TECHNICAL
REPORT

ISO/TR
18231

First edition
2016-05-01

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

Reference number
ISO/TR 18231:2016(E)

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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.*

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.

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.

3 Counter tests

3.1 Counter resolution

3.1.1 General

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:

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

$$\sigma = \sqrt{n} \tag{3}$$

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

$$\sigma = \frac{100}{\sqrt{n}} \left(\text{in}\,\%\right) \tag{4}$$

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):

$$n = \frac{E_\mathrm{x}}{V_\mathrm{i}} \tag{5}$$

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:

$$RES_\mathrm{th} = \frac{236 \times \sqrt{0{,}026\ 4}}{\sqrt{E_\mathrm{x}}} = \frac{38{,}4}{\sqrt{E_\mathrm{x}}} \tag{6}$$

Hence, for Cu Kα (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:

$$RES_\mathrm{th} = \frac{128}{\sqrt{E_\mathrm{x}}} \tag{7}$$

and for Cu Kα, 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):

$$RES_\mathrm{m} = k\ \ R \tag{8}$$

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 Kα 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 Kα or Fe Kα 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.

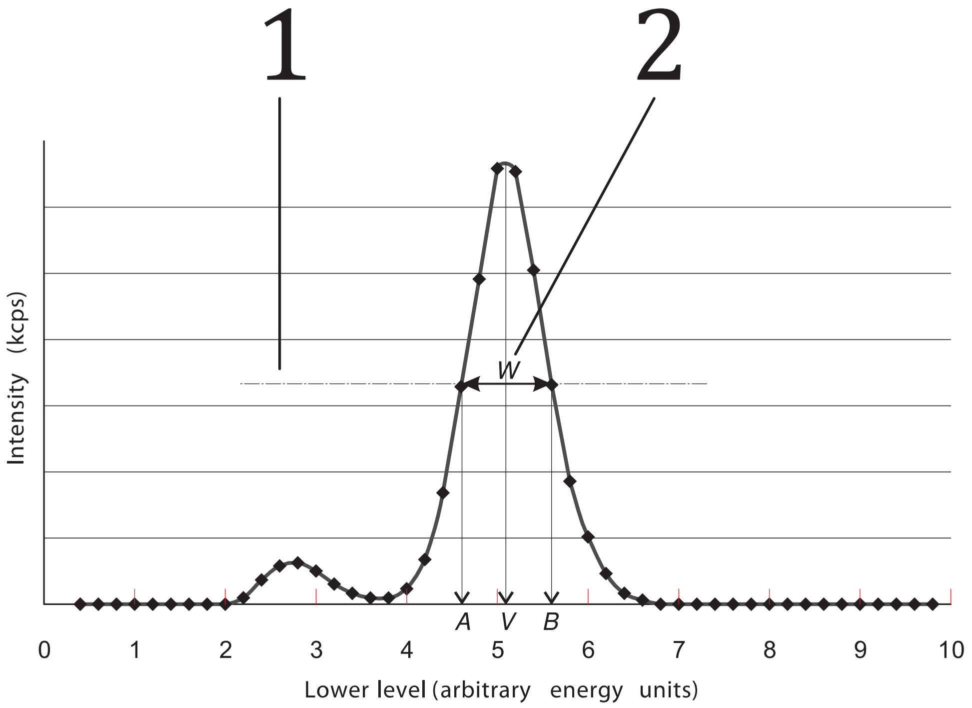
If the spectrometer does not provide automatic functions to determine RES_m then the following procedure should be used.

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.



Key

1 half peak height

2 peak width at half peak height

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

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

$$RES_m = \frac{B - A}{V} \times 100 \tag{9}$$

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. ~2Å but may have relatively little effect on short wavelengths, ~0.6Å. 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 Kα 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 µm 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 (≤1 µm polypropylene windows are commonly used in most modern spectrometers) varies from several months to more than a year. Where the spectrometer chamber is continuously under vacuum, the window life is longer than for those where the spectrometer is let down to normal air or Helium pressure frequently.

NOTE If the gas-flow proportional counter has a beryllium window, this test may be necessary to occasionally check for the formation of hairline cracks.

3.2.2 Procedure

3.2.2.1 Sequential spectrometers

The procedure for sequential spectrometers is as follows.

a) Carry out the test using K Kα radiation.

b) Using low X-ray tube power (low kV and mA), select a sample that gives a count rate of between 1 000 cps and 5 000 cps.

c) Set the 2θ angle and pulse height analyser using this sample and then, using these settings, measure the count rate for 10 s.

d) Replace the sample with one having a high potassium concentration (a briquette of potassium chloride or potassium hydrogen phthalate is particularly suitable or a sample advised by the instrument manufacturer); set the X-ray tube to such a power that the maximum count rate allowed by the manufacturer is achieved. Maintain these conditions for 2 min.

e) Reduce the X-ray tube power to its starting value and measure the count rate for the original sample again.

3.2.2.2 Simultaneous spectrometers

For simultaneous spectrometers, the test is made on those channels having gas-flow proportional counters fitted with thin plastic windows. The test is carried out in a similar manner to the procedure specified in 3.2.2.1, except that the radiation used is that specific to the selected channel.

NOTE Tests for simultaneous spectrometers are also applicable to fixed channels in a sequential spectrometer.

3.2.3 Assessment of results

If the window is conducting properly, the initial count rate will be within 5 % of the final count rate when the X-ray tube power is returned to the original settings. If the window is poorly conducting, a reduced count rate will be observed. In such cases, the count rate should slowly return to the original rate but for non-conducting windows, the time involved may be in excess of 12 h. The window should be replaced if there is any evidence of poor conduction.

3.3 Pulse shift corrector

3.3.1 General

At high count rates, high detector gains will result in a shift to lower pulse amplitudes. In modern spectrometers, the effects of pulse shift have been minimized by designing counters with a lower dependence on gas density and composition and by the use of automatic pulse shift correction electronics. Nevertheless, the effect of pulse shift errors on analytical accuracy can be significant.

