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Guidelines for the preparation of standard routine methods with wavelength-dispersive X-ray fluorescence spectrometry

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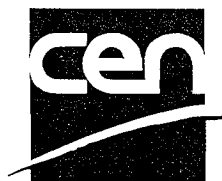
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EUROPEAN COMMITTEE FOR STANDARDIZATION
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1   Purpose of the guideline

X-ray Fluorescence Spectrometry (XRF) has been used for several decades as an important analytical tool for production analysis. XRF is characterised by its speed and high precision over a wide concentration range and since the technique in most cases is used as an relative method the limitations are often connected to the quality of the calibration samples. The technique is well established and most of its physical properties are well known.

This guideline is primarily intended to be used for analysis of metal alloys but it is also applicable to other materials although the sample preparation techniques differs. The purpose of this document is to describe general concepts and procedures for calibration and analysis with XRF.

2   Principals of the method

The sample is finished to a clean uniform surface and then irradiated by an X-ray beam of high energy. The secondary X-rays produced are dispersed by means of crystals and the intensities are measured by detectors at selected characteristic wavelengths. The measuring time is set to reach below a specified statistical counting error. Concentrations of the elements are calculated by relating the measured intensities of unknown samples to analytical curves prepared from reference materials of known concentrations

3.   Terminology - Definitions

3.1 Calibration

Calculation of the best fit of net intensities and concentrations from a number of calibration samples to an analytical curve.

3.2 Recalibration

Calculation of new calibration constants with a few number of samples, selected from the calibration samples and using the apparent concentrations calculated in paragraph 3.1.

3.3 Standardisation

To compensate for the instruments day to day variation a set of standardisation samples are measured, either one with a low and one with

a high concentration for each element (two-point standardisation) or one with a high concentration only for each element (one-point standardisation). The intensities are compared to the initial intensities stored during the calibration procedure and standardisation coefficients are calculated. Calibration constants are not changed.

3.4 Reference measurements

Instead of using net intensities to calculate the concentrations it is sometimes convenient to use the ratios between the intensities for the unknown sample and a reference sample.

Initial intensities for the reference samples are stored during the calibration procedure and the intensities are updated to compensate for day to day variations. The procedure is equivalent to the one-point standardisation procedure in paragraph 3.3.

3.5 Background Equivalent Concentration, BEC

The quantity of analyte which, when subjected to excitation, provides a net intensity equal to the spectral background, see Annex B.

3.6 Limit of Detection, LOD

The minimum concentration at which the signal generated by a given element can be positively recognised above any background signals with a specified degree of certainty, see Annex B.

3.7 Lower Limit of Detection, LLD

The minimum concentration at which the signal generated by a given element can be positively recognised above any background signals with a specified degree of certainty. Calculations based only on the counting statistical error, see Annex B.

3.8 Limit of Quantification, LOQ

The smallest concentration that can be determined with a specified degree of certainty, see Annex B.

3.9 Repeatability conditions, r

Precision under repeatability conditions as defined by ISO 5725 (Annex A, reference 7) e.g. same calibration, same operator, same instrument and shortest possible time between mesurements.

3.10 Reproducibility conditions, R

Precision under reproducibility conditions as defined by ISO 5725 (Annex A, reference 7) e.g. same method, identical test material, different laboratories, different operators using different instruments.

3.11 Accuracy

The closeness of agreement between test result and accepted reference value.

3.12 Trueness

The closeness of agreement between the average value obtained from a large series of test results and an expected reference value.

3.13 Sensitivity, S

The difference in intensities between a sample with a high concentration and one with a low concentration devided by the difference in concentration (sensitivity is expressed as counts per second per percent), see Annex B.

4. Instrumentation

The principle of two different X-ray Fluorescense Spectrometer concepts are shown in the figure 1 a-b below. Each detail will be described in the next paragraphs.

