,001	0,0005	<<	0,01	Rn	THE	<	0,001	0,0005	<<	0,01
Mn	ICP-MS	<	0,1	0,05	<<	0,01	Ba	ICP-MS	<	0,2	0,1	<<	0,01	Fr	THE	<	0,001	0,0005	<<	0,01
Fe	ICP-MS	<	1	0,5	<<	0,01	La	ICP-MS	<	0,001	0,0005	<<	0,01	Ra	THE	<	0,001	0,0005	<<	0,01
Co	ICP-MS	<	0,05	0,025	<<	0,01	Ce	ICP-MS	<	0,001	0,0005	<<	0,01	Ac	THE	<	0,001	0,0005	<<	0,01
Ni	ICP-MS	<	5	2,5	<<	0,01	Pr	ICP-MS	<	0,001	0,0005	<<	0,01	Th	ICP-MS	<	0,001	0,0005	<<	0,01
Cu	ICP-MS	<	5	2,5	<<	0,01	Nd	ICP-MS	<	0,001	0,0005	<<	0,01	Pa	THE	<	0,001	0,0005	<<	0,01
Zn	ICP-MS	<	0,08	0,04	<<	0,01	Pm	THE	<	0,001	0,0005	<<	0,01	U	ICP-MS	<	0,001	0,0005	<<	0,01
Ga	ICP-MS	<	0,2	0,1	<<	0,01	Sm	ICP-MS	<	0,001	0,0005	<<	0,01	Value contributes > 10 % to combined uncertainty						

BAM-A-primary-NaCl-1  
 LOT 22080

	matrix	impurity	sum 'above'	sum/2 'below'
	in %	in mg/kg	in mg/kg	in mg/kg
mass fraction	99,9837	163,34	47,00	116,34
abs. uncertainty	0,0045	45,35	17,00	40,05

Not relevant for  
 measurement

Upper limit value  
 (estimate)

H < 50																	He < 0,001	
Li < 4	Be < 1											B < 20	C < 50	O 47	F < 15	Ne < 0,001		
Na matrix	Mg < 0,4											Al	Si < 10	P < 0,011	S < 30	Cl matrix	Ar < 0,5	
K < 10	Ca < 5	Sc < 0,09	Ti < 0,04	V < 0,1	Cr < 0,4	Mn < 0,1	Fe < 1	Co < 0,05	Ni < 5	Cu < 5	Zn < 0,08	Ga < 0,2	Ge < 0,007	As < 5	Se < 0,25	Br < 15	Kr < 0,001	
Rb < 0,02	Sr < 0,5	Y < 0,05	Zr < 0,05	Nb < 0,001	Mo < 0,001	Tc < 0,001	Ru < 0,001	Rh < 0,001	Pd < 0,001	Ag < 0,2	Cd < 0,003	In < 0,004	Sn < 0,005	Sb < 0,005	Te < 0,005	I < 1	Xe < 0,001	
Cs < 0,001	Ba < 0,2	La < 0,001	Hf < 0,001	Ta < 0,001	W < 0,004	Re < 0,001	Os < 0,001	Ir < 0,004	Pt < 0,001	Au < 0,005	Hg < 0,005	Tl < 0,01	Pb < 0,5	Bi < 0,5	Po < 0,001	At < 0,001	Rn < 0,001	
Fr < 0,001	Ra < 0,001	Ac < 0,001																
			Ce	Pr < 0,001	Nd < 0,001	Pm < 0,001	Sm < 0,001	Eu < 0,001	Gd < 0,004	Tb < 0,004	Dy < 0,001	Ho < 0,004	Er < 0,001	Tm < 0,001	Yb < 0,001	Lu < 0,001		
			Th	Pa < 0,001	U < 0,001													

Figure 1: Summary of the results of impurity measurements of BAM-Y009. 'sum above' is the sum of all impurity values found above the respective limit of determination or upper limit; 'sum below' is the half of the sum of the respective limits of determination for impurities found below the limit of determination or impurities that are below an upper limit value.

