Guidelines for Chemical Analysis

Determination of the Elemental Content of Environmental Samples using ICP-MS

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**Guidelines for sampling, transport, storage and chemical characterisation
of environmental and human samples**
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1 German Environmental Specimen Bank

The German Environmental Specimen Bank (ESB) is an instrument for the monitoring of the environment. It is in the responsibility of the Federal Ministry for the Environment, Nature Protection and Reactor Safety (BMU) and technically and administratively coordinated by the Federal Environment Agency (Umweltbundesamt). The ESB collects ecologically representative environmental specimens as well as human samples, stores them and examines the archived material for environmental relevant substances.

The long-term storage is performed under conditions that exclude a change of state or a loss of chemical characteristics as far as possible during a period of several decades. By this means the archive provides specimens for a retrospective monitoring of such substances, whose hazard potential for the environment or human health are not yet known.

Comprehensive information on the German ESB is available at www.umweltprobenbank.de (English language pages available).

2 General information

This guideline for determining the elemental content of environmental samples by means of mass spectrometry following ionisation in inductively coupled plasma (ICP-MS: inductively coupled plasma mass spectrometry), describes a process for quantifying the dissolved elements arsenic, lead, cadmium, chromium, cobalt, copper, nickel, selenium and thallium in digests of plant and animal sample material. They can also be used for determining the content of other elements detectable by means of ICP-MS in biological and environmental samples.

This guideline is a continuation of the process guidelines developed by the German Environmental Specimen Bank (ESB) for analysing digests of environmental samples (UMWELTBUNDESAMT 1996). It includes references from DIN EN ISO 17294-2 (2005): ‘Water Quality – Use of Inductively Coupled Plasma Mass Spectrometry – Part 2: Determination of 62 Elements’ which is used for analysing acidic aqueous solutions (e.g. acidified drinking water, waste water and other water samples, as well as *aqua regia* extracts from soils and sediments).

3 Field of application

This guideline describes the procedure for examining digestions of environmental samples by means of ICP-MS. In the program of analysis pursued by the Environmental Specimen Bank, this guideline is regularly used for samples of the following types: bladder wrack, blue mussels, eel pout (muscle tissue and liver), herring gull eggs, zebra mussels, bream (muscle tissue and liver), spruce shoots, pine shoots, poplar leaves, beech leaves, earthworm, roe-deer liver, feral pigeon eggs. However no direct detection of selenium in bladder wrack is possible due to interferences. The use of the hydride generation method for analysis is possible (see separate ESB guideline). In the case of low arsenic and selenium contents in plant samples, analyses may also be distorted by interference. As an alternative, the hydride generation method may also be used here.

The method described below can also be applied to other biological sample types. Where samples are used for which no empirical data are yet available, a suitable validation process should be used before applying the method routinely (see section 7.6).

The lower range of application of the process described depends on the matrix in use and the errors connected therewith. For most elements this is between 1 ng/g (0.001 µg/g) and 0.1 µg/g (with reference to dry mass). With elements where interference may occur during analysis or which are liable to carry-over, the lower range of application may be higher.

For pure aqueous solutions (e.g. drinking water) the lower limits of the range stated in table 1 apply. The lower limits of the range converted for digested solid matter samples are also stated in the table. With digests of biological samples the lower limits of the range of application may be higher depending on the solid content and the completeness of digestion (i.e. reduction of carbon content).

4 Description of method

By standard mass spectrometry with inductively coupled plasma (ICP-MS) it is possible to detect and quantify elements in solutions. The solution under analysis is nebulised and the aerosol thus formed transported to a high-frequency plasma in which the analytes are atomised and ionised. The ions are extracted from the high-frequency plasma through a cone and separated according to their mass-charge ratio. Following separation, they are recorded in a detector and the signals created are evaluated by the software. Quantitative determination is possible following calibration with standard solutions since there is a linear relation between the intensity of the ion signals and the concentration of an element.

5 Apparatus

5.1 Vessels for element solutions

The stability of diluted element solutions (both sample and standard solutions) is determined substantially by the material of the vessels used. The suitability of the material for the intended purpose must always be ensured beforehand. For determining elements in the trace range, vessels of glass or polyvinyl chloride (PVC) should not be used. Vessels made of perfluoralkoxy plastics (PFA), hexafluoro-ethylene-propylene (FEP) or quartz glass are more suitable. In many cases, high-density polyethylene (e.g. HDPE vessels which are used for scintillation measurements) and polypropylene may also be used. When they are being re-used, the vessels must be rinsed with nitric acid or ‘steam cleaned’ with boiling concentrated nitric acid in closed systems

5.2 Mass spectrometer

Mass spectrometers with inductively coupled plasma (ICP-MS), suitable for the range 5 to 240 m/z. The resolution within this range must be at least 1 m_r/z (m_r = relative mass of an isotope; z = charge number).

The following components are important for reproducible operation:

- mass flow controller for the nebuliser gas and (if

Table 1: The lowest limit of the field of application achievable for this process for pure aqueous solutions and digested solid matter samples (reference: dry weight).