Fig. 1a Spectrometer geometry, used in sequential instruments
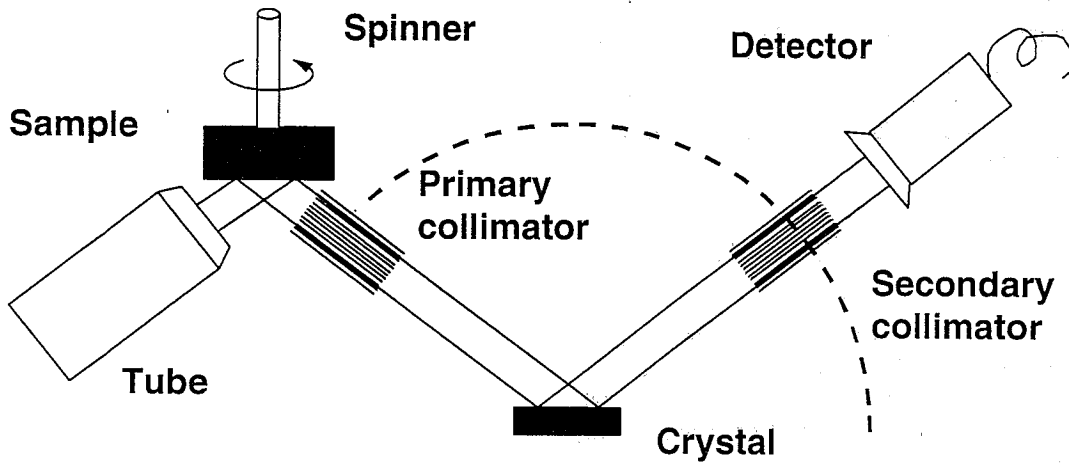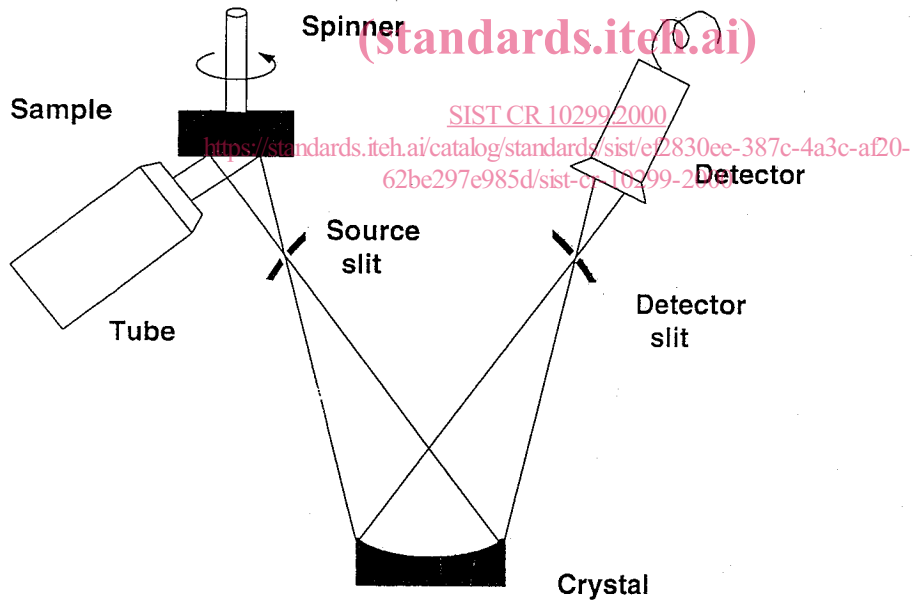

Fig. 1b Spectrometer geometry, used in simultaneous instruments

4.1 Tubes

Two different types of X-ray tubes are used: side-window tubes or end-window tubes. Table 1 gives a comparison of these two types. More favourable measuring conditions are usually obtained for light elements with an end-window tube due to the thinner window.

Table 1. Comparison of end window and side window tubes

	End window tubes	Side window tubes
Cooling	Two cooling circuits a) Direct cooling with deionized water b) Indirect cooling with tap water	One cooling circuit Direct cooling with tap water
Window	Slight thermal stressing: Thinner window	Greater thermal stressing: Thicker window
Service life	20 000 hours	5 000 hours

As target material, different high-purity elements like Rh, Ag, W, Cr or Au are used. For analysis of steels rhodium is usually used as a multipurpose tube with good excitation conditions for all elements of interest. If possible, the target material (anode) should not be made of an element to be determined. The applicability of the usual anode materials is summarised in table 2.