All modern spectrometers are fitted with automatic pulse shift correction but the operation of detectors should also be checked when the automatic shift correction is not operating at low count rates. The threshold count rate at which the automatic shift correction operates can vary between each detector type, instrument model and spectrometer manufacturer. This may even be programmable with automatic pulse shift disabled or enabled in software or hardware.

For gas-flow detectors, since the pulse shift is dependent on the gas composition (proportion of argon to methane and the level of contaminants) and gas density (temperature or pressure of the gas within the detector), pulse shift should be checked whenever the flow gas supply cylinder has been replaced or whenever the gas flow detector or gas density stabilizer has been repaired.

NOTE Leaks in the gas-flow circuitry may result in the erroneous entry of air, or helium in the case of liquid measurements, which will alter the flow gas composition.

As modern spectrometers are fitted with gas density stabilizers of significant volume, detector gas lines should be allowed to purge prior to checking pulse heights after any of the above work has been carried out. As the volume of flow gas circuits may be up to 3 l, the purging of lines may take up to 3 h unless the possibility exists for a higher purge rate for a short period of time. Advice from the manufacturer should be taken here.

3.3.2 Procedure

a) For all XRF instruments, use a sample whose radiation wavelength is suitable for the detector and crystal combination. Below are the recommended lines for each crystal:

    1) TlAP – Al Kα or Mg Kα;

    2) 2,5 nm to 5 nm 2d crystals (synthetic multilayer) — Al Kα, Na Kα or Mg Kα;

    3) 0,18 nm to 0,41 nm 2d crystals (LiF$_{200}$, LiF$_{220}$ & LiF$_{420}$) — Fe Kα or Cu Kα;

    4) Ge — S Kα;

    5) PE — Al Kα, Si Kα or P Kα;

    6) InSb — Si Kα.

b) Using high X-ray tube power (with high mA), select a sample, or samples, that give(s) a count rate near to that specified by the manufacturer as the maximum for the counter.

c) Measure the pulse height using a small step size (1 % to 2 % of the peak voltage) and a step time of not less than 1 s. Record the peak maximum position.

d) Check manufacturer instructions for the count rate at which the automatic pulse shift correction is enabled. Reduce the X-ray tube mA setting so that a count rate below this level is obtained or use a second sample.

e) Repeat the procedure c) and record the peak maximum position.

f) Repeat the whole procedure for each detector.

If the peak maximum positions at the low count rate and the high count rate differ by more than 5 % then the high voltage gain of the detector requires adjusting. This adjustment may require the skills of a qualified technician.

If the instrument uses pulse shift correction at all count rates, the test will check that the correction is working.

4 Spectrometer tests

4.1 General

X-ray spectrometers are mainly used for quantitative analyses. The degree of precision required in various applications varies considerably and the following tests are to determine whether the spectrometer can deliver the required precision.

Determining the measurement error component of the total analytical error can be achieved by measuring one sample 20 times (for example) and then processing the data to obtain the mean, standard deviation and % coefficient of variation ($\%CoV$) of the concentration or intensity values. The $\%CoV$ of the concentration values will be that of the intensity values multiplied by the matrix correction term for the element of interest. The standard deviation of the intensities should be close to the counting statistical error.

If the measurement error is outside of the statistical error limits given in Table 2 and also outside of the acceptable error for the analyses being carried out, then the following tests can be used to find the instrumental variables which are causing the problem and they can then have their influence on the total analytical error minimized.

For typical routine analyses, a $\%CoV$ of 0,1 % is generally satisfactory for analytical requirements. If higher precision is required, then the instrument should be carefully maintained and the testing frequency of parameters listed in Table 1 might need to be increased.

Testing of the spectrometer is carried out by making repeated measurements to determine the basic instrument stability and then the repeatability as various instrumental parameters are changed, one variable at a time, so that any error source can be found.

The statistical bounds of tests conducted present a probability distribution about the counting statistical error ($\%CSE$). For tests conducted at low levels of precision, it is frequently possible to obtain results that are less than the $\%CSE$. The probability of this occurring decreases when increasing the number of counts accumulated per measurement and when increasing the number of measurements.

At higher levels of precision, residual instrumental errors will have an increased impact on results and the $\%CoV$ will generally be greater than the $\%CSE$.

Precision measurements are made on the major element of the material to be analysed using a sensitive line. In the case below, the Fe Kα line is used.

Dead-time corrected intensities should be used for measurements since these intensity values are used to convert intensity data into concentration values during the analytical procedure. Such intensities are also used in calculating measuring times required to achieve the desired counting statistical error when setting up an analytical method.

The $\%CSE$ should theoretically be based on the actual counts a detector registers. At high count rates above about 1 000 000 cps, dead-time effects have an increasing effect on the calculated $\%CSE$ and this value is better established using the non-dead-time corrected count rate.

At high count rates, where dead time and pulse pile up effects are high, the time interval distribution of counts also varies from a Poisson distribution. However, such differences need not be considered when simply trying to determine if a spectrometer is capable of obtaining a required degree of analytical precision or if some component of the spectrometer needs to be fixed.

4.2 Precision

4.2.1 General

The precision of WD-XRF analytical methods is dependent on the error of sub-sampling the material brought to the laboratory for analysis, the sample preparation error and the sample measurement error. The total analytical error (T) is determined from contributing error components using Formula (10):

$$T = \sqrt{(\text{subsampling error})^2 + (\text{preparation error})^2 + (\text{measurement error})^2} \tag{10}$$

Factors contributing to measurement precision errors are counting statistical errors, instrumental stability errors, errors associated with moving instrumental parts and errors due to measurement parameter settings. These error sources will be addressed in the subclauses below.

The above errors are based on 1 standard deviation (*sd*). Generally, the precision of an analytical method is described using 2 *sd*, which corresponds to a 95 % probability that a result will be within those bounds. The maximum counting statistical error required for an analytical procedure can be calculated by rearranging Formula (10) and having minimized and knowing the sub sampling and sample preparation errors. These can be obtained experimentally.

4.2.2 Calculation of counting statistical error

For an infinite number of measurements and assuming no instrumental errors:

$$\%CSE = \%CoV = \frac{100}{\sqrt{N}} = 100 \times \frac{\sqrt{N}}{N} = 100 \times \frac{\text{Standard deviation}}{\text{Mean}} \tag{11}$$

where

N is the total counts accumulated per measurement.

