

Determination of elements by ICP-AES and ICP-MS

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SUMMARY

In cooperation with the Dutch Standardization Institute (NEN) an inventory has been made of existing standards and draft documents on the analysis of elements in relevant environmental matrices by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) and by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS).

Documents have been evaluated for their applicability as a horizontal standard.

From this evaluation draft horizontal standards were prepared for the determination of:

37 elements in aqueous solutions and digests of solids by ICP-AES;

66 elements in aqueous solutions and digests of solids by ICP-MS.

1 INTRODUCTION

This desk study covers an investigation into the potential for horizontal standardization of methods for the determination of elements in acid digests by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) and by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS).

The report contains:

- An evaluation of the potential for horizontal standardization based on existing standards, including the needs and material properties, identification of relevant fields and where possible including waste
- A draft horizontal standard for the determination by ICP-AES of trace elements in aqua regia and nitric acid digests.
- A draft horizontal standard for the determination by ICP-MS of trace elements in aqua regia and nitric acid digests.
- An itemized list of key point for discussion with recommended options.

2 ICP-AES STANDARDS

2.1.1 *List of relevant ICP-AES standards*

All standards and draft standards available from ISO, CEN and NEN using ICP-AES for the determination of elements in environmental matrices are given below:

- ISO 11885:1996 Water Quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy
- NPR 6425:1995 Inductively coupled plasma atomic emission spectrometry, general guidelines (In Dutch)
- NEN 6426:1995 Water – Determination of 40 elements by inductively coupled plasma atomic emission spectrometry (in Dutch)
- EPA Method 6010B:1996 Inductively coupled plasma atomic emission spectrometry

2.2 Description of standards for trace elements by ICP-AES

2.2.1 *ISO 11885:1996 Water Quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy*

ISO 11885 describes the determination of dissolved, particulate and total elements in raw, potable and wastewater. The 33 elements determined include all important trace elements in environmental analysis.

Filtered acidified samples (nitric acid) are analyzed to give dissolved elements; the filtrate is digested consecutively with nitric acid and hydrochloric acid to give particulate elements and the whole sample is digested with nitric acid to give total elements. The standard warns that the total elements procedure may only partially dissolve some elements like silicon, aluminum, tin, titanium and antimony.

Notice that the digestion matrix for the three measurands is not the same.

The technique is based on the measurement of the emission at one wavelength, which is highly selective for a specific element. Calibration matrix should match as much as possible the sample matrix. In practice it means that both acid compositions are the same. If the sensitivity of the element in the sample deviates considerably from that in the calibration matrix standard addition calibration is performed.

The method does not go into detail about calibration and how to minimize interference.

The standard leaves room for all types of ICP-AES instrumentation. There are no instrumental quality requirements.

Quality of data is controlled by quality control requirements:

- Independent calibration solution obtained from an outside source to verify the trueness of the standards applied (deviation less than 5%).
- Check standard after every 25 samples (deviation less than 5%)
- Inter-element and background correction check sample at the beginning, end, and at periodic intervals throughout the sample run (deviation within control limits).

The standard mentions typical detection limits, trueness and precision data:

- All trace elements have detection limits less than 0,1 mg/l.
- Systematic deviations are not significant.
- Coefficients of variation for (interlaboratory)reproducibility are less than 5% except for the alkali metals sodium, potassium, magnesium and calcium and the elements sulfur and vanadium.

2.2.2 NPR 6425:1995 Inductively coupled plasma atomic emission spectrometry, general guidelines (In Dutch)

NPR 6425 is a guideline. It describes:

- Principles of ICP-AES analysis.
- Instrumentation in detail.
- Signal generation, sources of interferences and matrix effects.
- Method development:
 - Wavelength selection, background correction, inter-element correction
 - Optimization of measurement conditions
 - Sample pretreatment.
 - Calibration, including standard addition calibration
 - Analysis
 - Validation
 - Quality control

The guide is meant to set up a measurement procedure. In practice it is the reference of specific measurement standards like NEN 6426.

2.2.3 NEN 6426:1995 Water – Determination of 40 elements by inductively coupled plasma atomic emission spectrometry (in Dutch)

NEN 6426 describes the determination of 40 elements in water, eluates and digests of water and solids. On top of the 33 elements of ISO 11885 seven other elements can be analyzed: cerium, lanthanum, neodymium, praseodymium, samarium and scandium.

The technique is similar to ISO 11885. Additionally, the guide recommends measuring, if possible, at two different wavelengths and using the difference of the measurement results as an indicator for interference.

The standard requires ICP-AES instrumentation equipped with a background correction system. Usually, background correction is included.

The standard refers to NPR 6425 for performance tests and performance limits. The standard does not give instructions for quality control during a run.

The standard mentions typical detection limits all less than 0,1 mg/l. Detection limits are achievable if the response is free of interference.
No data on trueness and precision are given.

2.2.4 EPA Method 6010B:1996 Inductively coupled plasma atomic emission spectrometry

EPA's method 6010B is applicable to 31 elements. Method 6010B mentions on top of the ISO 11885 list of elements mercury and thallium, but lacks bismuth, sulfur, tungsten and zirconium. It is applicable to different types of water, eluates and digests of waste, soil, sludge and sediments.

In principle, the method is similar to ISO 11885. However, it provides extensive information on:

- Interference and matrix effects including quantification and correction procedures.
- Memory effects.
- Setting up instrument parameters (optics, flows, data acquisition)
- Calibration: preparation of solutions, linear calibration functions and non-linear response curves obtained due to ionization and self-absorption.
- Quality control

Method 6010B is open for all computer-controlled ICP-AES instruments equipped with background correction. There are no specific instrumental performance requirements.

Quality of data is controlled by quality control requirements:

- Interference of uncorrected elements shall be less than 20% of the measured value.
- Change of inter-element correction shall be less than 10%. Inter-element correction is recommended for all listed interfering elements that may result in a response higher than the reporting limit.
- Difference between matrix spiked duplicate samples shall be within 20%.
- Post digestion spike recovery shall be between 75% and 125% (required when a new or unusual matrix is encountered).
- Difference between results for the original sample and the fivefold diluted sample shall be less than 10% (alternative test required when a new or unusual matrix is encountered).
- Calibration blank check shall be within 3 times the instrumental detection limit.
- Calibration check standard, at the beginning, end and after every 10 samples, shall be within 10%.
- Method blank (including preparations prior to ICP-AES analysis) required. No acceptance criteria given.

Method 6010B mentions typical detection limits, trueness and precision data:

- All trace elements have detection limits less than 0,05 mg/l.
- Systematic deviations for aqueous samples are not significant (the only deviating result, 20% for selenium, was obtained from only 2 laboratories).
- Systematic deviations for digests of fly ash and electroplating sludge were generally within 20%. Higher systematic deviations were obtained for silver, thallium for both types of sample (AAS results were taken as reference values).
- (Interlaboratory) coefficients of variation were approximately 20%.

2.3 Evaluation

2.3.1 Scope

Four standards have been identified for the determination of elements in relevant environmental samples:

- One ISO standard for water analysis

- Two Dutch standards of which one has the status of guide. Standards are applicable to aqueous samples and digests of other environmental samples.
- One US EPA standard applicable to aqueous samples and digests of other environmental samples.

All standards include important trace elements.

2.3.2 Procedures

The principle of all standards is the same; procedures are very similar. The differences are mainly the techniques to detect and/or minimise interference and the procedures for quality control.

ISO 11885 is only valid for water analysis. Generally, this matrix closely matches the calibration matrix, which means that differences in sensitivity are small and in case of fairly selective wavelengths also interference will be small.

Both NPR 6425/NEN 6426 and EPA method 6010B require actions to detect and correct for interferences, which may be substantial for waste, sludge and eluates. Both describe inter-element corrections for interfering elements detected during validation. These correction equations are updated every run. If no corrections are applied EPA requires verification of absence by analysis of an interference check sample. NPR 6425 recommends the routine analysis at two different wavelengths, where a substantial difference between the two results indicates interference. Unfortunately, a second selective and sensitive wavelength is not always possible. Both NPR 6425/NEN 6426 and EPA method 6010B require detection of matrix effects, by either additional analysis of a diluted sample or by recovery of a post digestion spike. Actions are matrix matching or standard addition calibration.

EPA method 6010B is very practically oriented. As a guide, NPR 6425 is more procedural and has a wider scope than water and digests. NEN 6425 is brief. It mentions essentials about water and digests analysis and refers to NPR 6426 to set up the procedure and work out problems during analysis. Remarkably, potential interferences are not listed.

