ORGANISATION INTERNATIONALE
DE MÉTROLOGIE LÉGALE

INTERNATIONAL RECOMMENDATION

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

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

OIML R 116

Edition 1995 (E)

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FOREWORD

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INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETERS FOR 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 legal measurements of metallic and some non-metallic pollutants in water. It does not intend to exclude any other equivalent means of analysis. An ICP system can be applied for rapid multielement determination of a large number of elements in samples of potable, surface, ground, and saline waters as well as domestic and industrial waste waters [1–5]. Measurement methods are beyond the scope of this Recommendation; however, reference to some relevant measurement methods is provided in Annex A.

1.2 ICP systems covered by this Recommendation are those which incorporate an argon inductively coupled plasma and which determine elements either in a simultaneous or sequential mode when applied for an 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.

2 Application

2.1 This Recommendation applies to an ICP system 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 are usually designed to 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 elements are below regulated limits.

2.2 Water samples may generally be analyzed directly by ICP systems after simple acidification and filtration. In some cases where the levels of the elements of interest are below the detection limit of the ICP systems, some type of preconcentration will be required. Samples of domestic and industrial waste water usually require processing to solubilize suspended material before analysis. Sludges, sediments and other types of solid samples may also be analyzed after appropriate pretreatment.

3 Terminology

Note: Definitions may be found in reference [6] for other basic and general terms used in metrology and in reference [7] for analytical spectroscopic methods.

3.1 Plasma

A 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

That region of the plasma monitored during the measurement process.

3.3 Radio frequency (r.f.) coil

A tube, wound around the outer quartz tube of the torch, through which the r.f. energy is transmitted to the argon. It is also referred to as the load coil.

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.

3.4 Nebulizer

A device that converts a 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

The flow of argon gas directed through the nebulizer that carries the sample aerosol through the injector and into the plasma.

3.6 Auxiliary flow

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

3.7 Coolant flow

The 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 of the tubes.

3.8 Blank test solution

A solution that is prepared in the same way as the sample solution but which does not contain the element(s) to be determined.

3.9 Reference standard solution

A solution with an accurately known concentration of a sample element(s) of interest used for testing and calibrating an instrument.

3.10 Detector

The 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

The 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. It 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 Linear range

The 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.

Note: For the ICP, the linear range is also its working range.

3.13 Repeatability

The 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: method of measurement, operator, measuring instrument, location, and environmental conditions.

3.14 Resolution

A measure of a spectrometer's ability to separate two adjacent spectral lines. It is commonly used to indicate the smallest distance between two adjacent spectral lines at which they can be distinguished from one another.

4 Description of the instrument

4.1 General

4.1.1 A diagram of an ICP system is shown in Figure 1. The major components of an ICP system consist of (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) data handling system.

4.1.2 An outline of the measurement process follows. A sample solution is introduced into a nebulizer which converts a fraction of the sample into an aerosol. The sample is then carried 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 through a coil in a radio frequency circuit. It is initiated by a high voltage electrical spark which seeds the flowing argon with ions. Elements in the sample are converted in the plasma to excited atoms and ions which 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 which allows the concentration of the particular element to be determined on the basis of previous measurements of reference standard solutions of that element. The output signals of the detector(s) are input into a data handling system for recording and subsequent analysis of the data.