## 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 sodium chloride in BAM-Y009. 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. Values of type 'ULV' are upper limit values, based on measurements. Values of type 'THE' are based on theoretical considerations. Values of type 'ULV-EST' are not based on measurements of the analyte concerned, but estimates. 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-Y009 element by element.

	type	result mg / kg	uncertainty mg / kg	method
89Ac	THE	0,001		THE
	1THE	0,001		THE
47Ag	ULV	0,2		ICP-MS
	1ULV	0,2		ICP-MS
	# 2VAL	7		DC-Arc-OES
13Al	ULV	0,04		ICP-MS
	1ULV	0,04		ICP-MS
	# 2LD	1		DC-Arc-OES
18Ar	THE	0,5		THE
	1THE	0,5		THE
33As	ULV	5		ICP-MS
	1ULV	5		ICP-MS
	# 2LD	20		DC-Arc-OES
85At	THE	0,001		THE
	1THE	0,001		THE

	type	result mg / kg	uncertainty mg / kg	method
	79Au ULV	0,005		ICP-MS
	1ULV	0,005		ICP-MS
	5B ULV	1,3		ICP-MS
	1ULV	1,31		ICP-MS
#	2LD	30		DC-Arc-OES
	56Ba ULV	0,2		ICP-MS
	1ULV	0,2		ICP-MS
#	2LD	7		DC-Arc-OES
	4Be ULV	1		ICP-MS
	1ULV	1		ICP-MS
	83Bi ULV	0,5		ICP-MS
	1ULV	0,5		ICP-MS
#	2LD	1		DC-Arc-OES
	35Br ULV	15		ICP-MS
	1ULV	15		ICP-MS
	6C LOD	20		HE
	1VAL	5,1		8,HE
	2LOD	20		HE
	20Ca ULV	5		ICP-MS
	1ULV	5		ICP-MS
#	2LD	1		DC-Arc-OES
	48Cd ULV	0,003		ICP-MS
	1ULV	0,003		ICP-MS
#	2LD	3		DC-Arc-OES
	58Ce ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	17Cl VAL	matrix		
	1VAL	99998		Coul
	27Co ULV	0,05		ICP-MS
	1ULV	0,05		ICP-MS
#	2LD	10		DC-Arc-OES
	24Cr ULV	0,4		ICP-MS
	1ULV	0,4		ICP-MS
#	2LD	1		DC-Arc-OES
	55Cs ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	29Cu ULV	5		ICP-MS
	1ULV	5		ICP-MS



	type	result	uncertainty	method
		mg / kg	mg / kg	
#	2LD	1		DC-Arc-OES
66Dy	ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
68Er	ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
63Eu	ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
9F	ULV-EST	15		ULV-EST
	1ULV-EST	15		ULV-EST
26Fe	ULV	1		ICP-MS
	1ULV	1		ICP-MS
#	2LD	1		DC-Arc-OES
87Fr	THE	0,001		THE
	1THE	0,001		THE
31Ga	ULV	0,2		ICP-MS
	1ULV	0,2		ICP-MS
#	2LD	1		DC-Arc-OES
64Gd	ULV	0,004		ICP-MS
	1ULV	0,004		ICP-MS
32Ge	ULV	0,007		ICP-MS
	1ULV	0,007		ICP-MS
#	2LD	1		DC-Arc-OES
1H	ULV-EST	50		ULV-EST
	1ULV-EST	50		ULV-EST
2He	THE	0,001		THE
	1THE	0,001		THE
72Hf	ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
80Hg	ULV	0,005		ICP-MS
	1ULV	0,005		ICP-MS
#	2LD	20		DC-Arc-OES
67Ho	ULV	0,004		ICP-MS
	1ULV	0,004		ICP-MS
53I	ULV	1		ICP-MS
	1ULV	1		ICP-MS
49In	ULV	0,004		ICP-MS
	1ULV	0,004		ICP-MS
#	2LD	5		DC-Arc-OES

