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GENERAL PAPER

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.

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.

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 materi-

Feature	

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score		
(ii) Choice of anode						

Feature	Definition and/or test procedures and guidance for assessment	Importance

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 m 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 m 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.			
9. Characteristics of lithium drifted silicon [Si(Li)] detector	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.					
(a) Resolution	The resolution of a Si(Li) detector is normally measured as the full width at half maximum (FWHM) of the Mn K 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 K –.74 keV and Zr K –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.	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 favourabl2(v)14.6(e]TJ /F7c)e8for nterest. gy01th 5268 5268/F1]TJf 0 9582 [(01th24by9 TD [mpb8f)-2(ac55268.654Tm 3000795la)0.1(wh			

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、 (8.6 keV) and Zn L、 (1.0 keV) peaks and calculate the ratio Zn L、/Zn K、. 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、/Ti K、 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、/Ba L、					

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 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.			
10. Pulse processing electronics						
(a) Time constant	The time (normally expressed in 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 becausel98 407.261.3284 TD 0.00059989 72 0 0 6.0e ree rexdesign ofccura-248.6(dead-time).3(rate)]T6.7(outp)]T6.TJ 0.4989 56.0idal'07.261.355.673 urocessingn4time that th					

Feature	

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.					