NPR 6425 warns not to use ordinary (unweighted) linear regression in case of multilevel calibration solutions. Because the spread is highly concentration dependent and usually the operational range of ICP-AES methods is large, the intercept calculated from calibration data has a much higher spread than expected from the spread of blanks. This problem of statistical nature is not tackled in the other standards.

2.3.3 Equipment

All standards require standard ICP-AES instrumentation. Only ISO 11885 does not require background correction, which is generally not necessary for water samples. Modern ICP-AES instruments are all equipped with a background correction system.

2.3.4 Quality Control

All standards require:

- Control of drift (calibration blank and calibration standard checks), every 10 to 25 samples.
- Method blank.
- Interference detection (check on inter-element correction factor).
- Recovery of post digestion matrix spike.

All mentioned quality control measures are useful. No additional checks are necessary. The magnitude of the five-fold dilution criterion (10%) in the EPA method is much more stringent than the $\pm 25\%$ criterion for recovery deviation. The value is the same as the 10% maximum de-

viation for the calibration check sample. 20% instead of 10% would be more in line with the recovery criterion.

2.4 Critical points and recommendations

2.4.1 Methodology

There are no conflicting approaches in the standards.

2.4.2 Scope of the method

Results of an interlaboratory comparison of EPA's method 6010B have shown that acceptable results can be obtained analysing solid waste digests (Coal fly ash and electroplating sludge). Other matrices concerned are as difficult or easier than the one analysed.

There is no reason not to draft a standard for water and digests of the following origin: water, eluates and digests of water, eluates, waste, soil, sludge and sediments.

The 30 elements given in ISO 11885 plus thallium, scandium and the rare earth elements cerium, lanthanum, neodymium, praseodymium and samarium can be taken into the draft standard.

2.4.3 Procedure and quality control

The normal ICP-AES procedure can be used. However, more attention must be given to the control of interference and matrix effects. It is the most critical point because of the possible variability of the matrix.

Quality control can be the same as summarised in 2.3.4.

2.4.4 Calibration

Attention must be paid to the limited application of ordinary linear regression in case of linear relationships and a large measurement range (see last paragraph of 2.3.2. As weighted linear regression is uncommon, alternative approaches must be introduced:

- Two point calibration and linearity check
- Multipoint calibration and ordinary linear regression forced through blank value
- Multipoint calibration and ordinary linear regression forced through zero combined with a check on the absence of a blank value.

In this respect also guidance should be given to non-linear calibration lines (EPA method 6010B).

2.5 Recommendation

Recommended for discussion:

- Stronger emphasis on interferent corrections and quality control related to (residual) interferences and matrix effects.
- The coverage and the magnitude of the quality control criteria.
- More flexibility in selecting own concentration levels of calibration. require 'range covered' and 'minimum number of levels and replicates).
- Dangers of applying ordinary linear regression in case of an large measurement range.

Recommend for action:

- Determination of detection limits, trueness and precision (CV_R) for digests of heavy matrices.
- Investigation to detect missing interferents for a few elements (Ce, La, Nd, Pr, Sc, Sm, Te).

2.6 Draft standard horizontal ICP-AES method

A draft of a horizontal ICP-MS standard is given in Annex 1.

3 ICP-MS STANDARDS

3.1 List of relevant ICP-MS standards

All standards and draft standards available from ISO, CEN and NEN using ICP-MS for the determination of elements in environmental matrices are given below:

- ISO/DIS 17294-1:2003 Water Quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of elements – Part 1: General guidelines and basic principles
- ISO 17294-2:2002 Water Quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 2: Determination of 61 elements
- NEN 6427:1999 (Draft) Water – Determination of 66 elements by inductively coupled plasma mass spectrometry (In Dutch)
- EPA Method 6020A:1998 Inductively coupled plasma - Mass spectrometry

3.2 Description of standards for trace elements by ICP-MS

3.2.1 ISO/DIS 17294-1:2003 Water Quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of elements – Part 1: General guidelines and basic principles

ISO/DIS 17294-2 is a guideline. It describes:

- Principles of ICP-MS analysis.
- Instrumentation in detail.
- Sources of interferences, matrix effects and techniques to minimize its effects.
- Tuning and adjustments
- Method development:
 - Isotope selection, interference correction
 - Optimization of measurement conditions
 - Sample pretreatment.
 - Calibration, including standard addition calibration
 - Analysis
 - Validation
 - Quality control

The guide gives a comprehensive list of elements, their isotopes, preferred isotope, abundance, detection limit, inter-element and polyatomic ions, generally relevant interference.

The guide is meant to set up a measurement procedure. In practice it is the reference of specific measurement standards ISO 17294-2.

3.2.2 ISO 17294-2:2002 Water Quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 2: Determination of 61 elements

ISO 17294-2 describes the determination of 62 elements in water (drinking water, surface water, groundwater, wastewater and eluates). The 62 elements determined include almost all elements in environmental analysis. Exceptions are halogens, noble gases, hydrogen, nitrogen and oxygen.

Filtered acidified samples (nitric acid) are analyzed to give dissolved elements and the whole sample is digested with nitric acid (ISO 15587-2) or *aqua regia* (ISO 15587-1) to give total ele-

ments. The standard warns that digestion for the total elements procedure may only partially dissolve some elements like silicon, aluminum, tin, tungsten, zirconium and antimony.

The technique is based on the measurement specific isotopes of elements. Corrections are made for isobaric interferences and interferences by polyatomics. Correction factors and correction equations are evaluated during the run by analyzing a so-called interference check solution. For non spectral interferences reference is made to ISO 17294-1 clause 6.2. This clause describes all effects that may lead to changes in sensitivity because of the matrix composition. No measures are taken in the procedure to verify the absence of sensitivity changes due to matrix effects.

Valuable instructions are given on the adsorption behavior of different elements at trace levels and on the use of super pure reagents.

Calibration is performed using calibration solutions at five different levels. The application of ordinary linear regression is given. However, reference is given to the comment in ISO 17294-1 clause 9.1 on the misfit of the intercept. See 2.3.2 last paragraph.

The use of an internal standard is recommended.

The required minimum specification for the ICP-MS apparatus allows (almost) all instrumentation on the market: resolution of 1.0 amu or better at 5% peak height.

Although quality control measures are taken no criteria are given:

- Stability, sensitivity and resolution check using an optimization solution prior to analysis
- Zero drift by a blank sample
- Accuracy check by analysis of a certified reference material.

The standard mentions typical detection limits and precision data:

- Trace elements have detection limits less than 1 µg/l, heavier elements down to 0,1 µg/l.
- Coefficients of variation for (interlaboratory)reproducibility are less than 15% for surface water except for chromium, tin, thallium and vanadium.
- Coefficients of variation for (interlaboratory)reproducibility are less than 15% (also 10%) for *aqua regia* digests except for arsenic, cadmium, thallium vanadium and zirconium.

3.2.3 NEN 6427:1999 (Draft) Water – Determination of 66 elements by inductively coupled plasma mass spectrometry (In Dutch)

NEN 6427 describes the determination of 66 elements in aqueous samples, and digests of solids. Palladium does not appear on this list. However, five more elements compared to ISO 17294-2 are given: iron, mercury, silicon, titanium and sulfur.

The technique is similar to ISO 17294-2.

The standard does not require minimum instrumental ICP-MS performance.

The standard refers to NPR 6428 (under development) for performance tests and performance limits. In the meantime ISO/DIS 17294-1 covers the contents of NPR 6428.

Detection limits are similar to those of ISO 17294-2.
No data on trueness and precision are given.

Quality control samples are recommended: spiked samples (recovery/sensitivity changes), reference material (accuracy), control sample (long term stability).

3.2.4 EPA Method 6020A:1998 Inductively coupled plasma - Mass spectrometry

EPA's method 6020A describes the analysis of at least 34 elements. 24 elements are dealt with in detail. All important trace elements are incorporated.

The method is applicable to all kinds of water, digests and waste eluates.

Method 6020A is similar to ISO 17294.

Method 6020A is open for ICP-MS instruments that have data systems that allow corrections for isobaric interferences and the application of the internal standard technique. The system should have a resolution better than or equal to 1.0 amu at 10% peak height.