Element	Isotope	Lowest limit of area of application (concentration in solution)	Lowest level of area of application (concentration in solid matter)§
Arsenic	^{75}As	0.1 µg/L	0.01 µg/g
Lead #	^{206}Pb ^{207}Pb ^{208}Pb	0.01 µg/L	0.001 µg/g
Cadmium	^{111}Cd ^{114}Cd	0.01 µg/L	0.001 µg/g
Chromium	^{53}Cr	0.1 µg/L	0.01 µg/g
Cobalt	^{59}Co	0.01 µg/L	0.001 µg/g
Copper	^{63}Cu ^{65}Cu	0.1 µg/L	0.01 µg/g
Nickel	^{60}Ni ^{62}Ni	0.1 µg/L	0.01 µg/g
Selenium	^{82}Se	1 µg/L	0.1 µg/g
Thallium	^{203}Tl ^{205}Tl	0.01 µg/L	0.001 µg/g

§ Calculation of content in the solid sample on the assumption that 200 mg of solid material is used for the digestion and is then replenished to 20.0 mL.

Since the lead-isotope conditions in the environment vary, the concentrations of all three Pb isotopes should be determined and the average value then calculated.

possible) also for the auxiliary and cooling gas;

- nebulising system with controlled low-pulsation pump;

- Argon, minimum purity 99.99 %.

6 Reagents

6.1 General notes

All chemicals used must be suitable for trace analysis. The digestion reagents must be of at least high-purity quality. Even better qualities are available for ultra-trace analysis. The reagents should be selected to ensure that the content of the element to be determined or interfering elements should be negligible in relation to the lowest element concentration to be determined.

If possible, nitric acid should always be used as preservation and digestion reagent as this minimises interference by polyatomic ions (see section 8.2.2).

NOTE: For element analysis carried out for the Environmental Specimen Bank, reagents (e.g. nitric acid) of 'suprapur' and 'ultrapur' qualities are used (supplier: Merck, Darmstadt). As an alternative, acid produced in-house by sub-boiling may also be used. Every charge is analysed to determine the content of the elements being analysed.

6.2 List of reagents

6.2.1 Water from a high-purity water system, Quality: specific resistance > 18.2 MΩ cm.

6.2.2 Nitric acid, $\rho(HNO_3) > 1.39$ g/mL ($\geq$ 65 %).

6.2.3 Diluted nitric acid (2.8 %), $c(HNO_3) = 0.5$ mol/L.

6.3 Element stock solutions

Commercially available solutions of the elements As, Cd, Co, Cr, Cu, Ni, Pb, Se, Tl (for each 1000 mg/L), as single or multi-element standard solutions, are used. The solutions are usable for several years. The shelf life stated by the manufacturer should always be observed. Only standard solutions with certificate should be used

6.4 Standard solutions 'internal standard'

The choice of the internal standard to be used depends on the task in question. For example, the elements In, Lu, Re, Rh and Y are suitable. An element should be selected which is in the average mass range of the elements being analysed and which occurs in the samples only in negligible concentrations.

NOTE: For the analysis of ESB samples, rhodium is taken as the internal standard. The solution is added to each sample and standard solution during the online measurement. The concentration of rhodium in the solution added is 10 µg/L in each case.

6.5 Multi-element standard solutions

The concentration of the elements in the standard solutions should be selected to ensure that the working range is covered. If necessary, further elements should be added to adapt the reference solution to the sample matrix.

The shelf life of diluted element solutions (1 to 100 µg/L) is limited. These should be replaced at regular intervals, and at the latest, every three months. Where solutions with low concentrations are required, these should be prepared freshly each day.

NOTE: For the analysis of samples for the Environmental Specimen Bank, multi-element standard solutions are used which are either purchased externally or prepared from single-element standards of the elements arsenic, lead, cadmium, chromium, cobalt, copper, nickel, selenium and thallium. Depending on the element, the lowest concentration is between 1 µg/L and 1 mg/L. To prepare the actual standard solutions, the solutions are diluted before the measurement on the day they are required.

6.6 Optimisation solution

An optimisation solution is used to test the mass calibration of the mass spectrometer and optimise the apparatus conditions. The purpose of optimisation is to achieve the maximum sensitivity of the mass spectrometer and keep the formation of oxides and double-charged ions to a minimum. For this reason, the optimisation solution contains elements of different masses which form oxides and double-charged ions at different rates. The element concentrations should be high enough to ensure that the impulse rates are between 10,000 and 100,000 impulses per sec. Always observe the instructions of the manufacturer on optimising the unit.

NOTE: To set the mass spectrometer for the analysis of ESB samples, an optimisation solution containing the following elements is used: Co, Ce, Tl, Y.

6.7 Chemical blank solutions

0.5 mol/L nitric acid (see 6.2.3) is used as chemical blank solution.