For a finite number of measurements and assuming Poisson statistics apply:

$$\%CoV = 100 \times \frac{\text{Standard deviation}}{\text{Mean}} \tag{12}$$

And the standard deviation = $\sqrt{\text{Mean}}$, as shown in Formula (11).

If the number of measurements (n) is <20, then the sample standard deviation (based on n−1) is used instead of the population standard deviation.

Where 20 measurements are made, the observed %*CoV* should not exceed 1,4 times (1 % probability[2]) the %*CSE*, as shown in Table 2.

Table 2 — %*CSE* and upper statistical limit for %*CoV*

Total counts (N)	%*CSE*[a]	1,4 × %*CSE*[a]	%*CSE*[b]	1,4 × %*CSE*[b]
1 000 000	0,100	0,140	0,116	0,160
10 000 000	0,032	0,044	0,037	0,051
20 000 000	0,022	0,031	0,026	0,036
25 000 000	0,020	0,028	0,023	0,033
40 000 000	0,016	0,022	0,018	0,026
100 000 000	0,010	0,014	0,012	0,016

[a] Using dead-time corrected counts at a count rate of 2 000 000 cps.

[b] Using non-dead-time corrected counts at a count rate of 1 481 636 cps

Counting statistical errors should be calculated on the counts actually detected by the detectors and not the dead-time corrected counts. At low count rates <1 000 000 cps, there will be little difference in the dead-time corrected and non-dead-time corrected %*CSE*. At high count rates, the difference becomes noticeable.

The non-dead-time corrected count rate can be calculated using the formula for extendable dead time [Formula (14)]. A dead time of 0,15 µs was used in the calculation, with the value entered in seconds, i.e. 0,000 000 15 s and the count rate in counts per second.

The total counts (N) in Table 2 are the dead-time corrected counts accumulated. Calculation of %*CSE*[b] is based on the same counting time used to accumulate the dead-time corrected counts with a non-dead-time corrected count rate of 1 481 636 cps.

The difference between $\%CSE^a$ and $\%CSE^b$ will decrease with decreasing count rate and increase with increasing count rate. There is little difference between the values below count rates of 1 million cps.

The $\%CSE^b$ values of Table 2 should be close approximations on the statistical limits obtained on flow counters at 2 000 000 cps for most modern instruments.

Test measurements are always carried out using the dead time corrected counts. Only the counting statistical limits are adjusted for dead-time effects.

If the $\%CoV$ for a precision test is larger than the values given in Table 2, which are limits based on statistics alone, then the measurements should be repeated. If the measurements are outside the limits again, then corrective measures should be taken to minimize the problem if the results do not satisfy analytical requirements. If the spectrometer cannot meet the required precision for an analysis, tests can be carried out at a lower count rate or its use should be limited to less precise work.

When testing spectrometers at the above levels of precision, it should be remembered that all spectrometers have some residual instrument errors and, therefore, will not pass precision tests when tested at some very high level of precision such as 100 million accumulated counts per measurement. However, most spectrometers are expected to be within the statistical limits or plus 20 % of the maximum limit when accumulating between 20 million to 40 million counts per measurement under standard laboratory conditions since measurement errors should be and are generally small.

4.3 Test specimen

4.3.1 General

The test specimen should be robust and stable and should have a flat analytical surface. A metal alloy or a glass disc into which the analyte(s) has/have been incorporated by fusion with a borate flux can be used. The use of compacted powder pellets is to be actively discouraged as these are not stable over long periods of time. The sample should be firmly fixed in the sample holder so that no movement is possible during measurement.

4.3.2 Sequential spectrometers

Any analytical line that gives a high count rate can be used for the precision test and it is appropriate to use the line of a major component of a typical sample. In the examples given below, Fe Kα is used and the amount of iron in the test specimen should be such that, under normal conditions of X-ray tube power, the maximum count rate stipulated by the manufacturer is not exceeded.

4.3.3 Simultaneous spectrometers

For simultaneous spectrometers, a test specimen that allows testing of several channels simultaneously is desirable. Several samples may be required to cover all element channels. The test specimen should be such that, under normal operating conditions of X-ray tube power, a count rate of around 10^5 cps or higher is obtained in each of the channels under test. For channels measuring very light elements, where such intensity may not be possible, use as high a count rate as is achievable. Very high count rates should be avoided as there will then be significant errors in the recorded counting times used unless three decimal places are available. Alternatively, use the fixed time method to collect sets of counts which are very close to the target value (N) for all power settings.

4.4 Instrumental conditions

4.4.1 General

The X-ray tube should be operated at the normal working power. The sample spinner should be used, if possible, unless otherwise stated in the specific test.

Where possible, measurements should be made using the pre-set count mode. The time, in seconds, required to accumulate the counts should be recorded to at least three decimal places. If a pre-set count facility is not available, or if the timer does not read to the required precision, the pre-set time mode should be used and the measuring time should be adjusted so that approximately the same number of counts is accumulated at each power setting. Alternatively, a pre-set counting statistical error mode can be used for the desired level of precision. The actual number of counts accumulated for each measurement should then be recorded for these alternate methods.

4.4.2 Sequential spectrometers

For sequential spectrometers, the collimator normally used for the major element being measured should be used if there is more than one available. The detector should also be that normally used for the element being measured.

A broad energy window should be used for the pulse height distribution (PHD) which may also include the escape peak.

Setting an upper energy level at a position where the intensity is still significantly higher than zero will lead to instability in a detector. This can be seen when comparing stability determinations between Fe Kα to Zn Kα radiation on a scintillation detector at similar count rates, with the Zn Kα peak being less broad, or when carrying out stability tests at high or lower intensity levels for a specific line.

4.4.3 Simultaneous spectrometers

A broad PHD window should be used with each channel under test. A trial measurement should be made to ascertain the correct PHD window width.

4.5 Stability test

When an X-ray tube is turned on, or when total power settings are changed, it may take some time for the output of the X-ray tube to stabilize. The period of instability, and its magnitude, varies even between instruments of the same manufacture and it should be determined for each spectrometer.