The main difference with other standards is quality control. In this method different types of interference are actively monitored and calibration drift is checked:

- Calibration blank check shall be within 3 times the instrumental detection limit.
- Calibration check standard, at the beginning, end and after every 10 samples, shall be within 10%.
- Difference between matrix spiked duplicate samples shall be within 20%.
- Post digestion spike recovery shall be between 75% and 125%.
- Difference between results for the original sample and the fivefold diluted sample shall be less than 10% (alternative test required when a new or unusual matrix is encountered).
- Method blank (including preparations prior to ICP-AES analysis) required. No acceptance criteria given.
- Change of correction factors between successive tests shall be less than 10%.
- Internal standard response of a sample shall be more than 30% of the response of a calibration solution.

Instrumental detection limits are not given.

Coefficients of variation for (interlaboratory)reproducibility for aqueous solutions are 10% on average.

Coefficients of variation for (interlaboratory)reproducibility for solid matrices are 25% on average.

3.3 Evaluation

3.3.1 Scope

Three standards have been identified for the determination of elements in relevant environmental samples:

- Two standards cover aqueous samples, eluates and digests of solids (NEN 6427 and EPA 6020A)
- One standard covers aqueous samples and digests of aqueous samples (ISO 17294-2).

More than 60 elements can be quantified by ISO 17294-2 and NEN 6427. EPA's method 6020A specifies 34 elements but provide procedures to add elements to the standard.

All standards cover the important trace components in the environment.

3.3.2 Procedures

The principles of all standards are the same; procedures are very similar. The differences are mainly the techniques to detect and/or minimise interference and the procedures for quality control.

ISO 17294-2 is only valid for water analysis. Generally, this matrix closely matches the calibration matrix, which means that differences in sensitivity are small and in case of fairly selective wavelengths also interference will be small.

Both NEN 6427 and EPA method 6020A require actions to detect and correct for interferences, which may be substantial for waste, sludge and eluates. Both describe inter-element corrections for interfering elements detected during validation. These correction equations are updated every run. EPA method 6020A and to a lesser extent NEN 6427 require detection of matrix effects, by either additional analysis of a diluted sample or by recovery of a post digestion spike. Actions are matrix matching or standard addition calibration.

ISO 17294-2 explicitly points at the problem of ordinary (unweighed) linear regression in case of multilevel calibration standards. It recommends to use a two point calibration instead. NEN 6427 refers to NPR 6425 where this problem is also addressed.

3.3.3 Equipment

All standards require standard ICP-AES instrumentation. Only EPA requires data systems capable of making corrections for isobaric interferences and the application of the internal standard technique.

3.3.4 Quality Control

Quality control required in at least two of the standards:

- Control of drift (calibration blank and calibration standard checks).
- Interference detection and control.
- Recovery of post digestion matrix spike.

All mentioned quality control measures are useful. No additional checks are necessary.

All mentioned quality control measures are useful. No additional checks are necessary. The magnitude of the five-fold dilution criterion (10%) in the EPA method is much more stringent than the $\pm 25\%$ criterion for recovery deviation. The value is the same as the 10% maximum deviation for the calibration check sample. 20% instead of 10% would be more in line with the recovery criterion.

3.4 Critical points and recommendations

3.4.1 Methodology

There are no conflicting approaches in the standards.

3.4.2 Scope of the method

Results of interlaboratory comparisons of EPA's method 6020A have shown that reasonable results can be obtained analysing solid matrices. Reproducibility for aqueous matrices using EPA's method 6020A and ISO 17294-2 are much better as is expected for these more simple matrices. There is no reason not to draft a standard for water and digests of the following origin: water, eluates and digests of water, eluates, waste, soil, sludge and sediments. 66 elements given in ISO 17294-2 minus mercury (not practical) plus palladium can be taken into the draft standard.

3.4.3 Procedure and quality control

The normal ICP-MS procedure can be used. However, more attention must be given to the control of interference and matrix effects. It is the most critical point because of the possible variability of the matrix.

Quality control can be the same as summarised in 3.3.4.

All standards focus on quadrupole instruments. Interference and detection limits are different for high-resolution ICP-MS and collision cell ICP-MS. The horizontal standard must explicitly allow these techniques.

3.4.4 Calibration

Attention must be paid to the limited application of ordinary linear regression in case of linear relationships and a large measurement range (see last paragraph of 2.3.2. As weighted linear regression is uncommon, alternative approaches must be introduced:

- Two point calibration and linearity check
- Multipoint calibration and ordinary linear regression forced through blank value
- Multipoint calibration and ordinary linear regression forced through zero combined with a check on the absence of a blank value.

3.5 Recommendation

Recommended for discussion:

- Stronger emphasis on interferent corrections and quality control related to (residual) interferences and matrix effects.
- The coverage and the magnitude of the quality control criteria
- More flexibility in selecting own concentration levels of calibration.require 'range covered' and 'minimum number of levels and replicates).
- Dangers of applying ordinary linear regression in case of an large measurement range.

Recommend for action:

- Determination of detection limits, trueness and precision (CV_R) for digests of heavy matrices.

3.6 Draft standard horizontal ICP-MS method

A draft of a horizontal ICP-MS standard is given in Annex 2.

ANNEX 1 STANDARD HORIZONTAL ICP-AES METHOD

Determination of dissolved elements by inductively coupled plasma atomic emission spectrometry (ICP-AES)

1 SCOPE

This international standard specifies the method for the determination of 37 elements in water (e.g. drinking water, surface water, groundwater, wastewater and eluates) and *aqua regia* and nitric acid digests of water, eluates, industrial and organic wastes, soils, sludges, sediments, and other solid wastes:

aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, cerium, chromium, cobalt, copper, lanthanum, lead, lithium, magnesium, manganese, molybdenum, neodymium, nickel, phosphorus, potassium, praseodymium, samarium, scandium, selenium, silver, sodium, strontium, tellurium, thallium, tin, tungsten, vanadium, zinc, and zirconium

Table 1 lists elements for which this method applies along with the recommended wavelength and typical instrumental detection limits for clean aqueous matrices.

2 NORMATIVE REFERENCES

The following normative documents contain provisions, which, through reference in this text, constitute provisions of <standard number>. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on <standard number> are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies.

ISO 3696:1987, *Water for analytical laboratory use. Specification and test methods.*

<*Aqua regia* horizontal standard> . *Digestion for the determination of selected elements . Part 1: Aqua regia digestion.*

<Nitric acid horizontal standard>. *Digestion for the determination of selected elements . Part 2: Nitric acid digestion.*

3 PRINCIPLE

This method describes multi-elemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. Additional interferences and matrix effects must be recognized and appropriate corrections made; tests for their presence are described.

Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

4 INTERFERENCES

Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (inter-element or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.

Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for inter-element contributions. Instruments that use equations for inter-element correction require the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. The interferences are listed in Table 1.

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer.

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis.

5 REAGENTS

5.1 General

For the determination of elements at trace and ultratrace level, the reagents shall be of adequate purity. The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared to the lowest concentration to be determined.

Use water according to Grade 1 of ISO 3696 for all sample preparation and dilutions.

5.2 Nitric acid, $\rho(\text{HNO}_3) = 1,4 \text{ g/ml}$.

NOTE Nitric acid is available both as $c(\text{HNO}_3) = 1,40 \text{ g/ml}$ ($w(\text{HNO}_3) = 650 \text{ g/kg}$) and $c(\text{HNO}_3) = 1,42 \text{ g/ml}$ ($w(\text{HNO}_3) = 690 \text{ g/kg}$). Both are suitable for use in this method provided there is minimal content of the interesting analytes.

5.3 Hydrochloric acid, $\rho(\text{HCl}) = 1,16 \text{ g/ml}$.

5.4 Hydrochloric acid, $c(\text{HCl}) = 0,2 \text{ mol/l}$.

5.5 Element stock solutions

Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, Sb, Sc, Se, Sm, Sn, Sr, Te, Tl, V, W, Zn, Zr, $\rho = 1\ 000 \text{ mg/l}$ each.

Both single-element stock solutions and multi-element stock solutions with adequate specification stating the acid used and the preparation technique are commercially available.

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

5.6 Anion stock solutions

Cl, PO_4 , SO_4 $\rho = 1\ 000 \text{ mg/l}$ each.

Prepare these solutions from the respective acids. The solutions are as well commercially available.

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

5.7 Multi-element calibration solutions

Depending on the scope, different multi-element standard solutions may be necessary. In general, when combining multi-element standard solutions, their chemical compatibility and the possible hydrolysis of the components shall be regarded. Care must be taken to prevent chemical reactions (e.g. precipitation).

The multi-element standard solutions are considered to be stable for several months, if stored in the dark.

