ORGANISATION INTERNATIONALE
DE MÉTROLOGIE LÉGALE

OIML

INTERNATIONAL RECOMMENDATION

Portable and transportable X-ray fluorescence spectrometers for field measurement of hazardous elemental pollutants

Spectromètres à fluorescence de rayons X portatifs et déplaçables pour la mesure sur le terrain d'éléments polluants dangereux

OIML R 123

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FOREWORD

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PORTABLE AND TRANSPORTABLE X-RAY FLUORESCENCE SPECTROMETERS FOR FIELD MEASUREMENT OF HAZARDOUS ELEMENTAL POLLUTANTS

1 Scope

1.1 This Recommendation provides requirements for defining, testing and verifying the performance of portable and transportable X-ray fluorescence (XRF) spectrometers which may be used for legal measurements of hazardous elemental pollutants found in various media, especially soil and waste water.

This Recommendation applies only to energy-dispersive X-ray spectrometers, but does not intend to exclude any other equivalent means of analysis.

Portable and transportable instruments are self-contained or integrated compact assemblies which can be used to carry out a complete analysis on site.

The portable instruments usually operate on battery (DC) power, and the transportable instruments usually operate on mains or generator (AC) power.

The major components specified in this Recommendation reflect examples of current technology and are not intended to exclude new developments. Laboratory-based instruments are not covered in this Recommendation.

1.2 Instruments that meet the requirements of this Recommendation have flexibility in some major components depending on their specific applications.

1.2.1 Essential instrument components are an excitation source, a means of providing reproducible presentation of the sample being measured, a detector, and a data processing system.

1.2.2 The excitation source may be either an X-ray tube with or without secondary targets or radioactive source(s). The principle X-ray fluorescence energies of the target elements of interest is from approximately 1 keV to 14 keV. Appropriate detectors currently available are gas-filled proportional detectors and semiconductor detectors.

1.3 Instrument performance better than the criteria prescribed in these applications may be achieved by optimizing the performance of each major component of the measuring system as well as new technological developments. In such cases, success may depend on the knowledge, skill and experience of the operator.

1.4 Sampling plans, sample preparation and measurement methods are beyond the scope of this Recommendation.

1.5 This Recommendation does not address safety requirements and tests necessary for personnel protection. Manufacturers and users should therefore determine that the instruments meet intrinsic safety and labeling requirements according to national regulations.

2 Application

2.1 Portable and transportable XRF spectrometers may be prescribed in national laws and regulations for field assessment and control of hazardous elemental pollutants. Examples are on-site analysis of pollutants in soils, ground water, waste water and sludge and particulate filter samples of ambient air at waste and industrial sites.

2.2 For successful applications, complete instructions shall be available for operating and testing an instrument's performance before and after field measurements. These instruments are expected to be operated by persons having a variety of backgrounds in education, training and skills.

2.3 For qualitative and quantitative analysis, XRF spectrometers should be calibrated with reference standards although generic site samples may be used to check or calibrate them. An instrument's performance and calibration should be checked periodically especially after maintenance and repair or when used under extreme environmental conditions.

3 Terminology

3.1 Accuracy

Closeness of the agreement between the result of a measurement and a true value of the measurand.

3.2 Detection limit

Concentration of an element which provides an output signal equivalent to three times the standard deviation of the background. It is the minimum quantity of an element that can be detected. For this Recommendation, it may be derived from the statistical variation in the background using the following equation:

$$D = 3\,(B/t)^{1/2}/S$$

where:

D = detection limit (unit of concentration);
B = background (counts per second);
t = measurement time (seconds);
S = sensitivity (counts per second per unit of concentration).

Note: When applied in a measurement method or for an analysis, the limit of quantitation of the instrument is an important parameter. It is defined as being a value equal to 10 times the standard deviation of the background and also would include the variations associated with sampling and analysis.

3.3 Detector

Device that converts the energy absorbed from the X-rays emitted by a sample into electric signals.

3.4 Working concentration range

Limits of concentration of an element in a sample over which the instrument operates within the performance requirements of this Recommendation.

3.5 Repeatability

Closeness of agreement between the results of successive measurements of the same sample using the same instrument, under the same defined conditions of use, and within a relatively short period of time.

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

3.6 Energy resolution

A parameter used as a measure of the ability of a detector to distinguish between two adjacent energy peaks arising from elements in a sample.

Note: For this Recommendation, it is expressed as the *full width at half maximum height* of the manganese K-alpha line (5.9 keV) in units of energy or in percent as related to the energy of the peak.

3.7 Sensitivity

Change in the response of a measuring instrument divided by the corresponding change in the stimulus.

3.8 Reference material

Material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or assigning values to materials.

Note: This term does not necessarily mean a certified reference standard.

3.9 Background

Signal produced in the detector resulting from the detection of X-rays other than X-rays from the analyzed element and from any noise produced elsewhere in the XRF spectrometer.