Instability can be observed by taking repetitive counts and plotting the count rate against time. Modern spectrometers often have this facility built into their software. The tests given below should be carried out after the spectrometer has stabilized. The time to reach stability is likely to be longer after an instrument is powered up after being turned off or set at low power overnight than when power changes are made during analyses. It will also be longer when stabilizing for the higher levels of precision.

The stability test should be carried out as follows.

a) Make 50 consecutive measurements on the test specimen in a static position. During this test, all the spectrometer parameters should remain fixed and the sample spinner should not be used while all measurements are made.

b) Calculate the %CoV.

The test should be performed using each of the detectors fitted to the spectrometer.

In this case, the calculated coefficient of variation should not exceed 1,23 times the counting statistical error (%CSE) for 50 consecutive measurements.[2] If the calculated value exceeds this, it may indicate a lack of stability in the equipment, as there is only a 1 % probability that a value in excess of 1,23 times the expected error will arise by chance.

If the error is greater than the limits given, the test should be repeated. If the error remains then the reason for the error should be determined and the fault should be corrected. Alternatively, the spectrometer can be tested at a lower level of precision if this is suitable for the analyses required.

Detectors can fail stability tests when tested for a high degree of precision at high count rates. This is also dependent on the PHD window settings. If highly precise analytical results are required, stability tests should be carried out to determine what the maximum usable count rate is to obtain the required degree of precision. This count rate should then not be exceeded in analytical work or in precision tests or dead-time determinations being carried out.

4.6 Specimen rotation test

Malfunction of the specimen rotation mechanism can cause measurement errors. If the stability test described in 4.5 passes, it should be repeated with specimen rotation turned on. Increased error may indicate a problem with the specimen spinner mechanism.

4.7 Carousel reproducibility test

For the carousel reproducibility test, 20 measurements are made on the test specimen but between each measurement, the carousel is rotated through one complete revolution. The results should be assessed as set out in 4.2.2. This tests all sample movement within the spectrometer but excludes sample holder loading and unloading. This test may or may not be appropriate for a particular spectrometer.

4.8 Mounting and loading reproducibility test

The mounting and loading reproducibility test is designed to check whether there are excessive errors associated with the remounting of a specimen in a sample holder and in reloading the sample holder into the carousel. It is also used to check for errors in directly loading a specimen into a sample holder in the carousel (see NOTE 1).

Twenty measurements are made on the test specimen but between each measurement, the test specimen is removed from the sample holder and then remounted and reloaded using the same sample holder and carousel position. The results should be assessed as set out in 4.2.2.

NOTE 1 For instruments which can load specimens directly into a carousel-mounted sample holder, a majority of the loading errors can be attributed to sample beads not being correctly seated in the sample holder.

NOTE 2 This is carried out using the same sample holder throughout.

4.9 Comparison of sample holders

In comparing sample holders, the number of sample holders tested will depend on the type and model of the spectrometer used and the measurement procedure adopted.

A measurement is made on the test specimen when mounted, in turn, in each of the sample holders being tested. The same carousel position is used throughout this test.

If the coefficient of variation of the results is excessive (see 4.2.2), the measurement should be repeated several times, if necessary, to determine which sample holders are giving excessively high or low results.

Sample holders that pass the test should be identified and used when precise analyses are being performed.

Sample holders that fail the test do so because they locate the sample at a different distance from the X-ray tube and measurement components. These holders should be returned to the manufacturer for replacement if recently purchased.

Differences between sample holders may be caused by wear from long term use. In this case, such sample holders should not be used for precise analyses.

NOTE In some spectrometers variations in the tube to sample distance by as little as 10 microns, due to variations in sample holders or carousel positions, can result in errors by as much as 0,07 %.

4.10 Comparison of carousel positions

To compare the combined radial and axial carousel positioning reproducibility, with the test specimen in the same sample holder, make 20 measurements in each carousel position.

If the coefficient of variation of all the results is excessive (see 4.2.2), the measurements for the individual carousel positions should be inspected to determine which positions are giving excessively high or low results. Where possible, errors arising from differences in carousel positions should be eliminated by adjustment of the carousel positions. This adjustment will normally be carried out by the spectrometer manufacturer or a qualified technician.

If empirical corrections are to be applied for each carousel position, the ratios should be determined for each wavelength where high precision is required. This is necessary as the ratios can vary with collimator and may even vary with crystal and angle.

NOTE Radial misalignment of carousel positions (in addition to resulting in poor precision between positions) may result in increased background concentrations of trace elements. In severe cases, elevated background concentrations are the result of the sample cup being measured as part of the analysis (giving an increase in the background concentration of sample cup constituents).

4.11 Angular reproducibility

For the angular reproducibility test, the test specimen remains in the spectrometer but between each measurement, the 2θ angle is altered by 10° to either the high or low angle side alternately and then returned to its original value. Twenty such measurements are required. The results should be assessed as set out in 4.2.2.

If the measuring sequence involves angular changes between sample and monitor measurements, then high angular reproducibility is essential.

These measurements can also be made on a scanning channel in a simultaneous spectrometer.

4.12 Collimator reproducibility (for sequential spectrometers fitted with an interchangeable collimator)

In the collimator reproducibility test, the test specimen should remain in the spectrometer while alternate measurements are made for each collimator. Twenty such sets of measurements are required for each collimator. The results for each collimator should be assessed separately as set out in 4.2.2.

4.13 Detector changing reproducibility (for sequential spectrometers fitted with more than one detector)

In the detector changing reproducibility test, the test specimen should remain in the spectrometer while alternate measurements are made for each detector. Twenty such sets of measurements are required. The results for each detector should be assessed separately as set out in 4.2.2.

For some spectrometers, the goniometer also moves when the detector is changed. For such spectrometers, consider the goniometer reproducibility when assessing the detector changing reproducibility test result.

4.14 Crystal changing reproducibility

In the crystal changing reproducibility test, the test specimen will remain in the spectrometer but between each measurement, the crystal is changed and then returned to its original position. Twenty measurements are required. The results should be assessed as set out in 4.2.2.

This test is also applicable to simultaneous instruments fitted with goniometer units which have programmable crystal changers.

