

Analytical Methods Committee

Evaluation of analytical instrumentation. Part XX Instrumentation for energy dispersive X-ray fluorescence spectrometry

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Abstract The reports of this series tabulate a number of features of analytical instruments that should be considered when making comparison between various systems. Scoring these features in a rational manner allows a scientific comparison to be made between instruments as an aid to selection. This is the XXth report

of the series and deals with instrumentation for energy dispersive X-ray fluorescence spectrometry.

Keywords Instrumentation · Overview · Evaluation · Energy dispersive X-ray fluorescence spectrometry

Introduction

The following report was compiled by the above sub-committee of the AMC, which consists of Professor S. Greenfield (chairman), Dr. M. Barnard, Dr. C. Burgess, Dr. D. Edwards, Professor S. J. Hill, Dr. K. E. Jarvis, Dr. G. Lord, Dr. M. Sargent, Dr. G. Lord, Dr. P. J. Potts, and Dr. M. West with Dr. E. J. Newman as secretary. The initial input of the features for consideration was undertaken by a working party comprising Drs. P. J. Potts and M. West to whom the committee expresses its thanks.

The purchase of analytical instrumentation is an important function of many laboratory managers, who may be called upon to choose between wide ranges of competing systems that are not always easily comparable. The objectives of the Instrumental Criteria Sub-Committee are to tabulate a number of features of analytical instruments that should be considered when making a comparison between various systems. As is explained below, it is then possible to score these features in a rational manner, which allows a scientific comparison to be made between instruments as an aid to selection.

The overall object is to assist purchasers in obtaining the best instrument for their analytical requirements. It is hoped that this evaluation will, to some extent, also help manufacturers to supply the instrument best suited to their customers' needs. It is perhaps pertinent to note that a number of teachers have found the reports to be of use as teaching aids.

No attempt has been made to lay down a specification. In fact, the committee considers that it would be invidious

to do so: rather it has tried to encourage the purchasers to make up their own minds as to the importance of the features that are on offer by the manufacturers.

The XXth report of the sub-committee deals with instrumentation for energy dispersive X-ray fluorescence spectrometry.

Notes on the use of this document

- Column 1 The features of interest.
- Column 2 What the feature is and how it can be evaluated.
- Column 3 The sub-committee has indicated the relative importance of each feature and expects users to decide on a weighting factor according to their own application.
- Column 4 Here the sub-committee has given reasons for its opinion as to the importance of each feature.
- Column 5 It is suggested that scores are given for each feature of each instrument and that these scores are modified by a weighting factor and sub-totals obtained. The grand total will give the final score that can contribute to the selection of the instrument that best suits the user's requirements.

Notes on Scoring

1. (PS) Proportional scoring. It will be assumed, unless otherwise stated, that the scoring of features will be by proportion, e.g., Worst/0 to Best/100.
2. (WF) Weighting factor. This will depend on individual requirements. All features mentioned in the tables have some importance. If, in the sub-committee's opinion,

some features are considered to be of greater importance, they are marked I. Those features of greatest importance are marked as VI (very important). A scale should be chosen for the weighting factor that allows the user to discriminate according to needs, e.g., $\times 1$ to $\times 3$ or $\times 1$ to $\times 10$.

3. (ST) Sub-total. Multiplying PS by WF obtains this.
4. In some circumstances where there is a fundamental incompatibility between a feature of the instrument and the intended application, it may be necessary to exclude an instrument completely from further consideration.

With these requirements in mind, the user should then evaluate the instruments available on the market, taking into account the following guidelines and any financial limitations. In many instances it will quickly become clear that a number of different instruments could be satisfactory and non-instrumental criteria and may then become important. However, in some specialized cases, only one or two instruments will have the ability or necessary features to be used in the intended application.

The guidelines are intended to be used as a checklist of features to be considered, mostly of the instrument itself, but also of service requirements and any existing relationship between the user and the manufacturer. The relative importance of these features will depend on a number of factors, which in some circumstances could be subjective. However, if all the points have been considered, the choice should be informed.

The committee considers that instrumentation for energy dispersive X-ray spectrometry is safe in normal use, but care should be taken to avoid exposure to X-ray radiation by ensuring that all safety features are fully operational and that instrumentation is used strictly in accordance with the manufacturer's instructions.

Finally, as many laboratories are now working to established quality standards, some consideration should be given to third-party certification of the manufacturer to standards such as the ISO Guide 9000 series. Such certification should extend to the service organisation.

An overview of energy dispersive X-ray fluorescence spectrometry (EDXRF)

Basic principles

X-ray fluorescence (XRF) is the phenomenon in which X-rays of energy characteristic of an atom are emitted following irradiation of a sample by energetic X-rays. An X-ray with sufficient energy can eject an inner shell electron of an atom leaving it in an excited or ionised state. As the atom is unstable, transitions can occur in which an electron from an outer orbital shell fills the vacancy left by the ejected electron. Accompanying each transition, a loss of energy must occur usually by the emission

of secondary 'characteristic' X-ray. Because the energy of these secondary 'fluorescence' X-rays is equal to the difference in energy between the two electron orbital levels involved in the transition, it is characteristic of the atom itself. The intensity of the radiation emitted is proportional to the concentration of that atom in the sample, so providing a means for quantification. The XRF technique is capable of measuring the elemental concentrations of almost all the elements in the periodic table (by convention from Na to U) in a wide range of sample types (solid, powders and liquids) to detection limits that under optimum conditions fall below the mg/kg level. The EDXRF analytical technique is simultaneous, non-destructive and widely applied in both routine production and research laboratory applications.

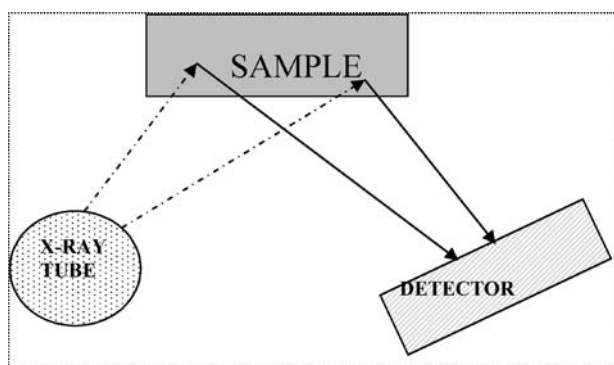
General description of instrumentation

XRF instrumentation comprises an X-ray excitation source positioned close to a sample, the X-ray fluorescence spectrum from which is detected using an X-ray spectrometer. Traditional instruments, which first became commercially available in the late 1950s, use wavelength dispersive spectrometers (see Part VI and VII). However, following rapid advances in semiconductor technology and the introduction of the lithium-drifted silicon detector, the alternative energy dispersive detectors became available from the 1970s. In its simplest form, EDXRF instrumentation comprises an X-ray tube excitation source used to excite the sample from which the X-ray fluorescence spectrum is detected with a solid-state energy dispersive detector. Although in early instruments, the Si(Li) detector was most commonly used, alternative detector types are available for installation in modern instruments and offer advantages in particular applications. These alternative detector types include Si(PIN) diodes and Si-drift detectors (which do not require cryogenic (liquid nitrogen) cooling), germanium, mercury (II) iodide and cadmium-zinc-telluride detectors (which extend the detection efficiency to the fluorescence spectrum above 20 keV).