The X-ray tube produces a continuous spectrum and a characteristic spectra depending on the selected anode material. For optimum excitation, a maximum excitation energy at least two to three times above the corresponding absorption edge of the element line to be measured is recommended.

At present, equipments are available which may be operated with acceleration voltages up to 100 KV and maximum power of 3KW. The limiting data of the apparatus should be given either by the high-voltage supply or the X-ray tube used. The use of acceleration voltages above 60 kV is only of advantage in a few cases e.g. for determining the trace elements of heavy elements.

The radiation from the sample is emitted uniformly in all directions. The sample volume, from where the characteristic lines for an element can be analysed is proportional to the mass number. Light elements are only penetrating a thin layer of the sample.

Table 2. Anod materials for X-ray tubes and their fields of application

Anode material	Application
Rh	Good excitation conditions for light and heavy elements
Cr	Good excitation conditions for light elements, specially for K, Ca Ti. Not so good for heavy elements
Mo	Good excitation conditions for heavy elements, specially for Rb, Sr
W	Good excitation conditions for heavy elements, specially for Fe, Ni
Au	Good excitation conditions for heavy elements, specially for Cu, Zn
Ag	Equivalent to Rh. Ag is used if Rh lines interfere with element of interest.
Double anode	Different applications according to the anode materials

4.2 Vacuum system

During the measurement, the sample is moved to the spectrometer chamber. Light elements ($Z<20$) shall be measured in vacuum as the absorption losses in air are so high that a meaningful measurement is no longer possible. For analysis of metal alloys it is recommended to measure all elements in vacuum in order to keep the instrument in stabile conditions. A pressure less than 40 Pa is required.

4.3 Sample spinner

Most instruments are equipped with a sample spinner in order to avoid effects from grinding striations. If that is not the case, orient the sample in such a way that the relation between the X-ray beam and the grinding striations are always the same from measurement to measurement.

4.4 Filters

If the target material (anode) in the tube is of the same element to be determined a filter has to be put in front of the exit window on the tube in order to eliminate the characteristic lines from the tube. The efficiency of a filter depends on the material and thickness. A filter made of titanium or aluminium is often used to eliminate the characteristic lines from a chromium tube. When a filter is used, the sensitivity of the element of interest will decrease several times. Sometimes a filter could be used to increase the peak to background ratio for heavy elements in low concentrations. Many instruments are supplied with a filter changer containing filters of different material and thickness.

4.5 Collimators or slits

In the flat crystal system (fig. 1a) only a portion of the secondary radiation is selected by a primary collimator and the parallel beam is allowed to fall into the plane surface of the crystal. The resolution of the spectrometer is affected not only by the crystals used, but also by the collimation of the radiation. The finer the collimator selected, the better is the resolution, but the lower is the intensity measured. Most sequential spectrometers of this type are supplied with at least two collimators, coarse and fine.

In a curved crystal geometry (fig. 1b) the use of collimators are not necessary since the light is focusized on the detector by a slit system.

4.6 Crystals

In order to isolate individual chacaracteristic lines emitted by the sample, large single crystals are used as dispersion media. To cover the usual wavelength range between 0.2 and 15 Å, crystals with different space between the atomic layer (d-value) are used. Commonly used analysing crystals are listed in table 3. To cover the whole wavelength range a minimum of three crystals is required, LiF(200), PE and TIAP or a multilayer for light elements.

4.7 Detectors

The selected fluorescent radiation in the spectrometer is recorded by means of appropriate counters (flow counter, gas counter, scintillation counter). As the sensitivity of the various counters is a function of the energy of the radiation to be measured, the most suitable counter shall be used for the particular element line in simultaneous apparatus.