Only one crystal needs to be checked when testing the crystal changing mechanism.

4.15 Other tests

Some spectrometers have a variety of other devices and where these are operated between the measurements of the monitor and those of the specimen, they can give rise to errors. If this is the case, they should be tested according to the criteria set out in 4.2.2. Examples of such devices are as follows:

a) primary beam filters;

b) collimator apertures;

c) attenuators (typically on simultaneous instruments).

4.16 Note on glass bead curvature

The sensitivity of a spectrometer to variations in bead curvature is a function of spectrometer design. This effect can be estimated by varying the tube to sample distance in a sample holder and taking intensity measurements.

The extent of bead curvature is a function of the curvature of the mould and it is further enhanced by fast cooling rates. The shape of bead variation from perfect flatness is normally not a symmetrical curve.

To determine the error due to variations in bead curvature on analytical results, prepare 20 beads of a homogeneous glass mixture in the same mould and then an equal number in each of the other moulds used for bead production. Measure the beads for the major element intensity and assess results in accordance to 4.2.2. A smaller number of beads per mould can be prepared but the statistical error will need to be adjusted accordingly for evaluation of results.

If the variation in results is too great, offending moulds need to be refurbished to flatten them.

5 Determination of the dead time and the maximum usable count rate of the equipment

5.1 General

In all counting equipment, there is a dead time, that is, after a count has been registered, there is a small time during which the equipment will not register another count; it is effectively “dead”.

The dead time for a particular spectrometer is not necessarily fixed. Commonly, it is different for proportional and scintillation counters and it can vary with electronic instrumental setting, e.g. PHA settings, integral and differential time constants. It may even vary with wavelength.

For any particular equipment, the factors that affect dead time can be determined only empirically; if precise analyses are to be made for a particular element, the dead time should be determined at that wavelength, with the electronic instrumental settings to be used during the analysis.

The dead time of the equipment results in counting losses that get relatively greater as the count rate increases. For observed count rates of <500 kcps, losses can be corrected using Formula (13) for non-extendable dead time:

$$R = \frac{R_0}{1 - R_0\ t} \qquad (13)$$

where

R is the count rate corrected for dead-time losses, in counts per second (cps);

R_0 is the observed count rate, in counts per second (cps);

t is the dead time, in seconds.

NOTE Formula (13) is valid only if the dead time is non-extendable.

For higher count rates (>500 kcps), Formula (14) should be used for extendable dead time:

$$R_0 = R \times \mathrm{e}^{-\mathrm{t}\mathrm{R}} \qquad (14)$$

where

R is the count rate corrected for dead-time losses, in counts per second (cps);

R_0 is the observed count rate, in counts per second (cps).

Formula (14) needs to be solved by an iterative technique using a stand-alone computer program when checking the accuracy of the pre-set dead-time value in the laboratory.

Automatic dead-time corrections provided by various instrument manufacturers may contain proprietary correction methods and algorithms. These methods may be an enhancement of Formula (14).

The purpose of this Technical Report is not to replace the manufacturer's dead-time correction procedure but to check how accurately the dead-time correction has been set. Thus, the formulae proposed here simply need to determine the small amount the set dead-time correction deviates from zero, giving consideration to measurement errors. If the deviation from zero is found to be large, then the manufacturer should be contacted to fix this with their own formulae since neither Formula (13) nor Formula (14) is probably the exact formula they are using for dead-time correction.

If the dead-time correction has been set to exactly zero, then within measurement precision, both correction methods [Formulae (13) and (14)] will give the same result. If the dead-time correction deviates just a little from zero, the difference between the dead-time values calculated by both methods will be small and both can be used to make a correction to the set dead time. At larger uncorrected dead-time values, the difference in calculated values from the two formulae will increase. Nonetheless, both methods will alert the user to have their dead-time correction checked by the manufacturer.

5.2 Methods of determination of dead time

5.2.1 General

A number of methods have been used for determining dead time but the most satisfactory ones involve changing the X-ray intensity by a fixed, but not necessarily known, ratio. The two intensities are recorded for a range of count rates and the dead time is calculated from these data.

The methods that have been used to obtain a fixed ratio between two count rates are as follows:

a) the insertion of an absorber into the fluorescent beam in front of the detector;

b) the insertion of an absorber (filter) into the fluorescent beam in front of the X-ray tube;

c) changing from one primary collimator to another;

d) changing collimator mask sizes;

e) changing crystals (for example, LiF_{200} and LiF_{220});

f) measurement of Kα and Kß lines on the one element;

g) using two samples that give different count rates for the same element.

Method a) is not easily carried out in modern sequential spectrometers, where the detectors are now positioned in the vacuum chamber. The required hardware can be incorporated in simultaneous spectrometers.

The mechanism for method b) exists on most sequential spectrometers but rarely on simultaneous instruments.

Methods c), d) and e) can be used where alternative collimators, collimator masks and crystals are available within the sequential spectrometer.

Method f) requires Kα and Kβ channels for one element which can easily be carried out on sequential instruments but requires two fixed channels or a high precision compact goniometer on a simultaneous spectrometer.

Method g) has the advantage that it can be used with all types of spectrometers but it requires that sample changing is very reproducible. It is the method recommended here if the sample changing error is equal to or smaller than the movement of other spectrometer parts.

5.2.2 Recommended method for determining dead time

5.2.2.1 Specimens

Two specimens should be prepared having analyte contents that differ by a factor of about three. Although pressed powder specimens can be used, there are advantages in using more robust and stable specimens; hence, the incorporation of the analyte into glass discs, via fusion with borate flux, is recommended although alloys could also be used. The analyte content of the higher specimen should be sufficiently high that at a little below full X-ray power, this sample gives a count rate just in excess of the manufacturer stated saturation count of the specific detector.

5.2.2.2 Setting the X-ray tube high voltage

The two specimens should be mounted in sample holders so that they can be measured alternately. With the higher analyte specimen in position, the tube current is set to the maximum and the voltage is adjusted to obtain the maximum count rate desired.

CAUTION — Most manufacturers stipulate a maximum current to voltage loading for their tubes and this should not be exceeded, as tube damage may result. This is usually restricted by the instrument internal controller.