4 Description of the instrument

4.1 The principle of measurement by an XRF spectrometer is based on interaction of X-rays from an external source with the atoms of the sample. This interaction may cause the ejection of inner shell electrons of the atoms. Electron transitions then occur to return the excited atoms to a stable state, resulting in the emission of characteristic X-ray photons. The emitted photons are called characteristic X-rays because their energies are unique to the identity of the excited atoms. The X-ray detector converts the characteristic X-ray energy into a related electric signal. The signals are processed electronically to yield an X-ray spectrum that can be displayed and from which elemental concentrations of the sample may be calculated.

Note: A more detailed description of the principle of XRF measurement may be obtained in References [1] through [4] - see page 17.

4.2 An XRF spectrometer is capable of multi-element analysis of a variety of materials including solids, liquids or powders. The instrument consists of 5 major components:

(a) a source that provides X-rays;
(b) a sample location or a sample presentation device;
(c) a detector which converts X-ray generated photons emitted from the sample into measurable electric signals;
(d) a data handling system that processes the signals into an X-ray energy spectrum from which elemental concentrations of the sample may be calculated;
(e) a data display and storage system.

A diagram of an XRF spectrometer is shown in Fig. 1.

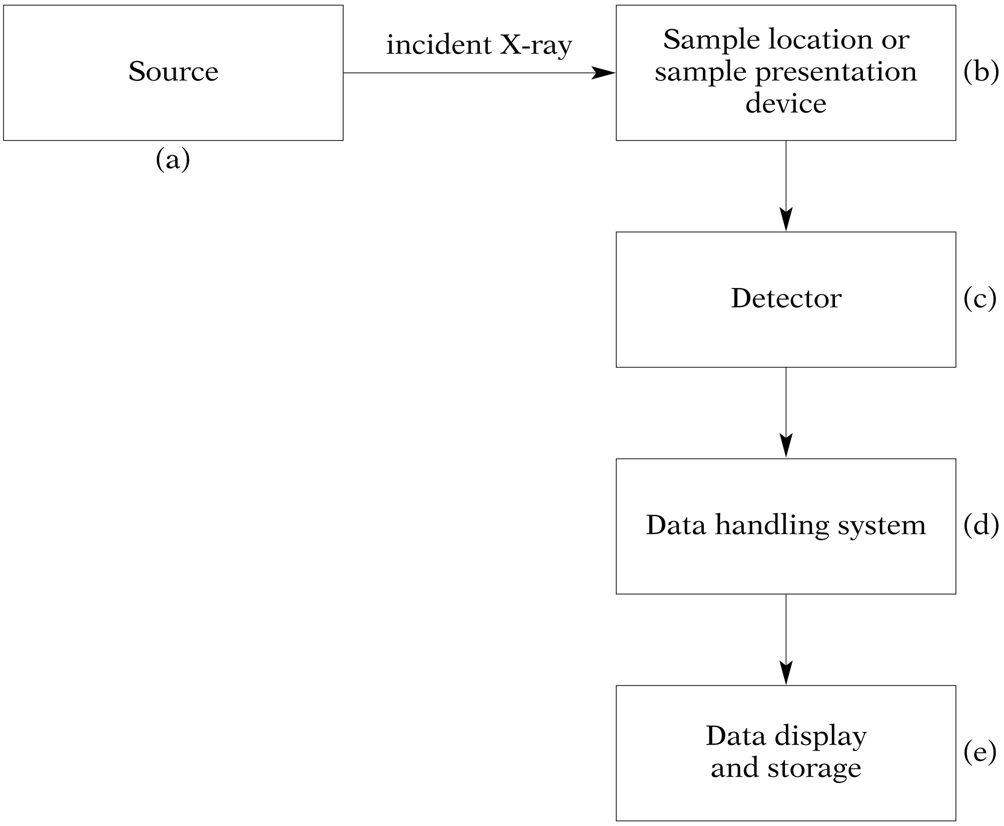

Fig. 1 Major components of an energy dispersive X-ray fluorescence spectrometer

4.3 Instrument components

4.3.1 An excitation source may be as specified in 4.3.1.1–4.3.1.3.

4.3.1.1 X-ray tube source

Positioned to direct incident X-rays onto the sample. A power supply provides a voltage between the filament and the anode. Electrons from the filament strike the anode and produce X-rays which then pass through a thin window towards the sample. The X-ray tube can emit a wide distribution of X-ray energies at high intensities. Various anode and filter materials may be used to produce and modify respectively the primary X-ray energies output prior to interaction with a sample.

4.3.1.2 Secondary target(s)

Employed in combination with an X-ray tube that produces monochromatic characteristic X-rays that then can strike a sample. A particular secondary target material may be selected to provide the optimum characteristic X-rays for exciting an expected element, or expected elements, in the sample.

4.3.1.3 Radioactive source(s)

This emits radiation of discrete energies for interaction with a sample. A source is provided in the form of a small sealed capsule containing an appropriate amount of a radioisotope. Various radioactive sources may be used to provide different X-ray energies suitable for exciting the expected elements in the sample (see Table 1).