Because ED detectors have the potential to detect the full spectrum emanating from a sample, a number of developments have occurred that are designed to modify the excitation and detection efficiency. By so doing, the detection of groups of elements in particular energy ranges of the fluorescence spectrum can be optimised. These developments include the use of primary beam metal foil filters (which modify the source spectrum reaching the sample to optimise detection characteristics) and a number of developments in excitation geometry. One of these advances is the secondary target excitation geometry in which a Cartesian optical path is used between tube, secondary target, sample and detector. The tube excites the secondary target, fluorescence radiation from which is then used to excite the sample. With a Cartesian optical path, a significant reduction in the continuum detected in the fluorescence spectrum is achieved because tube radiation is polarised when scatter occurs through a right angle and cannot then be scattered a

second time into the detector. If a low atomic number material is substituted as a secondary target [e.g., boron carbide, corundum or highly ordered pyrolytic graphite (HOPG)], the sample is now excited by the scattered tube spectrum (without additional characteristic lines from the secondary target). This arrangement leads to a further reduction in detected continuum referred to above. The importance of reducing this continuum derived by scatter of the source spectrum is that in doing so, detection limits are improved. A final refinement in the Cartesian arrangement is a configuration in which the sample is excited using the Bragg diffraction phenomenon. A few substrates are fortuitously capable of diffracting certain low energy characteristic lines from the X-ray tube (e.g., a Pd-L line) through a total diffraction angle of 90° . In this way, excitation of low atomic number elements by the tube L-line is enhanced because the efficiency of diffraction is significantly higher than any scatter, but at the same time the benefit of background suppression associated with a polarised excitation source is retained. The advantages of all these polarised excitation geometries can only be achieved effectively using an ED detector.

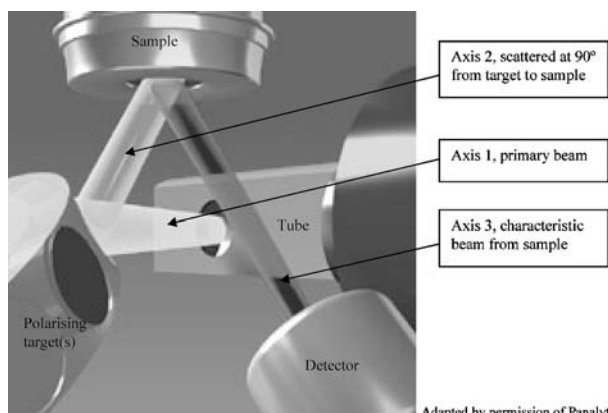
A schematic diagram of EDXRF instrumentation is shown below illustrating a direct tube excitation, and b Cartesian excitation geometries.



Primary X-rays----->

Secondary Characteristic X-rays----->

a) EDXRF with direct tube excitation



b) EDXRF with Cartesian geometry to provide polarised excitation

Further considerations

A further consideration in the design and performance of EDXRF instrumentation is the pulse processing electronics and spectrum deconvolution procedures. Semiconductor detectors have an intrinsic electronic noise level that makes a significant contribution to the measurement of X-ray photon events. As a result, there is a need to use relatively long time constants for signal processing circuits to compensate for the intrinsic noise in the signal. ED detectors therefore have a lower maximum count rate capability than WD systems and the accurate correction for dead time in the detector-signal processing circuits is an important consideration. Furthermore, the energy resolution of semiconductor detectors, (measured by convention as the full width at half the peak maximum height (FWHM) of the 5.9 keV Mn $K\alpha$ emission from a ^{55}Fe source) is inferior (at least in the 0 to 20 keV region) to that of a wavelength dispersive spectrometer. The potential for spectrum overlap interferences is therefore significantly greater in EDXRF than WDXRF, although a number of effective spectrum deconvolution procedures have been developed to compensate for this disadvantage.

A further technical issue that requires consideration is that like WDXRF, the detected EDXRF signal (fluorescence intensity) is not usually linearly proportional to concentration. Detected fluorescence intensities are affected, normally only to a small extent, by absorption and enhancement effects caused by other elements present in the sample. These so-called "matrix effects" can be overcome by the same correction procedures used in WDXRF spectrometry, provided effective software and the appropriate computer power are integrated into the instrument configuration.

The following review is designed to examine the overall system geometry and the function and characteristics of individual components of EDXRF instrumentation, and hence to draw attention to those aspects that are important in selection of an analytical system for a user's application.

Other techniques

WDXRF systems are configured as either simultaneous, sequential or a combination of both and as such tend to be larger and more expensive than the ED spectrometers. As mentioned above, WD systems typically offer better resolution and hence lower detection limits with the elemental range extending down to boron. Portable EDXRF systems provide the ability to take the spectrometer to the sample, thereby providing a powerful tool for "field" survey investigations. These portable systems do not provide a vacuum path between the sample and the analyser, thus limiting their use to elements from Ca upwards in the periodic table.

Other multi-element techniques generally "consume" the sample such as optical emission spectrometry (OES) for solid or powder samples, and inductively coupled plasma-

emission spectrometry (ICP-AES) or inductively coupled plasma-mass spectrometry (ICP-MS) for liquids.

Despite the better detection limit levels of some competitive techniques, ED-XRF is the instrument of choice for specific applications where simple dedicated instruments can meet regulatory requirements (e.g., S in fuel, Na, Al, Si, Ca in cement) and in multi-element applications in the analysis of a wide range of inorganic materials in research and development, production, and quality control/trouble shooting applications. EDXRF systems are

particularly appropriate for the analysis of geological, environmental, metallurgical and ceramic samples, as well as a wide range of other inorganic materials. In addition, there are specialised applications in the analysis of liquors and brines and other liquids of high salt content that are difficult to measure by competitive solution techniques or where competitive techniques have insufficient sensitivity for analytes such as halides or other electronegative elements.