In some cases, it may be necessary to work at a lower than maximum current if the analytical line considered requires a high excitation voltage. This may be the course of action if there are heavy element channels to be tested on a simultaneous instrument.

5.2.2.3 Measurements

The current should be reduced to a minimum or to a value that is no greater than 10 % of the maximum and, using the resulting count rate, the two theta angle should be determined. The upper and lower settings of the pulse-height analyser should be those used for analysis. These settings should be used to obtain in order, as follows:

a) the time to accumulate 10^6 counts for the higher analyte sample, t_1;

b) the time to accumulate 10^6 counts for the lower analyte sample, t_2;

c) the time to accumulate 10^6 counts for the lower analyte sample, t_2;

d) the time to accumulate 10^6 counts for the higher analyte sample, t_1.

Instead of 10^6 counts collected, other amounts such as 2×10^7 may be used depending on the precision required in the dead-time determination. A suitable formula capable of accounting for dead-time loss at the count rates obtained should also be used.

The above readings are obtained by using the pre-set count mode and recording the time to preferably three decimal places of seconds. If the timer does not read to the required number of decimal places, or if the equipment does not have a pre-set count facility, then a pre-set time may be used to collect around 10^6 counts.

The count rate is increased by increasing the current and the measurement is repeated. The voltage should remain fixed. This process of increasing the current and making the required measurements each time is continued until the maximum count rate (maximum current) is reached.

The current settings are not critical but if possible, they should be spaced to approximate a geometric progression (increments of 5 mA to 20 mA). The number of settings are not important but between 4 and 16 should be used.

5.2.2.4 Dead-time correction method I — Non extendable dead time

Formula (13) may also be written as Formula (15):

$$R = \frac{N_0}{t_0 - N_0\, t} \tag{15}$$

where

N_0 is the number of counts accumulated in t_0 seconds.

Where a pre-set number of counts are used, the counting time is corrected according to Formula (16):

$$t_c = t_0 - N_p\, t \tag{16}$$

where

t_0 is the observed time to accumulate the pre-set number of counts, N_p, in seconds;

t_c is the corrected time, in seconds;

t is the dead time in seconds.

To avoid using large numbers, possible round-off errors and excessive multiplications, t can be expressed in units of $\frac{t}{N}$. For example, if $N = 2 \times 10^7$, and when the dead time is expressed in units of 5×10^{-8} s, Formula (16) can then be expressed as:

$$t_c = t_0 - t \tag{17}$$

with t being expressed in seconds.

Rather than use such unusual units, if the pre-set time mode is used, or the number of counts accumulated is greater than 10^6, the measured data can be converted to the time required to accumulate 10^6 counts using Formula (18):

$$t_0 = \frac{10^6\, t'}{N} \tag{18}$$

where

t' is the time to accumulate N counts;

t_0 is time to accumulate 10^6 seconds.

Then, with $N_p = 10^6$ and $t = 10^{-6}$ s in Formula (16), t is expressed in seconds in Formula (17).

The reliability of the measured data is checked by calculating the overall coefficient of variation between the duplicate readings. The %*CoV* when accumulating $N = 10^7$ counts is 0,032 % and should not exceed 0,044 % as poor readings affect the reliability of the dead-time determination. The pairs of readings are averaged.

If more than 10^7 counts were accumulated, the %*CoV* should be smaller (see 4.2.2).

NOTE A method for calculating the coefficient of variation of duplicates is given in Annex A.

The basis of the calculation is that, when the count rates of the two specimens are corrected for dead time, the ratio of their corrected count rates will be constant and independent of the basic count rate (current setting).

If t_1 and t_2 are the times to accumulate N counts for the samples with higher and lower count rates respectively, the ratio (Q) of the two count rates after dead-time correction is, from Formulae (17) and (18), given by Formula (19):

$$Q = \frac{t_2 - t}{t_1 - t} \tag{19}$$

where

t is the dead time multiplied by 10^6, in seconds.

The value of t is adjusted by trial and error or by using an external mathematical fitting program to give the minimum coefficient of variation of Q and the error should be near that expected (see 4.2.2).

Often, it is not possible to find a value for t that will give a constant value for Q but if the values of Q are inspected for each dead time, it will be found that for a certain dead time, Q may be constant at the lower count rates but have reduced values at the higher count rates. In such cases, the highest count rate data should be deleted from the calculations to ascertain whether a value for t can be found to give close to the expected error for Q. If this is unsuccessful, the next highest count rate data should be deleted and so on.

The value of t for which the coefficient of variation of Q is a minimum, provided that this is not greater than 1,4 times the expected coefficient of variation, gives the dead time of the detector. However, this dead time can be applied only to count rates that give a constant value of Q, i.e. if it was necessary to drop high count rates from the calculations, then these rates should not be used for analytical work.

NOTE Formula (19) is in the form of a linear equation and a value for both Q and t could be found from a linear regression of t_1 against t_2. A normal linear regression, however, assumes errors in only one variable and further, that the errors are constant for the range of the variable. These assumptions can lead to small but significant errors in the dead time calculated from a simple linear regression. Also, using a linear regression would not indicate whether dead-time corrections are valid at the higher count rates.

5.2.2.5 Example of measurement data and dead-time calculations

A typical set of measurement data obtained, with Fe Kα as the analyte line at a maximum count rate of about 2 420 kcps, is given in Table 3. The calculations involved in establishing the dead time from these data are shown in Table 4.

In Table 3, the %*CoV* of the duplicates is within the statistical variation expected (a maximum of 0,028 %). Thus, the data is expected to be reliable.

It can be seen from Table 4 that, when $t = 0$, the value of Q increases with increasing count rate (increasing current), indicating that a lower value of t is necessary. Q values at $t = 0{,}01$ confirm this. With $t = -0{,}01$, the ratio varies to a lesser extent but the %*CoV* of the ratios is still much greater than 0,028 % limit. The final dead-time value of −0,007 8 µs gives a %*CoV* of 0,024 if the measurement at 160 mA is deleted from the calculations.