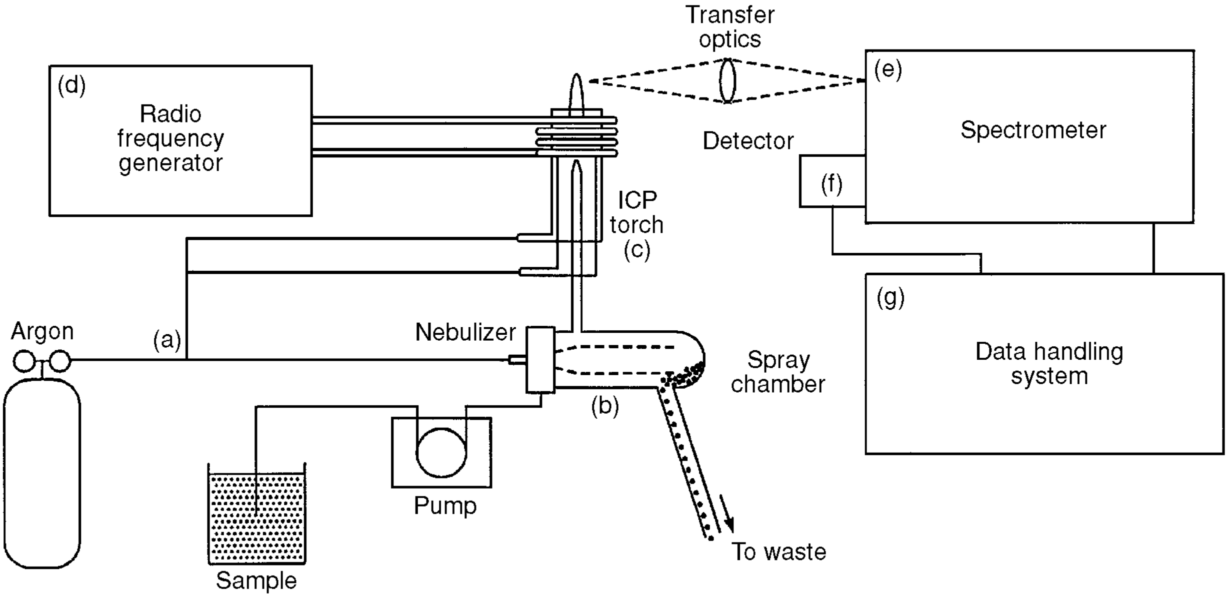

Figure 1. A diagram of an ICP System

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

Note: For a detailed discussion of spectral and nonspectral interferences and of means for correcting for them, see reference [5].

4.2 Major components

4.2.1 Gas flow control devices are those that control the flow of argon gas: (a) as a carrier flow for transferring the aerosol into the plasma, (b) as an auxiliary flow contained between the intermediate and center (injector) tubes of the torch, and (c) as a coolant flow contained between the outer and intermediate tubes of the torch.

4.2.2 A sample introduction device (i.e. 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: Its outer two tubes are usually made of quartz. Observation of the torch may be lateral or axial. (See Figure 2.)

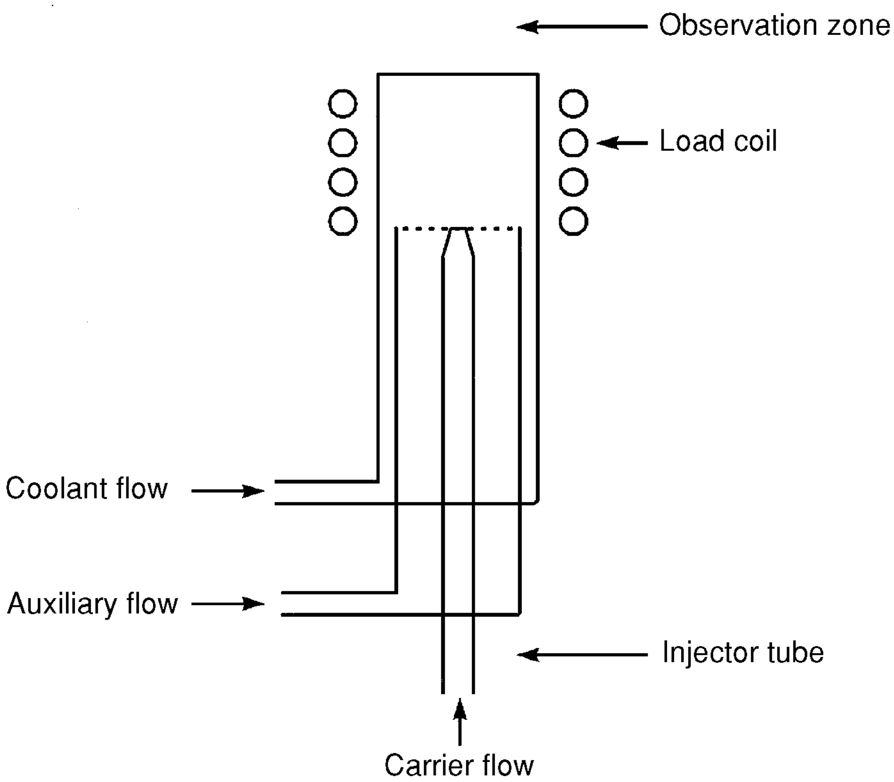

Figure 2. A diagram of the torch of an ICP System

4.2.4 An 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.

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 to be determined onto a light detector which 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 which may be arranged in an array.