This does not apply to multi-element standard solutions that are prone to hydrolysis, in particular solutions of Bi, Mo, Sn, Sb, Te, W, and Zr.

Multi-element standard solution A may contain the following elements:

Ag, Al, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, La, Li, Mn, Ni, Pb, Se, Sr, Tl, V, Zn.

Use nitric acid for stabilization of standard solution A.

Multi-element standard solution B may contain the following elements:

Mo, Sb, Sn, W, Zr.

Standard solution B needs hydrochloric acid for stabilization

Multi-element standard solutions with more elements are allowed provided that these solutions are stable.

Prepare in one or more steps calibration solutions at the highest concentration of interest. If more concentration levels are needed prepare those similarly.

Add acids (5.3 – 5.5) to match the acid concentration of samples closely.

If traceability of the values is not established check the validity by comparison with a (traceable) independent standard.

Check the stability of the calibration solutions.

5.8 Calibration blank

Prepare the calibration blank by acidifying water (5.2) to the same concentrations of the acids found in the calibration solutions and samples.

5.9 Method blank

The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.10 Calibration check solution

Prepare the calibration check solution in the same acid matrix using the same standards used for calibration at a upper concentration level.

5.11 Interference check solution

If interference cannot be excluded (see Table 1) prepare the interference check solution to contain known concentrations of interfering elements that will provide an adequate test of the correction factors.

Avoid two or more interferents for an analyte in the same interference check solution.

Spike the sample with the analytes of interest, particularly those with known interferences at 0.5 to 1 mg/L.

In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

6 APPARATUS

6.1 Inductively coupled argon plasma emission spectrometer:

- Computer-controlled emission spectrometer with background correction.
- Radio-frequency generator
- Optional mass flow controller for argon nebulizer gas supply.
- Optional peristaltic pump.
- Optional autosampler.
- Argon gas supply - high purity.

6.2 Volumetric flasks of suitable precision and accuracy.

6.3 Volumetric pipets of suitable precision and accuracy.

7 PROCEDURE

7.1 Test sample

The test sample is an acidified aqueous sample ($\text{pH} \leq 1$) free of particles or a particle free digest obtained by <Horizontal standard nitric acid digestion> or <Horizontal standard aqua regia digestion>.

7.2 Test portion

The test portion may be directly obtained for the test sample or may be diluted from the test sample to accommodate the measurement range or to dilute the matrix.

The acidity of the test portion must match the acidity of calibration solutions.

Ensure that all elements are present in a non-volatile form. Volatile species must be converted to non-volatile ones *e.g.* sulphide oxidation by hydrogen peroxide.

7.3 Set up of the procedure

Adjust the instrumental parameters of the ICP-AES system in accordance with the manufacturer's manual.

About 30 min prior to measurement, adjust the instrument to working condition.

Check the sensitivity and the stability of the system.

Check the wavelength calibration as often as required by the manufacturer.

Select wavelengths for measurement (Table 1) and for background subtraction (Clause 4). Alternatively, apply multivariate calibration procedures.

The use of an internal standard should be considered if the matrix is highly variable and matrix-matching is difficult.

Apply an element with a non-measurable concentration. Examples are scandium and yttrium.

Add the internal standard in measurable amounts to samples and calibration solutions.

Divide every analyte response by the internal standard response and use this ratio as the measurement signal.

Define the rinsing times depending on the length of the flow; in the case of largely varying mass concentrations in the measuring solutions, allow for longer rinsing periods.

7.4 Calibration

7.4.1 Linear calibration function

If more than two concentration levels, including zero, are used apply **weighted** linear regression to obtain the linear calibration function.

NOTE ICP-AES provide a large measurement range. The dispersion of blank measurements is usually much smaller than the dispersion at full scale. Ordinary linear regression assumes that the dispersion is constant over the entire range. As a consequence a much higher percentage of the calculated intercepts is out of the range expected from the spread of blanks: a non-zero blank value is calculated that is actually not there. Weighted linear regression forces the line through points of low dispersion, resulting in the expected intercept dispersion. Unfortunately, many data systems cannot handle weighted regression.
An alternative, but less efficient, approach is ordinary linear regression where the line is forced

through the blank value or through zero.

The most inexpensive way however is a (single or multiple) two point calibration. If calibration lines are linear, as they are usually in ICP-AES, this procedure is valid and efficient.

If weighted linear regression is not possible apply linear regression forced through the blank value or through zero. In the latter case check regularly by running a blank sample whether the assumption on the absence of a blank value is justified.

A two point calibration is allowed if the calibration function is linear, which usually is the case. Check regularly with a calibration solution of known dilution whether the assumption on linearity is justified.

Instead of one measurement per level more measurements can be performed to reduce the uncertainty of the calibration line.

7.4.2 Non-linear calibration function

Alkali and alkaline earth metals may have non-linear response curves due to ionization and self-absorption effects.

Calculate the calibration function from weighted polynomial regression (second degree).

If this option is not possible use polynomial regression under the condition that the function is forced through the blank or through zero. In the latter case check regularly whether the assumption on the absence of a blank value is justified.

7.4.3 Standard addition calibration

Add a known amount of analyte to the known amount of the sample portion. Calculate the corresponding concentration change. Measure the difference in concentration between the original and the spiked sample portion. Use the ratio 'true spike concentration' versus 'measured spike concentration' as a correction factor for the initially measured concentration of the sample portion. Minimise dilution or correct for spike dilution.

7.4.4 Inter-element correction

Investigate whether the interfering elements in Table 1 may result in measured values higher than three times the instrumental detection limit. If so, correct for interference.

Correction may be performed by:

- analysing one or more interferent check solutions (5.11),
- determining the ratio of supplied interferent concentration versus detected analyte concentration,
- using this ratio to calculate the interferent contribution from the measured interferent concentration of that specific test portion.

If sample composition strongly varies matrix matching may not be possible. Investigate the application of an internal standard to reduce the effect of the mismatch on analyte sensitivity (7.3). The internal standard method can be applied independently from the calibration procedure.

If the internal standard procedure insufficiently reduces matrix effects, apply standard addition calibration (7.4.3).

7.5 Sample measurement

Run one or more calibration solutions and calibration blanks.

Run the interference check solution(s) to establish interference correction or to check presence of interference.

Run all samples including one or more method blanks.

Every 25 samples or less and at the end, run a calibration blank and a calibration check solution. Run at least one spiked sample (digest or aqueous sample) from the series to check recovery.

NOTE If standard addition calibration is applied to all samples leave out the recovery check.

Whenever a new or usual sample matrix is encountered check:

- matrix effects by running the spike sample or
- matrix effects by running a fivefold diluted sample and
- inter-element interference analysing at a different wavelength.

8 CALCULATION

Calculate the element concentration in the aqueous sample:

$$\rho = (\rho_1 - \rho_0)f_d f_a$$

Calculate the element concentration in the digested solid sample:

$$w = (\rho_1 - \rho_0)f_a V/m$$

where:

ρ	is the concentration of the element in the aqueous sample in mg/l;
ρ_1	is the concentration of the element in the test sample in mg/l;
ρ_0	is the concentration of the element in the blank in mg/l;
f_d	is the dilution factor due to digestion of an aqueous sample; in all other cases $f_d = 1$;
f_a	is the dilution factor of the test portion;
w	is the mass fraction of the element in the solid sample in mg/kg;
V	is the volume of the test sample (digest) in litres;
M	is the mass of the digested sample in kg.

9 EXPRESSION OF RESULTS

State as many significant figures as are acceptable according to the precision of the measuring values, but not more than three significant figures.

10 QUALITY CONTROL

10.1 Blank

Result of the calibration blank check shall be within 3 times the instrumental detection limit.

10.2 Sensitivity

Result of the calibration check standard shall not deviate more than 10%.

10.3 Interference

Magnitude of uncorrected background and spectral interference shall not be higher than three times the instrumental detection limit.

Successive values of a correction factor shall not differ more than 20%.

10.4 Recovery

Spike recovery shall be between 75% and 125% or difference between results for the original sample and the fivefold-diluted sample shall be less than 20%.