Since it was necessary to delete the highest count rate in determining the dead time, this spectrometer should be limited to lower count rates. This count rate can be calculated by dividing 2,5 × 10^7 by the average counting time obtained at 140 mA on the higher concentration sample, which gives about 2 100 kcps. Since the maximum recommended count rate for the detector by the manufacturer is 2 000 kcps, this limit should be adhered to and can be used with confidence if the spectrometer also passed the other stability and precision tests at that count rate.

The spectrometer used in this test had automatic dead-time correction; hence, the measured dead time represents the error in addition to the setting of the original correction. In this case, the dead time was over corrected by 0,007 8 µs.

Table 3 — Typical measurement data

Tube current mA	**Time, s, to accumulate 2,5 × 10^7 counts:** $N = 2{,}5 \times 10^7$ **Higher iron sample** (t_1)	 **Lower iron sample** (t_2)
20	84,397 84,403	317,884 317,856
40	42,176 42,156	158,963 159,027
60	28,049 28,039	105,961 105,978
80	20,979 20,964	79,365 79,382
100	16,718 16,713	63,352 63,344
120	13,879 13,874	52,712 52,723
140	11,851 11,853	45,087 45,090
160	10,329 10,330	39,433 39,415
%*CoV* of duplicates[a]	0,027 %	0,018 %

[a] See Annex A.

Table 4 — Calculation of results

Tube current mA	**Average times to accumulate 10^6 counts, *s*** t_1	 t_2	$Q = (t_2 - t)/(t_1 - t)$ $t = 0$	 $t = 0{,}01$	 $t = -0{,}010$	 $t = -0{,}005$	 $t = -0{,}007\,8$
20	3,376	12,715	3,766 2	3,774 5	3,758 1	3,762 1	3,759 9
40	1,687	6,360	3,770 7	3,787 2	3,754 3	3,762 5	3,757 9
60	1,122	4,239	3,778 6	3,803 6	3,754 1	3,766 3	3,759 4
80	0,839	3,175	3,784 9	3,818 5	3,752 1	3,768 4	3,759 2
100	0,669	2,534	3,789 7	3,832 1	3,748 6	3,769 0	3,757 6
120	0,555	2,109	3,799 0	3,850 3	3,749 4	3,774 0	3,760 2
140	0,474	1,804	3,804 2	3,864 6	3,746 3	3,774 9	3,758 8
160	0,413	1,577	3,816 7	3,886 6	3,750 1	3,783 0	3,764 5
%*CoV* of *Q*			0,425 %	0,947 %	0,094 %	0,174 %	0,053 %
%*CoV* of *Q* (excluding 160 mA)			0,344 %	0,796 %	0,099 %	0,124 %	0,024 %

5.2.2.6 Dead-time correction method II and dead-time calculations — Extendable dead time

Formula (14), $R_0 = R \times e^{-tR}$, can be solved in an iterative scheme.

First, make an initial estimate of the dead time in seconds, e.g. 0,01 × 10^{-6} s.

Calculate the first estimate of R_1 from R_0 using Formula (20):

$$R_1 = \frac{R_0}{e^{-tR_0}} \tag{20}$$

Calculate a new estimate of the true intensity using Formula (21):

$$R_n = \frac{R_0}{e^{-tR_{n-1}}} \tag{21}$$

where

R_n is the count rate corrected for dead-time losses, in counts per second (cps), being determined by iteration;

R_0 is the observed count rate, in counts per second (cps);

t is the dead time, in seconds.

Repeat these steps until the difference between successive approximations of R_n is smaller than a preset amount.

For an example calculation, the data of Table 3 is converted to count rates for use in solving Formula (14) for R. The average of the count rates obtained from the high and low samples is given in Table 5.

Table 5 — Average count rates obtained from the data of Table 3

Tube current (mA)	**Count rates** (cps)	
	High	**Low**
20	296 209	78 653
40	592 892	157 238
60	891 445	235 918
80	1 192 103	314 965
100	1 495 607	394 647
120	1 801 572	474 227
140	2 109 322	554 470
160	2 420 296	634 133

Calculated corrected count rates in counts per second (cps) obtained when solving Formula (21) for five iterations are given in Table 6. Convergence is achieved after three iterations at the highest count rate due to the small residual dead time.

Table 6 — Calculated dead-time corrected count rates (cps) obtained from five iterations of Formula 21

Tube current (mA)	**Sample**	**Iteration number**				
		1	**2**	**3**	**4**	**5**
20	High	295 517	295 518	295 518	295 518	295 518
20	Low	78 604	78 604	78 604	78 604	78 604
40	High	590 121	590 134	590 134	590 134	590 134
40	Low	157 043	157 043	157 043	157 043	157 043
60	High	885 189	885 233	885 233	885 233	885 233
60	Low	235 479	235 480	235 480	235 480	235 480
80	High	1 180 929	1 181 033	1 181 032	1 181 032	1 181 032
80	Low	314 182	314 184	314 184	314 184	314 184
100	High	1 478 040	1 478 245	1 478 243	1 478 243	1 478 243
100	Low	393 419	393 422	393 422	393 422	393 422
120	High	1 776 113	1 776 470	1 776 465	1 776 465	1 776 465
120	Low	472 454	472 460	472 460	472 460	472 460
140	High	2 074 464	2 075 036	2 075 026	2 075 026	2 075 026
140	Low	552 047	552 057	552 057	552 057	552 057
160	High	2 374 459	2 375 319	2 375 303	2 375 303	2 375 303
160	Low	630 964	630 980	630 980	630 980	630 980

NOTE The data in this table was calculated using a dead time of −0,007 9 µs.

The converged values for the high sample count rates are then divided by the converged values of the low sample count rates for each mA setting to give a value for this division, *D*.

The value of *t* is adjusted by trial and error or by using an external mathematical fitting program to give the minimum coefficient of variation of *Q* and the error should be near that expected (see 4.2.2).

If it is not possible to find a value for *t* that will give a constant value for *D*, follow a similar strategy for determining constant *Q* values in 5.2.2.4 by eliminating the data set for the highest count rate and so on.

Table 7 contains the data obtained when determining the counter dead time by minimizing the %*CoV*, as was carried out in 5.2.2.4.