Table 1
Elements detectable and for testing with associated X-ray sources

X-ray source	Elements detectable (emission lines)		Elements for testing
X-ray tubes	Na through Ce: La through U:	K lines L lines	Cr, Cd Pb
Am^{241}	Cu through Tm: Hf through U:	K lines L lines	Cd Pb
Cd^{109}	Ca through Rh: Ba through U:	K lines L lines	Cr Pb
Cm^{244}	Ca through Se: La through Pb:	K lines L lines	Cr Pb
Fe^{55}	Al through Cr: Mo through Ba:	K lines L lines	Cr

4.3.2 The sample location or sample presentation device provides a means for obtaining a reproducible location for analysis of a sample.

4.3.3 A detector may be as specified in 4.3.3.1 and 4.3.3.2.

4.3.3.1 Solid-state detector

This is a semiconductor diode: the most commonly used materials for such diodes are silicon lithium-drifted crystals, germanium crystals and mercuric iodide crystals. An X-ray photon striking a biased solid-state crystal loses energy in the crystal through producing electron-hole pairs. The electric charge produced is collected and provides a current pulse that is directly proportional to the energy of the X-ray photon absorbed by the detector.

4.3.3.2 Gas-filled proportional detector

This is an ionization chamber filled with a mixture of noble and other gases. An X-ray photon entering the chamber ionizes the gas atoms. The electric charge produced is collected and provides an electric signal that is directly proportional to the energy of the X-ray photon absorbed in the gas of the detector.

4.3.4 A data handling system processes the signals from the detector. The result is an X-ray energy spectrum that provides a basis for the identification and quantification of elements present in the sample.

4.3.5 The data display and storage system presents and records the data for subsequent retrieval, manipulation and analysis.

4.4 Types of instruments

This Recommendation distinguishes instruments based on their principal components as follows:

Type I	Solid-state detector with X-ray tube source with or without secondary targets;
Type II	Solid-state detector with radioisotope source(s);
Type III	Gas-filled proportional detector with X-ray tube source with or without secondary targets;
Type IV	Gas-filled proportional detector with radioisotope source(s).

5 Metrological requirements

5.1 The manufacturers of instruments using X-ray tube and radioisotope sources shall specify the elements listed in Table 2 that can be analyzed with each instrument.

Note: Some instruments may be designed to measure only one element and may therefore require only one X-ray tube voltage or radioactive isotope source for the application. In such cases this Recommendation, which is more general, would serve as a model for specifying the necessary performance requirements.

5.2 Instruments with different detectors

Note: For instruments based on other design principles, the performance requirement in this subclause would apply to the spectrometer as a whole rather than to a detector (see also 1.1).

Table 2
Elements of interest in the analysis of elemental pollutants

Elements	**X-ray tube**	**Radioactive sources**			
[1]Sodium Na	↑				
[1]Magnesium Mg	│				
[1]Aluminum Al	│				↑
Sulfur S	│				│
Chlorine Cl	│				│
Potassium K	│				Fe^{55} K-lines
Calcium Ca	│		↑	↑	│
Vanadium V	│		│	│	│
[2]Chromium Cr	│		│	│	↓
Manganese Mn	│		│	│	
Iron Fe	│		│	│	
Cobalt Co	│		│	Cm^{244} K-lines	
Nickel Ni	│		Cd^{109} K-lines	│	
Copper Cu	│	↑	│	│	
Zinc Zn	│	│	│	│	
Arsenic As	│	│	│	│	
Selenium Se	│	│	│	↓	
Molybdenum Mo	│	Am^{241} K-lines	↓		↑
Silver Ag	│	│			Fe^{55} L-lines
[2]Cadmium Cd	│	│			│
Antimony Sb	│	│			│
Barium Ba	│	↓	↑		↓
Mercury Hg	│	↑	│	↑	
Thallium Tl	│	Am^{241} L-lines	Cd^{109} L-lines	Cm^{244} L-lines	
[2]Lead Pb	│	│	│	↓	
Uranium U	↓	↓	↓		

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[1] Determination of these elements requires a vacuum pump, necessary to evacuate the air from the spectrometer.

[2] Suggested elements for testing.

5.2.1 The maximum permissible error of the output display of the X-ray energies for the instrument shall be within ± 0.5 % for solid state detectors and ± 2 % for gas-filled proportional detectors over the specified operating energy range. The range of analyzable elements as specified according to 5.1 shall be taken into account by considering the energies of the principal K_α and L_α lines of the elements listed in Table 3.

5.2.2 The energy resolution of an instrument for characteristic X-rays for an element shall be expressed in terms of *full width at half maximum height* (FWHM). It shall be measured by irradiating the detector with a collimated, direct beam of 5.9 keV photons (Mn, K-alpha line) from an Fe^{55} source that can provide a total incident count rate (intensity) of at least l 000 counts/s.

5.2.2.1 The energy resolution for an instrument with a solid-state detector shall not be greater than 5 % at the Mn K-alpha line which corresponds to less than 300 eV FWHM.

