INTERNATIONAL
RECOMMENDATION

OIML R 116
Edition 2006 (E)

Inductively coupled plasma atomic emission
spectrometers for the measurement of metal
pollutants in water

Spectromètres à émission atomique de plasma couplé inductivement
pour le mesurage des polluants métalliques dans l'eau

OIML

ORGANISATION INTERNATIONALE
DE MÉTROLOGIE LÉGALE

INTERNATIONAL ORGANIZATION
OF LEGAL METROLOGY

Contents

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Inductively coupled plasma atomic emission spectrometers for the measurement of metal pollutants in water

1 Scope

1.1 This Recommendation provides requirements for defining, testing, and verifying the performance of inductively coupled plasma atomic emission spectrometers (ICP systems) when used for measuring metallic and some non-metallic pollutants in water as mandated by national laws and regulations. It does not intend to exclude any other equivalent means of measuring metal pollutants in water. An ICP system can be applied for rapid multi-element determination of a large number of elements in samples of potable, surface, ground, and saline waters as well as domestic and industrial waste waters. References [1]–[3] give a description of the ICP system and some applications.

1.2 ICP systems covered by this Recommendation incorporate argon inductively coupled plasma and determine elemental pollutants either in a simultaneous or sequential mode when applied for the analysis of water.

1.3 Performance better than the minimum requirements prescribed for these applications of an ICP system may be achieved by optimizing the performance of each major component of an instrument. In such cases, success may depend on the knowledge, skill, and experience of the analyst.

1.4 A sample usually requires undergoing a specific preparation technique prior to analysis with an ICP system. Sampling techniques and methods of analysis are beyond the scope of this Recommendation. As appropriate, relevant international, regional or national sampling techniques and reference methods of analysis shall be applied.

1.5 This Recommendation does not address requirements and tests that may be necessary for operator safety. Therefore, users should determine whether an instrument meets the safety and labeling requirements specified in national regulations.

2 Application

2.1 This Recommendation applies to ICP systems used for measuring metallic and some non-metallic pollutants in water. These instruments provide a means for monitoring and assessing water quality that may be prescribed by pollution control programs mandated by national laws or regulations. Such control programs usually cover both toxic and non-toxic pollutants in potable, surface, ground, and saline water, as well as domestic and industrial-waste waters to assess whether the concentrations of pollutants are within established regulated limits of concentration.

2.2 Normally after simple acidification and filtration, water samples may be analyzed directly by ICP systems. In cases of samples having concentrations of the elements of interest below the detection

limit of the ICP system, pre-concentration of samples before analysis is required. Samples of domestic and industrial waste water usually require processing to dissolve suspended soluble material before analysis. Sludge, sediments and other types of solid samples may also be analyzed after appropriate pretreatment.

3   Terminology

Note: Definitions of terms may be found in reference [4] for other basic and general terms used in metrology and in reference [5] for terms used in analytical spectroscopic methods.

3.1   Plasma

Gas having a large fraction of its atoms in an ionized state that excites and ionizes atoms of a sample introduced into an ICP system for analysis.

3.2   Observation zone

Region of the plasma monitored during the measurement process.

3.3   Radio frequency (r.f.) coil

Tube, wound around the outer quartz tube of the torch, through which the r.f. energy is transmitted to the argon.

Note: This coil is generally water-cooled, consists of 3 or 4 turns, and is constructed of a copper tube that may be plated with silver or gold and is also known as the load coil.

3.4   Nebulizer

Device used to transform the liquid sample into an aerosol.

Note: The nebulizer produces droplets of varying sizes that pass through the spray chamber where larger droplets remain on the chamber walls and are removed as waste.

3.5   Carrier flow

Flow of argon gas directed through the nebulizer for transporting the aerosol sample through the injector and into the plasma.

3.6   Auxiliary flow

Flow of argon gas between the intermediate and center (injector) tubes of an ICP torch that is used to adjust the position of the plasma optimally above the load coil.

3.7   Coolant flow

Flow of argon gas between the outer and intermediate tubes of an ICP torch at a rate depending on the torch design to maintain the plasma in the center of the torch and to prevent overheating the tubes.

3.8   Blank test solution

Solution that is prepared in the same way as the sample solution but does not contain the element or elements to be determined.

3.9   Reference standard solution

Solution with an accurately known concentration of a sample element or elements of interest used for testing and calibrating an instrument.

3.10   Detector

Device that responds to light signals passing through the exit slit of the polychromator or scanning monochromator of the ICP system.

