CCQM Inorganic Analysis Working Group

Roadmap for the purity determination of pure metallic elements

Basic principles and helpful advice

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1. Motivation

High purity materials can serve as a realisation of the *Système International d'Unitès* (SI) unit *amount of substance* for the specific element. Solutions prepared from such high purity materials using gravimetric preparation and the concept of molar mass are used as calibration solutions in many fields of analytical chemistry. Calibration solutions prepared this way provide the traceability to the SI and are the metrological basis in elemental analysis.

The preparation and characterization of such primary pure substances, representing the realisation of the SI unit amount of substance, is undertaken only by a small number of *National Metrology Institutes* (NMI) and *Designated Institutes* (DI).

Many other NMIs and DIs, however, prepare elemental calibration solutions as calibrants for their measurement services, such as the certification of matrix *Reference Materials* or the provision of reference values for *Proficiency Testing* schemes. The elemental calibration solutions used for this purpose are not a direct service to customers, such as preparing secondary calibration solutions, but provide the source of traceability for the other services. Hence, it is necessary for the NMI or DI to obtain data on the purity of the pure metals or other materials used to prepare the solutions with measurement uncertainties meeting the needs of the above described services. This is commonly undertaken as a "fit for purpose" assessment, appropriate for the uncertainty requirement of the service provided to customers.

As a consequence, total purity measurements are a long-term strategy of CCQM-IAWG. Several studies were conducted (CCQM-P107, CCQM-K72 and CCQM-P149) on the measurement of the purity of zinc. From these studies, several conclusions can be drawn for the purity assessment of a pure (metallic) element. These conclusions will be put together in this document in order to assist all NMIs/DIs in performing a purity assessment, whenever needed.

Structure

This roadmap describes three different cases:

Case 1: Purity determination of pure metallic elements to be used for calibration solutions using the metal assay approach with expanded uncertainties typically above 0.05 %

Case 2: Purity determination of pure metallic elements using the impurity assessment approach; expanded measurement uncertainties above 0.01 %, but equal to or less than 0.1 %

Case 3: Purity determination of pure metallic elements using the impurity assessment approach; expanded measurement uncertainties of equal to or less than 0.01 %

Note 1: When preparing calibration solutions from pure metallic elements typically a measurement uncertainty of 0.1 % on the purity is sufficient, because the vast majority of the instrumental techniques for elemental analysis are not capable of providing combined uncertainties at this low level. Only very few examples, such as isotope dilution mass spectrometry in combination with MC-ICPMS or electrochemical techniques both applied to the quantification of high purity solutions, can achieve measurement uncertainties at this level or below

Note 2: Many NMIs/DIs use external laboratories with specialised facilities for some aspects of metal purity assessment. It is recommended that for case 3 other NMIs/DIs with appropriate CMCs are used as external partners. For case 1 & 2 it is often satisfactory to use commercial subcontractors as their measurements make a negligible contribution to the overall uncertainty.

Note 3: For case 1 & 2 it is obvious that less effort will usually be undertaken as for case 3. Therefore, the work has to be clearly focused on the uncertainty level required by the NMI/DI for performing their specific analytical tasks or for providing service to customers. For selecting the critical / major impurities of course expert knowledge and / or additional information, e.g. analysis report from the material provider, may be used.

Note 4: It has to be considered, that for case 1 the produced calibration solution is assayed directly, in contrast to case 2 and 3, where the solid material is analysed. Therefore, impurities only affecting the mass of the pure metallic element, such as surface oxygen, do not affect the final result, the mass or amount content in the solution. All impurities affecting the direct quantification (e.g. coulometry, EDTA titrimetry) lead to a bias in the final result, the mass or amount content in the solution.

Note 5: In the purity determination using the impurity assessment approach many assumptions are used. To account for inaccuracies with those assumptions use of conventional uncertainty estimates is suggested as an alternative. The suggested conventional uncertainty estimates are based on the BAM approach for purity determination, which in essence is the basis for the impurity assessment approach for uncertainties of equal to or less than 0.01 %.

Note 6: Case 3 is recommended when primary pure substances are intended to be characterized.

Note 7: A roadmap on the purity determination of binary inorganic compounds will be collated separately.

Note 8: The guidance which follows for each of the three cases offers suggestions based on the experience of the IAWG participants. The suggestions are not intended as a protocol and other suitable approaches may be used if preferred.