	type	result	uncertainty	method
		mg / kg	mg / kg	
	77Ir	ULV	0,004	ICP-MS
		1ULV	0,004	ICP-MS
	19K	ULV-EST	10	ULV-EST
		ULV-EST	10	ULV-EST
#		2LD	2	DC-Arc-OES
	36Kr	THE	0,001	THE
		1THE	0,001	THE
	57La	ULV	0,001	ICP-MS
		1ULV	0,001	ICP-MS
	3Li	ULV	4	ICP-MS
		1ULV	4	ICP-MS
#		2LD	1	DC-Arc-OES
	71Lu	ULV	0,001	ICP-MS
		1ULV	0,001	ICP-MS
	12Mg	ULV	0,4	ICP-MS
		1ULV	0,4	ICP-MS
#		2LD	1	DC-Arc-OES
	25Mn	ULV	0,1	ICP-MS
		1ULV	0,1	ICP-MS
#		2LD	1	DC-Arc-OES
	42Mo	ULV	0,001	ICP-MS
		1ULV	0,001	ICP-MS
#		2LD	2	DC-Arc-OES
	7N	LOD	50	HE
		1Val	-3	11HE
		2LOD	50	HE
	11Na	VAL	matrix	
	41Nb	ULV	0,001	ICP-MS
		1ULV	0,001	ICP-MS
	60Nd	ULV	0,001	ICP-MS
		1ULV	0,001	ICP-MS
	10Ne	THE	0,001	THE
		1THE	0,001	THE
	28Ni	ULV	5	ICP-MS
		1ULV	5	ICP-MS
#		2LD	3	DC-Arc-OES
	8O	Val	47	17HE
		1Val	47	17HE

	type	result mg / kg	uncertainty mg / kg	method
	76Os ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	15P ULV	0,011		ICP-MS
	1ULV	0,011		ICP-MS
#	2LD	200		DC-Arc-OES
	91Pa THE	0,001		THE
	1THE	0,001		THE
	82Pb ULV	0,5		ICP-MS
	1ULV	0,5		ICP-MS
#	2LD	1		DC-Arc-OES
	46Pd ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	61Pm THE	0,001		THE
	1THE	0,001		THE
	84Po THE	0,001		THE
	1THE	0,001		THE
	59Pr ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	78Pt ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	88Ra THE	0,001		THE
	1THE	0,001		THE
	37Rb ULV	0,02		ICP-MS
	1ULV	0,02		ICP-MS
	75Re ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	45Rh ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	86Rn THE	0,001		THE
	1THE	0,001		THE
	44Ru ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	16S ULV-EST	30		ULV-EST
	1ULV-EST	30		ULV-EST
	51Sb ULV	0,005		ICP-MS
	1ULV	0,005		ICP-MS
#	2LD	7		DC-Arc-OES
	21Sc ULV	0,09		ICP-MS

	type	result mg / kg	uncertainty mg / kg	method
	1ULV	0,09		ICP-MS
	34Se ULV	0,25		ICP-MS
	1ULV	0,25		ICP-MS
	14Si ULV-EST	10		ULV-EST
	ULV-EST	10		ULV-EST
#	2LD	1		DC-Arc-OES
	62Sm ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	50Sn ULV	0,005		ICP-MS
	1ULV	0,005		ICP-MS
#	2LD	1		DC-Arc-OES
	38Sr ULV	0,5		ICP-MS
	1ULV	0,5		ICP-MS
#	2LD	10		DC-Arc-OES
	73Ta ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	65Tb ULV	0,004		ICP-MS
	1ULV	0,004		ICP-MS
	43Tc THE	0,001		THE
	1THE	0,001		THE
	52Te ULV	0,005		ICP-MS
	1ULV	0,005		ICP-MS
#	2LD	70		DC-Arc-OES
	90Th ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	22Ti ULV	0,04		ICP-MS
	1ULV	0,04		ICP-MS
#	2LD	2		DC-Arc-OES
	81TI ULV	0,01		ICP-MS
	1ULV	0,01		ICP-MS
#	2LD	1		DC-Arc-OES
	69Tm ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	92U ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
	23V ULV	0,1		ICP-MS
	1ULV	0,1		ICP-MS
#	2LD	2		DC-Arc-OES