7 ICP-MS measurement procedure

7.1 General notes

Mass spectrometers with inductively coupled plasma (ICP-MS) have a linear relationship several times the power of ten between the impulse rates measured and the concentration of an element. This means that quantification by means of external calibration with one straight reference line is possible. The calibration should be adjusted to the working range in question. Even for the lowest concentration values, sufficient measuring sensitivity and reproducibility must be assured

7.2 Preparation of the unit

The ICP-MS should be started and set in accordance with the instructions of the manufacturer. To ensure sufficient stability of the plasma, it should be started up at least half an hour before the measuring operation. An optimisation solution (see 6.6) is used to check the unit with regard to resolution, mass calibration, sensitivity and stability of the signal. In case of interferences (high rates of oxide formation, formation of double-charged ions) the settings are varied to reduce the disturbances as far as possible.

The masses of the elements being analysed are entered and relevant mathematical corrections selected (for As, see section 8.2.2). Should the concentrations of the measurement solutions vary strongly, the rinsing times may be increased.

7.3 Calibration of the ICP-MS system

Calibration is carried out on a daily basis using the appropriate program options of the apparatus. For each element being analysed, one straight calibration line with at least four concentrations should be determined (multi-element standard solutions to 6.5). One reagent blank solution is also measured in each case. For each measurement, at least three measurements are carried out automatically by the unit and then averaged.

The quality of the calibration function within the working range should be verified. The coefficient of correlation r should be > 0.995. Should r < 0.995 and the calibration still be used, the reason must be explicitly stated (e.g. calibration in the lowest application range of the method and resulting higher measurement uncertainty).

The correctness of the calibration is verified with an aqueous certified reference sample.

7.4 Measurement of digestion solutions

Following calibration of the mass spectrometer, the digestion solutions can be analysed. The correctness of the calibration is verified regularly. After analysing about 20 samples, an aqueous certified reference sample is also analysed. If the deviations from the target value are > 20% in the range up to five times the limit of quantification, the unit should be recalibrated. Reagent blank solutions are also measured at regular intervals to detect any possible carry-over.

7.5 Internal standard

During ICP-MS analysis, an internal standard (generally rhodium) is added online to each

Table 2: Selection of available reference materials

Designation	**Code**	**Certified by**	**Certified for (e.g.)**
Beech leaves	CRM 100	CRM	Ca, Cr, K, Mg
Spruce needles	CRM 101	BCR	Ca, Fe, Mg, Mn,
Cod muscle tissue	CRM 422	BCR	As, Cd, Cu, Pb, Se
Poplar leaves	GBE 07604	Institute of Geophysical and Geochemical Exploration (Langfang, China)	As, Cu, Cr
Mussel tissue	NIST 2976	NIST	As, Cd, Cu, Pb, Se
Powdered egg	NIST 8415	NIST	Ca, K, Mg, Mn
Bovine liver	NIST 1577b	NIST	Cd, Ca, Cu, Pb
Catfish liver	DOLT-2	National Research Council Canada	As, Cd, Co
Pine needles	NIST 1575a	NIST	Cd, Cu, As, Se
Sea lettuce (algae)	CRM 279	BCR	As, Cd, Cu, Pb, Se

sample and standard solution (see section 6.4).

7.6 Validation of method

For method validation, standard addition tests can be carried out. Different concentrations of the element being determined (e.g. approx. 50% and 100% of the concentration anticipated in the sample) are added to two parts of that sample. These partial samples along with a further partial sample (without addition of the element) are then analysed. By extrapolating the straight lines (measurement signal as linear function of the mass concentration of the analysis element) it is now possible to determine the original concentration of the sample. This procedure is described in detail in the German standard DIN 32633.

Another means of method validation is the analysis of a certified reference material.

NOTE: For the analysis of ESB samples, the ratio of digestion solutions to quality-assurance samples is always 2:1 at the most. Table 2 shows a selection of the reference materials used for element analysis of ESB samples.

With concentrations substantially above the limit of quantification, it is also possible to use the dilution method as a test method. To do this, a sample is first analysed in the undiluted state and then in the diluted state by a factor of between 5 and 10. If no interference occurs, the results converted for the original solution should be identical with due consideration of measurement uncertainty. The criterion of quality is a concordance of 100 $\pm$ 10 %.

For method validation, at least the following process parameters should be determined:

Selectivity / specificity: these are met if the amount measured for the chemical blank value is less than the lowest validated concentration.

Reproducibility: the reproducibility is calculated from the relative standard deviation (S_{rel}) of the recovery data of the reference materials. This condition is fulfilled if the following applies: $S_{rel} <$ 10 % ($n \geq 5$).

Lowest limit of measuring range: the lowest limit of the method is the calibration point for which the signal-noise ratio is no less than 6:1.

Limit of detection / limit of quantification: The limit of detection is calculated from reagent blank analyses (DIN 32645: blank-test method, quick estimate). The limit of quantification is produced by multiplying the detection limit by a factor of 3.