Case 1. Purity determination of pure metallic elements to be used for calibration solutions using the metal assay approach with expanded uncertainties typically above 0.05 %

1) The direct approach is applicable for relative standard uncertainties of ≥ 0.05 % for the purity statement.
2) Analytical methods, which can be used are e.g. EDTA titrimetry or coulometry.
3) Select a suitable specimen of the element under investigation with sufficiently high purity. This high purity element should fulfil the following requirements:
    a. Metallic purity of (preferably) better than 0.999 kg/kg.

   b. Suitable price of the material.

4) Define an etching or other cleaning procedure for removing the surface layer containing oxidation products and adsorbed impurities.

5) Perform a first screening of the material, e.g. using GDMS and/or ICPMS, and identify the major impurities and their homogenous/inhomogeneous distribution in the material.

6) Quantify those impurities which interfere with the analytical method applied (e.g. EDTA titration) and are above 5 mg/kg according to the screening.

7) For interfering impurities significantly above 100 mg/kg the use of higher order calibration approaches is advised such as standard addition or isotope dilution mass spectrometry. Alternatively, two independent analytical techniques may be applied instead.

8) Calculate the relative contribution to the assay of the metal based on the impurities found and the conditions of the assay.

9) Provide the molar mass or the atomic weight of the element. In case isotope variations occur and the atomic weight of the element differs from that listed in the IUPAC tables or in case the IUPAC tables only list an interval for the atomic weight, it is recommended to determine the atomic weight, because many user work with mass fraction instead of amount of substance concentration. This mainly applies for elements such as Li, B and Pb.

   Note: The molar mass of an element X can be obtained from the IUPAC listed atomic weight $A_r(X)$, more exactly the relative atomic mass, by the following equation:

   $M(X) = A_r(X) \cdot M_u$

   with M_u being the molar mass constant with its exact value of $1 \cdot 10^{-3}$ kg mol^{-1}. Thus, the relative atomic masses can be directly converted into the molar masses without changing their values and uncertainties.

10) Make all treatment, measurements and calculations transparent and document them. Optionally, a report on the whole purity determination might be produced.

Case 2. Purity determination of pure metallic elements using the impurity assessment approach; expanded measurement uncertainties above 0.01 %, but less than 0.1 %

1) For achieving relative standard uncertainties between 0.1 % and 0.01 % for the purity statement, the impurity assessment approach is highly recommended.

2) Select a suitable specimen of the element under investigation with sufficiently high purity. This high purity element should fulfil the following requirements:

   a. Total purity of (preferably) better than 0.999 kg/kg.

   b. The material should offer a low surface-to-volume ratio to reduce the amount of adsorbed gases and the degree of oxidized surface material: compact materials such as bars or ingots are recommended.

Note: Some compact materials may contain higher mass fractions of impurities such as oxides, depending on the production technique: an example for this are spheres which are produced by rolling a metal sheet into a ball or sphere.

c. Powders are not suitable due to the large surface leading to high oxide levels.

d. Stability of the material.

e. Suitable price of the material

3) Define an etching or other cleaning procedure for removing the surface layer containing oxidation products and adsorbed impurities.

4) Perform a first screening of the material, preferably with GDMS or with ICPMS after dissolution, and identify the major impurities.

5) Make an approximate estimate on the homogeneity of the material based on point 4.

6) Quantify the individual impurities in the pure metallic element:

   a. Apply analytical procedures offering detection limits in the solid metal preferably below 40 mg/kg for the major non-metals and metalloids (H, C, N, O, S, Si) and below 1 mg/kg for metals.

   b. Quantify all impurities with mass fractions present above the detection limit.

   Note: Point 6b focuses on mass fractions in the medium (H, C, N, O, S, Si) or low mg/kg range. For analytical procedures offering detection limits far below the values mentioned in point 6a, upper limit values may be estimated for the range in between (see points 8a and 8d) in order to save resources.

7) Whenever the measured mass fraction of a single impurity and its associated uncertainty compromises the target uncertainty of the purity statement:

   a. The use of higher order calibration approaches is advised such as standard addition or isotope dilution mass spectrometry.

   b. Alternatively, two independent analytical techniques may be applied instead.

   c. Relative standard uncertainties of several percent are sufficient in most cases.