	type	result mg / kg	uncertainty mg / kg	method
#	74W ULV	0,004		ICP-MS
	1ULV	0,004		ICP-MS
	2LD	20		DC-Arc-OES
	54Xe THE	0,001		THE
	1THE	0,001		THE
	39Y ULV	0,05		ICP-MS
	1ULV	0,05		ICP-MS
	70Yb ULV	0,001		ICP-MS
	1ULV	0,001		ICP-MS
#	30Zn ULV	0,08		ICP-MS
	1ULV	0,08		ICP-MS
	2LD	100		DC-Arc-OES
#	40Zr ULV	0,05		ICP-MS
	1ULV	0,05		ICP-MS
	2LD	5		DC-Arc-OES

### 13 Technical details of Chemical Analysis

The limit of determination has been measured using the blank value method according to [8], which is:

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

*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 (NaCl). Typically the standard addition using BAM-Y009 was applied, 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 chloride using coulometry

The measurements by constant current coulometry have been performed by M. Breitenbach and C. Oberröder under the responsibility of D. Lück in 2003.

From two measurements a result of  $w(\text{NaCl, BAM-Y009}) = (0,999\ 98 \pm 0,000\ 03)$  kg/kg (standard deviation) was reported.

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

The measurement by HR-ICP-MS have been performed by S. Richter using an 'Element I' spectrometer Finnigan MAT equipped with an HF resistant inlet system. Technical details can be found in [9].

The sample was pretreated as described in chapter 7. Four sub-samples of 1 g each were used. The decomposition was performed using 50 mL water + 10 mL HNO<sub>3</sub> (sub-boiled) for 1 g of material BAM-Y009. The solution was heated for 2 h at 40- 65 °C. After dilution to a concentration of about 1 mg/L the samples were analysed by ICP-MS applying an addition calibration. From the results obtained, the upper limit values as given in Table 5 were reported.

Table 5: Measured values and upper limit values of impurities in BAM-Y009.

element	mass fraction/ mg/kg	element	mass fraction/ mg/kg
Ac	-	Na	Matrix
Ag	< 0,2	Nb	< 0,001
Al	< 0,04	Nd	< 0,001
As	< 5	Ni	< 5
Au	< 0,005	Os	< 0,001
B	< 1,3	P	< 0,01
Ba	< 0,2	Pa	-
Be	< 1	Pb	< 0,5
Bi	< 0,5	Pd	< 0,001
Br	< 15	Pr	< 0,001
Ca	< 5	Pt	< 0,001
Cd	< 0,003	Rb	< 0,02
Ce	< 0,001	Re	< 0,001
Co	< 0,05	Rh	< 0,001
Cr	< 0,4	Ru	< 0,001
Cs	< 0,001	S	-
Cu	< 5	Sb	< 0,005
Dy	< 0,001	Sc	< 0,09
Er	< 0,001	Se	< 0,25
Eu	< 0,001	Si	-
Fe	< 1	Sm	< 0,001
Ga	< 0,2	Sn	< 0,005
Gd	< 0,004	Sr	< 0,5
Ge	< 0,07	Ta	< 0,001
Hf	< 0,001	Tb	< 0,004
Hg	< 0,005	Te	< 0,005

Ho	< 0,004	Th	< 0,001
I	< 1	Ti	< 0,04
In	< 0,004	Tl	< 0,01
Ir	< 0,004	Tm	< 0,001
K	-	U	< 0,001
La	< 0,001	V	< 0,1
Li	< 4	W	< 0,004
Lu	< 0,001	Y	< 0,05
Mg	< 0,4	Yb	< 0,001
Mn	< 0,1	Zn	< 0,08
Mo	< 0,001	Zr	< 0,05

### 13.3 Measurements by CG-HE / combustion analysis

Oxygen and Nitrogen were measured in 2002 by H. Kipphardt using classical carrier gas hot extraction. The sample was molten in a carbon crucible with Ni flux. The CO/CO<sub>2</sub> produced was swept to an infra-red detector by a He flow and measured. N<sub>2</sub> was measured after removal of CO/CO<sub>2</sub> by thermal conductivity. Technical details can be found in [10].