8 Interferences

8.1 General

In exceptional cases, the measurement may be affected by spectral or non-spectral interference. The most important causes are mass-coincidences and physical interference by the sample matrix. The most common spectral interferences of the isotopes concerned here are listed in table 3. In order to identify interferences, several isotopes of one element should be analysed wherever possible. Should this not be possible, under some circumstances mathematical correction of the disrupted measurement signal is possible. Drifting and fluctuation of intensities can be adjusted by means of internal standards. In order to avoid physical and spectral interference, the proportion of dissolved solids and the acid content should not exceed 3%.

Many types of interferences can be avoided by usage of a high-resolution ICP mass spectrometer or collision cell technology.

8.2 Spectral interferences

8.2.1 Interference by isobaric elements

Interference of this kind occurs where there are isobaric elements which cannot be isolated by mass spectrometers with low resolutions (e.g. ^{114}Cd and ^{114}Sn). Interferences by isobaric elements can be corrected mathematically (available as option in the software of modern ICP-MS units). However, this depends on the interference-free measurement of another isotope of the interfering element. With regard to the elements under consideration here, the following types of interference by isobars may occur: ^{114}Cd (by ^{114}Sn), ^{58}Ni (by ^{58}Fe).

8.2.2 Interference by poly-atomic ions

Poly-atomic ions may be created by the encounter of constituents of the plasma gas, reagents and the sample matrix (e.g. interference in determining ^{75}As by ^{40}Ar^{35}Cl and ^{40}Ca^{35}Cl or ^{77}Se caused by ^{40}Ar^{37}Cl). Such interference can be corrected in the same way as interference caused by isobars (see section 8.2.1). The elements As, Cr and Ni are often subject to interference by poly-atomic ions. For each series of analyses it should be ascertained whether interference by poly-atomic ions is likely. This applies particularly to low concentrations. For the elements concerned here, the most important types of interference are listed in table 3.

If a mathematical adjustment is being made, it should be remembered that interference can be due to the composition of the plasma as well as the concentration of interfering elements. Possible ways of calculating adjustments on the basis of signal intensities and mass concentrations are described in the standard DIN EN ISO 17294-2.

NOTE: In the analysis of samples for the Environmental Specimen Bank, equations are used for adjusting the element As which are described in U.S. EPA methods (EPA METHOD 200.8, 1994 and EPA METHOD 6020, 1994).

8.2.3 Interference by double-charged ions

Another source of interference are the double-charged ions which may be created under plasma conditions. These are of importance for elements with low secondary ionisation energy such as Ba. The ration of relative mass to charge creates a false signal at half the isotope mass of the interfering element (e.g. ^{69}Ga^{+} by ^{138}Ba^{2+}). To reduce this effect, an upper limit of 3% for the ratio of m/z 70 (Ce^{2+}) to m/z 140 (Ce^{+}) is fixed when the apparatus settings are being optimised.

If possible, such interference should be prevented by selecting a non-interfered isotope (or carrying out an adjustment in the same way as that described in section 8.2.2). However, this type of interference is usually not significant for elements under consideration here.

8.3 Non-spectral interferences

8.3.1 Interference by carry-over

Residues in the sample-infeed unit or in the inlet system of the mass spectrometer may cause carry-over in the analyses of subsequent samples (‘memory effect’). Where there are significant differences in concentration within one series of measurements, an adequate rinsing time should be set and checks carried out by means of reagent blank solutions.

8.3.2 Interference through deposits

Where the solutions contain high concentrations of salts, deposits may form in the sample-infeed system, in particular in the inlet system (cone) of the mass spectrometer, which then could cause an interference. In such cases, the apparatus should be thoroughly cleaned. Wherever possible, the solutions should be diluted to avoid such problems.

8.3.3 Interference through physical properties of the analysis solution

Differences in the physical characteristics of the analysis solutions (e.g. viscosity) may affect the infeed of the sample and cause distortions through increased or decreased signal intensities. The use of an internal standard (see 7.5) may compensate for this kind of interference. Alternatively, matrix-adjusted standard solutions may also be used or measurements carried out with standard additions. Where an element has several isotopes, isotope-dilution analysis can also be applied.

Table 3: Spectral interferences according to DIN EN ISO 17294-2 (2005) and other sources.