Note: These requirements are necessary to provide a means of detection and analysis of adjacent elements in a multi-element sample.

5.2.2.2 The energy resolution for an instrument with a gas-filled proportional detector shall not be greater than 15 % at the Mn K-alpha line which corresponds to approximately 890 eV FWHM.

5.3 Instrument test under reference conditions

5.3.1 During pattern approval and initial and subsequent verification, the repeatability of the entire instrument shall be tested in a laboratory using reference materials under the following reference conditions:

- ambient temperature: 22 °C ± 5 °C and stable to within ± 1 °C over the period of testing;
- relative humidity (RH): 60 % ± 20 %;
- source type: specified by manufacturer;
- detector: specified by manufacturer;
- relative mass fraction (mg/kg) of the elements in the reference material from approximately 3 times the detection limit up to 0.1 % of Pb, Cd and Cr in a stable matrix;
- acquisition time: up to 300 s per element.

5.3.2 Under the reference conditions and for the prescribed reference standard in 5.3.1 at a relative mass fraction (k) of about 10 times the detection limit, the repeatability of the instrument shall have a relative standard deviation (σ_r) less than 5 % as determined from the results of a minimum of 10 repeated measurements.

Note: The relative standard deviation shall be calculated from the following equation:

$$\sigma_r = \frac{\sigma}{\bar{Y}} \times 100\ \%$$

where: $$\sigma = \left[\frac{\Sigma\, (Y_i - \bar{Y}\,)^2}{n - 1} \right]^{1/2}$$

Y_i is the individual result, and

$\bar{Y}$ is the average result for n number of repeated measurements.

Table 3
Principal X-ray fluorescence energies of elements of interest

Elements	K_α lines (keV)	$L_{\alpha1}$ lines (keV)
Sodium Na	1.041	
Magnesium Mg	1.254	
Aluminum Al	1.487	
Sulfur S	2.307	
Chlorine Cl	2.622	
Potassium K	3.312	
Calcium Ca	3.690	
Vanadium V	4.949	
Chromium Cr	5.411	
Manganese Mn	5.895	
Iron Fe	6.400	
Cobalt Co	6.925	
Nickel Ni	7.472	
Copper Cu	8.041	
Zinc Zn	8.631	
Arsenic As	10.532	
Selenium Se	11.210	
Molybdenum Mo	17.443	2.293
Silver Ag	22.104	2.984
Cadmium Cd	23.109	3.133
Antimony Sb	26.274	3.605
Barium Ba	32.065	4.467
Mercury Hg		9.987
Thallium Tl		10.266
Lead Pb		10.549
Uranium U		13.613

5.3.3 A linear least-squares fit of the data of the output signal of an instrument versus the relative mass fraction shall be carried out using reference materials with elements and relative mass fractions specified for testing under reference conditions (see Annex A). The correlation coefficient, r, of the fitted curves shall be determined, and r^2 shall not be less than 0.95.

5.3.4 The detection limit of an instrument depends on the sample matrix (in which the elements are contained) and on the measurement time. Type I, Type II, Type III and Type IV instruments shall meet the detection limits specified in Table 4 for the reference elements in an oil matrix (reference material) under the following conditions of measurement:

- a homogeneous mixture of the element in the oil matrix having a relative mass fraction within ± 2 % of the specified value;
- a sample cup having a diameter of 31 mm or as specified by the manufacturer;
- a window having a thickness of 5 µm of polypropylene or a thickness and material as specified by the manufacturer;
- a sample thickness as specified by the manufacturer;
- a measurement time of 300 s per element.

Table 4
Detection limits for reference elements

Reference element	Detection limit (mg/kg)			
	Type I	Type II	Type III	Type IV
Pb (L series)	3.0	5	30	5
Cd (K series)	3.0	50	30	15
Cr (K series)	3.0	60	60	60

Note: For special applications, a manufacturer may identify another reference element for which the value of the detection limit shall be specified for the instrument. For example, sulfur or chlorine may be specified for a Type III instrument with a detection limit of 30 mg/kg.

5.3.5 For the measurements obtained in 5.3.2, the mean relative mass fraction value, $\bar{Y}$, determined from the instrument response in 5.3.2, shall not differ from the relative mass fraction value (k) of the reference material used by more than ±5 %.

5.3.6 The procedures for an overall test of the instrument under reference conditions are given in Annex A.

5.4 Influence factors

5.4.1 During pattern evaluation, the entire instrument shall be tested as described in Annex B using the relevant conditions specified in 5.3.1 for the following influence factors:

- low voltage indicator for battery power;
- variation in mains or portable generator voltage and frequency;

- mechanical shock;
- vibration (sinusoidal);
- electrostatic discharge;
- electromagnetic fields;
- temperature range;
- damp heat.

5.4.2 The result of the tests specified in 5.4.1 shall meet the requirements of 5.3.2. A description of the performance tests for influence factors is given in Annex B.

6 Technical requirements

6.1 The instrument shall be self-contained, i.e. all instrument components shall be in a single unit or located together in an integrated compact assembly including an external detector probe, if applicable. It may be portable or transportable.