3.11   Detection limit

Concentration of an element that provides an output signal equivalent to three times the standard deviation of the mean of the output signal of a blank solution and is the minimum quantity measured before it can be concluded that an element has been detected.

Note: In this Recommendation, this term refers to the determination of an element in a reference solution free of interfering elements. The baseline noise is established by measuring the output signal of several aliquots of the blank test solution.

3.12   Working range

Range of concentrations over which the output signal of the instrument is directly proportional to the concentration of the element being measured to within specified limits.

3.13   Repeatability

Closeness of agreement between successive measurements of the same measurand carried out under the same conditions and within a short period of time.

Note: The same conditions include the following: the method of measurement, the operator, the measuring instrument, the location, and the environmental conditions.

3.14   Resolution

Measure of a spectrometer's ability to separate two adjacent spectral lines.

Note: It usually indicates the smallest distance between two adjacent spectral lines at which they can be distinguished one from the another.

4   Description of the instrument

4.1   General

4.1.1   A diagram of an ICP system is shown in Figure 1. It shows the following major components:

     (a) gas-flow control devices for the carrier, auxiliary, and coolant argon supplies,

     (b) a sample introduction device,

     (c) a torch,

     (d) a radio frequency (r.f.) generator,

     (e) transfer optics and a spectrometer,

     (f) one or more detectors, and

     (g) the data handling system.

4.1.2 An outline of the measurement process follows. A sample solution is introduced into a nebulizer that converts a fraction of the sample into an aerosol. Then, the sample is transported by an argon gas stream into an argon plasma at a temperature between 6 000 °C and 8 000 °C. The plasma is produced and maintained by electromagnetic coupling by a coil in a radio frequency circuit and is initiated by a high voltage electrical spark that ionizes some of the flowing argon atoms. Atoms of metal elements in the sample are converted in the plasma to excited atoms and ions that emit characteristic wavelengths of radiation when they return to the ground energy level or any lower energy excited state. Photons thus emitted are focused by transfer optics into a spectrometer (either a polychromator or a monochromator) which in turn resolves the light into its discrete wavelengths and directs that dispersed radiation onto a detector. The detector converts the radiation intensity of a specific wavelength into an electrical signal that allows the concentration of the particular element to be determined on the basis of previous measurements of reference standard solutions of elements of interest. The output signals of the detector or detectors are input into a data handling system for recording and subsequent analysis of the data.

4.1.3 For an accurate measurement of emitted radiation from certain elements, the ICP system requires a means to correct for contributions to the emitted-radiation intensity at the wavelength of interest not caused by the element or elements of interest. This background emission may be due to the black body continuum radiation from the plasma, electron-atom recombination, molecular emission, and/or sample matrix component emission other than from the element or elements of interest.
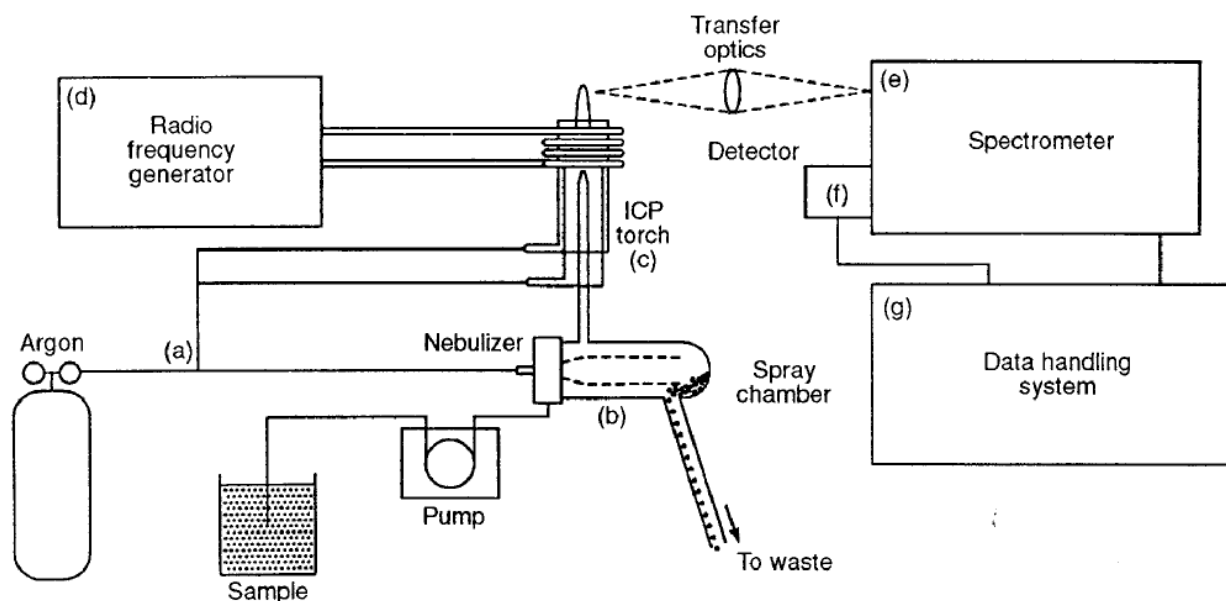
Figure 1 Diagram of an ICP system