Instrumental criteria sub-committee instrument evaluation form

| Type of instrument: Energy dispersive X-ray fluorescence spectrometer | | | | | |
|---|--|------------|--|----------------|--|
| Manufacturer: | | | | | |
| Model No: | | | | | |
| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | |
| <i>A. Non Instrumental Criteria</i> | | | | | |
| <i>1. Selection of manufacturer</i> | | | | | |
| | Laboratories in possession of other spectrometers should score highest for the manufacturer with the best past record based on the following sub-features. | | | PS WF ST | |
| (a) Previous instruments | | | | | |
| (i) Innovation | Company's record for developing instruments with innovative features. | I | The manufacturer should be alert to developments in design, excitation and detector technologies. | PS WF ST | |
| (ii) Reliability record | Company's record for instrument reliability. | I | Indicates history of sound design/manufacturing concepts. | PS WF ST | |
| (iii) Similarity of operation, layout and design (including software) to existing instruments in the laboratory | For routine purposes, this may be important. However, this may be less important for research applications. | I | Similarity of design and operation means that operators can draw on in-house expertise, resulting in reduced costs and time for training. It may also maximise the use of spares and fittings. | PS WF ST | |
| (iv) Confidence in the supplier | Confidence gained from past personal experience. | I | The benefits arising from good working relationship already in place. | PS WF ST | |
| (b) Servicing | | | | | |
| (i) Service contract | Score according to manufacturers' claims and past record, judged by the sub-features (i) to (v) below. Availability of a suitable service contract from the supplier, agent or third-party contractor. | VI | Essential to ensure reliable operation over the planned working life of the instrument. Often ensures preferential service and guarantees a specific response time to call-outs. | PS WF ST | |
| (ii) Availability and delivery of spares | Range of stock carried by, or quickly available to, the manufacturer/agent/contractor. | I/VI | Rapid delivery of spares reduces down time. | PS WF ST | |
| (iii) Call-out time | The time for the engineer to reach the laboratory following a call. | I | A rapid response keeps the laboratory in operation by reducing down time. Note that the guaranteed call out time may depend on the selected service contract. | PS WF ST | |
| (iv) Effectiveness of service engineers | The ability of the service engineer to identify and repair faults as judged from previous experience and reports of others. | I | Ability to repair on-site avoids return visit or removal of equipment for off-site repair so reduces down time and may reduce service cost. | PS WF ST | |
| (v) Cost of call out and spares | It may be inappropriate to score this feature if in-house servicing is contemplated or the call out is included in the service contract. | I | The proximity of the service centre may be a factor in travel costs. Note that many service contracts exclude 'consumables,' the provision of which may contribute a significant additional cost. | PS WF ST | |
| (c) Technical support | | | | | |
| (i) Applications department | Score according to manufacturers' claims and past record, judged by the sub-features (i) to (vi) below. The advice and training available from the manufacturer's applications department. | | This helps in-house staff to optimise measurements for new applications. | PS WF ST | |
| (ii) Technical literature | The range and quality of technical literature including the operating manual. | I | The availability of quality technical literature helps operators optimise the use of the instrument. Note that on many modern instruments, operating instructions are available online as part of the instrument operating software. | PS WF ST | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | |
|--|---|----------------------------------|--|----------------|--|--|
| (iii) Telephone assistance | Willingness of the manufacturer, supplier or contractor to give effective advice over the telephone. This can normally only be evaluated by reference to existing users. | I | Rapidly available technical help reduces the number of call outs and enhances productivity. | PS WF ST | | |
| (iv) Remote diagnostics | Facility that allows an engineer to assess the status of an instrument by telephone/modem access from a remote location. Score for the availability of this feature if appropriate. | I | Remote diagnostics often help in reducing downtime by facilitating rapid identification of faults. Networking may also enable engineers to interrogate the instrument from a distance. | PS WF ST | | |
| (v) Training | This includes initial training when setting up the instrumentation and follow up courses for more advanced users. | VI | A comprehensive training scheme will ensure that operators and instrumentation are working effectively. | PS WF ST | | |
| (vi) User Group Meetings | Meetings and technical briefings organised for users of instrumentation by the manufacturer or third party. | I | Other users are often the best source of advice on problems, solutions and applications. | PS WF ST | | |
| <i>B. Instrumental Criteria</i> | The specific tests recommended in this report should be discussed with the instrument manufacturer in advance of any evaluation to ensure that any testing is undertaken in a practical and effective manner. | | | | | |
| <i>2. General Features</i> | | | | | | |
| Facilities required for: | | | | | | |
| (a) Access, and location of the connections and controls on the instrument | Score according to convenient access taking into account the proposed location of the instrument. | I | Depending on bench position and layout, connections and controls may limit accessibility for servicing and installation particularly at the rear of the instrument. | PS WF ST | | |
| (b) Power requirements | Score maximum for compatibility with existing electrical supply, both with regard to loading and stability. | Varies with user's circumstances | Additional power requirements may significantly increase installation costs. Most modern instruments only require a standard electrical supply. | PS WF ST | | |
| (c) Size of equipment | Score according to practicality of installation. | I/VI | The instrument must be compatible with existing laboratory accommodation otherwise expensive alterations will be required. The size of instrumentation may be critical if space is limited. | PS WF ST | | |
| (d) Environmental control | EDXRF instruments are installed in a wide variety of environments, from laboratories to industrial plants. Score according to the tolerance of the instrument to factors such as temperature, humidity, vibration and dust, as relevant to the environment in which the instrument is to be installed. | VI | Additional installation costs may be considerable, if control of environmental factors is necessary. | PS WF ST | | |
| <i>3. Choice of category of instrument</i> | | | | | | |
| Energy dispersive X-ray fluorescence instruments are available with a number of different excitation sources and excitation geometries. These design characteristics are summarised in the following entries and should be scored in relation to the advantages they offer in the intended application of the instrument as judged from the details given below. | | | | | | |
| (a) Direct tube excitation | Instruments using direct tube excitation are designed with a conventional excitation-detection geometry in which the sample is excited directly by the output of an X-ray tube. The X-ray path from tube to detector is designed to subtend an angle of about 90° at the sample to minimise the detection of scattered radiation from the sample. | VI | The different excitation sources, excitation geometries and detection systems offer different analytical characteristics that can give analytical advantages in a particular application. By appropriate selection of tube anode, primary beam filter (see below) and tube operating conditions (kV/mA), excitation may be optimised to determine ranges of elements. Depending on choice of tube anode, characteristic and continuum radiation from the tube is effective in exciting fluorescence lines in approximately the 1 to 30 kV range of the spectrum. This category of instrument has particular advantages in the excitation of the low atomic number elements (e.g., Na to Si) and is suited for the rapid qualitative analysis of unknown samples. Excitation conditions can be optimised for ranges of elements that can be determined from fluorescence lines in the 4 to 35 kV region of the spectrum by selection of an appropriate secondary target material. For extended multi-element analysis under optimum conditions, several fluorescent spectra must be recorded using a series of secondary targets. Satisfactory excitation of the low atomic number elements (Na-Cl) can only be achieved by reverting to direct tube excitation. | PS WF ST | | |
| (b) Excitation using characteristic radiation from a secondary target | In this form of instrumentation, the sample is excited by the X-ray emission from a secondary target which is itself excited by output radiation from an X-ray tube. If the X-ray path (tube—secondary target—sample—detector) is designed with an orthogonal geometry, additional benefits arise from the reduction of background radiation from the X-ray tube, scattered off the sample. | | | | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | |
|--|--|------------|--|----------------|--|--|
| (c) Excitation using scattered tube radiation | In this design of instrument, the secondary target is made of a low atomic number material such as boron carbide which does not emit characteristic fluorescence lines but has high efficiency in scattering the tube spectrum onto the sample. | | By appropriate selection of tube anode and tube operating conditions (kV/mA), excitation conditions may be optimised to determine ranges of elements from fluorescence lines in the 1 to 20 kV range of the X-ray spectrum that can be excited efficiently by characteristic and continuum radiation from the tube scattered onto the sample. By designing the instrument with Cartesian excitation geometry, advantages arise from the reduction of background radiation originating from the tube so enhancing detection limits. To compensate for the inefficient scattering off the secondary target, instrumentation must normally be fitted with a high power generator than a standard ED-XRF instrument. | | | |