   Note: The homogeneity of impurities in the mg/kg range in high purity metals may be worse than those typically obtained in matrix reference materials. Thus, it makes no sense to obtain very small uncertainties, because the sample analysed might not be a representative sample at such low uncertainty levels.

8) Calculation of the purity and its associated uncertainty:

   a. For impurities with mass fractions below the LOD or where an upper limit value is reported, it is suggested to estimate an amount with an associated uncertainty as follows. A mass fraction of half of the LOD/upper limit value should be assumed. For the uncertainty, a rectangular distribution can be assumed and the uncertainty can be calculated as:

   $$U = \frac{k \cdot LOD}{2\sqrt{3}}$$

   Alternatively, a conventional approach with a relative expanded uncertainty of 100 % can be applied.

   b. Mass fractions of impurities above the LOD are taken unchanged with their associated uncertainty. A conventional approach with a minimum expanded uncertainty of 30 % might be applied alternatively.

   c. For mass fractions obtained with higher order calibration approaches or at least two methods the individually calculated uncertainty is taken.
   d. For impurities not quantified by measurement, but by expert knowledge/best state of knowledge upper limit values shall be estimated and treated as described in 8a.
   e. Finally, all impurity values are summed up and are subtracted from 1 kg/kg. The uncertainty is calculated accordingly.

9) Provide the molar mass or the atomic weight of the element to the user. In case isotope variations occur and the atomic weight of the element differs from that listed in the IUPAC tables or in case the IUPAC tables only list an interval for the atomic weight, the atomic weight has to be determined. This mainly applies for elements such as Li, B and Pb.

   Note: The molar mass of an element X can be obtained from the IUPAC listed atomic weight $A_r(X)$, more exactly the relative atomic mass, by the following equation:

   $M(X) = A_r(X) \cdot M_u$

   with M_u being the molar mass constant with its exact value of $1 \cdot 10^{-3}$ kg mol^{-1}. Thus, the relative atomic masses can be directly converted into the molar masses without changing their values and uncertainties.

10) Make all treatment, measurements and calculations transparent and document them. Optionally, a report on the whole purity determination might be produced.

Case 3. Purity determination of pure metallic elements using the impurity assessment approach; expanded measurement uncertainties of equal to or less than 0.01 %

1) For the purity determination of pure metallic elements with expanded measurements uncertainties below 0.01 % only the impurity assessment approach assessing all elemental impurities is applicable.

2) Select a suitable specimen of the element under investigation with sufficiently high purity. This high purity element should fulfil following requirements:
   a. Total purity of (preferably) better than 0.999 kg/kg.
   b. The material should offer a low surface-to-volume ratio to reduce the amount of adsorbed gases and the degree of oxidized surface material: compact material such as bars or ingots are recommended.

   Note: Some compact materials may contain higher mass fractions of impurities such as oxides, depending on the production technique: an example for this are spheres which are produced by rolling a metal sheet into a ball or sphere.

   c. Powders are not suitable due to the large surface leading to high oxide levels.
   d. Stability of the material.
   e. Suitable price of the material.

3) Define an etching or other cleaning procedure for removing the surface layer containing oxidation products and adsorbed impurities.

4) Perform a first screening of the material, preferably with GDMS or with ICPMS after dissolution, and identify the major impurities.

5) Get a rough estimate on the homogeneity of the material based on point 5.

6) Quantify or assess all individual impurities in the pure metallic element:

   a. With analytical procedures offering detection limits preferably below 40 mg/kg for the major non-metals and metalloids (H, C, N, O, S, Si) and below 1 mg/kg for metals

   b. Include a measurement or assessment for all 91 elemental impurities.

7) Whenever the measured mass fraction of a single impurity and its associated uncertainty compromises the target uncertainty of the purity statement:

   a. The use of higher order calibration approaches is advised such as standard addition or isotope dilution mass spectrometry.

   b. Alternatively, two independent analytical techniques may be applied instead.

   c. Relative standard uncertainties of several percent are sufficiently low in most cases.

   <u>Note:</u> The homogeneity of impurities in the mg/kg range in high purity metals may be worse than those typically obtained in matrix reference materials. Thus it makes no sense to obtain very small uncertainties, because the sample analysed might not be a representative sample at such low uncertainty levels.