4.2 Major components

*4.2.1* Gas flow control devices regulate the flow of argon gas. They control the following functions:

   (a) the carrier flow for transferring the aerosol into the plasma,

   (b) the auxiliary flow contained between the intermediate and center (injector) tubes of the torch, and

   (c) the coolant flow contained between the outer and intermediate tubes of the torch.

4.2.2   A sample introduction device called the nebulizer converts a liquid sample into an aerosol.

4.2.3   A torch is a device consisting of three concentric tubes used to support the plasma and to introduce the sample into the plasma through the injector tube.

Note: The two outer tubes are usually made of quartz. Observation of the torch may be lateral or axial as shown in Figure 2.

4.2.4   A r.f. generator is the power source that maintains the plasma in the torch by coupling its energy to the argon ions through an r.f. load coil located around the outer tube of the torch.

Argon Ion Plasma
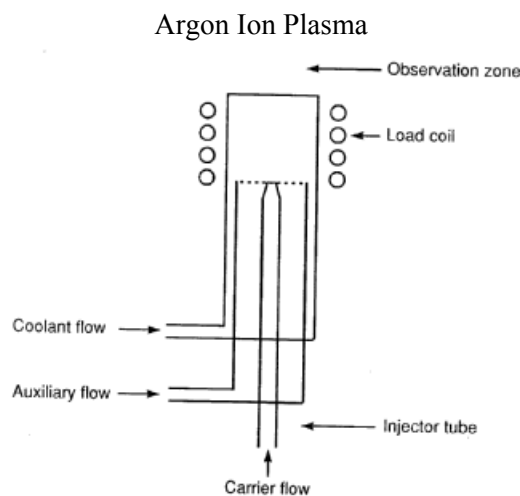
Figure 2 Diagram of the torch of an ICP system

4.2.5   Transfer optics consist of optical components such as mirrors and/or lenses used to collect light emitted from the plasma and then to focus that light onto the entrance slit of the spectrometer.

4.2.6   *Spectrometers*

4.2.6.1 A diagram of a polychromator of an ICP system is shown in Figure 3. The light from the torch is focused onto the entrance slit of the spectrometer by transfer optics. The light passing through that slit is then dispersed by a diffraction grating through an array of exit slits. Each exit slit is precisely aligned to pass a specific wavelength of a particular element of interest onto a light detector that converts the radiation intensity into an electrical signal. The polychromator ICP system is capable of determining many elements simultaneously. The number of elements determined simultaneously is limited by the number of exit slits and associated detectors usually arranged in an array.
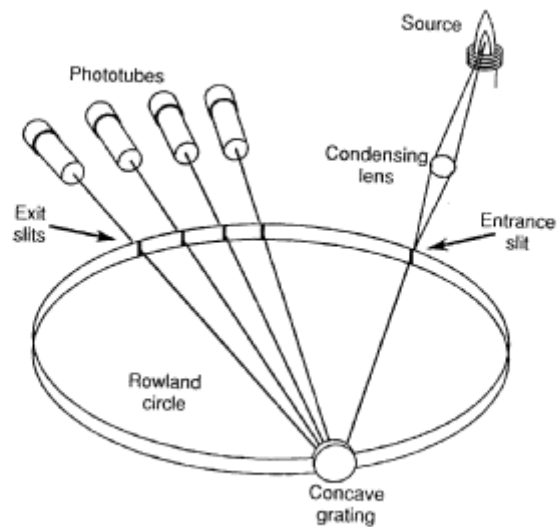
Figure 3 Diagram of the polychromator of an ICP system