Element	**Isotope**	**Interferences by poly-atomic ions**	
Arsenic	$^{75}\mathrm{As}$	$^{40}\mathrm{Ar}^{35}\mathrm{Cl}$, $^{40}\mathrm{Ca}^{35}\mathrm{Cl}$	
Lead	$^{206}\mathrm{Pb}$	$^{171}\mathrm{Yb}^{35}\mathrm{Cl}$, $^{205}\mathrm{Tl}^{1}\mathrm{H}$	(Lit. 1)
	$^{207}\mathrm{Pb}$	$^{170}\mathrm{Er}^{37}\mathrm{Cl}$, $^{206}\mathrm{Pb}^{1}\mathrm{H}$	
	$^{208}\mathrm{Pb}$	$^{171}\mathrm{Yb}^{37}\mathrm{Cl}$, $^{207}\mathrm{Pb}^{1}\mathrm{H}$	
Cadmium	$^{111}\mathrm{Cd}$	$^{95}\mathrm{Mo}^{16}\mathrm{O}$, $^{94}\mathrm{Mo}^{16}\mathrm{O}^{1}\mathrm{H}$	
	$^{114}\mathrm{Cd}$	$^{98}\mathrm{Mo}^{16}\mathrm{O}$, $^{97}\mathrm{Mo}^{16}\mathrm{O}^{1}\mathrm{H}$	
Chromium	$^{52}\mathrm{Cr}$	$^{40}\mathrm{Ar}^{12}\mathrm{C}$, $^{35}\mathrm{Cl}^{16}\mathrm{O}^{1}\mathrm{H}$	
	$^{53}\mathrm{Cr}$	$^{37}\mathrm{Cl}^{16}\mathrm{O}$, $^{36}\mathrm{Ar}^{16}\mathrm{O}^{1}\mathrm{H}$	
Cobalt	$^{59}\mathrm{Co}$	$^{43}\mathrm{Ca}^{16}\mathrm{O}$ (Lit. 1), $^{24}\mathrm{Mg}^{35}\mathrm{Cl}$ (Lit. 1)	
Copper	$^{63}\mathrm{Cu}$	$^{40}\mathrm{Ar}^{23}\mathrm{Na}$, $^{31}\mathrm{P}^{16}\mathrm{O}_2$, $^{26}\mathrm{Mg}^{37}\mathrm{Cl}$	
	$^{65}\mathrm{Cu}$	$^{49}\mathrm{Ti}^{16}\mathrm{O}$ (Lit. 1), $^{23}\mathrm{Na}^{40}\mathrm{Ca}$ (Lit. 1), $^{32}\mathrm{S}^{16}\mathrm{O}_2{}^{1}\mathrm{H}$	
Nickel	$^{58}\mathrm{Ni}$	$^{40}\mathrm{Ca}^{18}\mathrm{O}$, $^{44}\mathrm{Ca}^{14}\mathrm{N}$, $^{23}\mathrm{Na}^{35}\mathrm{Cl}$, $^{24}\mathrm{Mg}^{34}\mathrm{S}$	
	$^{60}\mathrm{Ni}$	$^{44}\mathrm{Ca}^{16}\mathrm{O}$, $^{43}\mathrm{Ca}^{16}\mathrm{O}^{1}\mathrm{H}$, $^{23}\mathrm{Na}^{37}\mathrm{Cl}$	
Selenium	$^{77}\mathrm{Se}$	$^{40}\mathrm{Ar}^{37}\mathrm{Cl}$, $^{36}\mathrm{Ar}^{40}\mathrm{Ar}^{1}\mathrm{H}$	(Lit. 2)
	$^{78}\mathrm{Se}$	$^{40}\mathrm{Ar}^{38}\mathrm{Ar}$, $^{38}\mathrm{Ar}^{40}\mathrm{Ca}$	
	$^{82}\mathrm{Se}$	$^{12}\mathrm{C}^{35}\mathrm{Cl}_2$	
Thallium	$^{203}\mathrm{Tl}$	$^{187}\mathrm{Re}^{16}\mathrm{O}$, $^{163}\mathrm{Dy}^{40}\mathrm{Ar}$	(Lit. 1)
	$^{205}\mathrm{Tl}$	$^{165}\mathrm{Ho}^{40}\mathrm{Ar}$, $^{189}\mathrm{Os}^{16}\mathrm{O}$	

Lit. 1: Agilent (2001); Lit. 2: Taylor (2001).

9 Evaluation

The analysis data are evaluated by the software in the mass spectrometer. The automatic evaluation must be verified for plausibility. During evaluation, the analysis data are calculated in accordance with the mathematical corrections selected and then related to the internal standard. For the purposes of calibration, linear regression is carried out in order to calculate the slope, ordinate intercepts and the coefficients of correlation (r). The concentrations of all the analysis solutions (blank values, aqueous reference materials, digestion solutions) are determined on the basis of the straight calibration lines.

Any dilution operations must also be taken into account in all calculations. It must be possible to reconstruct all the calculations carried out by means of the electronically stored data or by means of archived printouts.

When examining digested samples of solids, the results must refer to the solid (i.e. to dry mass or fresh mass). The concentrations of the elements in the digestion solutions are generally determined by the ICP-MS software. The further calculation of the element contents in the solid matter is done by means of the following equation:

$$\omega_E = V / M * \rho_E * F$$

where:

ω_E	proportion by mass of the element in the solid matter, stated, for example as µg/g;
M	mass of the sample used, stated in mg (e.g. 200 mg);
V	volume to which replenished, stated in mL (e.g. 20.0 mL);
ρ_E	concentration of the element under consideration in the digestion solution, stated for example in µg/L;
F	conversion factor (1 L/mL * mg/g).

10 Statement of results

The results refer to the amount of solid material used (dry mass or fresh mass).

All results should be stated to three significant digits.

EXAMPLES: thallium (Tl) 123 ng/g; arsenic (As) 12.3 µg/g; lead (Pb) 1.23 µg/g; nickel (Ni) 0.123 µg/g.