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 by a grating whose angle with respect to the incident light is varied in order to direct a specific wavelength through the exit slit onto a single light 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, but also a number of different wavelengths within its measuring range for analysis of each sample.

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.

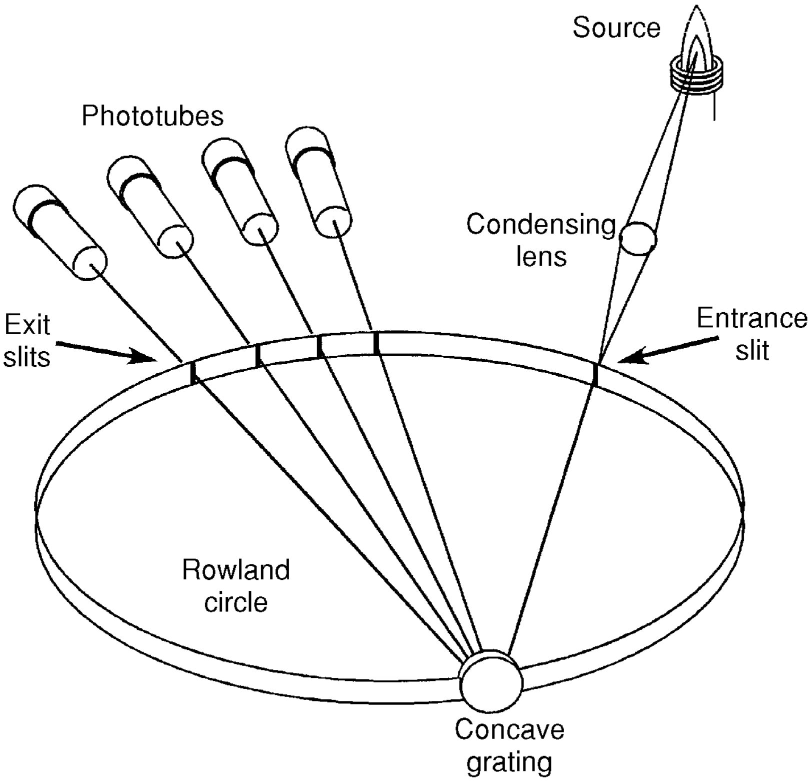

Figure 3. A diagram of the polychromator of an ICP System

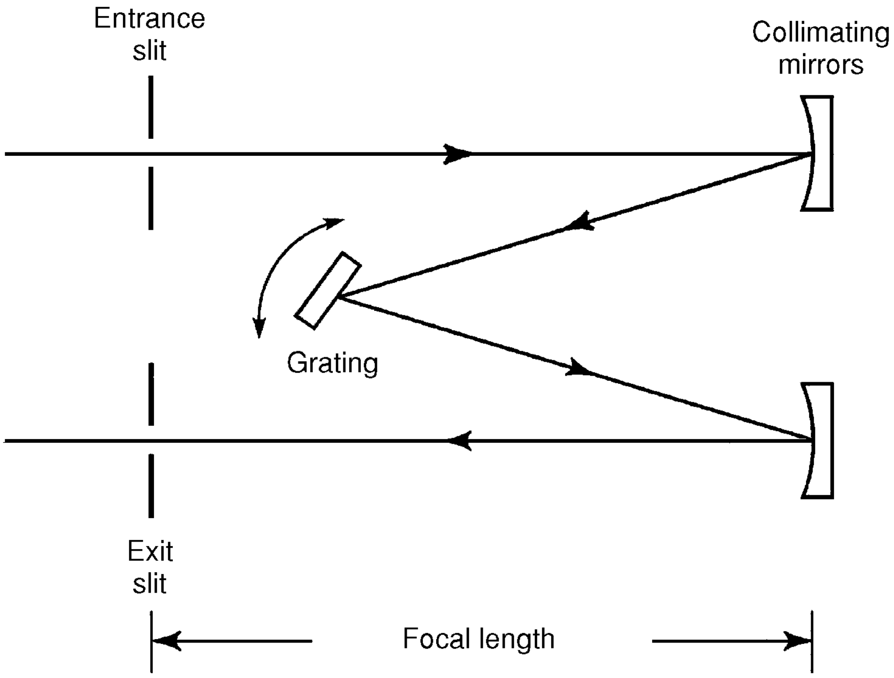

Figure 4. A diagram of a scanning monochromator of an ICP System

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(s) and calculating the concentration of the element(s) in the sample analyzed. Some data systems also provide automatic control and adjustment of injection, argon flow, r.f. generator, spectrometer, and other instrument parameters as well as data analysis and report format.

5 Metrological requirements

5.1 For elements that are important in the analysis of water pollutants, values of the detection limits and upper limits of concentration at an appropriate wavelength are given in Table 1. An ICP system shall achieve these minimum requirements for elements determined under optimum measurement conditions consistent with the instrument's design and its nominal operating parameters; therefore, measurements shall be made to confirm these values using blank and reference standard solutions free of interfering elements.

Notes:(1) Annex B provides recommended concentrations of reference standard solutions of the elements listed in Table 1. For samples containing elements other than the element of interest, which may cause interference at the detection wavelength, alternative wavelengths for detection may be more appropriate; however, at such wavelengths, the detection limits specified in Table 1 do not apply.

(2) For samples containing materials other than the element(s) of interest, it may not be possible to achieve the detection limits specified in Table 1. For guidance on recommended wavelengths and corresponding detection limits for elements expected in raw, potable, and waste water, see ISO/CD 11 885 (ISO/TC147/WG2 No. 234 dated 1992-10-20).

5.2 The repeatability shall be such that the relative standard deviation of the mean measured value shall be no greater than 2 for the concentration range from 100 times the detection limit to the upper limit of concentration.

5.3 The spectrometer shall be capable of analyzing radiation with wavelengths over a range of at least 190 nm to 770 nm and shall have a spectral resolution of at least 0.05 nm.