An LECO TC436DR equipped with a EF500 furnace was used. The sample was pretreated as described in chapter 7. Due to the huge vapour pressure the analysis of sodium chloride by carrier gas hot extraction is rather difficult. About 110 mg of material was used for each analysis. Calibration was performed using Fe<sub>2</sub>O<sub>3</sub> for oxygen and KNO<sub>3</sub> for nitrogen (ultra-micro balance). 120 mg of tin was added as flux. Addition of Fe<sub>2</sub>O<sub>3</sub> to the sodium chloride material gave no indication for incomplete extraction. For nitrogen and oxygen, values of  $w(\text{O, BAM-Y009}) = (47 \pm 17) \mu\text{g/g}$  and  $w(\text{N, BAM-Y009}) = (-3 \pm 11) \mu\text{g/g}$  (expanded uncertainty with  $k=2$ ) were reported. The corresponding limit of determination was  $w(\text{N, BAM-Y009}) < 50 \mu\text{g/g}$ .

Carbon and sulphur were measured by H. Kipphardt in 2002 by combustion analysis with IR detection. Technical details can be found in [11]. The sample was pretreated as described in chapter 7. Due to the formation of chlorine oxides, the analysis of sodium chloride by combustion analysis is rather difficult. About 0,4 g of material, 2,5 g W and 88 mg Sn (capsule) were used. BaCO<sub>3</sub> was used for calibration of carbon, BaSO<sub>4</sub> was used for calibration of sulphur (ultra micro balance). Addition of BaCO<sub>3</sub> to the sodium chloride material gave no indication for incomplete extraction, however, the addition of BaSO<sub>4</sub> gave the indication that the extraction of sulphur is incomplete. From the six sub-samples a value of  $w(\text{C, BAM-Y009}) = (5,1 \pm 8,5) \mu\text{g/g}$  (expanded uncertainty with  $k=2$ ) was reported. The corresponding limit of determination was  $w(\text{C, BAM-Y009}) < 20 \mu\text{g/g}$ .

### 13.4 Estimates for the not yet measured analytes H, F, K, Si and S

For sodium chloride as supplied, typical values for potassium and silicon are stated to be well below 2 mg/kg. Assuming the hydrogen to be bound to oxygen, an upper limit for the mass fraction of hydrogen is 3 µg/g. Assuming the sulphur to be present as sulphate, an upper limit for the mass fraction of sulphur is 23 µg/g. Fluorine is not likely to be present more than bromine. From this, The conservative estimates as given in Table 6 have been made to account for the elements, which have not been measured yet.

Table 6: Estimated values for elements, which have not been measured yet.

Element $E$	$w(E, \text{BAM-Y009}) / \text{mg/kg}$
H	< 50
F	< 15
K	< 10
Si	< 10
S	< 30

### 13.5 Estimates for noble gases

Estimates have been made for the noble gases: Helium, Neon, Argon, Krypton and Xenon. There is no indication seen, that noble gases should be present in the material in significant amounts. If at all, the gas most likely to find is Argon, because of technological reasons. Assuming a ‘natural’ noble gas impurity, the other noble gases should be present even 1000 fold less. The presence of Argon however would be detected as Nitrogen when using carrier gas hot extraction for the measurement of Nitrogen with heat conductivity detector. From this the values as given in Table 7 are used for the mass fraction of the noble gases.