11 TEST REPORT

The test report shall contain the following information:

- a reference to this standard
- a reference to the digestion method used
- a complete identification of the sample
- the results of the determination
- any deviation from the standard

TABLE 1: Recommended wavelengths, spectral interferences and estimated instrumental detection limits

Element	Line (nm)	Interfering elements	Instrumental
Ag	328,068		7
	338,289	Cr	15
Al	308,215	Mn, V, Fe	50
	396,152	Mo, Cu	10
	167,08	Fe	1
As	193,696	Fe, Al	50
	197,197	Fe, Al	75
	189,042	Al	
B	208,959	Al, Mo	10
	249,678	Fe, Cr	5
	249,773	Fe	5
Ba	233,527	Fe, V	5
	455,403		1
Be	493,409		1
	313,042	V	2
	234,861	Fe	30
Bi	313,107		
	223,061	Cu	30
	306,772	Fe, V	75
Ca	315,887	Co	30
	317,933	Fe, V	20
	393,366		0,2
Cd	214,438	Fe	3
	226,502	Fe	3
	228,802	As, Co	3
Ce	394,275	?	70
	413,380	?	50
Co	228,616	Ti	7
Cr	205,552	Fe, Mo	6
	267,716	Mn, V	7
	283,563	Fe, Mo	7
	284,325	Fe	7
Cu	324,754	Ti, Fe	5
	327,396		10
Fe	259,940		6
	238,20	Co	1
K	766,490	Mg, Ar	6
	769,90		
La	333,749	?	10
	379,478	?	10
Li	460,286	Fe	
	670,784		6
	279,079		30
Mg	279,553		0,1
	285,21	Fe	
	257,610	Fe, Mo, Cr	1
Mn	293,306	Al, Fe	1
	202,030	Al, Fe	8
	204,598		10
Na	588,995	Ar	70
	588,995		

Element	Line (nm)	Interfering elements	Instrumental
	330,237		
Nd	406,109	?	100
	430,358	?	75
Ni	231,604	Co	25
P	178,287	I	15
	213,618	Cu, Fe, Mo, Zn	7
	214,914	Cu, Al, Mg	7
	177,428	Cu	
Pb	220,353	Al, Co, Ti	40
	283,306		
Pr	390,844	?	40
	414,311		40
S	182,036	Cr, Mo	15
	180,669	Ca	13
Sb	206,833	Cr, Mg, Co, Mn	30
	217,581		40
Sc	357,635	?	0,3
	361,384	?	0,3
Se	196,026		75
	203,985		100
Si	251,611		10
	212,412		15
	288,158		30
Sm	359,260	?	40
	388,529	?	80
Sn	235,848	Mo, Co	100
	189,980		25
Sr	407,771		0,3
	421,552		0,3
	460,733		70
Te	214,281	?	40
	225,902	?	180
Ti	334,941	Ca, Cr, Si	4
	336,121		5
	337,280		7
	368,520	Co, Cr	10
V	290,882	Fe, Mo	8
	292,402	Fe, Mo, Cr	8
	310,230		7
	311,071	Fe, Mn, Ti, Cr	10
W	207,911		30
	209,860		40
	239,709		60
	222,589	Cu	60
	202,998		75
Zn	206,191	Cr	6
	213,856	Cu, Ni, Fe	7
Zr	343,823		10
	354,262		7
	339,198		7

ANNEX 2 STANDARD HORIZONTAL ICP-MS METHOD

Determination of dissolved elements by inductively coupled plasma mass spectrometry (ICP-MS)

1 Scope

This standard specifies a method for the determination of the dissolved elements aluminium, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, caesium, calcium, cerium, chromium, cobalt, copper, dysprosium, erbium, europium, gadolinium, gallium, germanium, gold, hafnium, holmium, indium, iridium, iron, lanthanum, lead, lithium, lutetium, magnesium, manganese, molybdenum, neodymium, nickel, palladium, phosphorus, platinum, potassium, praseodymium, rubidium, rhenium, rhodium, ruthenium, samarium, scandium, selenium, silicon, silver, sodium, strontium, sulfur, terbium, tellurium, thorium, thallium, thulium, tin, titanium, tungsten, uranium, vanadium, yttrium, ytterbium, zinc, and zirconium in water (e.g. filtered drinking water, surface water, groundwater, wastewater, eluates) and *aqua regia* and nitric acid digests of water, eluates, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, .

Taking into account the specific and additionally occurring interferences, these elements can also be determined in digests of water, sludges, sediments and soil (e.g. digests of water according to <Aqua regia horizontal standard> and <Nitric acid horizontal standard>).

The working range depends on the matrix and the interferences encountered.

In drinking water and relatively unpolluted waters, the detection limit is between 0,1 µg/l and 1,0 µg/l for most elements (see Table 1).

The detection limits of most elements will be affected by blank contamination and this will depend predominantly on the laboratory air-handling facilities available.

The detection limit will be higher in cases where the determination is likely to be interfered (see clause 4) or in case of memory effects (see clause 8.2 of ISO 17294-1).

2 Normative references

The following normative documents contain provisions, which, through reference in this text, constitute provisions of <standard number>. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on <standard number> are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies.

ISO 3696:1987, *Water for analytical laboratory use. Specification and test methods*.

<Aqua regia horizontal standard> . *Digestion for the determination of selected elements . Part 1: Aqua regia digestion*.

<Nitric acid horizontal standard> . *Digestion for the determination of selected elements . Part 2: Nitric acid digestion*.

ISO 17294-1, *Water quality . Application of inductively coupled plasma mass spectrometry (ICP-MS) . Part 1: General guideline*.

3 PRINCIPLE

This international standard describes the multi-elemental determination of analytes by ICP-MS in aqueous and nitric acid or *aqua regia* digests. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer.

The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

4 INTERFERENCES

4.1 General

Detailed information on spectral and non-spectral interferences is given in clause 6.1 of ISO 17294-1.

4.2 Spectral interferences

4.2.1 Isobaric elemental interferences

Isobaric elemental interferences are caused by isotopes of different elements of the same nominal mass-to-charge-ratio and which cannot be separated due to an insufficient resolution of the mass spectrometer in use (e.g. ^{114}Cd and ^{114}Sn).

Element interferences from isobars may be corrected for taking into account the influence from the interfering element (see Table 1). The isotopes used for correction shall be free of interference. Correction options are often included in the instrument software. Common isobaric interferences are given in Table 2.

4.2.2 Isobaric molecular and doubly charged ion interferences

Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Examples include $^{40}\text{Ar}^{35}\text{Cl}^+$ and $^{40}\text{Ca}^{35}\text{Cl}^+$ ion on the ^{75}As signal and $^{98}\text{Mo}^{16}\text{O}^+$ ions on the $^{114}\text{Cd}^+$ signal. Natural isotope abundances are available from the literature. However, the most precise coefficients for an instrument will be determined from the ratio of the net isotope signals observed for a standard solution.

The accuracy of these types of equations is based upon the constancy of the observed isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g., oxide levels can vary with operating conditions. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent.

The magnitude of isobaric molecular and doubly charged interferences shall be corrected for if their impact can be higher than three times the instrumental detection limit.

4.3 Non spectral interferences

Physical interferences are associated with the sample nebulization and transport

processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers. Total solid levels below 0.2% (2,000 mg/L) is recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30 % of the signals in the calibration solution) will be observed. Dilution of the sample fivefold will usually eliminate the problem.

5 REAGENTS

5.1 General

For the determination of elements at trace and ultratrace level, the reagents shall be of adequate purity. The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared to the lowest concentration to be determined.

If possible nitric acid preservation and digestion should be used in order to minimize interferences by polyatoms. Bi, Mo, Sn, Sb, Te, W, Hf and Zr may need hydrochloric acid for preservation and digestion.

5.2 Water

Use water according to Grade 1 of ISO 3696 for all sample preparation and dilutions.

5.3 Nitric acid, $c(\text{HNO}_3) = 1,4 \text{ g/ml}$.

NOTE Nitric acid is available both as $\rho(\text{HNO}_3) = 1,40 \text{ g/ml}$ ($w(\text{HNO}_3) = 650 \text{ g/kg}$) and $\rho(\text{HNO}_3) = 1,42 \text{ g/ml}$ ($w(\text{HNO}_3) = 690 \text{ g/kg}$). Both are suitable for use in this method provided there is minimal content of the interesting analytes.

5.4 Hydrochloric acid, $c(\text{HCl}) = 1,16 \text{ g/ml}$.

5.5 Element stock solutions

Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, $\rho = 1\,000 \text{ mg/l}$ each.

Both single-element stock solutions and multi-element stock solutions with adequate specification stating the acid used and the preparation technique are commercially available.

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

5.6 Anion stock solutions

Cl, PO_4 , SO_4 $\rho = 1\,000 \text{ mg/l}$ each.

Prepare these solutions from the respective acids. The solutions are as well commercially available.