5.4 The output signal of an ICP system shall be linear within ± 0.05 % as determined by a least square fit of the data for each element being determined over the working range; i.e., the range from its detection limit to its upper-limit concentration as specified in Table 1.

TABLE 1

THE METROLOGICAL CHARACTERISTICS OF AN ICP SYSTEM

Element	Wavelength (nm)	Detection limit (µg/L)	Upper limit concentration (mg/L)
Aluminium	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

5.5 The gas used to supply the torch shall be argon and its purity shall be at least 99.95 percent or better.

5.6 The stability of the power output of the radio frequency generator shall be within ± 0.05 % for the power range from 0.5 kW to 2 kW. It shall operate at a frequency within the range from 1 MHz to 60 MHz.

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

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 flow-rate values that provide appropriate operating and measurement conditions.

6.2 An appropriate sample introduction device shall be used to meet the requirements of 5.1.

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, samples containing particulates or samples with a high content of dissolved solids. A peristaltic pump may be used to regulate the sample delivered to the nebulizer.

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

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

6.4 The spectrometer shall be designed to operate in the simultaneous and/or sequential mode.

6.5 The detector(s) used shall be selected so that the spectral response matches the wavelengths of the elements to be determined.

6.6 The spectrometer shall incorporate a means for measuring the background light signal on either or both sides of a wavelength peak in order to make any necessary corrections.

6.7 The data handling system shall be capable of producing a correct 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 for efficiency and precision of measurements. For connection to external computer systems, it shall be possible to output data over a standard communication bus such as EIA RS-232C [8] or IEEE-488 [9].

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 emissions should be provided according to national regulations.

7 Practical instructions

7.1 An inductively coupled plasma atomic emission spectrometer requires high voltage and generates high temperatures and corrosive and/or toxic gases during normal operation. Warning labels shall be placed conspicuously on the instrument to alert the user to these potential hazards. Instrument installation and operation, particularly with respect to the exhaust of heat and corrosive and/or toxic gases, shall be consistent with national safety regulations.

7.2 Manufacturers of an ICP system shall supply a manual which describes requirements for its installation, operation, and routine maintenance.