| (d) Radioisotope excitation | The sample is excited using an appropriate radioactive source, so avoiding the requirement for X-ray tube and generator. Although a high resolution Si(Li) detector can be used, relatively cheap and compact instruments are also available incorporating a gas-filled proportional counter as a detector. | | The excitation characteristics of this category of instrument (and therefore the fixed range of elements that can be analysed successfully) depend on the choice of radioactive isotope. Instrumentation can be designed to be relatively cheap, portable and battery operated, being thus suitable for field measurements and production control in laboratory and non-laboratory environments. Bench-top instruments with single (or restricted) element capabilities (e.g., S, Cl) are also available. | | | |
| Particular features relevant to each of these categories of instrumentation will now be considered as follows: | | | | | | |
| 4. Direct tube excitation | | | | | | |
| (a) X-ray generator | | | | | | |
| (i) Design of generator | Generator power supplies are invariably of solid-state design for this type of instrument; it is inappropriate to score this feature. | | For a low power output, optimum performance and economy of design are satisfied by a solid-state power supply. | | | |
| (ii) Power rating | For direct tube excitation, a maximum power rating of 50 W is normally adequate and it may be inappropriate to score this item providing this power level can be achieved. | | The coupling efficiency for excitation by this type of instrument is high and power rating of the generator does not normally limit the performance. | | | |
| (iii) Maximum voltage | If the instrument is to be used to measure the K-lines of the higher atomic number elements ($Z > 26$), a maximum kV of at least 50 is required. If applications involve the lower atomic number elements (and L-lines of the heavier elements), a maximum generator of 30 kV may be adequate. Score according to application. | I | A restriction in the maximum voltage setting will limit the sensitivity and, therefore, range of elements that can be determined satisfactorily. Elemental sensitivity is also affected by choice of tube anode (see below). | PS WF ST | | |
| (iv) Steps in voltage and current setting | Score maximum for the provision of adequately small steps in generator voltage and current settings. | I | Steps in generator voltage setting of 1 kV permits excitation conditions to be optimised for individual groups of elements (particularly $Z < 26$). Steps in the generator current setting of 0.01 mA permit excitation conditions to be optimised to the count rate capacity of the detector system. | PS WF ST | | |
| (v) Stability | Score maximum for generators with the best stability specification. | VI | The output of the X-ray tube is subject to both short term fluctuations and long term drift which are affected by changes in mains voltage and laboratory environment. Any instability will affect overall performance of the instrument and the frequency with which recalibrations must be undertaken. | PS WF ST | | |
| (vi) Pulsed-tube capability | The facility to interrupt the output from the X-ray tube for the duration required by the pulse processing electronics to process a detected X-ray photon. Score for the provision of this facility. | I | This facility reduces the 'extended' dead time caused by pulse pile-up rejection which occurs if a second X-ray photon is detected before the first has been fully processed. By reducing this effect in pulsed tube mode, the overall output count rate of the detector system can be increased by a factor of up to three. | PS WF ST | | |
| (b) X-ray tube | | | | | | |
| (i) Type of tube | Most instruments use a side window X-ray tube of conventional design fitted with a beryllium window, which, in conjunction with primary beam filters, affords maximum flexibility in optimising excitation conditions for a wide range of elements. An alternative tube design is available with a transmission target which, though ineffective in the exciting low atomic number elements, may have applications in the determination of specific groups of higher atomic number elements. Score according to application. | I | Maximum flexibility in exciting a wide range of elements is offered by the conventional tube and primary beam filter. If applications involve only a restricted range of higher atomic number elements, the transmission target tube may offer some simplification in instrumentation. | PS WF ST | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | |
|--|--|------------|---|----------------|--|--|
| (ii) Choice of anode | Score maximum for the availability of a range of tubes having anodes relevant to the envisaged application. | VI | The group of elements that may be excited with optimum sensitivity depends on the X-ray tube anode material and its characteristic spectrum. In practice, Pd, Ag, Rh, Gd or Mo anode tubes are most widely used in this type of instrument, although others have more specialised applications. Choice of tube anode is based on matching the energy of the characteristic tube lines with the energy of the absorption edges of the suite of elements to be determined. | PS WF ST | | |
| (iii) Ease of replacement/ interchange of X-ray tube | Score according to the ease of the tube exchange procedure | I | In some applications, it may be necessary to change tube types to extend the range of elements that may be determined to optimum sensitivity. This is only likely to be an important consideration in research applications. Occasional replacement may also be necessary following tube failure. It is important that these operations can be undertaken simply. Changing tubes should only be undertaken by a fully qualified engineer. | PS WF ST | | |
| (iv) Safety interlocks | Safety features, which include warning lights, appropriate safety switches and interlocks, are devices to prevent accidental exposure to either ionising radiations or hazardous voltages during operation or maintenance of the instrument. The provision and operation of safety interlocks must satisfy current national and international regulations and be maintained in full working order. | VI | Failure to meet these standards precludes legal operation of instrumentation. Operation of the X-ray tube must be inhibited unless mounted in the instrument with all shielding in place. | | | |
| (v) Tube cooling | The facility to dissipate the heat generated during operation of an X-ray tube. Providing external cooling water is not required, scoring this feature is inappropriate. | | X-ray tubes of moderate to high power (e.g., 200–4000 W) require effective cooling using a recirculating system to avoid destructive overheating. This facility is unnecessary for low power tubes (say <50 W) fitted to EDXRF instrumentation as air cooling is then normally effective. | | | |
| (c) Primary beam filters | Score maximum for the provision of the widest range of exchangeable primary beam filters. | VI | The use of a filter (usually a thin foil of metal, cellulose or other suitable material) placed between X-ray tube and sample has the important property of modifying the tube spectrum available to excite the sample. By judicious selection of filter (material and thickness), excitation conditions for elements determinable from various regions in the spectrum may be optimised. | PS WF ST | | |
| (d) Masks | Score according to the provision of a range of suitable masks that restrict the area of the excited sample that can be viewed by the detector. This feature is only likely to be important if applications involve the analysis of samples that are smaller than the diameter of a standard sample cup. | Maybe I | If small samples are to be analysed, the mask avoids detection of radiation from sample cup and sample support medium that could otherwise cause spectrum interferences or enhanced backgrounds. | PS WF ST | | |
| <i>5. Excitation using an X-ray tube in Cartesian geometry to achieve polarisation</i> | | | | | | |
| (a) Generator and tube power rating | For Cartesian geometry excitation, a higher power rating is required compared to direct tube excitation. Providing this can be attained, it may be inappropriate to score this feature. | I | To compensate for losses in intensity during the scatter process, a higher power generator is required to achieve satisfactory sensitivity. Consideration of the features of high power generators has been reported previously in Part VI of this series of reports. | | | |
| (b) Cooling of the X-ray tube | A recirculating coolant system may be required to dissipate heat from the higher power X-ray tube. Providing effective cooling is provided, it may be inappropriate to score this point. | | Instruments require adequate cooling to dissipate heat from the more highly rated X-ray tube. This facility can normally be provided by a simple recirculating system. | | | |
| (c) Choice of targets | Score maximum for the provision of a range of targets appropriate for the application; score additionally for ease of selection of targets under computer control. | VI | Cartesian excitation geometries use either (i) secondary targets that normally comprise metallic foils, the characteristic lines from which are capable of exciting the range of elements of interest, or (ii) polarisation targets (e.g., corundum, boron carbide or HOPG) that scatter the entire tube spectrum onto the sample. A selection of secondary or polarisation targets may, therefore, be required to permit the excitation of an extended range of elements under optimum conditions. | PS WF ST | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | |
|--|---|-------------------------------------|--|----------------|--|--|
| (d) Suppression of scattered background | Score maximum for the instrument offering the highest peak-to-background ratio for the elements of interest from a test sample relevant to the application. | VI | The inherent advantage of Cartesian excitation geometry is that the background originating from scatter of X-ray photons present in the tube spectrum off the sample into the detector is suppressed so potentially enhancing peak-to-background ratios. This occurs because following scatter off the target, photons from the X-ray tube spectrum are polarised and cannot in theory be scattered a second time into the detector. However, this ideal suppression is unlikely to be fully realised owing to multiple scatter events and solid angle effects that reduce the degree of polarisation. | PS WF ST | | |
| (e) Optimum excitation of low atomic number elements | If relevant to the intended application, score for the best peak to background ratio for these elements. This may be achieved by a facility to revert to direct tube excitation or by using a special form of polarisation by Bragg diffraction of a low energy characteristic tube line off a suitable crystalline substrate. | I | Secondary or conventional polarising target excitation does not achieve optimum excitation of low atomic number elements (particularly the K-lines of Na to Cl). If these elements are to be determined to the highest sensitivity, one of the specified alternative excitation options must be used. | PS WF ST | | |
| <i>6. Radioisotope excitation</i> | | | | | | |