Table 7 — Calculation of results

Tube current (mA)	$D = R_{\mathrm{High}}/R_{\mathrm{Low}}$				
	$t = 0{,}010$	$t = 0{,}005$	$t = -0{,}005$	$t = -0{,}010$	$t = -0{,}007\,9$
20	3,774 3	3,770 1	3,761 9	3,757 9	3,759 6
40	3,787 3	3,778 9	3,762 5	3,754 4	3,757 8
60	3,803 8	3,791 1	3,766 3	3,754 2	3,759 3
80	3,818 7	3,801 6	3,768 4	3,752 3	3,759 0
100	3,832 5	3,810 9	3,769 1	3,749 0	3,757 4
120	3,850 9	3,824 6	3,774 1	3,750 0	3,760 0
140	3,865 5	3,834 3	3,775 1	3,747 0	3,758 7
160	3,887 7	3,851 5	3,783 3	3,751 1	3,764 5
%*CoV* of D	0,957 %	0,687 %	0,177 %	0,086 %	0,054 %
%*CoV* of D (excluding 160 mA)	0,804 %	0,571 %	0,127 %	0,092 %	0,023 %
NOTE Dead times (*t*) are given in microseconds.					

The results are similar to those obtained when using Formula (13) to correct for dead time, with the higher count rates needing to be excluded. This equipment should not be used for higher count rates higher than 2 100 kcps. Since the maximum recommended count rate for the detector by the manufacturer is 2 000 kcps, this limit should be adhered to and can be used with confidence if the spectrometer also passed the other stability and precision tests at that count rate.

Annex A
(informative)

Calculation of the coefficient of variation of duplicates

For each of the two samples (higher iron, lower iron, see 5.2.2.1), a number of measurements are taken in duplicate at varying currents. The coefficient of variation of duplicates for either sample is calculated as follows.

a) Coefficient of variation for one pair of readings:

$$\%CoV = \frac{\sigma}{\bar{x}} \times 100 \qquad \text{(A.1)}$$

$$\bar{x} = \frac{x_1 + x_2}{2} \qquad \text{(A.2)}$$

where

x_1 is the first reading of sample at a given current;

x_2 is the second reading of sample at the same current;

σ is standard deviation of Formula (A.3).

$$x_1, x_2 = x_1^2 + x_2^2 - \frac{\left(x_1 + x_2\right)^2}{2} \qquad \text{(A.3)}$$

b) Coefficient of variation of duplicates:

$$\%CoV\left(\text{duplicates}\right) = \sqrt{\frac{\sum\left(\frac{\sigma}{\bar{x}} \times 100\right)^2}{n}} \qquad \text{(A.4)}$$

where

n is the number of different current readings.

From Table 3, Tables A.1 and A.2 may be formulated, for the higher and lower iron samples, respectively.

Table A.1 — Data for determination of coefficient of variation of duplicates — Higher iron sample

Tube current mA	x_1	x_2	σ	$\%CoV$	$(\%CoV)^2$	$\Sigma(\%CoV)^2$
20	84,397	84,403	0,004 2	0,005 0	$2{,}53 \times 10^{-5}$	$2{,}53 \times 10^{-5}$
40	42,176	42,156	0,014 1	0,033 5	$1{,}13 \times 10^{-3}$	$1{,}15 \times 10^{-3}$
60	28,049	28,039	0,007 1	0,025 2	$6{,}36 \times 10^{-4}$	$1{,}79 \times 10^{-3}$
80	20,979	20,964	0,010 6	0,050 6	$2{,}56 \times 10^{-3}$	$4{,}34 \times 10^{-3}$
100	16,718	16,713	0,003 5	0,021 2	$4{,}47 \times 10^{-4}$	$4{,}79 \times 10^{-3}$
120	13,879	13,874	0,003 5	0,025 5	$6{,}49 \times 10^{-4}$	$5{,}44 \times 10^{-3}$
140	11,851	11,853	0,001 4	0,011 9	$1{,}42 \times 10^{-4}$	$5{,}58 \times 10^{-3}$
160	10,329	10,330	0,000 7	0,006 8	$4{,}69 \times 10^{-5}$	$5{,}63 \times 10^{-3}$

From Table A.1:

$$\sum\left(\frac{\sigma}{x}\times 100\right)^2 = 0{,}005\ 63$$

and

$n = 8$

Therefore,

$$\%CoV(\text{duplicates}) = \sqrt{\frac{0{,}005\ 63}{8}} = 0{,}027\ \%$$

Table A.2 — Data for determination of coefficient of variation of duplicates — Lower iron sample

Tube current mA	x_1	x_2	σ	$\%CoV$	$(\%CoV)^2$	$\Sigma(\%CoV)^2$
20	317,884	317,856	0,019 8	0,006 2	$3{,}88 \times 10^{-5}$	$3{,}88 \times 10^{-5}$
40	158,962	159,027	0,046 0	0,028 9	$8{,}36 \times 10^{-4}$	$8{,}75 \times 10^{-4}$
60	105,961	105,978	0,012 0	0,011 3	$1{,}29 \times 10^{-4}$	$1{,}00 \times 10^{-3}$
80	79,365	79,382	0,012 0	0,015 1	$2{,}29 \times 10^{-4}$	$1{,}23 \times 10^{-3}$
100	63,352	63,344	0,005 7	0,008 9	$7{,}97 \times 10^{-5}$	$1{,}31 \times 10^{-3}$
120	52,712	52,723	0,007 8	0,014 8	$2{,}18 \times 10^{-4}$	$1{,}53 \times 10^{-3}$
140	45,087	45,090	0,002 1	0,004 7	$2{,}21 \times 10^{-5}$	$1{,}55 \times 10^{-3}$
160	39,433	39,415	0,012 7	0,032 3	$1{,}04 \times 10^{-3}$	$2{,}59 \times 10^{-3}$

From Table A.2:

$$\sum\left(\frac{\sigma}{x}\times 100\right)^2 = 0{,}002\ 59$$

and

$n = 8$

Therefore,

$$\%CoV(\text{duplicates}) = \sqrt{\frac{0{,}002\ 59}{8}} = 0{,}018\ \%$$

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ICS 73.060.10

Price based on 26 pages