Measurement results are subject to a degree of uncertainty. In the working range of a method, the measurement uncertainty increases as the concentration in the sample decreases. The degree of uncertainty of a measured value can be determined in a number of ways which are described in the 'ISO Guide to the Expression of Uncertainty in Measurement (GUM)' (ISO, 1995) and guideline 'Quantifying Uncertainty in Analytical Measurement' (EURACHEM/CITAC, 2000). A practical means of determining uncertainty is the so-called Nordtest process (MAGNUSSON ET AL., 2003; Handbook for calculation of measurement uncertainty in environmental laboratories).

NOTE: For the analysis of Environmental Specimen Bank samples, generally six sub-samples from one homogenate are used. The standard deviation of the average value is regarded as the measurement uncertainty of the result. The correctness of the results is verified with the help of certified reference materials. Representative data are given in the appendix.

11 Analysis report

The following data should be documented in the analysis report:

- Reference to this guideline,
- Sample identity,
- Data on preliminary sample treatment and digestion,
- Concentration of the elements in question with reference to the percentage of solid matter (depending on material used, with reference to fresh or dry mass),

- Statement of measurement uncertainty if applicable,
- Data on preliminary treatment of sample and digestion,
- Any deviations from this guideline.

12 Representative analysis results

Representative results of analyses are given in the appendix:

a) Results of the analysis of certified reference materials,

b) Results of the analysis of reference materials from the Environmental Specimen Bank,

c) Results of the analysis of representative samples from the Environmental Specimen Bank.

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Appendix: Representative Analysis Results

a) Results of the analysis of certified reference materials.

Reference material	**Element**	**Certified Content**	**Recovery**	**Comment**
Spruce needles BCR CRM 101	Cr	2.71 µg/g	88 ± 5 (n = 10)	Information value
	Cu	4.90 µg/g	78 ± 5 (n = 11)	Information value
	Cd	0.345 µg/g	82 ± 4 (n = 12)	Information value
	Pb	2.60 µg/g	100 ± 7 (n = 11)	Information value
Beech leaves BCR CRM 100	Cr	7.34 µg/g	98 ± 6 (n = 10)	Certified value
	Co	0.265 µg/g	99 ± 6 (n = 10)	Own average value
	Cd	0.269 µg/g	102 ± 5 (n = 10)	Own average value
	Pb	16.3 µg/g	93 ± 2 (n = 7)	Own average value
	Tl	55.4 ng/g	85 ± 5 (n = 8)	Own average value
	Ni	7.31 µg/g	103 ± 6 (n = 10)	Own average value
	Cu	11.8 µg/g	87 ± 3 (n = 8)	Information value
Poplar leaves GBW07604	As	0.37 ± 0.06 µg/g	85 ± 6 (n = 3)	Certified value
	Co	0.42 ± 0.02 µg/g	113 ± 4 (n = 5)	Certified value
	Cr	0.55 ± 0.05 µg/g	81 ± 3 (n = 6)	Certified value
	Cu	9.3 ± 0.5 µg/g	92 ± 5 (n = 6)	Certified value
	Cd	0.32 ± 0.05 µg/g	101 ± 5 (n = 6)	Certified value
	Ni	1.9 ± 0.2 µg/g	93 ± 3 (n = 6)	Certified value
	Pb	1.5 ± 0.2 µg/g	103 ± 5 (n = 6)	Certified value
Whole egg powder NIST 8415	Cu	2.70 ± 0.35 µg/g	97 ± 5 (n = 10)	Certified value
	Pb	61 ± 12 ng/g	119 ± 11 (n = 8)	Certified value
	Se	1.39 ± 0.17 µg/g	79 ± 4 (n = 7)	Certified value
Sea lettuce (algae) BCR CRM 279	As	3.09 ± 0.20 µg/g	96 ± 9 (n = 6)	Certified value
	Cd	0.274 ± 0.022 µg/g	80 ± 6 (n = 6)	Certified value
	Cr	11.6 µg/g	94 ± 11 (n = 6)	Information value
	Cu	13.14 ± 0.37 µg/g	98 ± 4 (n = 6)	Certified value
	Ni	15.9 µg/g	108 ± 6 (n = 6)	Information value
	Pb	13.48 ± 0.36 µg/g	102 ± 19 (n = 5)	Certified value
	Tl	37.6 ng/g	93 ± 16 (n = 6)	Information value
Mussel tissue NIST 2976	As	13.3 ± 1.8 µg/g	100 ± 8 (n = 20)	Certified value
	Cd	0.82 ± 0.16 µg/g	102 ± 6 (n = 20)	Certified value
	Co	0.61 ± 0.02 µg/g	104 ± 6 (n = 20)	Reference value
	Cu	4.02 ± 0.33 µg/g	102 ± 11 (n = 20)	Certified value
	Ni	0.93 ± 0.12 µg/g	107 ± 17 (n = 18)	Reference value
	Se	1.80 ± 0.15 µg/g	97 ± 9 (n = 15)	Certified value
	Pb	1.19 ± 0.18 µg/g	96 ± 8 (n = 19)	Certified value
Dogfish liver DOLT-3	Cd	19400 ± 600 ng/g	86 ± 9 (n = 70)	Certified value
	Cu	31.2 ± 1.0 µg/g	105 ± 7 (n = 70)	Certified value
	Pb	320 ± 50 ng/g	91 ± 13 (n = 62)	Certified value
Cod muscle tissue BCR CRM 422	As	21.1 ± 0.05 µg/g	89 ± 5 (n = 14)	Certified value
	Cu	1.05 ± 0.07 µg/g	109 ± 11 (n = 11)	Certified value
	Se	1.63 ± 0.07 µg/g	89 ± 5 (n = 14)	Certified value
	Pb	85 ± 15 ng/g	83 ± 12 (n = 12)	Certified value