| (a) Choice of isotope | The selected radioisotope source(s) must be capable of effectively exciting the range of elements relevant to the application. However, as appropriate sources are likely to be available from all manufacturers, it is inappropriate to score this feature. If provision is made in the instrument for installing multiple sources to extend the range of elements that may be determined and this facility is relevant to the application, score accordingly. | VI | Individual radioisotope sources are only capable of exciting effectively a restricted range of elements and are, therefore, normally less versatile excitation sources than an X-ray tube. Choice of radioisotope source must be made according to application, normally from the following list (characteristic X-ray emissions in parenthesis): ⁵⁵ Fe (Mn K lines), ¹⁰⁹ Cd (Ag K lines), ²⁴¹ Am (60 keV plus some weaker gamma emission lines). | PS WF ST | | |
| (b) Activity of sources | The activity of a radioactive source, specified in megabecquerels (MBq). Providing the source has sufficient activity to provide sufficient sensitivity for the range of elements relevant to the application, it is inappropriate to score this feature. | | The intensity of X-ray emission from a radioactive source depends on the decay characteristics of the selected isotope, but is directly proportional to source activity. A compromise must be achieved between adequate excitation capability, cost and safety. | | | |
| (c) Useful working life | The effective working life of the source which depends on its initial activity and intrinsic half-life. It is inappropriate to score this feature. | | The half-lives of commonly used sources are as follows: 2.7 years (⁵⁵ Fe), 18 years (²⁴⁴ Cm), 1.3 years (¹⁰⁹ Cd), 458 years (²⁴¹ Am). Users should be aware that instrument performance (in terms of excitation efficiency) will decline with age of source. This effect is normally accounted for by a mathematical correction that compensates for radioactive decay. | | | |
| (d) Cost of replacing sources | Score maximum for the most cost effective service offered by the manufacturer. | I | This operation should be entrusted to the manufacturer's service engineers and may contribute to the longer term running costs of instrumentation. | PS WF ST | | |
| (e) Disposal of spent sources | Score for a disposal service offered by the manufacturer during source replacement. | I | If the manufacturer does not dispose of the source, the user will have to pay a specialist contractor to undertake this task. | PS WF ST | | |
| (f) Safety considerations | The provision of appropriate interlocks and adequate shielding to prevent accidental exposure are statutory requirements, without which an instrument cannot be legally operated. It is inappropriate score these items. | | Any exposure to ionising radiations represents a potential hazard to health. | | | |
| <i>7. Sample changer and presentation</i> | | | | | | |
| (a) (i) Number of samples | For instruments that are used for the routine analysis of large batches of samples, score maximum for the provision of a sample changer that can accommodate the largest number of samples. | VI | Essential if unattended operation is envisaged for routine analysis. In contrast with many WDXRF systems, most EDXRF instruments incorporate an internal carousel with a fixed number of positions. | PS WF ST | | |
| (ii) Large samples | If justified by the application, score maximum for the largest sample that can be readily accommodated inside the sample chamber. This facility is important for the semi-quantitative analysis of large non-standard samples. | I (depending on application) | In some applications, it is advantageous to be able to analyse directly large irregular objects. The ability to move such samples across the analysis position to obtain spatial distribution data may also be useful. | PS WF ST | | |
| (b) (i) Vacuum system | Score, if appropriate to the application, for the provision of a vacuum system. Score additionally for the fastest pump-down time, combined with automatic analysis initiation. | VI (depending on application) | For elements with an atomic number of ≤ 17 , a vacuum system is required to avoid unwanted attenuation in air of low-energy X-ray signals. However, vacuum operation is not suitable for the analysis of liquids nor normally loose powders. | PS WF ST | | |
| (ii) Helium flush option | Score for the provision of a facility to change to an atmosphere of He in the sample chamber. Score additionally for automatic control of He flow to ensure the most economical use of the gas, and for an interlocking arrangement that will avoid accidentally evacuating the helium flush atmosphere when liquid or powdered samples are being analysed. | Maybe VI (depending on application) | This option is essential if low atomic number elements are to be determined in volatile liquid or loose powder samples. Accidental evacuation of the sample chamber when containing these types of sample will seriously contaminate the instrument. | PS WF ST | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | |
|---|---|------------|---|----------------|--|--|
| (c) Positioning and alignment of sample | Score maximum for the best mechanical precision in repositioning a sample in the analysis position. | VI | Even small discrepancies in mechanical alignment will affect the precision of measurements, owing to consequential changes in excitation and detection efficiency. | PS WF ST | | |
| (d) Sample spinning | Score for the ability to rotate the sample continuously throughout the analysis period. This facility is only justified if the aim is to achieve the highest precision in measurements. | I | Averaging the excitation produced from the sample surface will reduce the effects caused by minor sample inhomogeneity and surface defects. | PS WF ST | | |
| (e) Sample holders | Score maximum for the availability of sample holders in a suitable range of materials and designs. | VI | Sample holders may introduce unwanted fluorescence signals and, if of poor design, will restrict the area of sample excited. Selection of holders from a range of materials and designs will enable the user to minimise such problems. Different designs are required to accommodate solid, liquid or thin film samples. | PS WF ST | | |
| 8. Choice of detectors | Several categories of energy dispersive detector are available. Scoring may be inappropriate unless particular characteristics of the detector type are relevant to the application. | Maybe VI | Although lithium-drifted silicon Si(Li) detectors are widely used, Si-PIN diodes, Si-drift detectors, germanium, mercuric iodide and gas proportional counters all possess some distinctive characteristics that may offer advantages in a particular applications as summarised in the next paragraphs. | PS WF ST | | |
| (a) Lithium drifted silicon [Si(Li)] detector | A detector based on a high purity silicon crystal into which lithium atoms are drifted to compensate for residual impurities and improve its semi-conductor properties. This detector type is normally made from a wafer 3 or 5 mm thick of area 10 to 50 mm ² . Si(Li) is capable of offering a typical resolution of 140 eV at 5.9 keV with an effective detection range 1 to 30 keV. The provision of a high transmission window extends the use down to about 0.2 keV. Si(Li) detectors offer a stable and enduring performance but require cooling normally using liquid nitrogen. | | Si(Li) detectors represent well-proven technology and are generally regarded as the bench-mark against which other devices are compared. The use of Si(Li) in XRF applications is currently declining in favour of more recently introduced Si(PIN) and Si drift detector types (see below). | | | |
| (b) Si(PIN) detector | A detector comprising high purity silicon wafer of typical thickness 300 µm and active area 7 to 25 mm ² . The Si(PIN) does not require cryogenic cooling (a small degree of Peltier cooling is sufficient). Best resolutions are in the order of 180 eV FWHM at 5.9 keV and the detector has similar maximum count rate capabilities to the Si(Li) detector but with an effective energy range of 1 to 20 keV. | | Si(PIN) detectors are compact and the are increasingly being substituted for Si(Li) detectors because they offer similar performance characteristics, without the need for cryogenic cooling. | | | |
| (c) Silicon drift detector | A particular design of detector in which the capacitance is minimised by the overall detector design and by the integration of the first stage signal amplification onto the detector wafer. This detector is normally designed on a wafer 300 µm thick and requires a small degree of Peltier cooling, can offer resolutions of better than 140 eV FWHM at 5.9 keV and because of the low inherent capacitance, will operate successfully at input count rates > 10 ⁵ s ⁻¹ . | | Silicon drift detectors offer significant advance in performance compared to Si(Li) because of their high count rate capability without the need for cryogenic cooling. However, these detectors are significantly more expensive, and represent a device that is subject to intensive further development. | | | |
| (d) Germanium detector | A detector based on a hyper-pure germanium semi-conductor crystal (sometimes erroneously called intrinsic germanium). This detector offers better resolution than a Si(Li) detector (down to about 115 eV at 5.9 keV) coupled with a higher detection efficiency that allows it to be used for an extended energy range up to 80–100 keV. Problems caused by incomplete charge collection that result in low energy tailing of peaks have been overcome with recent advances in technology. Ge escape peaks may cause overlap interferences in general XRF applications. Ge detectors require cooling to liquid nitrogen temperatures to achieve optimum performance. | | The principal attraction of germanium detectors is that their detection efficiency extends (to 80–100keV) substantially beyond the range of silicon detectors. This gives this detector type substantial advantages when high energy excitation sources (e.g., an X-ray tubes operated at 100 kV) are used to excite the K-lines of higher atomic number elements. The better resolution characteristics offer advantages in the detection of low energy X-ray spectra (especially <5 keV) but are unlikely to be an issue of choice in XRF applications. | | | |
| (e) Mercuric iodide detector | An energy dispersive X-ray detector based on high-purity mercury (II) iodide semiconductor crystal. The principal property of this device is that it offers a reasonably good resolution response (about 250 eV at 5.9 keV) with a small degree of Peltier cooling. Furthermore, detection efficiency is also high (better than that for a germanium detector) allow their use in measuring the higher energy fluorescence spectrum. Escape peaks from Hg (L lines) and I (K lines) may cause spectral overlap interferences in some applications. | | Mercuric iodide detectors represent an evolving technology in which further improvements are likely to occur. Room temperature operation gives these detectors an advantage over germanium detectors which has been exploited in field portable XRF instrumentation. | | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | |
|--|--|------------|---|----------------|--|--|
| (f) CZT | Cadmium-zinc-telluride represents one of a number of semiconductor materials that are being investigated for their X-ray detection properties. | | New detector materials will need to show clear advantages in detection characteristics, longevity and/or robustness compared with the detector types described in the above sections. | | | |
| (g) Gas proportional counters | An energy dispersive X-ray detector based on a gas filled proportional counter similar to the devices used as detectors on WD spectrometers. As a multichannel X-ray detector, these devices offer poor resolution performance (typically > 1000 eV at 5.9 keV). Efficiency range depends on gas filling but these detectors offer inferior efficiency in comparison with other detectors mentioned above, about 10–15 keV. Instrumentation is light, robust, operates at room temperature and is cheap to construct and maintain. | | Proportional counters represent well-proven technology and offer particular advantages in radioisotope XRF instruments designed for: (1) The determination of single elements in relatively simple matrices (e.g., S in oil; Cl in liquors). (2) Element specific field portable XRF instrumentation in applications where spectral overlap interferences do not degrade performance to an unacceptable extent. | | | |
| <i>9. Characteristics of lithium drifted silicon [Si(Li)] detector</i> | | | | | | |
| (a) Resolution | <p>The features of the Si(Li) detector are considered here in detail, but with suitable adaptation, these details may be used to evaluate other categories of detector, where appropriate.</p> <p>The resolution of a Si(Li) detector is normally measured as the full width at half maximum (FWHM) of the Mn Kα line at 5.9 keV. Counting conditions should be selected to reflect those likely to be encountered in routine analysis. Additional measurements of FWHM should also be made on other element lines (e.g., Si Kα–74 keV and Zr Kα–15.7 keV) to cover the full spectrum range of interest to the user. Furthermore, if applications require the measurement of very low energy X-ray lines (e.g., < 1 keV), additional FWHM measurements should be made on the lowest energy X-ray line of interest. Score maximum for the best overall resolution.</p> <p>This feature may be measured independently of the instrument using radioactive sources, ⁵⁵Fe being the standard source for FWHM measurements at 5.9 keV. However, all instruments should be compared using the same test procedure as the signal-to-noise ratio is likely to be better with the detector on the bench than when installed in an instrument and detector resolution will vary with count rate.</p> | VI | Detector resolution varies not only as a function of photon energy, but also with the count rate at which measurements are made, the time constant selected for pulse processing electronics and the size, shape, active area and quality of the detector crystal. Manufacturers' measurements are usually made at 5.9 keV under the most favourable counting conditions (⁵⁵ Fe source excitation at an input count rate of < 10 ³ s ⁻¹), so it is advisable that measurements are made on specified peaks that cover the full spectrum range of interest under conditions typical of their application. Allowances should then be made when making comparisons with manufacturers' data. Detector performance cannot be reliably predicted prior to manufacture, so any purchase order should specify that on commissioning, the detector should meet an agreed FWHM specification over the spectrum range of interest. | PS WF ST | | |
| (b) Active area of detector crystal | Detector crystals are normally available in a range of standard sizes identified by the 'active' area of the front face of the crystal that is sensitive to X-ray photons. Score maximum for the availability of the crystal size appropriate to the application. | I | The size of the detector crystal affects resolution, sensitivity and peak shape, standard sizes being 10, 30 and 50 mm ² . Crystals with larger active areas usually give poorer resolution but are favoured in some XRF applications to increase sensitivity by maximising the solid angle of detection. | WF | | |
| (c) Quality of detector crystal | The quality of the detector crystal may be evaluated from the shape of the peak response and the signal-to-background ratio by measuring (i) the ratio of the FWHM to the full width one tenth maximum (FWTM) of the Mn-K α peak and (ii) the ratio in intensity of the Mn-K α peak to the lower energy background. Score maximum for maximum values in both these parameters. This test is best carried out with a ⁵⁵ Fe source. | I | Spectrum response in terms of peak shape, resolution and the degree of low energy background tailing are affected by the quality of the detector crystal. By careful attention to design and manufacture, charge trapping effects, that increase the tailing of detected peaks and enhance lower energy backgrounds can be minimised. For a Gaussian peak, the ideal FWHM/FWTM ratio is 1.85. | PS WF ST | | |
| (d) Collimation | Test for changes in peak shape and signal-to-background ratio as described under (c) above with the detector mounted in the instrument using the excitation source supplied with the instrument. Provided there is no significant change in these parameters, indicating that a collimator of appropriate dimensions is fitted, it is inappropriate to score this feature. | I | Satisfactory collimation minimises the acquisition of adventitious X-rays scattered off the specimen chamber and restricts the area of the detector crystal in which the spectrum is recorded to the central 'active volume', so minimising charge collection problems. Whereas, use of too small a collimator may optimise the test parameters, the count rate capability of the detector may then be restricted to an unacceptably low level. | PS WF ST | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | |
|---|---|----------------------------------|---|----------------|--|--|
| (e) Detector efficiency | To test for low energy detection efficiency for standard applications involving spectrum analysis down to 1 keV, measure the area of the Zn K α (8.6 keV) and Zn L α (1.0 keV) peaks and calculate the ratio Zn L α /Zn K α . Score maximum for the highest value of this ratio. In SEM applications where provision of a window-less detector or one fitted with an ultra-thin window permits measurements to be extended down to the lower energy range, this test should be repeated by ratioing the intensity of the Ti L α /Ti K α lines at 0.45 and 4.5 keV. Comparisons between instruments, must be undertaken using identical sample types and identical excitation conditions (e.g. X-ray tube and applied kV). To test the detection efficiency to higher energy X-ray photons, measure the ratio of Ba K α /Ba L α at 32.2 and 4.5 keV (or from an element that emits a suitable alternative fluorescence K line in the higher energy spectrum range of interest). Score maximum for the highest value of this ratio. | VI (depending on application) | The relative detection efficiency depends on a number of factors. Efficiency towards low X-ray energy photons varies with the thickness of the 'dead layer' (or the presence of unexpected contamination) on the front surface of the detector crystal and, more importantly, on the type and thickness of the entrance window fitted to the detector. The degree of attenuation cannot be predicted reliably prior to manufacture, so any purchase order should specify that on delivery, the detector will meet an agreed performance target. The fall-off in detection efficiency for higher photon energies depends largely on the thickness of the detector crystal. Above 20 to 30 keV, an increasing proportion of X-rays will pass straight through a standard Si(Li) crystal without interaction. The specified tests permit comparative measurements to be made between different ED detectors. | PS WF ST | | |
| (f) Choice of window | If applications involve high sensitivity measurements of the low energy X-ray spectrum \ll 2 keV, score according to the availability of, and facility to use, high transmission window materials. | VI | Standard detectors are fitted with a beryllium window of nominal thickness 6 μ m, which causes significant attenuation of X-ray photons of energy lower than 2 to 3 keV. The resulting detection efficiency is usually acceptable in ED-XRF applications. However, for some specialised EDXRF (as well as SEM/EPMA) applications which involve measurement of the lower energy X-ray spectrum, detection efficiency must be enhanced by use of thinner window materials. This can be achieved by use of a detector fitted with an ultra-thin polymer window (capable of withstanding a pressure differential of one atmosphere). Alternatively, an exchangeable window assembly may be used, comprising a standard beryllium window, an ultra-thin membrane window and an opening for windowless operation. Window selection of this device must be interlocked with the instrument vacuum system to prevent rupture of the membrane window or contamination of the detector crystal which would occur if the vacuum failed | PS WF ST | | |
| (g) Cooling | All Si(Li) detector crystals require cooling, normally to liquid nitrogen temperatures. Scoring is inappropriate. | | Cooling is necessary to minimise electronic noise in the detector and first stage of the signal amplification circuits (field effect transistor). | | | |
| (i) Liquid nitrogen cooling | It is inappropriate to score this item as all manufacturers offer this feature. | | Liquid nitrogen is capable of cooling components to -196°C and in comparison with alternative Peltier cooling devices, minimises the electronic noise contribution to the detector signal, so optimising spectrum resolution. Disadvantages include the requirement for both a bulky storage cryostat and a reliable refilling schedule. | | | |
| (ii) Capacity and hold time of cryostat | The length of time taken for liquid nitrogen to evaporate from a full cryostat. Score for the longest hold time for a cryostat that can be fitted to the instrument, taking into account the practical limitations of size. | VI | In practice, hold time is likely to depend not only on design and capacity of cryostat and ambient temperature, but also whether or not the detector end of the assembly is held in an evacuated chamber. As a guide, the refill schedule should be at least two and a half times shorter than the hold time. | PS WF ST | | |
| (iii) Liquid nitrogen consumption | Score maximum for the system with the lowest consumption of liquid nitrogen. | I | Reduces running costs. | PS WF ST | | |
