
**Iron ores — Wavelength dispersive
X-ray fluorescence spectrometers —
Determination of precision**

*Minerais de fer — Spectromètres à fluorescence à rayons X à longueur
d'onde dispersive — Détermination de la précision*

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Contents

Page

Foreword	iv
Introduction	v
1 Scope	1
2 Frequency of testing	1
3 Counter tests	2
3.1 Counter resolution.....	2
3.1.1 General.....	2
3.1.2 Procedure.....	4
3.1.3 Assessment of results.....	6
3.2 Conductivity of the gas flow proportional counter window.....	6
3.2.1 General.....	6
3.2.2 Procedure.....	7
3.2.3 Assessment of results.....	7
3.3 Pulse shift corrector.....	7
3.3.1 General.....	7
3.3.2 Procedure.....	8
4 Spectrometer tests	8
4.1 General.....	8
4.2 Precision.....	9
4.2.1 General.....	9
4.2.2 Calculation of counting statistical error.....	10
4.3 Test specimen.....	11
4.3.1 General.....	11
4.3.2 Sequential spectrometers.....	11
4.3.3 Simultaneous spectrometers.....	11
4.4 Instrumental conditions.....	11
4.4.1 General.....	11
4.4.2 Sequential spectrometers.....	12
4.4.3 Simultaneous spectrometers.....	12
4.5 Stability test.....	12
4.6 Specimen rotation test.....	13
4.7 Carousel reproducibility test.....	13
4.8 Mounting and loading reproducibility test.....	13
4.9 Comparison of sample holders.....	13
4.10 Comparison of carousel positions.....	14
4.11 Angular reproducibility.....	14
4.12 Collimator reproducibility (for sequential spectrometers fitted with an interchangeable collimator).....	14
4.13 Detector changing reproducibility (for sequential spectrometers fitted with more than one detector).....	14
4.14 Crystal changing reproducibility.....	14
4.15 Other tests.....	15
4.16 Note on glass bead curvature.....	15
5 Determination of the dead time and the maximum usable count rate of the equipment	15
5.1 General.....	15
5.2 Methods of determination of dead time.....	16
5.2.1 General.....	16
5.2.2 Recommended method for determining dead time.....	17
Annex A (informative) Calculation of the coefficient of variation of duplicates	24
Bibliography	26

Foreword

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The committee responsible for this document is ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

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Introduction

If an X-ray fluorescence spectrometer is to be used for precise analyses, it needs to be functioning correctly to specification, that is, the errors associated with the various functions of the instrument have to be very small. It is important therefore that the spectrometer be tested to ensure that it is indeed functioning to deliver the required precision. The objective of this Technical Report is to set out tests that can be used to ascertain the extent of the errors and to suggest procedures for their rectification. These tests are not used to ascertain whether the instrument is operating optimally but to determine whether the instrument is capable of giving a preselected precision.

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Iron ores — Wavelength dispersive X-ray fluorescence spectrometers — Determination of precision

1 Scope

This Technical Report describes methods of test that can be applied to wavelength dispersive X-ray fluorescence (WD-XRF) spectrometers to ensure that the spectrometers are functioning in a manner that allows precise analyses to be made.

The tests outlined are designed to measure the errors associated with the operation of certain parts of the spectrometer. They are not designed to check every part of the spectrometer but only those parts that may be the common sources of error.

It is assumed that the performance of the instrument has been optimized according to the manufacturer's instructions. For all tests, the two-theta angle should be carefully set for the line being measured. The pulse height window should be set according to the manufacturer's instructions and should have a broad setting which may also include the escape peak for gas proportional counters. The instrument and detector gas environment should be as specified by the manufacturer, as should the power supply to the instrument.

NOTE Where no distinction has been made, it is assumed that a test is applicable to both sequential and simultaneous spectrometers.