8) Calculation of the purity and its associated uncertainty:

   a. For impurities with mass fractions below the LOD or where an upper limit value is reported, it is suggested to estimate an amount with an associated uncertainty as follows. A mass fraction of half of the LOD/upper limit value shall be assumed. For the uncertainty, a rectangular distribution can be assumed and the uncertainty can be calculated as:

   $$U = \frac{k \cdot LOD}{2\sqrt{3}}$$

   Alternatively, a conventional approach with a relative expanded uncertainty of 100 % can be applied.

   b. Mass fractions of impurities above the LOD are taken unchanged with their associated uncertainty. A conventional approach with a minimum expanded uncertainty of 30 % might be applied alternatively.

   c. For mass fractions obtained with higher order calibration approaches or at least two methods the individually calculated uncertainty is taken.

   d. For impurities not quantified by measurement, but by expert knowledge/best state of knowledge upper limit values shall be estimated and treated as described in 8a.

   e. Finally, all impurity values are summed up and are subtracted from 1 kg/kg. The uncertainty is calculated accordingly.

9) Check the isotopic composition of the pure material, whether isotopic variations occur. When the material corresponds to the IUPAC listed isotopic composition, include the corresponding molar mass in the certificate and provide it to the user. Provide the molar mass or the atomic weight of the element to the user. In case isotope variations occur and the atomic weight of the element differs from that listed in the IUPAC tables or in case the IUPAC tables only list an interval for the atomic weight, the atomic weight has to be determined and it has to be noted explicitly that

the material has a specific isotopic composition and that the molar mass differs from that listed by IUPAC. This mainly applies for elements such as Li, B and Pb.

Note: The molar mass of an element X can be obtained from the IUPAC listed atomic weight $A_r(\mathrm{X})$, more exactly the relative atomic mass, by the following equation:

$M(\mathrm{X}) = A_r(\mathrm{X})\cdot M_u$

with M_u being the molar mass constant with its exact value of $1\cdot10^{-3}$ kg mol^{-1}. Thus, the relative atomic masses can be directly converted into the molar masses without changing their values and uncertainties.

10) Make all treatment, measurements and calculations transparent and produce a report on the whole purity determination.

Appendix 1: List of all 91 impurities to be measured or assessed, when applying case 3 , plus 6 transuranium elements; for case 1 and 2 the list of elements to be measured or assessed strongly depends on the individual application

“X” means preferable measured or assessed respectively

Element	Measurement	Assessment	Comment	Element	Measurement	Assessment	Comment
H	X			Sb	X		
He		X	noble gas	Te	X		
Li	X			I	X	X	halogen
Be	X			Xe		X	noble gas
B	X			Cs	X		
C	X			Ba	X		
N	X			La	X		
O	X			Ce	X		
F	X	X	halogen	Pr	X		
Ne		X	noble gas	Nd	X		
Na	X			Pm		X	radioactive
Mg	X			Sm	X		
Al	X			Eu	X		
Si	X			Gd	X		
P	X			Tb	X		
S	X			Dy	X		
Cl	X	X	halogen	Ho	X		
Ar		X	noble gas	Er	X		
K	X			Tm	X		
Ca	X			Yb	X		
Sc	X			Lu	X		
Ti	X			Hf	X		
V	X			Ta	X		
Cr	X			W	X		
Mn	X			Re	X		
Fe	X			Os	X		
Co	X			Ir	X		
Ni	X			Pt	X		
Cu	X			Au	X		
Ga	X			Hg	X		
Ge	X			Tl	X		
As	X			Pb	X		
Se	X			Bi	X		
Br	X	X	halogen	Po		X	radioactive
Kr		X	noble gas	At		X	radioactive
Rb	X			Rn		X	radioactive
Sr	X			Fr		X	radioactive
Y	X			Ra		X	radioactive
Zr	X			Ac		X	radioactive
Nb	X			Th	X		radioactive
Mo	X			Pa		X	radioactive
Tc		X	radioactive	U	X		radioactive
Ru	X			Np		X	radioactive
Rh	X			Pu		X	radioactive
Pd	X			Am		X	radioactive
Ag	X			Cm		X	radioactive
Cd	X			Bk		X	radioactive
In	X			Cf		X	radioactive
Sn	X						