| (iv) Peltier cooling device | Peltier cooling is an alternative form of cooling based on a solid-state thermoelectric device and its availability may be important in some applications. Score according to application. In the case of other detector types (see above) a small degree of Peltier cooling is all that is required for successful operation. | VI (for some installations) | For some applications liquid nitrogen is not readily available or the location in which the ED spectrometer must operate does not permit regular refilling with liquid nitrogen. In these circumstances, Peltier cooling offers a viable alternative. For other detector types that do not require cryogenic cooling, there is a considerable benefit in size and simplicity of detector design. | PS WF ST | | |
| (v) Warm-up protection | Score for the provision of a device that monitors the operating temperature of the detector crystal and automatically trips off the high voltage supply to the detector if the temperature rises above a preset value. | VI | Irreparable damage can occur to the detector crystal if it is allowed to warm up to room temperature with the high voltage bias still applied. | | | |
| (vi) Recycling to room temperature | The ability to allow the detector crystal to warm to room temperature (with the high voltage bias switched off) and re-cool to liquid nitrogen temperatures without loss of performance specification. Score according to the warranty available from the manufacturer. | VI | There is a risk that the detector crystal will become irreversibly damaged on warming to room temperature due to migration of lithium ions. Performance (particularly resolution) may not be restored on re-cooling. With advances in semiconductor technology, this problem is less likely to affect modern detector crystals. | PS WF ST | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | |
|---|---|------------|---|----------------|--|--|
| (h) Microphonics | Microphonics is the phenomenon whereby detector performance is affected by noise and vibration. This phenomenon can only be tested satisfactorily by undertaking measurements of FWHM and spectrum background in the working environment and comparing the degradation in signal quality with data recorded in an instrument laboratory. Score according to the warrantee offered by the manufacturer if tests cannot be made in situ. | I | Under some conditions, detector performance (in particular peak resolution and ambient background) may be degraded appreciably by noise induced vibration. The magnitude of this effect may be influenced by the frequency of ambient noise. Careful design of the ED spectrometer will minimise this effect. | PS WF ST | | |
| (i) Escape peak intensity | A spectral artefact which is observed at an energy of 1.74 keV below that of the most intense lines in a spectrum. Escape peaks are an intrinsic property of all Si(Li) detectors and it may be inappropriate to score this feature. | | Escape peaks are caused by the escape from the detector of Si K α X-ray photons (which themselves result from fluorescence of the detector crystal). The intensity of the escape peak may be affected by the size, shape and quality of the detector crystal, however little difference is likely to be observed in the performance of modern detector designs. | | | |
| <i>10. Pulse processing electronics</i> | | | | | | |
| (a) Time constant | The time (normally expressed in μ s and selectable by the user) that controls the integration time of the pulse processing electronic circuits. Score maximum for the widest range of appropriate time constant settings. | I | Short time constants provide the ability to operate at high data acquisition rates at the expense of reduced spectral resolution. Longer time constants can be used to optimise spectral resolution but restrict maximum data acquisition rates. | PS WF ST | | |
| (b) Count rate capability | Score maximum for the system that offers maximum data acquisition rates under equivalent pulse processing conditions (in particular time constant setting) representative of those that will be used in the application. | VI | As input count rate is progressively increased, all systems eventually suffer a roll-over effect in which the output count rate starts to decrease in magnitude. Maximum data acquisition rates are influenced by design of the entire detection and pulse processing system. | PS WF ST | | |
| (c) Response stability with count rate | An increase in FWHM resolution and shift in spectrum gain and spectrum origin occur as the data acquisition rate is increased. Score maximum for the system that offers minimum variation in these parameters under equivalent pulse processing conditions representative of those that will be used in the application. | VI | For accurate quantification of spectral intensities, changes in system response as a function of count rate will cause errors unless they are accurately compensated for. | PS WF ST | | |
| (d) Accuracy of dead-time correction | Dead-time is the proportion of time that the counting system is unavailable for the acquisition of new data because it is 'busy' processing an existing pulse. The accuracy with which the 'real' count time is extended to compensate for this effect can be measured by evaluating the linearity between the intensity (area) of a selected fluorescence line as a function of tube current, other conditions remaining identical. Scoring is inappropriate as all instruments will be provided with reliable dead time correction. | | Excitation conditions are often selected to give a pulse processing dead-time of 20–40%. Accurate correction for this effect is necessary so that intensities from spectra recorded at different spectral dead-times may be compared directly. | | | |
| (e) Pulse pile-up suppression | Pulse pile-up is the coincident detection of two X-ray events that appear as a spectrum artefact having the sum of the energy of the two individual events. The appearance of sum peaks is most apparent at high count rates. Score maximum for the system that offers minimum value in the ratio of the intensity of a suitable K α \pm K α sum peak relative to the intensity of the parent K α peak. | VI | Pulse processing systems include a pulse pile-up rejector designed to recognise pulse-pile-up events and suppress their detection. However, at high count rates, near-coincident pulses will not be distinguished as individual events and so give a pulse pile-up peak. This can cause ambiguity in the qualitative interpretation of spectra and bias in quantitative analysis. | PS WF ST | | |
| (f) Gain | Score maximum for an appropriate range of user-selectable gain settings which permit acquisition of spectral data over a range of energies appropriate to the application. | VI | Spectral data is accumulated into a fixed number of channels in the multichannel analyser (normally 1024 or 2048 channels). By adjusting the pulse processor gain, the appropriate energy range (e.g., 0–10 keV, 0–20 keV or 0–40 keV) can be stored and displayed. | PS WF ST | | |
| <i>11. Spectrum evaluation</i> | | | | | | |
| (a) Qualitative interpretation | | | | | | |
| (i) Spectrum display | Score for the ability to display the spectrum during data acquisition. | I | Permits the interpretation of spectral data during data acquisition. | PS WF ST | | |
| (ii) Spectrum manipulation | Score for the ability to change the scales of the spectrum display axes with the option to select a logarithmic or linear intensity scale to facilitate user interpretation of data. | I | This facility aids the rapid identification of features of interest, but may depend on user preferences. | PS WF ST | | |
| (iii) Peak identification | Score for the facility to display K-L-M markers on spectra. Score additionally for markers that are displayed in proportion to the line intensity and for indications of the position of escape and sum peaks. | I | Markers aid unambiguous element identification, which is normally based on the recognition of a line pattern. | PS WF ST | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | |
|--|---|------------|--|----------------|--|--|
| (iv) Options for hard copy | Score for the capability of producing hard copy output of spectra, if appropriate by transfer for external printing. | I | Many users prefer to have available a permanent visual record. | PS WF ST | | |
| (v) Automatic identification of peaks | Score for the provision of this facility, providing its accuracy and reliability can be established using an appropriate range of test samples. | I | Automatic identification of peaks is particularly useful for inexperienced operators, bearing in mind that accuracy of such procedures in the analysis of complex spectra may be about 90–95%. | PS WF ST | | |
| (b) Quantifying spectra | | | | | | |
| (i) Choice of spectrum analysis procedures | Score for the provision of a selection of spectrum analysis procedures for measuring the intensities of fluorescence peaks appropriate to the application. The most common types of programme from which selection can be made are listed below. One of these options is required for quantitative analysis and is classified as VI* in such an application. | VI | Different spectrum analysis procedures offer different advantages—simpler procedures may be inappropriate for the analysis of more complex spectra. | PS WF ST | | |
| (ii) Region of interest integration | The channel limits of an X-ray peak are identified and the designated area integrated, a background correction being made by linear interpolation between the limiting channels. | * | This procedure is most effective for intensity measurements on single X-ray peaks that do not suffer overlap interferences and where the background varies in a linear manner. If these assumptions are not met, bias may occur in results. | PS WF ST | | |
| (iii) Background modelling and peak fitting | The spectral background is modelled using an adaptation of Kramer's equation, (including, in more sophisticated procedures, the presence of absorption edges). Spectral peaks are then accounted for by a least squares fit of peaks of the appropriate shape (often Gaussian) at selected energies corresponding to $K\alpha$ lines of interest. Corresponding $K\beta$ peaks are normally accounted for by calculating the intensity of the peak using precalibrated data for the intensity of the $K\alpha/K\beta$ ratio. Procedures normally allow for the correction of escape peaks. | * | This procedure is effective in analysing complex spectra that include K-line overlaps. Without further adaptation, such procedures are not as effective in analysing spectra containing L-line peaks. For the highest accuracy, a correction must be made to account for any drift in spectrum origin and gain and the change in spectrum resolution as a function of count rate. | PS WF ST | | |