2 Frequency of testing

Testing is not required to be carried out with each batch of analyses. The frequency of testing varies depending on the test involved. [Table 1](#) lists the suggested frequency with which each test should be carried out. Where specific problems are encountered, more frequent testing may be required and remediation work performed.

Table 1 — Suggested frequency of precision tests

Frequency	Test
Monthly	Resolution of the gas-flow proportional counter Resolution of the scintillation and sealed gas counters Operation of the pulse height shift corrector ^a
Half yearly	Conductivity of gas-flow proportional counter window General stability Collimator reproducibility Detector changing reproducibility Crystal changing reproducibility Angular reproducibility
Yearly	Carousel reproducibility Comparison of carousel positions Comparison of sample holders Sample loading and unloading
^a The position of the pulse height peak should also be checked after changing a bottle of detector gas since a variation in the methane content of the gas will change the position of the peak.	

The frequencies with which the tests listed in [Table 1](#) are carried out are suggested on the basis that there have been no changes to the spectrometer. If mechanical or electronic maintenance of a major nature is carried out, the appropriate tests should be made before the spectrometer is taken back into routine service.

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3 Counter tests

3.1 Counter resolution

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3.1.1 General

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3.1.1.1 Theoretical resolution

Impurities in the flow gas and contamination of the anode wire may cause gas flow proportional counters to gradually deteriorate, which will result in both a shift and a broadening of the energy distribution (pulse height) curve. Similarly, scintillation counters and sealed gas counters may, for various reasons, exhibit the same gradual deterioration. This can, ultimately, adversely affect the measurements. Impurities in detector gas can be minimized by the use of gas filters.

The resolution (*RES*) of a counter is related to its energy distribution curve, and is given by the measured peak width at half height (*W*) expressed as a percentage of the maximum of the pulse amplitude distribution (*V*), using Formula (1) where the values of *W* and *V* are in terms of arbitrary units (which vary between instrument manufacturers) obtained from the X-axis (see [Figure 1](#)):

$$RES = \frac{W}{V} \times 100 \tag{1}$$

The theoretical resolution (*RES_{th}*), using the full width at half height of a Gaussian distribution, can be calculated using the following formulae:

$$RES_{th} = 2,36 \sigma \tag{2}$$

$$\sigma = \sqrt{n} \quad (3)$$

Expressed as a percentage relative to n , Formula (3) becomes:

$$\sigma = \frac{100}{\sqrt{n}} \text{ (in \%)} \quad (4)$$

where

n is the number of primary electrons per incident photon (gas counters) or number of photoelectrons collected by the first dynode of the photomultiplier tube (scintillation counters), calculated using Formula (5):

$$n = \frac{E_x}{V_i} \quad (5)$$

E_x is the energy of the incident radiation, in kilo electron volts (keV);

V_i is the effective ionization potential of Argon for a flow counter, in kilo electron volts (keV) = 0,026 4.

Substituting Formula (5) into Formula (4), and Formula (4) into Formula (2) gives:

$$RES_{th} = \frac{236 \times \sqrt{0,026\ 4}}{\sqrt{E_x}} \frac{38,4}{\sqrt{E_x}} \quad (6)$$

Hence, for Cu $K\alpha$ ($E = 8,04$ keV), the theoretical resolution of an Ar gas counter is 13,5 %.

3.1.1.2 Scintillation counter

For a scintillation counter:

$$RES_{th} = \frac{128}{\sqrt{E_x}} \quad (7)$$

and for Cu $K\alpha$, the resolution should be approximately 45 %.^[1]

3.1.1.3 Practical resolution

In practice, however, the measured resolution achieved (RES_m) is given in Formula (8):

$$RES_m = k R \quad (8)$$

where

k is a factor that varies with the design of the counter, phosphor efficiency (scintillation counters), diameter, cleanliness and composition of the anode wire (gas counters).

For a well-designed and clean gas-flow proportional counter, k should be less than 1,15. Hence, for such a counter, RES_m should be less than 15,6 % for Cu $K\alpha$ radiation. For the scintillation counter, this value should be less than 52 %.