b) Results of analysis of Environmental Specimen Bank reference materials;
IS UPB – Informationssystem Umweltprobenbank (information system of the German ESB).

Reference material	Element	Content (from IS UPB)	Recovery
Spruce shoots, Warndt (0110/0/0385/02201/0/xxx)	Co	0.55 µg/g	91 ± 5 (n = 5)
	Ni	5.15 µg/g	74 ± 6 (n = 5)
	Cu	4.35 µg/g	83 ± 4 (n = 5)
	Cd	0.27 µg/g	75 ± 5 (n = 5)
	Pb	6.32 µg/g	105 ± 3 (n = 5)
Beech leaves, Bornhöved (0410/0/0893/03103/0/xxx)	Co	0.08 µg/g	75 ± 5 (n = 8)
	Ni	1.04 µg/g	89 ± 8 (n = 10)
	Cu	5.04 µg/g	84 ± 8 (n = 10)
	Cd	0.08 µg/g	75 ± 2 (n = 6)
	Pb	0.85 µg/g	83 ± 4 (n = 10)
Poplar leaves, Völklingen-Werbeln/Velsen (0310/0/0889/02103/0/xxx)	As	0.265 µg/g	95 ± 7 (n = 6)
	Cd	1.26 µg/g	80 ± 3 (n = 4))
	Co	1.40 µg/g	81 ± 3 (n = 5)
	Cu	7.73 µg/g	85 ± 3 (n = 6)
	Ni	2.71 µg/g	97 ± 11 (n = 6)
	Pb	6.46 µg/g	88 ± 5 (n = 6)
Roe-deer liver, Warndt (1021/0/0098/02200/2/xxx)	Cd	1.1 µg/g	93 ± 5 (n = 15)
	Co	0.32 µg/g	95 ± 6 (n = 15)
	Ni	0.07 µg/g	110 ± 16 (n = 7)
	Se	1.19 µg/g	85 ± 5 (n = 14)
Feral pigeon egg content, Saartal (1211/0/0093/02100/0/xxx)	Cu	3.46 µg/g	97 ± 2 (n = 6)
	Pb	408 ng/g	96 ± 6 (n = 6)
	Se	0.98 µg/g	78 ± 6 (n = 4)
Bladder wrack (4000/0/0089/07102/0/xxx)	As	56.36 µg/g	70 ± 2 (n = 6)
	Cd	1.21 µg/g	70 ± 5 (n = 6)
	Co	2.89 µg/g	96 ± 7 (n = 6)
	Cu	3.60 µg/g	105 ± 4 (n = 6)
	Ni	8.10 µg/g	93 ± 4 (n = 6)
	Pb	0.63 µg/g	96 ± 6 (n = 16)
Blue mussel, south of Lister Hafen (4110/0/0086/07102/0/xxx)	As	9.82 µg/g	109 ± 10 (n = 6)
	Cd	0.850 µg/g	94 ± 9 (n = 6)
	Co	0.62 µg/g	94 ± 9 (n = 6)
	Cu	5.32 µg/g	108 ± 9 (n = 6)
	Ni	2.01 µg/g	94 ± 10 (n = 6)
	Pb	1.04 µg/g	95 ± 7 (n = 6)
Zebra mussel, Konstanzer Trichter (3010/0/1092/04101/0/xxx)	As	6.04 µg/g	90 ± 10 (n = 10)
	Cd	1.06 µg/g	91 ± 10 (n = 10)
	Co	0.515 µg/g	90 ± 9 (n = 9)
	Cu	13.4 µg/g	90 ± 10 (n = 8)
	Ni	12.3 µg/g	89 ± 6 (n = 9)
	Pb	0.48 µg/g	78 ± 7 (n = 6)
Eelpout muscle, Darßer Ort (4210/0/0796/06103/0/xxx)	As	2.19 µg/g	84 ± 6 (n = 6)
	Cu	0.843 µg/g	94 ± 5 (n = 6)
	Pb	21.2 ng/g	90 ± 24 (n = 6)
	Se	1.03 µg/g	94 ± 6 (n = 6)

c) Examples of results from representative ESB samples (LOQ - limit of quantification).