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

7.3 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 Pattern approval

8.1.1 Pattern approval testing shall provide means for attesting the conformity of a sample, or samples, of an instrument's pattern, or type, to the requirements of this Recommendation.

8.1.2 The manufacturer shall provide the responsible national body with the required number of instruments and an operating manual. In addition, manufacturer's test data, calibrations, and other relevant information for determining whether an instrument's pattern meets the requirements of this Recommendation may be provided.

8.1.3 The instrument's operating manual shall be reviewed for completeness and clarity of instructions.

8.1.4 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:

- specification of gas purity (5.5)
- argon flow control devices (6.1)
- r.f. generator (5.6)
- adjustable height of the torch (6.3)
- background correction (6.6)
- data systems (6.7)
- markings (6.8).

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

- repeatability (5.2 and C.5)
- wavelength range (5. 3, Table 1, and C.5)
- the detection limit (5.1, Table 1, and C. 6)
- upper limit of concentration (5.1, Table 1, and C.7)
- linearity and working range (5.4, Table 1, and C.7)

8.1.6 The procedures for an overall performance test of an ICP system are given in Annex C.

8.1.7 The results of the tests referred to in 8.1.5 shall contain as a minimum the elements (information) according to the format specified in Annex D. A specific report form may be developed according to national preference. The manufacturer shall receive specific information or comments on failures.

8.2 Initial and subsequent verification

8.2.1 Traditional legal metrological controls of initial and subsequent verification may not be practicable for all instruments placed in service. However, the responsible national body should consider adopting the control procedures specified in 8.3 as a means for ensuring the continued metrological integrity of an ICP system.

8.2.2 Such control procedures may be established for specific analytical methods and may include a means for assessing laboratories using ICP systems. Appropriate assessment procedures may include the following: accreditation of the user laboratory; self certification by the user laboratory; and proficiency testing through intercomparisons of measurements among user laboratories.

8.3 User tests and records

8.3.1 An initial test of an ICP system shall be performed according to the manufacturer's instructions. The results of this test shall be within the specifications provided by the manufacturer.

8.3.2 Routine tests shall be carried out frequently (for example, once per work period) to determine and maintain the optimum operating conditions of the instrument for a particular method of analysis. Annex E provides such a test.

8.3.3 An overall test of the entire ICP system should be carried out occasionally using reference standard solutions that are appropriate for the analytical method for the class of sample compounds. Reference samples may be used daily together with quality control charts to verify the working range of the instrument. Some of the procedures of the overall performance test for an ICP system in Annex C may be appropriate for routine tests. Appropriate reference and certified reference materials may be available as indicated in references [10–12].

8.3.4 Procedures published by the responsible national body should specify performance tests, calibration procedures, and routine tests for ICP systems appropriate for methods of analysis of specific pollutants. The time interval between such tests should be specified, as appropriate.

8.3.5 Records containing the following information shall be maintained for each ICP system (in chronological order):

- results of initial and overall performance tests
- results of routine tests
- identification of the reference sample, sample introduction device, instrumental operating conditions, mode of operation, detectors, and the data system used for the quality control test
- identification of operator
- description of malfunctions and corrective actions taken
- extent 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] Gabarino, J.R. and Taylor, H.E. *Recent Developments and Applications of Inductively Coupled Plasma Emission Spectroscopy to Trace Elemental Analysis of Water,* Trace Analysis, Volume 4, J.F. Lawrence, Ed., Academic Press, Inc., pp 186-237 (1985) ISBN 0-12-682104-6

[3] 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

[4] DIN 38 406, Part 22, *German Standard Method for the Examination of Water, Waste Water, and Sludge,* Beuth Verlag Gmbh, Postfach 11 45, D-1000 Berlin, Germany (1988)

[5] Australian Standard AS 3641.2-1990, *Recommended Practice for Atomic Emission Analysis, Part 2: Inductively Coupled Plasma Excitation*

[6] Joint Working Group of BIPM, IEC, ISO, and OIML, *International Vocabulary of Basic and General Terms in Metrology*, ISO (1993)

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

[8] EIA RS-232D-86, *Interface Between Data Terminal Equipment and Data Communication Equipment Employing Serial Binary Data Interchange* (Including Bulletin No. 9, Application Notes, R1981) Electronic Industries Association, Washington D.C., U.S.A