Table 7: Estimated values for the noble gases.

Element $E$	$w(E, \text{BAM-Y009}) / \text{mg/kg}$
He	< 0,001
Ne	< 0,001
Ar	< 0,5
Kr	< 0,001



Xe < 0,001

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### 13.6 Estimates for radioactive elements

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 [12] are given in Table 8. There is no indication seen to assume significant amounts of the artificial and radioactive elements in BAM-Y009. For the calculation of the mass fraction of sodium chloride 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 9. These values are treated in the same way as the values which are found to be below the limit of determination.

Table 8: Mass fractions of radioactive elements in the earth's crust according to [12].

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 9: Estimated values for the artificial and radioactive elements.

Element $E$	$w(E, \text{BAM-Y009}) / \text{mg/kg}$
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

### 13.7 Information from manufacturer

Information from the supplier [13] for batch 22080 of the sodium chloride are given in Table 10 and Table 11. The measurements have been performed using DC-Arc-OES.

Table 10: Values for impurities in sodium chloride batch 22080 as given by the supplier.  
 “Elements sought and limits of detection”

	Ag	Al	As	B	Ba	Bi	Ca
w / mg/kg	1	1	20	30	7	1	1
	Cd	Co	Cr	Cu	Fe	Ga	Ge
w / mg/kg	3	10	1	1	1	1	1
	Hg	In	K	Li	Mg	Mn	Mo
w / mg/kg	20	5	2	1	1	1	2
	Ni	P	Pb	Sb	Si	Sn	Sr
w / mg/kg	3	200	1	7	1	1	10
	Te	Ti	Tl	V	W	Zn	Zr
w / mg/kg	70	2	1	2	20	100	5

Table 11: Values for impurities in sodium chloride batch 22080 as given by the supplier.  
 „Elements detected“

	Al	Ca	Ag	Si
w / mg/kg	< 1	< 1	7	< 1

## 14 Acknowledgements

The editor would like to thank all who contributed to the successful certification of BAM-Y009 and especially R. Matschat who developed the underlying concept of this project and made it run.

## 15 References

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1 Certificate BAM-Y009, BAM(2004).

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- 2 Guide to the Expression of Uncertainty in measurement, ISO, Geneve, (1993).
  - 3 IUPAC: 'Atomic weights of the elements 1993' Pure & Appl. Chem. 68 (1996), 2339-2359.
  - 4 <http://www.bipm.fr/en/convention/mra/> (2004).
  - 5 BIPM Comptes-rendus 14<sup>th</sup> Conférence Générale des Poids et Mesures 1971, Resolution 3, (1972), 78.
  - 6 Quantifying Uncertainty in Analytical Measurement, 2<sup>nd</sup> edition, EURACHEM, (2000).
  - 7 ISO Guide 35: Certification of reference materials – General and statistical principles, draft (2003).
  - 8 DIN 32645: 'Chemical analysis; decision limit; detection limit and determination limit; estimation in case of repeatability; terms, methods, evaluation', (1994).
  - 9 S. Richter: 'ICP-MS Analysenergebnisse Alfa JM, NaCl LOT 22080 Kandidat primäres Kalibriernormal vom Typ A', Internal Report, BAM, (August 2002).
  - 10 H. Kipphardt: 'Messung von Sauerstoff und Stickstoff in NaCl LOT 22080 Kandidat primäres Kalibriernormal Typ A' Internal Report BAM/HKi/02-16, BAM (2002).
  - 11 H. Kipphardt: 'Messung von Kohlenstoff und Schwefel in NaCl LOT 22080Kandidat primäres Kalibriernormal Typ A, Internal Report BAM/HKi/02-24, BAM (2002).
  - 12 Hollemann-Wiberg: 'Lehrbuch der Anorganischen Chemie', 91-100 Aufl. (1985), De Gruyter, Berlin.
  - 13 Certificate of Analysis for Sodium Chloride 99,999 %, batch 22080, Alfa Aesar.