6.2 The mass of a portable instrument shall not be more than 15 kg.

6.3 Transportable instruments are classified into two types according to their mass and power source: Type A and Type B. The mass of a Type A transportable instrument shall not be more than 30 kg, and the mass of a Type B transportable instrument shall be more than 30 kg.

6.4 Portable and Type A transportable instruments shall be powered by a battery capable of continuous operation for at least 4 hours and shall have a means for indicating low battery voltage. They may also be operated on AC power when available. Type B transportable instruments shall be AC powered by mains or generators.

6.5 The instrument shall provide a means for presenting the sample in a reproducible position with respect to the source and detector, or the manufacturer shall specify the means by which an operator can reproducibly present the sample.

6.6 The voltage applied across an X-ray tube source shall be fixed or be selectable for a value or range within 6–50 kV or within the voltage range specified by the manufacturer which meets the requirements of this Recommendation.

6.7 The intensity of the source shall be sufficient to meet the requirements for detection limits of 5.3.4 over the time period specified by the manufacturer.

Note: The use of radioactive sources may require separate approval by the national body responsible for their safe application. In particular, a warning light is usually required to indicate when the X-ray source is operational.

6.8 If the detector requires cooling below ambient temperature for proper operation, the manufacturer shall provide a means for maintaining the detector at the required temperature.

6.9 The ambient temperature working range shall be from 5 °C to 35 °C for portable and Type A transportable instruments and from 10 °C to 30 °C for Type B transportable instruments.

6.10 The manufacturer shall specify a procedure by which the energy calibration shall be routinely checked and shall provide a means for adjustment.

6.11 The data handling system shall be capable of providing a qualitative and quantitative analysis on site, and the display and storage system shall be capable of providing an accurate and accessible record of a measurement.

6.12 For portable instruments, the manufacturer shall recommend a procedure for decontaminating the instrument.

6.13 Markings shall be attached conspicuously to the instrument as follows:

- name of manufacturer;
- instrument model and serial number;
- type designation;
- power requirements;
- safety requirements according to national regulations.

7 Practical instructions

7.1 Manufacturers of XRF spectrometers shall provide a manual which clearly and concisely describes the instrument's operation and routine maintenance.

7.2 Before an instrument is used, all environmental factors related to the specific application should be considered. If the conditions are different to those specified for the instrument, the manufacturer should be consulted.

7.3 Any necessary precautions or warnings for instrument operators shall be explicitly indicated in the manufacturer's operating manual and shall be clearly displayed on the instrument when applicable.

8 Metrological controls

8.1 Pattern evaluation

8.1.1 Manufacturers shall provide the national responsible body with an operating manual for the instrument and may provide data and other information on performance tests and calibrations that support a determination of whether the design of the instrument meets the requirements of this Recommendation.

8.1.2 The instrument manual shall be reviewed by the national responsible body for its completeness and clarity of operating instructions. The instrument shall be visually inspected in conjunction with the manufacturer's specifications to determine the instrument's compliance with the requirements of 6.1 through 6.13.

8.1.3 The national responsible body shall carry out the following performance tests, or may accept the manufacturer's test data, to confirm acceptable performance for:

- range of analyzable elements (5.1 and 5.2.1);
- maximum permissible errors for display of X-ray energies (5.2.1 and A.2);
- detector resolution (5.2.2 and A.3);
- repeatability (5.3.2);
- linearity of response with relative mass fraction (5.3.3 and A.5);
- detection limit (5.3.4 and A.5.9);
- low voltage indicator for battery power (5.4 and B.1);
- variation in mains or portable generator voltage and frequency, if applicable (5.4 and B.2);
- mechanical shock (5.4 and B.3);
- vibration (sinusoidal) (5.4 and B.4);
- electrostatic discharge (5.4 and B.5);
- electromagnetic fields (5.4 and B.6);
- temperature working range (5.4 and B.7);
- damp heat (5.4 and B.8).

Note: References to the clauses containing the requirements and a brief description of associated tests are indicated in parenthesis.

8.1.4 The report on instrument tests carried out during pattern evaluation shall at least contain the items of information according to the format provided in Annex C. A specific form may be developed according to national preference. The manufacturer shall be provided specific comments on any test failures.

8.2 Initial verification

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

8.2.2 The repeatability test under the reference conditions specified in 5.3.2 shall be carried out.

8.2.3 Any other instrument tests specified under 8.1.3 which may be considered to be critical to the specific application shall be performed.

8.2.4 The period of validity of this verification shall be specified by the national responsible body.

8.2.5 An instrument shall undergo subsequent verification equivalent to initial verification after repair or replacement of component parts or units of its electrical control and readout system.

8.3 Routine tests carried out by the user

8.3.1 The national responsible body shall provide information on methods for using instruments to measure specific pollutants. Some measurement methods may be appropriate for use as quality control in assessing an instrument's performance.