[9] IEEE 488-1.87 *Standard Digital Interface for Programmable Instrumentation,* Institute of Electrical and Electronic Engineers, New York, NY, U.S.A

[10] International Organization for Standardization, *ISO Directory of Certified Reference Materials,* Geneva, Switzerland

[11] United States National Institute of Standards and Technology, *NBS Standards Reference Materials Catalogue,* Gaithersburg, MD 20899, U.S.A (NBS SP260, GPO)

[12] United States Environmental Protection Agency, *EPA Analytical Reference Standards and Supplement PB 85-143766 Pesticides,* 81-172744 Pesticides

ANNEX A

REFERENCES TO METHODS OF ANALYSIS

A.1 Joint Editorial Board, American Public Health Association, American Water Works Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater,* 18th Edition 1992 ISBN 0-87553-207-1

A.2 U.S. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes,* EPA-600/4-79-020 (1983) PB-84- 128677

A.3 M.W. Skougstad, et al., Editors, U.S. Geological Survey, *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments,* USGS-TWSI Book 5, Chapter Al (1979)

A.4 Association of Official Analytical Chemists, *Official Methods of Analysis of the Association of Official Analytical Chemists,* Methods Manual, 15th Edition. ISBN 0-935584-42-0

A.5 U.K. Standing committee of Analysts, *Methods for the Examination of Waters and Associated Materials* (in series), HMSO, London

A.6 ASTM, Annual Book of Standards on Water. Vol. 11.01, 11.02, 11.03, 11.04 (1993), 1916 Race Street, Philadelphia, PA 19103- 1187

A.7 International Organization for Standardization (ISO) Standards of ISO/TC 147 on “Water Quality”, Latest Issues

A.8 U. S. Environmental Protection Agency, *Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled-Atomic Emission Spectrometry,* Method 200.7 Revision 3.3, 4/91 pp 31-82, as found in *Methods for the Determination of Metals in Environmental Samples,* EPA/600-4-91/010, 6/91 PB91-231498

ANNEX B

REFERENCE STANDARD SOLUTIONS

(Mandatory)

B.1 Preparation of reference standard solutions

B.1.1 A stock solution of each element of interest shall either be obtained from commercial sources or 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 to prepare the stock standard solutions and subsequent dilutions shall have an electrical conductivity at 25 °C of less than 0.1 mS/m (grade 2 water according to ISO 3696).

Notes (1) Stock standard solutions usually have a concentration of the element(s) of interest of 1 000 mg/L or 10 000 mg/L.

(2) Stock standard solutions should be prepared using standard methods such as those prescribed in Method 3120 of Reference A.1 or Reference A.8.

(3) All salts used as a source for an element should be dried at 105 °C for one hour with the exception of carbonates which should be dried at 140 °C for one hour.

B.1.2 The concentrations of the reference standard solutions shall be those specified in Table 2 and shall be prepared by appropriate dilution of the stock standard solutions described in B.1.1. The selection of an acid and its concentration shall be made so as to provide compatibility for any mixed standards being prepared.

B.1.3 Stock standard solutions shall be monitored to ensure their stability with time.

B.2 Preparation of mixed reference standard solutions

B.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 2. Before preparing the mixed reference standard solutions, the stock standard solutions to be used shall be analyzed to identify any potential spectral interferences at the wavelengths selected for analysis.

B.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: The acids used as a preservative should be compatible with the elements selected.

Table 2

RECOMMENDED REFERENCE STANDARD SOLUTION CONCENTRATIONS

Element	Reference standard solution concentration (mg/L)
Aluminium	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

B.2.3 The following mixed reference standard solutions may be used:

- Mixed reference standard solution I: manganese, beryllium, cadmium, lead, selenium, and zinc
- Mixed reference standard solution II: barium, copper, iron, vanadium, and cobalt
- Mixed reference standard solution III: molybdenum, silicon, arsenic, strontium, and lithium
- Mixed reference standard solution IV: calcium, sodium, potassium, aluminium, chromium, and nickel
- Mixed reference standard solution V: antimony, boron, magnesium, silver, and thallium.