Table 3. Crystals and their fields of application

Crystal	Lattice planes	2 d values (nm)	For the measurement of the Ka-lines of
Lithium fluoride (LiF)	(220)	0,2848	Ti, V, Cr, Mn, Fe, Co, Ni
Lithium fluoride (LiF)	(200)	0,4027	K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, V
Germanium (Ge)	(111)	0,6532	P, S, Cl
Pyrolytic graphite (PG)	(002)	0,6715	P, S, Cl
Pentaery- thritol (PE)	(002)	0,8742	Al, Si, P, S, Cl
Ammonium dihydrogen phosphate (ADP)	(101)	1,0642	Mg, Na
Thallium hydrogen phtalate (Tl AP)	(100)	2,575	F, Na, Mg, Al
Multi-layer crystal	-	Variable	Elements z < 11

With sequential apparatus, flow and scintillation counters are generally used at the same time and are connected in series (tandem connection).

For elements with atomic number less than 25 the flow counter is used and for atomic number higher than 30 the scintillation counter is used. For atomic numbers between 25 and 30 both counters are used in tandem, if possible. In

simultaneous instruments 'gas counters filled with Kr or Xe are often used for atomic numbers between 20 and 40.

All counters can record only a limited number of pulses per unit of time, because the measuring process for each pulse requires a fixed amount of time which is in the order of 1 to 100 µs. Other pulses cannot be detected in this time. It is defined as dead time τ. Therefore, care shall be taken to ensure that the maximum pre-set pulse rate is not exceeded. This is possible, for example, by connecting attenuation filters (simultaneous equipment's) or decrease the tube current. Otherwise, there will be no linearity between the intensity of the X-ray radiation and the pulse rate measured.

The dead time of the counters may have an effect from a pulse rate of approximately 10^5 pulses per second. However, higher pulse rates may be used if the instrument is supplied with an electronic dead time corrector.

The counters used register pulses at different intensities as a function of the energy of the X-ray radiation. Therefore, specific pulses or energies may be filtered out by the selection of an electronic "window" (Pulse Height Discriminator). This pulse height discrimination eliminates interference pulses.

4.8 Sequential- Simultaneous instruments

The X-ray fluorescence apparatus can be sub-divided into two categories: sequential apparatus and simultaneous. Simultaneous apparatus have several fixed goniometers (channels) arranged around the sample so that the individual element lines may be measured at the same time with the same excitation conditions. Each channel is optimised for each element. In the sequential apparatus the user has the flexibility to optimise the measuring conditions independently for all selected elements and their backgrounds. The goniometer can be set to an pre-defined angle (5-150°) and the excitation conditions can be optimised separately for all elements.

Simultaneous apparatus are often used in a production environment where speed is important and the sample matrix is known. In modern instruments sequential and simultaneous functions can be combined.

5. Sampling and sample preparation

In any analytical work the sample preparation is a critical procedure (Annex A, reference 8). In XRF analysis of metal alloys usually a flat solid sample with a diameter of at least 25 mm and thickness of at least 1 mm is prepared. Samples with a smaller size could be analysed, even down to a diameter less then 10 mm, but the sensitivity will decrease significantly. Chips or small pieces of metals may be transformed into a suitable sample by remelting in inert gas environment. The preparation is divided into several steps, cutting of the sample to a suitable size and then grinding to a certain surface smoothness. There are different equipments on the market for sample preparation.

In order to obtain an accurate test result, the measuring surface should be free of defects. Commonly used grinding papers are aluminiumoxid, silicon carbide or zirconium oxide. The material in the paper will disable the determination of the corresponding element (Al, Si, Zr) in the sample, specially in low concentrations <0,1%. The grain size of the grinding material will strongly influence the standard deviation on repeated measurements. For steels a grain size between 120 to 220 mesh is often used. With manual grinding a paper with a grain size not less than 180 mesh should be used since the sample surface will be different from one operator to another and the reproducibility will decrease.

Often the metal surface, from a macroscopic point of view, could be treated as a homogenous sample but that is not always true. In some cases structure effects could influence the measured intensity due to non-metallic inclusions particularly of carbides, sulphides and nitrides. It has been reported (Annex A, reference 1) that those effects can be reduced. It is therefore very important that the calibration samples and the unknown samples have the same metallurgical structure.

6. Evaluation methods

The intensities measured should be corrected as described below:

6.1 Dead time correction

The dead time τ is a function of the type of counter and can be calculated. If n is the