8.3.2 An instrument operator shall carry out a test with a suitable reference sample, which includes specific elemental pollutants, in the field in order to document the performance of the instrument before, after and periodically during field measurements.

Note: The instrument should be checked especially in the field when used near known or suspected sources of electromagnetic interference.

8.3.3 A chronological written record shall be maintained for each instrument and shall contain at least the following information:

- results of all routine tests;
- results of energy and quantitative calibration checks;
- extent of maintenance and repair;
- identification of major components replaced;
- identify of the operator(s) who performed the indicated tasks.

REFERENCES

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[4] Tertain, R. and Claisse, F., Principles of Quantitative X-ray Fluorescence Analysis, John Wiley and Sons, New York, 1982.

ANNEX A
OVERALL PERFORMANCE TEST FOR THE INSTRUMENT
(Mandatory)

A.1 The objective of this test is to check the following characteristics of an instrument in order to evaluate its overall performance for measuring elemental pollutants over the specified working range of the instrument:

- detector resolution;
- maximum permissible errors for display of fluorescence X-ray energies;
- range of analyzable elemental pollutants;
- repeatability;
- linearity with concentration of elemental pollutants;
- detection limits.

A.2 For the maximum permissible errors for the display energies of fluorescence X-rays, the requirements of 5.2.1 shall be met. Energies of fluorescence X-rays from at least three specific elements identified in Table 3 within the range of analyzable elements shall be measured for this determination.

A.3 For detector resolution, the requirements of 5.2.2 shall be met.

A.4 For repeatability, the requirements of 5.3.2 shall be met.

A.5 Linearity with concentration and detection limit

A.5.1 The test shall be carried out at reference conditions as specified in 5.3.1 with a reference sample in an oil matrix.

A.5.2 Obtain or prepare at least 4 reference materials having mass fractions from approximately 3 times the expected detection limit up to and including 1 000 mg/kg, respectively, of Pb, Cd, and Cr in an oil matrix. The accuracy of the mass fraction of each reference material shall be 1.0 % or better.

Notes:

1) With particle sizes in the range of μm, such reference materials can easily be fabricated to be homogenous and can be stabilized to have a relatively long shelf life (one year or more);
2) Other reference materials may be selected which would provide an equivalent performance test for some specific applications.

A.5.3 Select the appropriate source for the element to be measured.

A.5.4 Carry out at least 4 repeated measurements of each reference material for a total count of at least 10 000 or an acquisition time of no more than 300 s.

A.5.5 For each measurement, record the acquisition time and total number of counts per second in the peak area for each element.

A.5.6 From the results of A.5.5, calculate the mean of the 4 repeated measurements for each element, i.e. the average number of counts in each peak area per unit time.

A.5.7 Determine the sensitivity and background signal by plotting the results of A.5.6 for the recorded number of counts per second versus the mass fraction (mg/kg). Make a linear least-squares fit to this data for the four reference materials having different mass fractions. The results shall meet the requirements of 5.3.3.

Note: The correlation coefficient, r, gives an indication of how well the data fits the least-squares regression curve. A perfect fit would be $r = \pm 1$ or $r^2 = 1$. The square of the correlation coefficient (r^2) can be calculated from the slope(s) and the standard deviation of the mass fraction (σ_x) and the output signal in number of counts per second (σ_y) as follows:

$$r^2 = \left[s \cdot \frac{\sigma_x}{\sigma_y} \right]^2$$

where:

$$s = \frac{n \, \Sigma X_i Y_i - \Sigma X_i \, \Sigma Y_i}{n \, \Sigma X_i^2 - (\Sigma X_i)^2}$$

$$\sigma_x = \left[\frac{\Sigma (X_i - \bar{X})^2}{n - 1} \right]^{\frac{1}{2}}$$

$$\sigma_y = \left[\frac{\Sigma (Y_i - \bar{Y})^2}{n - 1} \right]^{\frac{1}{2}}$$

X_i = individual measurements of the mass fraction
Y_i = individual measurements of counts per second

A.5.8 The slope of the resulting curve in A.5.7 is the sensitivity, and the intercept of the extrapolation of this curve to zero mass fraction yields the background signal.

A.5.9 Calculate the detection limit according to the equation in 3.2 using the results obtained in A.5.7 and A.5.8 for the sensitivity and background signal, respectively, and for the acquisition time in A.5.4. The results shall meet the requirements listed in Table 4.

A.5.10 The difference between the mean value of the relative mass fraction (k) for each of the reference materials used for determining the linear least-squares, curve and the mean value ($\bar{Y}$) determined by the instrument response shall be no greater than ±5 %.

ANNEX B
PERFORMANCE TESTS FOR INFLUENCE FACTORS
(Mandatory)

B.1 Low voltage indicator for battery power

For portable and transportable Type A instruments, the instrument's power source shall be replaced by a variable DC power source. The voltage of this source shall initially be set at the DC level specified by the manufacturer and shall then be reduced until a low voltage indicator is activated. After being switched on, the voltage shall be increased to a level such that the low voltage indicator is just deactivated. At this last voltage level, the tests specified in 5.3 shall be carried out, and the requirements of 5.3.2 shall be met.