4.2.6.2 A diagram of a scanning monochromator of an ICP system is shown in Figure 4. The radiation from the torch is focused through the entrance slit of the spectrometer onto the collimating mirror of the monochromator. The radiation is then dispersed in wavelength by a diffraction grating. This grating is then rotated with respect to the incident light in order to direct a specific wavelength through the exit slit onto a single detector. An alternate configuration may be used in which the grating angle is fixed with respect to the incident light while the exit slit/detector is moved to a specific location on an arc with respect to the grating in order to direct a specific wavelength to the detector. The scanning monochromator ICP system is capable of selecting not only a particular wavelength of interest but also a number of different wavelengths within its measuring range for analysis of each sample.
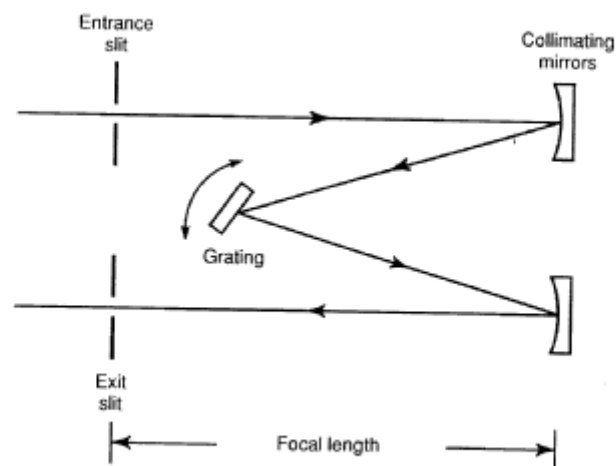
Figure 4 Diagram of a scanning monochromator of an ICP system

4.2.6.3 Both the polychromator and scanning monochromator systems can be used with either conventional, high-groove density diffraction gratings or with low-groove density echelle diffraction gratings. A conventional diffraction grating is finely ruled, has an efficiency characteristic varying

only slightly with wavelength in the primary order in which it is intended to be used, and is generally used in a single order throughout the wavelength range for which it is designed. Higher orders of diffraction (up to four in some cases), however, may be used to measure radiation with higher resolving power at wavelengths in the visible range when the grating has been optimized for use in the ultraviolet range. Order sorting filters may be required for measurements in higher orders. An echelle diffraction grating is a low-groove density grating, intended to be used in very high orders of diffraction with large (> 45°) angles of incidence of the radiation to achieve greater resolving power in a physically smaller system. When the many multiple high orders of echelle grating are intended to be viewed simultaneously, an order-sorting or cross-dispersing optical component is required.

4.2.7 A detector converts the radiation passing through the exit slit of the spectrometer into an electrical signal.

4.2.8 The data system provides a means for recording and displaying the output signal from the detector or detectors and calculating the concentration of the element or elements being analyzed. It may provide some control and adjustment of the instrument operating parameters.

5 Metrological requirements

5.1 The metrological characteristics of the ICP system are given in Table I.

5.2 During type evaluation and initial and subsequent verification, the repeatability, detection limit, and working range of the output signal of the instrument shall be tested in a laboratory using reference sample solutions under reference conditions as follows:

- mean ambient temperature of between 20 °C and 27 °C and stable to within ± 3 °C during the measurement; and
- relative humidity (RH) between 30 % and 80 %.

5.3 The manufacturer shall specify the following components and other conditions under which the instrument is to be tested:

- torch assembly and height;
- gas flow control devices and flow rates;
- sample introduction device;
- frequency of the r.f. generator;
- any necessary programming for detection of the element of interest.

5.4 The repeatability of measurements shall be checked. The procedure shall include measuring 10 repeated samples of a reference standard solution of at least five elements. The concentration of the reference standard solutions shall be equivalent to approximately 100 times the detection limit value of the elements being determined. The relative standard deviation of the measurement results for each element shall be ≤ 2 %.

Note: Recommended concentrations of stock concentrations for preparing reference standard solutions are given in Annex A.

5.5 The detection limits of the five elements selected for 5.4 shall be checked. The procedure shall include measuring 10 repeated samples of a blank solution at the wavelength of detection for each element selected. The detection limit for each element is determined by multiplying the standard

deviation of the measurement results by three. It shall be equal to or less than the value given in Table 1.

5.6   The working range and nominal instrument linearity shall be determined by fitting a curve to data obtained for at least five different concentrations of reference standard solutions for at least one of the elements (preferably copper) selected for 5.4. The concentrations of the reference standard solutions shall be within the values of the working ranges indicated in Table 1 and include a lower limit of approximately 100 times the detection limit and the specified upper limit. At each concentration, 10 successive measurements shall be performed, and the mean value and standard deviation shall be calculated. A linear curve shall be fitted to the mean values calculated at the five different concentrations.