Sample	Element	Content (from IS UPB)	Comment
Spruce shoots, Scheyern 2004 0110/0/0304/16101/0/xxx	Cr	0.326 µg/g (n = 6)	
	Co	0.573 µg/g (n = 6)	
	Ni	4.02 µg/g (n = 6)	
	Cu	3.55 µg/g (n = 6)	
	Cd	0.085 µg/g (n = 6)	
	Tl	25.6 ng/g (n = 6)	
	Pb	0.484 µg/g (n = 6)	
Spruce shoots, Dübener Heide 2004 0210/0/0304/11200/0/xxx	Cr	0.750 µg/g (n = 6)	
	Co	0.217 µg/g (n = 6)	
	Ni	2.06 µg/g (n = 6)	
	Cu	3.83 µg/g (n = 5)	
	Cd	0.144 µg/g (n = 6)	
	Tl	18.1 ng/g (n = 6)	
	Pb	0.707 µg/g (n = 6)	
Beech leaves, Solling 2003 0410/0/0803/14102/0/xxx	Cr	0.518 µg/g (n = 6)	
	Co	0.068 µg/g (n = 6)	
	Ni	0.846 µg/g (n = 5)	
	Cu	6.33 µg/g (n = 6)	
	Cd	0.061 µg/g (n = 6)	
	Tl	- (n = 6)	< LOQ
	Pb	0.560 µg/g (n = 6)	
Poplar leaves, Leipzig 2003 0310/0/0803/11111/0/xxx	Cr	0.471 µg/g (n = 6)	
	Co	0.657 µg/g (n = 6)	
	Ni	1.47 µg/g (n = 5)	
	Cu	6.85 µg/g (n = 6)	
	Cd	1.16 µg/g (n = 6)	
	Tl	3.12 ng/g (n = 6)	
	Pb	0.651 µg/g (n = 5)	
Earthworm, Saartal 2003 2211/0/1003/02100/0/xxx	Co	8.16 µg/g (n = 6)	
	Cd	8.77 µg/g (n = 6)	
Bladder wrack, Königshafen 2003 4000/0/0003/07101/0/xxx	Cr	0.947 µg/g (n = 6)	
	Co	1.75 µg/g (n = 6)	
	Ni	5.09 µg/g (n = 5)	
	Cu	3.33 µg/g (n = 6)	
	As	41.3 µg/g (n = 6)	
	Cd	0.479 µg/g (n = 6)	
	Tl	7.87 ng/g (n = 5)	
	Pb	0.689 µg/g (n = 6)	
Blue mussel, Königshafen 2003 4110/0/0003/07101/0/xxx	Co	0.757 µg/g (n = 6)	
	Ni	2.72 µg/g (n = 6)	
	Cu	6.74 µg/g (n = 5)	
	As	16.2 µg/g (n = 6)	
	Se	3.04 µg/g (n = 6)	
	Cd	1.06 µg/g (n = 6)	
	Pb	1.40 µg/g (n = 5)	

Sample	Element	Content (from IS UPB)	Comment
Eelpout muscle, Meldorfer Bucht 2004 4210/0/0504/07202/0/xxx	Cu	0.711 µg/g (n = 6)	
	As	4.86 µg/g (n = 6)	
	Se	0.871 µg/g (n = 6)	
	Tl	- (n = 6)	< LOQ
	Pb	24.1 ng/g (n = 6)	
Herring gull egg content, Trischen 2004 4311/0/0504/07201/0/xxx	Cu	2.77 µg/g (n = 6)	
	As	0.468 µg/g (n = 6)	
	Se	2.59 µg/g (n = 6)	
	Tl	2.68 ng/g (n = 6)	
	Pb	30.7 ng/g (n = 5)	
Zebra mussel, Elbe / Prossen 2003 3010/0/1103/10110/0/xxx	Co	1.06 µg/g (n = 6)	
	Ni	18.9 µg/g (n = 6)	
	Cu	13.5 µg/g (n = 5)	
	As	6.43 µg/g (n = 6)	
	Se	2.89 µg/g (n = 6)	
	Cd	0.456 µg/g (n = 6)	
	Pb	2.46 µg/g (n = 6)	
Bream muscle, Elbe / Prossen 2004 3111/0/0804/10110/0/xxx	Cu	1.26 µg/g (n = 6)	
	As	0.274 µg/g (n = 6)	
	Se	2.28 µg/g (n = 6)	
	Tl	3.74 ng/g (n = 6)	
	Pb	98.5 ng/g (n = 5)	
Bream liver, Elbe / Prossen 2003 3121/0/0703/10110/0/xxx	Cd	1860 ng/g (n = 6)	
	Pb	310 ng/g (n = 6)	
Roe-deer liver, Solling 2003 1021/0/0503/14000/0/xxx	Co	0.218 µg/g (n = 6)	
	Se	0.557 µg/g (n = 6)	
	Cd	0.628 µg/g (n = 6)	
Feral pigeon egg content, Halle 2003 1211/0/0003/11101/0/xxx	Cu	3.11 µg/g (n = 6)	
	Se	0.725 µg/g (n = 6)	
	Pb	213 ng/g (n = 6)	