B.2 Variation in mains or portable generator voltage and frequency

If applicable for transportable Type A and Type B instruments, the instrument shall be tested for its susceptibility to changes from the nominal voltage and frequency when operated by an AC power source. The instrument's power shall be changed from its nominal rated values specified by the manufacturer as follows: Mains or generator voltage by ±10 % and mains or generator frequency by ±2 %. While the change specified for each nominal power source rated value is maintained in turn for the instrument, the tests specified in 5.3 shall be carried out, and the requirements specified in 5.3.2 shall be met.

B.3 Mechanical shock

The part of the instrument containing the electronic components shall be placed on a rigid surface in its normal operational orientation. It shall then be tilted about one bottom edge to a height of at least 50 mm for portable and transportable Type A instruments and 25 mm for transportable Type B instruments, and then allowed to fall once to the surface. After this shock, the tests specified in 5.3 shall be carried out, and the requirements specified in 5.3.2 shall be met.

B.4 Vibration (sinusoidal)

The instrument shall be mounted on a rigid surface such that the gravitational force acts in the same direction as it would in normal use. It shall then be subjected to the following conditions of sinusoidal vibrations in turn on its three mutually perpendicular main axes:

- frequency range from 10–50 Hz;
- maximum acceleration level of 2 m/s^2;
- 20 sweep cycles per independent axis.

After these vibrations, the tests specified in 5.3 shall be carried out, and the requirements specified in 5.3.2 shall be met.

B.5 Electrostatic discharge

The instrument shall be tested for its susceptibility to electrostatic discharges from a suitable DC voltage source of 8 kV connected through a capacitor of 150 pF. The instrument shall be grounded or placed on a grounded surface. Those surfaces of the instrument which are normally accessible to the user shall be subjected to electrostatic discharges using an electrode with a resistance of at least 150 Ω. The electrode shall be brought into close contact with the instrument until a discharge occurs, and shall then quickly be removed before applying another discharge. At least 10 discharges shall be applied, leaving at least 10 s between each. After this exposure, the tests specified in 5.3 shall be carried out, and the requirements specified in 5.3.2 shall be met.

B.6 Electromagnetic fields

The instrument shall be tested for its susceptibility to interference from electromagnetic fields in the range 0.1–1 000 MHz. The field strengths may be generated as follows:

- by using a “strip line” for frequencies in the range 0.1–150 MHz;
- by “dipole antennae” or “antennae with circular polarization” for frequencies in the range 150–1 000 MHz;
- by using areas of known electromagnetic fields.

During exposure to these electromagnetic fields at a field strength of 1 V/m, the instrument shall be subjected to the tests specified in 5.3, and the requirements of 5.3.2 shall be met.

B.7 Temperature range

For portable and transportable Type A instruments, the instrument shall be placed in an environmental chamber and warmed up to 35 °C at a relative humidity of 60 % ± 20 % until the instrument is in thermal equilibrium at that temperature. At 35 °C, tests shall be carried out to determine the relative standard deviation of the output signal. The instrument shall be cooled down to achieve thermal equilibrium at 5 °C. The rate of cooling or warming shall not exceed 1 °C/min and the final relative humidity shall be within 60 % ± 20 %. At 5 °C, the same tests shall be conducted as at 35 °C. The tests shall be the same as specified in 5.3 but for these conditions, and the requirements specified in 5.3.2 shall be met.

B.8 Damp heat

For portable and transportable Type A instruments, the instrument shall be placed in an environmental chamber and warmed up to 35 °C, at a rate not exceeding 1 °C/min and at a relative humidity of 93 %, until the instrument is in thermal equilibrium without condensation. If the detector is cooled by liquid nitrogen, the upper limit of relative humidity shall be 80 %. Under these conditions, the tests specified in 5.3 shall be carried out, and the requirements in 5.3.2 shall be met.

ANNEX C
TEST REPORT FORMAT
(Mandatory)

Introduction

This *Test report format* presents a standardized format for the results of the various tests and examinations to which a pattern of an XRF spectrometer shall be submitted with a view to its approval.

It is recommended that all metrology services or laboratories evaluating patterns of XRF spectrometers according to OIML R 123 or to national or regional regulations based on OIML R 123 use this *Test report format*, directly or after translation into a language other than English or French.

It is also recommended that this *Test report format* in English or French (or in both languages) be transmitted by the country performing the tests to the relevant authorities of another country, under bi- or multi-lateral cooperation agreements. In the framework of the OIML Certificate System for measuring instruments, use of the *Test report format* is mandatory.

The test report shall include the following information:

Report No. ....

OIML Recommendation No. .... Edition (year) ....

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

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

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C.3 Name and address of the manufacturer

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

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

- instrument type ....
- trade name ....
- model number ....
- serial number ....
- requirements for: voltage ....
  frequency ....
  current ....

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

Comments: ....

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

C.7.1 Analyzable elements: From .... To ....

Comments: ....