The correlation coefficient, r, of the fitted curve shall be determined, and r^2 shall be ≥ 0.95. This procedure shall also confirm the upper limit of concentration.

Table 1 Metrological characteristics of an ICP system

Element	Wavelength (nm)	Detection limit (μg/L)	Upper limit of concentration (mg/L)
Aluminum	308.215	20	100
Antimony	206.833	50	100
Arsenic	193.696	50	100
Barium	455.403	0.5	50
Beryllium	313.042	0.5	10
Boron	249.773	5	50
Cadmium	226.502	5	50
Calcium	317.933	10	100
Chromium	267.716	7	50
Cobalt	228.616	6	50
Copper	324.754	3	50
Iron	259.940	3	100
Lead	220.353	50	100
Lithium	670.784	3	100
Magnesium	279.079	30	20
Manganese	257.610	2	50
Molybdenum	202.030	5	100
Nickel	231.604	10	50
Potassium	766.491	200	100
Selenium	196.026	100	100
Silicon	288.158	60	100
Silver	328.068	5	50
Sodium	588.995	50	100
Strontium	407.771	0.5	50
Thallium	190.864	50	100
Vanadium	292.402	5	50
Zinc	213.856	3	100

6 Technical requirements

6.1 Gas-flow regulating devices shall be available to control the carrier, auxiliary and coolant gas flows. The instrument manufacturer's operating instructions shall specify nominal flowrate values that provide the appropriate operating and measurement conditions.

6.2 The manufacturer shall specify the type and the purity of the gas used to supply the torch.

Note: Argon is the normal gas used with typical purity of at least 99.995 % depending on the impurities and detection requirements.

6.3 An appropriate sample introduction device shall be used to meet the requirements of clause 5.

Note: The commonly used sample introduction device is a pneumatic nebulizer. Various nebulizer designs are generally applicable; however, a special design may be required to handle viscous samples, such as those containing particulate material or having a high content of dissolved solids. A peristaltic pump may be used to regulate the sample delivered to the nebulizer.

6.4 The r.f. generator shall have a power range of 0.5 kW to 2 kW with a stability of ± 0.5 %. It shall operate within a frequency range of 1 MHz to 60 MHz.

Note: Generator frequencies of 27.12 MHz and 40.68 MHz are industrial standards in some countries.

6.5 The relative height of the torch assembly shall be adjustable with respect to the entrance slit of the spectrometer.

Note: Some instruments may offer programmable adjustments of the observation zone.

6.6 The spectrometer shall cover the wavelength range from 190 nm to 770 nm, with a resolution of less than or equal to 0.02 nm.

6.7 The data handling system shall be capable of producing an accurate and accessible record of measurements. It shall also be used for displaying, recording and storing ICP system signal outputs and for data processing and may be used for instrument control of some instrument parameters.

Note: The data handling system usually provides a means for adjusting the torch, making background corrections, and controlling other parameters associated with analysis.

6.8 Markings shall be attached conspicuously to all major components of the ICP system as follows:
- name of the manufacturer;
- instrument model, serial number, and date (month and year) of manufacture;
- voltage, frequency, and current requirements.

Note: Labels or declarations concerning safety of personnel and radio frequency interference emission should be provided according to national regulations.

6.9 Manufacturers of an ICP system shall supply an instrument manual that describes requirements for its installation, operation, and routine maintenance.

Note: Manufacturers may also provide service manuals and analytical methods manuals.

7 Practical instructions

7.1 During normal operation, an ICP system requires high voltage and generates high temperatures and corrosive and/or toxic gases. Instrument installation and operation shall take into account these requirements particularly with respect to the exhaust of heat and corrosive and/or toxic gases. Warning labels shall be placed conspicuously on the instrument to alert users of these potential hazards. Such labels shall be consistent with national safety regulations.

7.2 Before installation of an ICP system, all laboratory environmental factors shall be considered. Manufacturers shall provide specifications for the rated power of the instrument including allowable variations from the rated mains voltage and frequency. Specifications shall also be provided for rated heat dissipation and operational conditions for ambient temperature, humidity, and exhaust-gas venting.

8 Metrological controls

8.1 Type evaluation

8.1.1 The manufacturer shall provide the responsible national body with an ICP system and its operating manual, and may also provide test data and other relevant information that support a decision with regard to the system meeting the requirements of this Recommendation.