| (iv) Digital filtering with least squares fitting of library spectra | The spectral background and channel-by-channel noise is suppressed by applying a simple digital filter to spectral data. Peak intensities in the resulting 'convoluted' spectral data are then quantified by fitting selected single element 'library' spectra which have themselves been convoluted by the digital filter function. Basic 'library' spectra are normally provided in the operating programme by the manufacturer, but can be supplemented by additional spectra recorded by the user to extend applications. Procedures normally account for the presence of escape peaks. | * | This procedure is effective in the analysis of complex spectra containing overlap interference from K and/or L lines (as there are no restrictions on the selection of library spectra). However, no account is normally made for the presence of absorption edges (which may appear as a minor background features in some spectra). A series of appropriate library spectra must be pre-recorded from a set of samples in which spectral overlaps on the lines of interest are absent. For the highest accuracy, a correction must be made to allow for any drift in spectrum origin and gain and the change in spectrum resolution as a function of count rate. | PS WF ST | | |
| <i>12. Quantification and analysis software</i> | | | | | | |
| (a) Quantitative analysis | Score for the provision, as appropriate to the application, of software features such as: (1) Calibration using various data fitting modes for linear and non-linear functions. (2) Matrix correction for absorption and enhancement effects by empirical and/or fundamental parameter procedures. (3) Options to store results for further processing and comparison as well as editing and outputting data in a report format. (4) The facility to transfer files of results in the appropriate computer format to an external device. (5) Statistical process control software for quality control applications. | VI | Calibration functions and matrix corrections must be applied to raw intensity data to obtain quantitative analysis results. In many applications, results are supplied to the user in a standardised report format. To satisfy quality control criteria, statistical treatment of sets of data is essential before results can be released to the user for interpretation. | PS WF ST | | |
| (b) Semi-quantitative analysis | Score for the provision of a software package capable of estimating concentration levels from measured intensity data without recourse to calibration using a full matrix specific set of standard materials. | VI | In applications where limited numbers of calibration standards are available, the user's requirements may be satisfied by a semiquantitative analysis in which intensity data are converted to concentrations using a theoretical correction based on fundamental equations of excitation and absorption. | PS WF ST | | |
| <i>13. Instrument control, data acquisition and measurement</i> | | | | | | |
| (a) Instrument control | Score maximum for the largest number of instrument functions that are under computer control. | VI | Computer control of instrumental parameters ensures reliable and reproducible operation of the instrument by trained, but non-expert operators and also prevents the selection of instrument errors (e.g., conflicting settings) which could lead to instrumental malfunction or even damage. Furthermore, computer control is essential if unattended operation is required for extended periods, for which the operating system should permit the sequential execution of several analytical programmes. | PS WF ST | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | |
|---|---|------------------------------|--|--------------------------|--|--|
| (b) Operating program | Score maximum for a user-friendly operating system, which allows the user to develop versatile analytical programmes tailored to the application. | VI | Difficult or repetitive keyboard interactions and complex access codes can lead to operator frustration and errors. The use of a graphical user interface (e.g., pull-down menu options) and/or soft keys or other devices for reducing setting up times and initiating analytical programmes reduces training requirements. | PS WF ST | | |
| (c) Instrument status | Score maximum for an adequate display of instrument status parameters and alarm functions that monitor whether the instrument is operating within its design envelope for the selected analytical programme. | VI | A comprehensive display of instrument parameters will confirm to the operator that the required analytical programme is being followed. Effective monitoring of instrument status may give early warning of malfunction. | PS WF ST | | |
| (d) Instrument performance diagnostics | Score for an instrument with the most comprehensive set of self-checks on power up and has easy to use qualification routines. | I | It is vital that the system performs 'fail safe' diagnostic checks on power up; this information must be recorded. | PS WF ST | | |
| (e) Data collection and application software | Define the requirements before scoring these items. | | | | | |
| (i) Specialised software options | Score, where appropriate for the application, for the provision of software enabling the instrument to be used for more specialised tasks such as: (1) Alloy/metal sorting. (2) Thickness measurements of multilayer samples. (3) Analysis of dust. (4) Other fingerprinting applications. It is important that such software packages are verified using a range of suitable test samples. | I (depending on application) | The provision of appropriate software enhances instrument performance if specialised applications are envisaged. | PS WF ST | | |
| (ii) Storage of instrumental parameters and spectral data | Score highest if all parameters can be set and stored with the spectral data to ensure that all future analyses can be performed under the same instrumental conditions. | VI | Essential for many regulatory requirements e.g., GLP, GMP and all regulated industries. | PS WF ST | | |
| (iii) Display software routines | Score maximum for the most versatile set of spectral display routines. | VI | Simple versatile spectral display routines are vital (see also 12(a) for spectral manipulation options). Graphical displays are essential especially when spectra may be overlaid, transient signals may be plotted, calibration curves inspected, etc. | PS WF ST | | |
| (iv) Intuitive and flexible software | Score for software that is user friendly, versatile and flexible. Score highly for a system that offers help functions, error messages, complete libraries of relative intensity, interferences and corrections. Score additionally for databases of matrices, methods, results and QC standards. | VI | Versatile and user friendly application software varies considerably between manufacturers. It is often useful to communicate with existing users when evaluating software options. Software that enables a choice of matrix correction procedures and reanalysis of acquired data under amended matrix or calibration parameters provides the user with valuable flexibility. In addition, quality control procedures such as re-analysis options based on periodic QC standards, sample out of calibration range protocols and calibration failure protocols e.g., re-calibrate, ignore erroneous standards, etc., facilitate the validation of the method. Ideally, the software should be intuitive, and a comprehensive help function is highly desirable. Meaningful error messages rather than merely error numbers are also an advantage. A comprehensive library of line intensity along with prospective interferences as well as a database of matrices and methods can assist the analyst in the choice of suitable operating parameters. | PS WF ST WF | | |
| (v) Validation software | Score maximum for a system that best complies with any regulating authority's standards with respect to validation routines. | VI | Essential in many laboratories for regulatory requirements. | PS WF ST | | |
| (vi) Custom reporting | Score for a flexibility of reporting format. Score additionally when reports may be generated from stored data. | VI | The possibility of different reporting formats, e.g., full statistics with replicates and methods, full statistics alone or only a summary report gives the analyst flexibility. The capacity to generate a report from stored data extends the flexibility further. | PS WF ST | | |
| (f) Data storage | Data may be stored on various media and increasingly via networks. Score for compatibility with existing data processing facilities and requirements. | VI | The vast majority of modern instruments have data storage options that enable further data processing to be easily performed. ASCII data can be exported to and manipulated by many external software packages. The nature of the data output may need to be compatible with LIMS systems, if in use. This expands the scope of data manipulation and chemometric routines available to the user and provides security and backup. | PS WF ST | | |
| (g) Ability to be networked | Score if networking, for example, to a laboratory information management systems, is required. | I | In many laboratories, instruments are run from a PC and, at a suitable time, the data is transferred to a server. | | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | |
|---|--|------------|--|-------------------|--|--|
| <i>14. Safety considerations</i> | | | | | | |
| (a) Regulatory compliance | In the UK, design and construction of instrumentation and all safety features, including interlocks, must comply with the appropriate legislation. Other countries have similar National Regulations with which instrument design and construction must comply. Reject any instrument that does not comply with any of these requirements. | VI | Apart from the obvious hazard, operation of instrumentation in contravention of statutory regulations is illegal. | | | |
| (b) Shielding of ionising radiations | In the UK, to comply with the Ionising Radiations Regulations 2000, leakage of ionising radiation from an instrument must fall below a specified maximum value. Score for shielding and additional features that minimise leakage of extraneous radiation below the regulatory limits. | VI | Any exposure to ionising radiation is potentially hazardous. Instruments must be designed to ensure that any external leakage is as low as reasonably practicable. | | | |
| | | | | Sum of sub-totals | | |
| <i>15. Value for money (points per currency unit)</i> | | | | | | |
| | Sum of the previous sub-totals divided by the purchase price of the instrument. Subject to proportional scoring and weighting factors, including ST in grand total. | | 'Simple' instruments are often good value for money, whereas those with unnecessary refinements are often more costly. | PS WF ST | | |
| | | | | Grand total | | |

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