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

5.7 Multi-element standard solutions

Depending on the scope, different multi-element standard solutions may be necessary. In general, when combining multi-element standard solutions, their chemical compatibility and the possible hydrolysis of the components shall be regarded. Care must be taken to prevent chemical reactions (e.g. precipitation).

The multi-element standard solutions are considered to be stable for several months, if stored in the dark.

This does not apply to multi-element standard solutions that are prone to hydrolysis, in particular solutions of Bi, Mo, Sn, Sb, Te, W, Hf and Zr.

Multi-element standard solution A at the mg/l level may contain the following elements: Ag, Al, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, La, Li, Mn, Ni, Pb, Rb, Sr, Th, Tl, U, V, Se, Zn. Use nitric acid for stabilization of standard solution A.

Multi-element standard solution B at the mg/l level may contain the following elements: Au, Mo, Sb, Sn, W, Zr.

Standard solution B needs hydrochloric acid for stabilization.

Multi-element standard solutions with more elements are allowed provided that these solutions are stable.

5.8 Multi-element calibration solutions

Prepare in one or more steps calibration solutions at the highest concentration of interest.

If more concentration levels are needed prepare those similarly.

Add acids (5.3 – 5.4) to match the acid concentration of samples closely.

If traceability of the values is not established check the validity by comparison with a (traceable) independent standard.

Check the stability of the calibration solutions.

5.9 Internal standard solution

The choice of elements for the internal standard solution depends on the analytical problem. The solution of this/these internal standard(s) should cover the mass range of interest. The concentrations of the selected elements in samples should be negligibly low. The elements In, Lu, Re, Rh and Y have been found suitable for this purpose.

Generally, a suitable concentration of the internal standard in samples and calibration solutions is 50 µg/l.

5.10 Calibration blank

Prepare the calibration blank by acidifying water (5.2) to the same concentrations of the acids found in the calibration solutions and samples.

5.11 Method blank

The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.12 Optimization solution

The optimization solution serves for mass calibration and for optimization of the apparatus conditions, e.g. adjustment of maximal sensitivity with respect to minimal oxide formation rate and minimal formation of doubly charged ions.

It should contain elements covering the total mass range, as well as elements prone to a high oxide formation rate or to the formation of doubly charged ions. An optimization solution containing Mg, Cu, Rh, In, Ba, La, Ce, U and Pb is suitable. Li, Be and Bi are less suitable because they tend to cause memory effects.

The mass concentrations of the elements used for optimization should allow count rates of more than 10 000 counts per second.

5.13 Interference check solution

The interference check solutions serve to determine the correction factors for the corresponding equations. High demands are made concerning the purity of the basic reagents due to the high mass concentrations.

Interference check solutions shall contain all the interferents of practical relevance given in Table 1, at a concentration level that is at least as high as in samples.

Leaving out an interferent of Table 1 is permitted if it can be demonstrated that its impact is negligible and lasting.

In extreme situations also the other interferents of Table 1 shall be investigated for relevance.

NOTE An example of the composition of an interferent check solution is:
 $\rho(\text{Ca}) = 200 \text{ mg/l}$; $\rho(\text{Cl}^-) = 300 \text{ mg/l}$; $\rho(\text{PO}_4) = 25 \text{ mg/l}$ and $\rho(\text{SO}_4) = 100 \text{ mg/l}$.

6 APPARATUS

6.1 General requirements

The stability of samples, measuring, and calibration solutions depends to a high degree on the container material.

The material shall be checked according to the specific purpose. For the determination of elements in a very low concentration range, glass or polyvinyl chloride (PVC) should not be used. Instead, it is recommended to use perfluoroalkoxy (PFA), hexafluoroethene propene (FEP) or quartz containers, cleaned with hot, concentrated nitric acid in a closed system. For the determination of elements in a higher concentration range, HDPE or PTFE containers are also allowed for the collection of samples.

Immediately before use, all glassware should be washed thoroughly with warm diluted nitric acid (e.g. $w(\text{HNO}_3) = 10 \%$), and then rinsed several times with water (5.2).

The use of piston pipettes is permitted and also enables the preparation of lower volumes of calibration solutions.

The application of dilutors is also allowed. Every charge of pipette tips and single-use plastics vessels shall be tested for impurities.

For more detailed information on the instrumentation see clause 5 of ISO 17294-1.

6.2 Mass spectrometer

A mass spectrometer with inductively coupled plasma (ICP) suitable for multi-element and isotope analysis is required. The spectrometer should be capable of scanning a mass range from 5 m/z (AMU) to 240 m/z (AMU) with a resolution of at least 1 m_r/z peak width at 5 % of peak height (m_r = relative mass of an atom species; z = charge number). The instrument may be fitted with a conventional or extended dynamic range detection system.

Most quadrupole ICP-MS, high-resolution ICP-MS and collision cell ICP-MS instrumentation is fit for purpose.

6.3 Mass-flow controller

A mass-flow controller on the nebulizer gas supply is required. Mass-flow controllers for the plasma gas and the auxiliary gas are also useful. A water-cooled spray chamber may be of benefit in reducing some types of interferences (e.g. from polyatomic oxide species).

NOTE The plasma is very sensitive to variations in the gas flow rate.

6.4 Nebulizer with variable speed peristaltic pump

6.5 Argon gas supply

Argon gas with high purity grade, i.e. > 99,99 %

6.6 Glassware

Volumetric flasks, 50 ml, 100 ml, 500 ml and 1 000 ml;

Erlenmeyer flasks, 100 ml;

Pipettes, 1 ml, 2,5 ml, 10 ml, 20 ml and 25 ml.

6.7 Storage bottles for the stock, standard, calibration and sample solutions

Preferably made from perfluoroalkoxy (PFA) or hexafluoroethene propene (FEP). For the determination of elements in a higher concentration range, HDPE or PTFE bottles may be sufficient for the storage of samples.

7 PROCEDURE

7.1 Test sample

The test sample is an acidified aqueous sample ($\text{pH} \leq 1$) free of particles or the digest obtained by *<Horizontal standard nitric acid digestion>* or *<Horizontal standard aqua regia digestion>*.

7.2 Test portion

The test portion may be directly obtained for the test sample or may be diluted from the test sample to accommodate the measurement range or to dilute the matrix.

The acidity of the test portion must match the acidity of calibration solutions.

Ensure that all elements are present in a non-volatile form. Volatile species must be converted to non-volatile ones e.g. sulfide oxidation by hydrogen peroxide.

7.3 Instrument set up

Adjust the instrumental parameters of the ICP-MS system in accordance with the manufacturer's manual.

About 30 min prior to measurement, adjust the instrument to working condition.

Before each series of measurement check the sensitivity and the stability of the system and minimize interference e.g. by using the optimization solution (5.12).

Check the resolution and the mass calibration as often as required by the manufacturer.

Define the relative atomic masses and the corresponding corrections. Alternatively, apply multi-variate calibration procedures.

Define the rinsing times depending on the length of the flow; in the case of largely varying mass concentrations in the measuring solutions, allow for longer rinsing periods.

The use of an internal standard is recommended. Add the internal standard solution (5.9) to the interference check solution (5.13), to all multi-element calibration solutions (5.8), to the blank calibration solutions (5.10), and to all measuring solutions.

The mass concentration of the reference-elements shall be the same in all solutions. A mass concentration of $\rho(Y, Re) = 50 \mu\text{g/l}$ is often suitable.

NOTE ICP-MS has excellent multi-element capability. Nevertheless it does not mean, that all elements can be analyzed during one measurement run. The sensitivity of determination depends on plenty of parameters (nebulizer flow, radio-frequency power, lens voltage, lens voltage mode etc.). The optimal instrument settings can not be reached for all elements at once.

7.4 Calibration

7.4.1 Linear calibration function

If more than two concentration levels, including zero, are used apply **weighted** linear regression to obtain the linear calibration function.

NOTE ICP-AES provides a large measurement range. The dispersion of blank measurements is usually much smaller than the dispersion at full scale. Ordinary linear regression assumes that the dispersion is constant over the entire range. As a consequence a much higher percentage of the calculated intercepts is out of the range expected from the spread of blanks: a non-zero blank value is calculated that is actually not there. Weighted linear regression forces the line through points of low dispersion, resulting in the expected intercept dispersion. Unfortunately, many data systems cannot handle weighted regression.
An alternative, but less efficient, approach is ordinary linear regression where the line is forced through the blank value or through zero.
The most inexpensive way however is a (single or multiple) two point calibration. If calibration lines are linear, as they are usually in ICP-AES, this procedure is valid and efficient.