8.1.2 The operating manual shall be reviewed for its completeness and clarity of instructions.

8.1.3 The responsible national body shall visually inspect the instrument in conjunction with a review of its operating manual to determine that the following requirements are met:

- argon flow control devices (6.1);
- specification of gas purity (6.2);
- sample introduction device (6.3);
- r.f. generator (6.4);
- adjustable height of the torch (6.5);
- wavelength range and resolution (6.6);
- data systems (6.7);
- markings (6.8).

8.1.4 The responsible national body shall carry out the following tests, or may accept the manufacturer's test data, that confirm acceptable performance of the following performance requirements:

- repeatability (5.4 and B.3);
- detection limit (5.5, Table 1, and B.4);
- working range (5.6 and Table 1, and B.5).

8.1.5 A test procedure for an ICP system shall be carried out according to that given in Annex B.

8.1.6 The report on tests of the ICP system carried out during type evaluation shall contain as a minimum the items of information according to the format specified in Annex C. A specific report form may be developed according to national preference. The manufacturer shall be provided with specific information or specific comments about any failures.

8.2   Initial and subsequent verification

8.2.1   The documentation provided by the manufacturer shall be examined to ensure compliance with 8.1.

8.2.2   Tests shall be carried out under reference conditions specified in 5.3.

8.2.3   Any of the tests specified for the ICP system under 8.1.4 that are considered critical to the specific application shall be performed.

8.2.4   The national responsible body shall specify the period of validity of the verification.

8.2.5   An instrument shall undergo subsequent verification equivalent to initial verification after repair or replacement of any major components of the system or after the period of time specified by the national responsible body.

8.3   Routine tests by a user

8.3.1   The national responsible body shall identify methods for using an ICP system to measure specific pollutants. Some measurement methods may be appropriate for use in assessing the performance of an ICP system.

8.3.2   The user of an ICP system shall carry out a test with a reference sample solution before and after a series of measurements in the laboratory. The results of these tests shall be within the limits established by the national responsible body.

8.3.3   In addition to the requirements of 8.3.2, the user shall carry out a performance test of the entire ICP system related to and before a specific application.

8.3.4   A chronological written record shall be maintained for each ICP system and shall contain at least the following information:

 ▪ results of all routine tests;
 ▪ results of calibrations;
 ▪ identification of any major components replaced;
 ▪ dates and summaries of maintenance and repair.

References

[1]   Thompson, Michael and Walsh, J. Nicholas, A Handbook of Inductively Coupled Plasma Spectrometry. Blackie, Glasgow and London (1983), 2nd Ed. 1989 ISBN 0-412-00371-6

[2]   Boumans, P.W.J.M. ed., Inductively Coupled Plasma Emission Spectrometry Part 2: Application and Fundamentals. John Wiley and Sons (1987). ISBN 0-471-85378-X

[3]   Montaser, A. and Golightly, D.W. eds., Inductively Coupled Plasma in Analytical Atomic Spectrometry, VCH Publishers, New York (1987), ISBN 089573334X

[4]   BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML, International Vocabulary of Basic and General Terms in Metrology. Published by ISO (1993).

[5]   ISO 6955 International Organization for Standardization, Analytical Spectroscopic Methods - Flame Emission, Atomic Absorption, and Atomic Fluorescence - Vocabulary, ISO6955, First edition 1982-07-15.

Annex A

Reference standard solutions

(Mandatory)

A.1 Preparation of reference standard solutions

A.1.1 A stock solution of each element of interest shall either be obtained from commercial sources or be prepared from ultra-high purity grade elements or their salts. These solutions shall be prepared using ultra-high purity grade hydrochloric acid or nitric acid, as appropriate, and shall have an acid concentration such as to produce a stable solution of the element of interest. The water used in preparation of the stock standard solutions and in subsequent dilutions shall have an electrical conductivity at 25 °C of less than 0.1 mS/m (grade 2 water according to ISO 3696).

Note 1: Stock standard solutions usually have a concentration of the element or elements of interest of 1 000 mg/L or 10 000 mg/L.

Note 2: Stock standard solutions should be prepared using appropriate and documented standard methods.

Note 3: All salts used as a source for an element should be dried at 105 °C for one hour except for carbonates, which should be dried at 140 °C for one hour.

A.1.2 The concentrations of the reference standard solutions shall be those specified in Table A.1 and shall be prepared by appropriate dilution of the stock standard solutions described in A.1.1. The selection of an acid and its concentration shall be made so as to provide compatibility for any mixed solutions being prepared.

A.1.3 Stock standard solutions shall be monitored periodically for stability.