3.1.2 Procedure

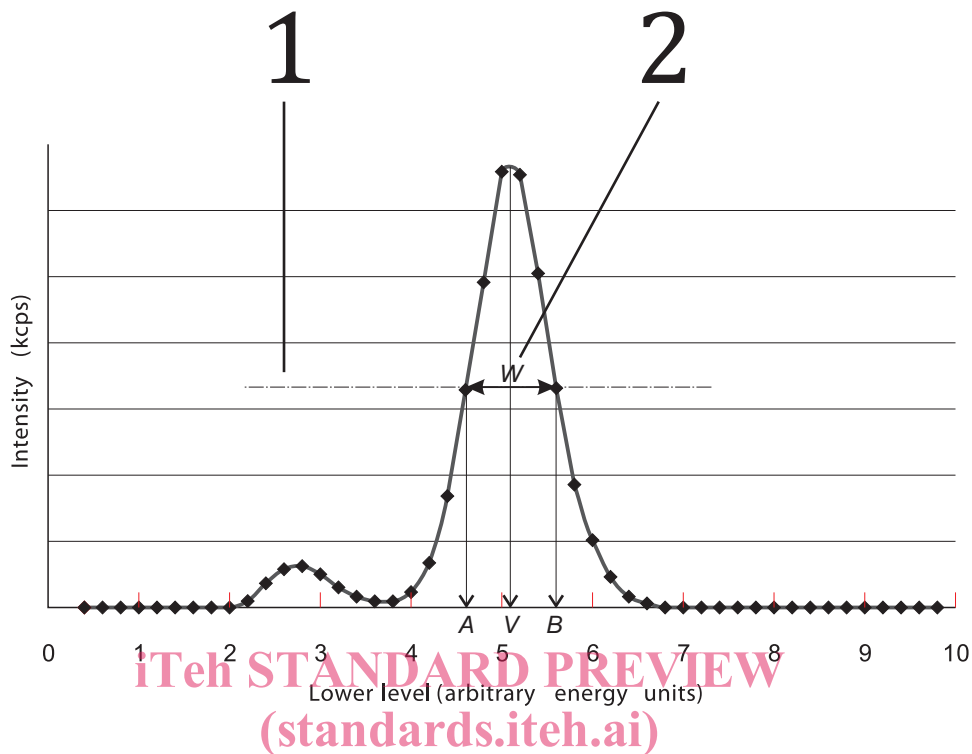
This test should be carried out on all counters used in the spectrometer. Most modern instruments provide the facility to measure pulse height distributions and to print out the counter resolution and this facility should be used if available.

For sequential spectrometers, it is recommended that the test be carried out using either Cu K α or Fe K α radiation for both detectors. However, if these lines are measured using only the scintillation counter in actual analysis, measure an X-ray line of a major element analysed with the gas proportional counter for testing.

If the spectrometer does not provide automatic functions to determine RES_m then the following procedure should be used.

- a) Select a sample containing the appropriate analyte and, using a lower level setting and the pulse height analyser (PHA) window set to “threshold” (no upper level), adjust the X-ray tube power to give a count rate of about 2×10^4 cps (counts per second).
- b) Select a narrow pulse height window (2 % to 4 % of the peak voltage V of [Figure 1](#)) and decrease the lower level setting until the count rate drops to essentially zero.
- c) Increase the lower level stepwise, noting the count rate at each step, until the peak has been passed and the count rate drops again to a very low value. Each step should be of the same width as the pulse height window width, i.e. if the pulse height window width corresponds to 0,2 units, then each step of the lower level should be 0,2 units.
- d) Plot the count rate obtained at each step against the lower level values. An example is shown in [Figure 1](#).