Note: Special procedures are required to ensure that silver does not precipitate out of mixed reference standard solution V.

B.2.4 The mixed reference standard solutions shall be monitored periodically for stability.

ANNEX C

AN OVERALL PERFORMANCE TEST FOR AN ICP SYSTEM

(Mandatory)

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

C.2 Select at least five elements, two of which shall be thallium and potassium. Prepare mixed or individual reference standard solutions for these elements in the concentrations recommended in Table 2. The following elements may be considered:

Tl	190.864 nm	Zn	213.856 nm
Mn	257.610 nm	Cu	324.754 nm
Ba	455.403 nm	Na	588.995 nm
Li	670.784 nm	K	766.491 nm

C.3 Prepare a blank test solution to be associated with each of the solutions prepared in C.2.

C.4 Start-up procedures

C.4.1 Allow the instrument warm up and make any necessary adjustments according to manufacturer's instructions before beginning the analysis.

C.4.2 Calibrate the instrument using the blank test solutions and the reference standard solutions prepared according to C.2 and C.3.

C.5 Repeatability and wavelength range check

C.5.1 Perform 10 replicate measurements for the analysis of each reference standard solution selected in C.2 at the appropriate wavelengths according to Table 2.

C.5.2 Compute the mean and standard deviation of the sample element concentration of C.5.1 as determined at each wavelength of interest.

C.5.3 The relative standard deviations of all mean values determined in 5.2 shall be no greater than 2 %.

C.5.4 The results for thallium (190 nm) and potassium (766 nm) shall meet the requirements of C.5.3 in order to satisfy the wavelength range requirements of the ICP system.

C.6 Instrument detection limit check

C.6.1 Use the mean and standard deviation of the result of C.5.2 as determined at each wavelength of interest.

C.6.2 Multiply each standard deviation obtained in C.5.3 by three and compare the result with the corresponding detection limits of Table 1. These determined detection limits shall be equal to or better than those indicated in Table 1.

C.7 Upper limit of concentration and linearity check

C.7.1 For each element selected according to C.2, prepare a reference solution with a concentration equal to or slightly more than the upper limit concentration as specified in Table 1. From that reference solution, prepare three to five more reference solutions by dilution to different concentrations none of which shall be less than 100 times the detection limit.

C.7.2 Perform at least three replicate measurements for each reference solution prepared in C.7.1 and compute the means of the values measured.

C.7.3 A least-squares curve fitted to a plot of the data obtained in C.7.2 shall be linear to within ± 5 % for each element selected.

ANNEX D

TEST REPORT FORMAT

Note: This Annex is informative with regard to implementation of this Recommendation in national regulations; however, use of the test report format is mandatory for application of the Recommendation within the OIML Certificate System.

A test report intended for use in the OIML Certificate System or for other purposes shall include the following information.

Report No. _______

OIML Recommendation No. _______, Edition (year) _______

D.1 Name and address of the testing laboratory(ies)

____

____

____

D.2 Location at which tests were performed if other than that indicated in D.1

____

____

____

D.3 Name and address of the manufacturer

____

____

____

D.4 Name and address of applicant if other than the manufacturer

____

____

____

D.5 Identification of the instrument (pattern) tested

- trade name ________________________
- model number _____________________
- serial number ______________________
- date of manufacture ________________
- requirements for voltage _______, frequency _______, current _______

D.6 Review of the operating manual: acceptable _______, deficient _______
Comments: ____

____

____

D.7 Summary of the visual inspection and information in the operating manual

D.7.1 Specification of gas purity: value _______
pass _______, fail _______
Comments: ____

____

____

D.7.2 Argon flow control devices and instructions:
pass _______, fail _______
Comments: ____
____
____

D.7.3 r.f. generator: power range from ____ kW to ____ kW; stability _____
pass _______, fail _______
Comments: ____
____
____

D.7.4 Adjustable height of the torch: yes ____, no ____
Comments: ____
____
____

D.7.5 Background correction: yes ____, no ____
Comments: ____
____
____

D.7.6 Markings: pass ____, fail ____
Comments: ____
____
____

D.8 Summary of the results of tests carried out according to 8.1.5

D.8.1 Conditions of testing:

- ambient temperature ____________________
- humidity ________________________________
- argon gas 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: for display of output _______, reduction of data _______, control of other instrument parameters (list)

____
____
____

D.8.2 Determination of repeatability and instrument detection limit

Elements →	1.	2.	3.	4.	5.
Wavelength →					
Concentatrion →					
Repetition ↓ 1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
Average					
σ_τ					
D.L.					