A.2 Preparation of mixed (multi-element) reference standard solutions

A.2.1 Mixed (multi-element) reference standard solutions containing several elements of interest in the same solution shall be prepared using suitable combinations and dilutions of the stock standard solutions at the concentrations recommended in Table A.1. Prior to preparing the mixed reference standard solutions, the stock standard solutions to be used shall be analyzed to identify any potential spectral interference at the wavelengths selected for analysis.

A.2.2 The mixed reference standard solutions shall contain elements that are compatible with each other and stable in the mixture. The compatibility of the anions shall also be considered.

Note: Any acids added to preserve the mixture shall be compatible with the elements included.

A.2.3 The mixed reference standard solutions shall be monitored periodically for stability.

Table A.1 Recommended reference standard solution concentrations

Element	Reference standard solution concentration (mg/L)
Aluminum	10.0
Antimony	10.0
Arsenic	10.0
Barium	1.0
Beryllium	1.0
Boron	1.0
Cadmium	2.0
Calcium	10.0
Chromium	5.0
Cobalt	2.0
Copper	1.0
Iron	10.0
Lead	10.0
Lithium	5.0
Magnesium	10.0
Manganese	2.0
Molybdenum	10.0
Nickel	2.0
Potassium	10.0
Selenium	5.0
Silicon	10.0
Silver	2.0
Sodium	10.0
Strontium	1.0
Thallium	10.0
Vanadium	1.0
Zinc	5.0

Annex B

Test procedure

(Mandatory)

B.1   This test procedure involves determining trace amounts of various elements in several reference standard solutions over the wavelength range of the instrument.

B.2   Use the following initial procedures:

B.2.1   Set up the instrument according to the manufacturer's instructions, making any necessary adjustments or calibrations.

B.2.2   Select at least five elements listed in Table 1 including copper with two elements being selected at the extreme wavelengths of anticipated analysis, for example thallium and potassium. Prepare stock reference standard solutions of these elements individually or as mixtures in the concentrations recommended in Table A.1 of Annex A.

B.2.3   Prepare a blank test solution.

B.3   Repeatability

B.3.1   Perform 10 replicate measurements for the analysis of an appropriate sample of each of the five reference standard solutions of the elements selected. The concentration of the reference standard solutions shall be equivalent to approximately 100 times the detection limit value of the elements being determined according to Table 1, and each shall be measured at its specified wavelength.

B.3.2   Compute the mean and relative standard deviations of the results of the measurements performed according to B.3.1 at each reference solution at the appropriate wavelength using the following formulas:

$$s_r = \frac{s}{\bar{x}} \cdot 100 \ \%$$

where:

$$s = \left[\frac{\sum \left(x_i - \bar{x}\right)^2}{n-1} \right]^{1/2}$$

x_i = the individual result, and

$\bar{x}$ = the average result for n number of repeated measurements.

B.3.3   The relative standard deviations of all mean values determined in B.3.2 shall meet the requirements of 5.4.

B.4   Detection limit

B.4.1   Perform 10 replicate measurements of the blank test solution at each of the wavelengths of the elements selected for analysis in B.3.1.

B.4.2   Compute the mean value and standard deviation of the results obtained in B.4.1.

B.4.3   Multiply each standard deviation value obtained in B.4.2 by three. The detection limits results determined for all elements selected shall meet the requirements of 5.5.

B.5   Working range

B.5.1   For at least one element selected according to B.2 (preferably copper), prepare a reference standard solution with a concentration equal to or slightly more than the upper limit concentration as specified in Table 1. From that reference standard solution, prepare at least 4 more reference standard solutions by dilution to different concentrations with the lowest concentration being approximately 100 times the detection limit.

B.5.2   Perform 10 successive measurements for each concentration of the reference standard solution prepared in B.5.1 and compute the mean of the results of each set of measurements.

B.5.3   A linear least-squares analysis is applied to a plot of the data obtained in B.5.2. Plot the results to the mean value determined for each concentration and fit a linear least-squares regression, determining the slope, *m*, intercept, *b*, and correlation coefficient, *r*, parameters from the general linear equation model:

$$y = mx + b$$

Calculate the square of the correlation coefficient for the least-squares regression curve using:

- the sum of the squared residuals, S_{xy}^2,
- the standard deviation of the known concentration values, s_x, and
- the standard deviation of the measured signal values, s_y,

from the data as follows:

$$r^2 = \frac{S_{xy}^2}{s_x s_y}$$

where:

$$S_{xy} = \Sigma \left(x_i - \bar{x} \right)\left(y_i - \bar{y} \right)$$

$$s_x = \Sigma \left(x_i - \bar{x} \right)^2$$

$$s_y = \Sigma \left(y_i - \bar{y} \right)^2$$

B.5.4 The correlation coefficient, r, determined for the fitted curve in B.3.5.2 shall be such that r^2 is ≥ 0.95.