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C.7.2 If portable, mass of the instrument ....kg

If transportable, Type A ....kg

Type B ....kg

Comments: ....

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C.7.3 Means of orienting sample with respect to source and detector: Yes ☐ No ☐

Comments: ....

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C.7.4 Source parameters specified: Yes ☐ No ☐

Comments: ....

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C.7.5 Detector requires cooling and means of maintenance specified: Yes ☐ No ☐

Comments: ....

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C.7.6 Data handling system capable of providing qualitative and quantitative analysis of data on site: Yes ☐ No ☐

Comments: ....

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C.7.7 Markings: Pass ☐ Fail ☐

Comments: ....

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C.8 Summary of the results of the tests carried out according to 8.1.3

C.8.1 Reference conditions for testing:

- ambient temperature ....
- relative humidity..
- source type ....
- detector(s) type ....

C.8.2 Detector resolution: Value .... Pass ☐ Fail ☐

Comments: ....

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C.8.3 Displayed energies: maximum permissible error

Values for elements 1 .... 2 .... 3 ....

Pass ☐ Fail ☐

Comments: ....

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C.8.4 Repeatability

Elements	Pb	Cd	Cr
Mass fraction (k)	.... mg/kg	.... mg/kg	.... mg/kg
Acquisition time			
Repetition: 1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
$\bar{Y}$			
σ_r			

Pass ☐ Fail ☐

Comments ....

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C.8.5 Linearity and detection limits (Ds)

Elements	Pb	Cd	Cr
Mass fraction (k)	.... mg/kg	.... mg/kg	.... mg/kg
Counts/second			
Acquisition time			
Repetition: 1			
2			
3			
4			
$\bar{Y}$			
$\bar{Y}-k$			
Mass fraction (k)	.... mg/kg	.... mg/kg	.... mg/kg
Counts/second			
Acquisition time			
Repetition: 1			
2			
3			
4			
$\bar{Y}$			
$\bar{Y}-k$			
Mass fraction (k)	.... mg/kg	.... mg/kg	.... mg/kg
Counts/second			
Acquisition time			
Repetition: 1			
2			
3			
4			
$\bar{Y}$			
$\bar{Y}-k$			

C.8.5 Linearity and detection limits (Ds) *(continued)*

Elements	Pb	Cd	Cr
Mass fraction (k)	.... mg/kg	.... mg/kg	.... mg/kg
Counts/second			
Acquisition time			
Repetition: 1			
2			
3			
4			
$\overline{Y}$			
$\overline{Y}-k$			
r^2			
D			

Linearity (r^2): Pass ☐ Fail ☐

Detection limits (Ds): Pass ☐ Fail ☐

Difference $\overline{Y}-k$: Pass ☐ Fail ☐

Comments ....

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C.8.6 Battery powered: Yes ☐ No ☐

Battery power low voltage indicator

Elements	Pb	Cd	Cr
Mass fraction (k)	.... mg/kg	.... mg/kg	.... mg/kg
Acquisition time			
Repetition: 1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
$\bar{Y}$			
σ_r			

Pass ☐ Fail ☐

Comments ....

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C.8.7 Variation in voltage or frequency

Elements	Pb	Cd	Cr
Mass fraction (k)	.... mg/kg	.... mg/kg	.... mg/kg
Acquisition time			
Repetition: 1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
$\bar{Y}$			
σ_r			

Pass ☐ Fail ☐

Comments ....

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C.8.8 Mechanical shock

Elements	Pb	Cd	Cr
Mass fraction (*k*)	.... mg/kg	.... mg/kg	.... mg/kg
Acquisition time			
Repetition: 1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
$\bar{Y}$			
σ_r			

Pass ☐ Fail ☐

Comments ....

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C.8.9 Vibration (sinusoidal)

Elements	Pb	Cd	Cr
Mass fraction (*k*)	.... mg/kg	.... mg/kg	.... mg/kg
Acquisition time			
Repetition: 1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
$\bar{Y}$			
σ_r			

Pass ☐ Fail ☐

Comments ....

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C.8.10 Electrostatic discharge

Elements	Pb	Cd	Cr
Mass fraction (k)	.... mg/kg	.... mg/kg	.... mg/kg
Acquisition time			
Repetition: 1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
$\bar{Y}$			
σ_r			

Pass ☐ Fail ☐

Comments ....

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C.8.11 Electromagnetic fields

Elements	Pb	Cd	Cr
Mass fraction (k)	.... mg/kg	.... mg/kg	.... mg/kg
Acquisition time			
Repetition: 1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
$\bar{Y}$			
σ_r			

Pass ☐ Fail ☐

Comments ....

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C.8.12 Temperature working range

Elements	Pb	Cd	Cr
Mass fraction (k)	.... mg/kg	.... mg/kg	.... mg/kg
Acquisition time			
Repetition: 1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
$\bar{Y}$			
σ_r			

Pass ☐ Fail ☐

Comments ....

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

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

Name: ....

Title: ....

Signature: ....

Date: ....