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**Key**

- 1 half peak height <https://standards.iteh.ai/catalog/standards/sist/90fd7043-78cc-4ec3-8283-25cf02aead51/iso-tr-18231-2016>
- 2 peak width at half peak height

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Figure 1 — Intensity as a function of lower level setting (arbitrary energy units) displayed for Fe K α radiation measured on a flow counter

The measured counter resolution RES_m (in %) is obtained from the plot as follows:

$$RES_m = \frac{B - A}{V} \times 100 \quad (9)$$

where

B and A are the lower level settings at the half height positions on either side of the peak;

V is the lower level setting at the maximum of the pulse height distribution.

The pulse height distribution should be determined at a count rate indicated by the instrument manufacturer, or just below 2×10^4 cps (see [Figure 1](#)).

When determining the pulse height distribution automatically, A , B , V and W are not usually displayed, but the graph, peak position and detector resolution are shown together with instrument specific data.

3.1.3 Assessment of results

3.1.3.1 Gas flow proportional counter

Since the resolution of a proportional counter depends on design, an absolute resolution value cannot be given but the value should be near to that given in Formula (6). The optimum resolution of a particular counter may be specified by the manufacturer or it may be found with use. When RES_m increases by a factor of 1,2 times that value, the counter should be serviced.

3.1.3.2 Scintillation and sealed gas counters

These counters usually do not exhibit significant changes in resolution unless the counter is beginning to fail, which can be quite early for some sealed gas counters for light elements and where they have been used at very high flux for extended periods. Their resolution can be calculated according to Formula (9) but the k factor is instrument specific. Hence, it is sufficient to measure their resolution experimentally on a regular basis. If a significant increase in resolution is noted or the pulse height distribution extends outside the energy window when it did not on installation, then the counter should be replaced.

Scintillation counters can fail due to leaks in the beryllium window, thereby admitting moisture to the very hygroscopic NaI crystal. The effect of such moisture reduces count rates for the longer wavelengths, e.g. $\sim 2\text{\AA}$ but may have relatively little effect on short wavelengths, $\sim 0.6\text{\AA}$. As more moisture reacts with the crystal, its sensitivity will be reduced for all wavelengths.

Similarly, the sensitivity of sealed counters will reduce due to leaks in the detector window. A leaking sealed gas counter window will result in a loss of gas density and thus gas amplification.

Although a reduction in sensitivity of the scintillation and sealed gas counters does not affect counting precision, the signal-to-noise ratio will be reduced and longer counting times will be required to achieve a given precision. Furthermore, if the reduction in sensitivity is due to failure of the window, then this reduction will be continuous and total detector failure will be imminent.

The best method of detecting deterioration of such counters is to set aside a stable specimen (such as an instrument monitor) and to periodically measure the intensity of a reasonably long wavelength line (for example, Fe $K\alpha$ for the scintillation counter). Any pulse height shift or decrease of intensity over time should be investigated to ascertain whether the scintillation (or sealed gas) counter requires replacing.

3.2 Conductivity of the gas flow proportional counter window

3.2.1 General

The gas-flow proportional counter window consists of a thin layer of plastic material (such as Mylar or polypropylene) coated with a very thin electrically conductive layer (typically aluminium). For practical considerations, the window material should be able to support atmospheric pressure without breakage. Where air or helium paths are frequently used over a period of time, this material may stretch and cause the aluminium coating to suffer from micro-cracks, resulting in the window becoming non-conducting.

A gas-flow proportional counter having a poorly conducting or non-conducting window appears to function normally in most respects. However, measurements made with such a counter will be in error, as the counter will give reduced count rates for samples which would normally give a high count rate. This is especially noticeable when low and high count rates are measured consecutively.

Where $6\ \mu\text{m}$ windows are used, loss of conductivity is seldom encountered, as the window usually has a life of some years, requiring replacement only when the counter is serviced for other reasons. The useful life of thinner windows ($\leq 1\ \mu\text{m}$ polypropylene windows are commonly used in most modern spectrometers) varies from several months to more than a year. Where the spectrometer chamber