Note: The correlation coefficient, r, interprets how well the data fits the least-squares regression curve. A perfect fit would be $r = \pm 1$ or $r^2 = 1$.

Annex C
Test report format
(Mandatory)

A test report intended for use within the scope of the *OIML Certificate System for Measuring Instruments* or for other purposes shall include the following information:

Report No. _____

OIML Recommendation R 116, Edition 2006

C.1 Name and address of the testing laboratory or laboratories:

_____
_____
_____
_____

C.2 Location at which the tests were performed, if other than that indicated in C.1:

_____
_____
_____
_____

C.3 Name and address of the manufacturer:

_____
_____
_____
_____

C.4 Name and address of applicant, if other than the manufacturer:

_____
_____
_____
_____

C.5   Identification of the instrument (type) tested:

Instrument type: polychromator system   _____

                        or scanning monochromator system   _____

Wavelength range and resolution (nm):

Minimum   _____

Maximum   _____

Resolution   _____

Trade name: _____

Model number: _____

Serial number: _____

Date of manufacture: _____

Requirements for voltage: _____ frequency: _____ current: _____

C.6   Review of the operating manual: □ Acceptable   □ Deficient

Comments: _____

_____

_____

_____

C.7   Summary of a visual inspection of the instrument and review of information in the operating manual:

C.7.1   Specification of gas type and purity: type _____   purity _____

Comments: _____

_____

_____

_____

C.7.2   Argon flow control devices and instructions: □ Yes   □ No

Comments: _____

_____

_____

_____

C.7.3   r.f. generator: voltage range from _____kW to _____ kW   stability: _____

Comments: _____

_____

_____

_____

C.7.4   Adjustable height of the torch: □ Yes   □ No

Comments: _____

_____

_____

_____

C.7.5   Background correction: ☐ Yes   ☐ No

Comments: _____

_____

_____

_____

C.7.6   Markings: ☐ Pass   ☐ Fail

Comments: _____

_____

_____

_____

C.8   Summary of the results of tests carried out according to 8.1:

C.8.1   Conditions of testing:

Ambient temperature: _____

Humidity: _____

Gas type: _____ purity: _____

Flow device settings carrier gas: _____ auxiliary flow: _____

Coolant flow: _____

r.f. generator settings frequency: _____ power: _____

Nebulizer type: _____

Torch height: _____

Spectrometer type: _____

Detector(s) type: _____

Background correction: ☐ Manual   ☐ Automatic

Data handling system display data outputs: _____

Reduction of data: _____

Control of other instrument parameters (list):

_____

_____

_____

_____

C.8.2   Determination of repeatability

Elements →	1	2	3	4	5
Wavelength →					
Concentration →					
Repetition ↓ 1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
$\overline{X}$					
σ_r					

Relative standard deviation:

- Element 1: ☐ Pass   ☐ Fail
- Element 2: ☐ Pass   ☐ Fail
- Element 3: ☐ Pass   ☐ Fail
- Element 4: ☐ Pass   ☐ Fail
- Element 5: ☐ Pass   ☐ Fail

Comments: _____

_____

_____

_____

_____

C.8.3 Determination of detection limit

Elements →	1	2	3	4	5
Wavelength →					
Concentration →					
Repetition ↓ 1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
$\overline{X}$					
σ_r					
D.L.					

Detection limit (D.L.): - Element 1: Pass ☐ Fail ☐
- Element 2: Pass ☐ Fail ☐
- Element 3: Pass ☐ Fail ☐
- Element 4: Pass ☐ Fail ☐
- Element 5: Pass ☐ Fail ☐

Comments: _____

_____

_____

_____

C.8.4   Determination of working range and linearity

Element: _____

wavelength setting: _____

Measurement Concentration → repetition ↓	1	2	3	4	5
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
$\overline{X}$					
σ_r					

r^2:_____

Pass ☐   Fail ☐

Comments: _____

_____

_____

_____

C.9   Brief statement of conclusions as to whether the instrument tested meets the requirements of this Recommendation.

_____

_____

_____

C.10   Person(s) responsible for the testing:

Signature(s) and title(s): _____

_____

_____

Date: _____