Relative standard deviation (σ_τ): pass _______, fail _______
Detection limit (D.L.): pass _______, fail _______
Comments: ____
____

D.8.3 Wavelength range (190 nm - 770 nm):
pass _______, fail _______

D.8.4 Determination of linearity

Element 1 _______					
Concentrations →					
Repetition ↓ 1					
2					
3					
4					
5					
Average					

Deviation from linearity: value _______, pass _______, fail _______
Comments: ____
____

Element 2 _______					
Concentrations →					
Repetition ↓ 1					
2					
3					
4					
5					
Average					

Deviation from linearity: value _______, pass _______, fail _______
Comments: ____
____

Element 3 _______					
Concentrations →					
Repetition ↓ 1					
2					
3					
4					
5					
Average					

Deviation from linearity: value _______, pass _______, fail _______
Comments: ____
____

Element 4 _______					
Concentrations →					
Repetition ↓ 1					
2					
3					
4					
5					
Average					

Deviation from linearity: value _______, pass _______, fail _______
Comments: ____

____

Element 5 _______					
Concentrations →					
Repetition ↓ 1					
2					
3					
4					
5					
Average					

Deviation from linearity: value _______, pass _______, fail _______
Comments: ____

____

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

____

____

____

____

D.10 Person(s) responsible for testing:
Signature(s) and title(s)..

____

____

Date: _________

ANNEX E

A ROUTINE INSTRUMENT TEST
(Informative)

E.1 This is a routine test procedure for resetting the plasma of a polychromator system to a preselected observation zone of the plasma by adjusting the carrier gas flow rate entering the plasma prior to calibration and use in analysis.

E.2 This test procedure shall be carried out using a precise and sensitive gas flow control device that maintains the flow rate under varying pressure conditions.

E.3 The optimum operating conditions of the instrument for the analysis of the reference standard solution specified shall be selected prior to this test. These conditions may include adjustments of the r.f. power output; the flow rates of the carrier, auxiliary and coolant gases; the rate of delivery of sample, and the observation height of the torch.

Note: Optimum conditions are those which provide the lowest reliable detection limits.

E.4 Establishing test criteria

E.4.1 Allow the instrument to warm up after being turned on according to manufacturer's instructions, and set the instrument to the selected optimum operating conditions.

E.4.2 Profile the entrance slit for proper alignment to the exit slits for maximum signal response.

E.4.3 Select a reference standard solution containing only copper (Cu) and manganese (Mn) and having an equal concentration (within the range of 1 mg/L to 10 mg/L) of each element.

E.4.4 Introduce the Cu-Mn reference standard solution into the instrument through the nebulizer.

E.4.5 Perform and record ten replicate measurements of the output signal from both Cu and Mn at their selected wavelengths according to Table 1.

E.4.6 From each set of replicate measurements, compute the ratio for the Cu to the respective Mn output signal (Cu/Mn) together with the mean value and the standard deviation of the ratios.

E.4.7 Any change in selected instrument operating conditions (E.3) or replacement of instrument components requires that test criteria be re-established.

E.5 Resetting the plasma emission zone

E.5.1 Begin each period of analysis by following the steps of E.4.1 through E.4.5.

E.5.2 From the ten replicate measurements, compute the mean value and the ratio for Cu to Mn (Cu/Mn). Compare the results with those established according to E.4.6.

E.5.3 If the ratio determined from E.5.2 is within two standard deviations of the established mean value determined in E.4.6, the plasma is within acceptable limits, i.e., adjustment is not required and the instrument is ready for calibration and analysis.

E.5.4 If the ratio determined from E.5.2 is not within two standard deviations of the established mean value determined in E.4.6, corrective action should be taken. Adjust the aerosol sample carrier gas flow rate until the requirement of E.5.3 is achieved. Decreasing the carrier gas flow rate will decrease the ratio, and increasing the flow rate will increase the ratio.

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