If weighted linear regression is not possible apply linear regression forced through the blank value or through zero. In the latter case check regularly by running a blank sample whether the assumption on the absence of a blank value is justified.

A two point calibration is allowed if the calibration function is linear, which usually is the case. Check regularly with a calibration solution of known dilution whether the assumption on linearity is justified.

Instead of one measurement per level more measurements can be performed to reduce the uncertainty of the calibration line.

7.4.2 **Standard addition calibration**

Add a known amount of analyte to the known amount of the sample portion, or its dilution. Calculate the corresponding concentration change. Measure the difference in concentration between the original and the spiked sample portion. Use the ratio 'true spike concentration' versus 'measured spike concentration' as a correction factor for the initially measured concentration of the sample portion.

Minimise dilution or correct for spike dilution.

7.4.3 **Determination of correction factors**

In order to evaluate and to update the correction factors, measure the interference check solutions (5.13) at regular intervals within a measuring cycle.

Subsequent correction factors shall not change more than 20%.

7.4.4 **Variable isotope ratio**

Take into account the possible discrepancies in the isotope composition between the calibration solutions and the measuring solutions (e.g. relevant for Li, Pb, U).

7.5 **Sample measurement**

Run one or more calibration solutions and a calibration blank.

Run the interference check solution(s) to establish interference correction or to check presence of interference.

Run all samples including one or more method blanks.

Every 25 samples or less and at the end, run a calibration blank and a calibration check solution.

Run at least one spiked sample (digest or aqueous sample) from the series to check recovery.

NOTE 1 If standard addition calibration is applied to all samples leave out recovery check.

Some elements (for example Ag, B, Be, Li, Th) are rinsed very slowly from the sample inlet system. Check whether a high sample count rate has an effect on the next measurement result.

Whenever a new or usual sample matrix is encountered check:

- matrix effects by running the spike sample or
- matrix effects by running a fivefold diluted sample and
- inter-element interference analysing a different isotope.

8 **CALCULATION**

Calculate the element concentration in the aqueous sample:

$$\rho = (\rho_1 - \rho_0) f_d f_a$$

Calculate the element concentration in the digested solid sample:

$$w = (\rho_1 - \rho_0) f_a V/m$$

where:

ρ	is the concentration of the element in the aqueous sample in $\mu\text{g/l}$;
ρ_1	is the concentration of the element in the test sample in $\mu\text{g/l}$;
ρ_0	is the concentration of the element in the blank in $\mu\text{g/l}$;
f_d	is the dilution factor due to digestion of an aqueous sample; in all other cases $f_d = 1$;
f_a	is the dilution factor of the test portion;
w	is the mass fraction of the element in the solid sample in $\mu\text{g/kg}$;
V	is the volume of the test sample (digest) in litres;
M	is the mass of the digested sample in kg.

9 EXPRESSION OF RESULTS

State as many significant figures as are acceptable according to the precision of the measuring values, but not more than three significant figures.

10 QUALITY CONTROL

10.1 Blank

Result of the calibration blank check shall be within 3 times the instrumental detection limit.

10.2 Sensitivity

Result of the calibration check standard shall not deviate more than 10%.

10.3 Internal standard response

Internal standard response of a sample shall be more than 30% of the response of a calibration solution.

10.4 Interference

Magnitude of uncorrected isobaric molecular and doubly charged interferences shall not be higher than three times the instrumental detection limit.

Successive values of a correction factor shall not differ more than 20%.

10.5 Recovery

Spike recovery shall be between 75% and 125% or difference between results for the original sample and the fivefold-diluted sample shall be less than 20%.

11 TEST REPORT

The test report shall make reference to this international standard and contain the following details:

- Complete identification of the sample;
- Expression of results as indicated in clause 9;
- Sample pre-treatment, if appropriate;
- Any deviations from this method, and details of all circumstances which could have affected the result.

Tabel 1. Selected isotopes, spectral interferences and detection limits for quadrupole ICP-MS instruments

Element	Isotope	Abundance (%)	Method detection limit ^A $\mu\text{g/L}$	Theoretical interferences		Interference with practical relevance	Best usable isotopes	
				Interelement	Polyatomic ions		Preference	Reason
Ag	107	51,8	1		ZrO YO	⁹¹ Zr ¹⁶ O	x	least interference
	109	48,2	1		ZrO ZrOH NbO	-		
Al	27	100	5		BeO BO CN HCN		x	
As	75	100	1	Sm ²⁺ Eu ²⁺ Nd ²⁺	ArCl CoO Ar ₂ H ArK CaO ₂ NaCAr CPD ₂ CaCl	⁴⁶ Ar ³⁵ Cl	x	
Au	197	100	0,5		HfO TaO		x	
B	10	19,9	10				x	free of interference, low background
	11	80,1	10		BH			
Ba	135	6,6	3					
	137	11,2	3				x	highest abundance, least interference
	138	71,7	0,5	La Ce		La, Ce		
Be	9	100	0,5				x	
Bi	209	100	0,5				x	
Ca	43	0,14	100	Sr ²⁺	MgO BO ₂ AlO CaH CNO CO ₂	Sr ²⁺	x	low background, least interference
	44	2,1	50	Sr ²⁺	CaH MgO AlO BO ₂ CNO SiO CO ₂ N ₂ O	Sr ²⁺ , ¹² C ¹⁶ O ₂	x	lowest detection limit
Cd	111	12,8	0,5		MoO MoOH ZrOH K ₂ O ₂ H	⁹⁴ Zr ¹⁶ O ¹ H, ⁹⁶ Mo ¹⁶ O		
	113	12,2	0,5	In	MoO ZrOH Ca ₂ O ₂ H Ar ₂ O ₂ H RuO	In, ⁹² Mo ¹⁶ O	x	for high Sn
	114	28,7	0,3	Sn	MoO MoOH RuO	Sn, ⁹⁶ Mo ¹⁶ O	x	lowest detection limit, least interference
Ce	140	88,5	0,1				x	
Co	59	100	0,2	Sn ²⁺	CaO CaOH MgCl ArNa ArOH ArF	⁴³ Ca ¹⁶ O	x	
Cr	52	83,8	1		SO ArO ArC ArN ClO HClO ClN ArNH	⁴⁶ Ar ¹² C	x	for low C and high Cl
	53	9,5	5		H ₂ O ArC HClO ClO ArOH ArN ArNH SO	³⁷ Cl ¹⁶ O	x	for high C and low Cl
Cs	133	100	0,1		RuO ₂		x	
Cu	63	69,2	1		TiO PO ₂ ArNa MgCl NaCa CaOH ArCNH NCCl ClO	⁴⁷ Ti ¹⁶ O, ⁴⁶ Ar ²³ Na	x	for low Na and Ti, lowest detection limit
	65	30,8	2	Ba ²⁺	TiO PO ₂ SO ₂ SO ₂ H ArMg CaOH ArN ₂ H S ₂ COCl	⁴⁹ Ti ¹⁶ O, ³² S ¹⁶ O ₂ ¹ H, ⁴⁶ Ar ²⁵ Mg	x	for medium Mg, S and Ti and high Na
Dy	163	24,9	0,1		NdO SmO		x	
Er	166	33,6	0,1		SmO NdO		x	
Eu	151	47,8	0,1		BaO			
	153	52,2	0,1		BaO		x	

(Table 1 continued)

Element	Isotope	Abundance (%)	Method detection limit ^A , µg/L	Theoretical interferences		Interference with practical relevance	Best usable isotopes	
				Inter-element	Polyatomic ions		Preference	Reason
Fe	54	5.8	20	Cr	HClO ArO ArN ArNH ArOH SO ClO	ArN Cr	x	abundance and background determine choice
	57	2.2	50		CaO ArO ArOH CaC CaN CaOH MgO ₂ ArF	⁴² Ar ¹⁶ O ¹ H ⁴² Ca ¹⁶ O ¹ H	x	
Ga	69	60.1	0.3	Ce ²⁺ Ba ²⁺ La ²⁺	ClO ₂ ArP VO ArS SO ₂ S ₂	Ba ²⁺		
	71	39.9	0.3	Ni ²⁺ Ce ²⁺	ArP ClO ₂ ArCl SO ₂ ArS CrO		x	least interference
Gd	157	15.7	0.1		CeO PrO LaO BF		x	least interference
	158	24.8	0.1	Dy	CeO PrO NdO	Dy		
Ge	74	35.9	0.3	Se Sm ²⁺ Nd ²⁺	ArS Cl ₂ Ar ₂	Se	x	
Hf	178	27.3	0.1		GdO DyO ErO		x	
Hg	200	23.1	5		WO	¹⁸⁴ W ¹⁶ O		
	201	13.2	10		WO	¹⁸⁴ W ¹⁷ O	x	least interference of WO
	202	29.9	5		WO	¹⁸⁶ W ¹⁶ O		
Ho	165	100	0.1		SmO		x	
In	115	95.7	0.1	Sn	RuO	Sn	x	
Ir	193	62.7	0.1		HfO LuO		x	
K	39	93.3	50		ArH		x	
La	139	99.9	0.1				x	
Li	6	7.5	10					
	7	92.5	1				x	lowest detection limit
Lu	175	97.4	0.1	Hf	GdO TbO	Hf	x	
Mg	24	79.0	1	T ²⁺ Ca ²⁺	LiO NaH C ₂		x	lowest detection limit, least interference
	25	10.0	10	T ²⁺	LiO BeO C ₂ C ₂ H			
	26	11.0	10		BeO BO CN C ₂ H ₂ C ₂ H		x	for higher Mg concentrations
Mn	55	100	3		HClO ArN ClO NaS ArOH ArNH KO ArN ArO ArF	ArNH	x	
Mo	95	15.9	0.5		ArKO BrO			
	96	24.1	0.3	Ru	BrO K ₂ O	Ru	x	lowest detection limit
Na	23	100	10	T ²⁺ Ca ²⁺	LiO		x	
Nd	146	17.2	0.1		BaO RuO ₂		x	
Ni	58	68.1	1	Fe	CaO ArO CaN NaCl MgS CaOH Si ₂ ArOH	Fe	x	for low Fe
	60	26.2	3		CaO CaOH MgCl NaCl	⁴⁴ Ca ¹⁶ O	x	least interference
	61	1.1	5		CaOH ScO	⁴⁴ Ca ¹⁶ O ¹ H, ⁴⁶ Sc ¹⁶ O		
P	31	100	2		SH NO NOH N ₂ H CO COH	NO	x	
Pb	206 ^B	24.1	0.2		PtO		x	Sum of 205, 207 and 208
	207 ^B	22.1	0.2		IrO		x	Sum of 205, 207 and 208
	208 ^B	52.4	0.1		PtO		x	Sum of 205, 207 and 208
Pd	105	22.3	0.5		YO ArCu			
	106	26.5	0.5	Cd	MoO ZrO	Cd	x	
Pr	141	100	0.1				x	
Pt	195	33.8	0.5		HfO		x	
Rb	85	72.2	0.1	Yb ²⁺ Er ²⁺			x	

(Table 1 continued)

Element	Isotope	Abundance (%)	Method detection limit ^A , µg/L	Theoretical interferences		Interference with practical relevance	Best usable isotopes	
				Inter-element	Polyatomic ions		Preference	Reason
Re	185	37,4	0,1		TmO ErO		x	least interference
	187	62,6	0,1	Os	TmO YbO	Os	x	highest abundance
Rh	103	100	0,1	Pb ²⁺	SrO ArCu RbO		x	
Ru	101	17,0	0,2		ArNi NiCl			
	102	31,6	0,1	Pd	SrO	Pd	x	lowest detection limit, least interference
S	34	4,2	1000		O ₂ SH NOH O ₂ H	O ₂	x	
Sb	121	57,4	0,2		PdO		x	least interference
	123	47,6	0,2	Te	ZrO	Te		
Sc	45	100	5	Zr ²⁺	CO ₂ SiO BO ₂ AlO CaH CHO ₂ SiOH N ₂ OH	¹³ C ¹⁶ O ₂ , ²⁸ Si ¹⁶ O	x	
Se	77	7,6	10	Sm ²⁺ Gd ²⁺	ArCl Ar ₂ H CaCl CFNO ₂	⁴⁰ Ar ³⁷ Cl	x	for low Cl
	78	23,8	10	Kr Gd ²⁺ Dy ²⁺	Ar ₂ CaCl ArCa	³⁸ Ar ⁴⁰ Ar	x	for high Cl and Br
	82	8,7	10	Kr Ho ²⁺ Er ²⁺ Dy ²⁺	Ar ₂ H BrH CCl ₂ SO ₃ Ar ₂ H ₂ ArCa	Kr, ⁸¹ Br ¹ H	x	for low Br
Si	29	4,7	10		CO N ₂ BO SiH AlH COH N ₂ H		x	
Sm	147	15,0	0,1		RuO ₂		x	
Sn	118	24,2	1	U ²⁺	MoO RuO PdO		x	least interference
	120	32,6	1	Te	RuO PdO	Te		
Sr	86	9,9	0,5	Kr Yb ²⁺	RbH			
	88	82,6	0,3	Yb ²⁺ Lu ²⁺			x	lowest detection limit, least interference
Tb	159	100	0,1		NdO PrO		x	
Te	125	7,1	5				x	least interference
Te	126	19,0	2	Xe	PdO	Xe	x	lowest detection limit
Th	232	100	0,1				x	
Ti	47	7,3	10	Zr ²⁺	NO ₂ PO SiO CCl SNH SiOH SN N ₂ NO ₂ H	³¹ P ¹⁶ O	x	least interference
	48	73,8	1	Ca Zr ²⁺	ArC CCl SO NO ₂ PO SN NN ₂ C ₄	Ca, ³² S ¹⁶ O		
	49	5,5			SOH	³² S ¹⁶ O ¹ H		
Ti	203	29,5	0,2		WO ReO WHO			
	205	70,5	0,1				x	lowest detection limit, least interference
Tm	169	100	0,1		EuO		x	
U	238	99,3	0,1				x	
V	51	99,8	1		HSO ClO ClN ArNH ArC ArN SN SO	³⁶ Cl ¹⁶ O	x	
W	182	26,3	0,3		HoO DyO ErO		x	least interference
	184	30,7	0,3	Os	ErO YbO	Os		
Y	89	100	0,1				x	
Yb	172	21,9	0,2		DyO SmO GdO		x	least interference
	174	31,8	0,2	Hf	DyO GdO	Hf		
Zn	64	48,6	1	Ni	TiO CaO PO ₂ SO ₂ AlCl S ₂ PO ₂ H ArN ₂ ArMg	Ni, ⁴⁶ Ti ¹⁶ O, ³² S ¹⁶ O ₂ , ⁴² Ar ²⁴ Mg		
	66	27,9	2	Ba ²⁺	TiO VO SO ₂ PCI FeC S ₂ SO ₂ H	⁵⁰ Ti ¹⁶ O, ³² S ¹⁶ O ₂	x	for medium Ti ans S
	68	18,8	3	Ba ²⁺ Ce ²⁺	VO ClO ₂ SO ₂ TiO ArS FeN PCI FeC S ₂ ArN ₂ ArSi	Ba ²⁺ , ⁴⁶ Ar ²⁴ Si	x	for low Ba and Si
Zr	90	51,5	0,2				x	

^A Method detection limit for relatively clean aqueous samples to be interpreted as an instrumental detection limit

^B Signals of the isotopes summed due to natural variation of abundances

Table 2. Examples of equations for correcting spectral interferences

Element	Recommended isotope and inter-element correction
As	$^{75}\text{As} - 3,127(^{77}\text{Se} - 0,815^{82}\text{Se})$ or $^{75}\text{As} - 3,127(^{77}\text{Se} + 0,3220^{78}\text{Se})$
Ba	$^{138}\text{Ba} - 0,0009008^{139}\text{La} - 0,002825^{140}\text{Ce}$
Cd	$^{114}\text{Cd} - 0,02684^{118}\text{Sn}$
Ge	$^{74}\text{Ge} - 0,1385^{82}\text{Se}$
In	$^{115}\text{In} - 0,01486^{118}\text{Sn}$
Mo	$^{98}\text{Mo} - 0,1106^{101}\text{Ru}$
Ni	$^{58}\text{Ni} - 0,04825^{54}\text{Fe}$
Pb	$^{208}\text{Pb} + ^{207}\text{Pb} + ^{206}\text{Pb}$
Se	$^{82}\text{Se} - 1,009^{83}\text{Kr}$
Sn	$^{120}\text{Sn} - 0,01344^{125}\text{Te}$
V	$^{51}\text{V} - 3,127(^{53}\text{Cr} - 0,1134^{52}\text{Cr})$
W	$^{184}\text{W} - 0,001242^{189}\text{Os}$