Report by the Analytical Methods Committee

Evaluation of Analytical Instrumentation. Part VII
Simultaneous Wavelength Dispersive X-ray Spectrometers

Analytical Methods Committee
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A method is provided for comparing the features of wavelength dispersive X-ray spectrometers.

The Analytical Methods Committee has received and approved the following report from the Instrumental Criteria Sub-Committee.

Introduction

The following report was compiled by the above Sub-Committee of the AMC, which consisted of Professor S. Greenfield (Chairman), Dr. P. J. Potts, Mr. D. Squirrell and Mr. P. Warren, with Mr. C. A. Watson as Honorary Secretary.

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

The over-all object is to assist purchasers in obtaining the best instrument for their analytical requirements. It is also hoped that, to a degree, it will help manufacturers to supply the instrument best suited to their customers' needs.

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 seventh* report of the Sub-Committee deals with X-ray fluorescence spectrometers that are designed as *simultaneous* instruments.

* The first six reports were as follows: 'Atomic Absorption Spectrophotometers, Primarily for Use with Flames', *Analytical Proceedings*, 1984, **21**, 45; 'Atomic Absorption Spectrophotometers, Primarily for Use With Electrothermal Atomisers', *Analytical Proceedings*, 1985, **22**, 128; 'Polychromators for Use in Emission Spectrometry With ICP Sources', *Analytical Proceedings*, 1986, **23**, 109; 'Monochromators for Use in Emission Spectrometry With ICP Sources', *Analytical Proceedings*, 1987, **24**, 3; 'Inductively Coupled Plasma Sources for Use in Emission Spectrometry', *Analytical Proceedings*, 1987, **24**, 266; 'Wavelength Dispersive X-ray Spectrometers', *Analytical Proceedings*, 1990, **27**, 324.

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 applications.
Column 4. Here the Sub-Committee has given reasons for its opinion as to the importance of each feature.
Column 5 onwards. 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 addition of the sub-totals will give the final score for each instrument.

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. An indication of the Sub-Committee's opinion of the relative importance of each feature is indicated as follows: VI (very important), I (important) and NVI (not very important). A scale is chosen for the weighting factor which allows the user to discriminate according to needs, *e.g.*, ×1 to ×3, or ×1 to ×10. The factor could amount to total exclusion of the instrument.
3. (ST) Sub-total. This is obtained by multiplying PS by WF.
4. Simultaneous X-ray fluorescence spectrometers have recently developed along two pathways. As well as spectrometers with high power X-ray tube generators, low power instruments designed with a compact excitation geometry are now available to provide a performance approaching that of the conventional high power generator instrument but in a smaller and less expensive instrument. It is therefore necessary to decide which of these two types of instrumentation is appropriate for a particular application (see section 1).

Technical considerations may then be made to decide between available instruments within the particular category. The scoring of the features concerned with the number of channels, sensitivity, size, cooling, power requirements and cost should enable this choice to be made.

INSTRUMENTAL CRITERIA SUB-COMMITTEE INSTRUMENT EVALUATION FORM

Type of Instrument: Simultaneous wavelength dispersive X-ray spectrometer

Manufacturer:

Model No:

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
1. *Choice of category of instrument*								
(*a*) Number of channels	Score maximum for the type of instrument with sufficient channels to meet analytical requirements.	VI	Simultaneous instruments require one 'monochromator' channel for each element and as the provision of additional channels increases cost and complexity, the type of instrument chosen should not have more channels than is justified by the analytical application. Low power instruments (~150 W), which rely on a compact geometry, are normally restricted to 10–14 channels, while high power instruments (3 kW) can accommodate up to 30 channels.	PS WF ST				
(*b*) Sensitivity	Score maximum for the type of instrument which has adequate sensitivity and detection levels to meet analytical requirements.	VI	In general, high power instruments have better sensitivity and detection limits. However, if a low power instrument can meet analytical requirements, there is little point in using a high powered instrument.	PS WF ST				
(*c*) Excitation geometry	Score maximum for the provision of an excitation geometry designed to excite the lower surface of a sample if applications demand the analysis of liquid, powder or granular samples that cannot be prepared as brickettes.	Depends on application.	Such a geometry permits the analysis of liquid and loose powder/granular samples. This type of sample cannot be readily analysed on instruments designed to only excite the upper surface.	PS WF ST				
(*d*) Costs and services	Score maximum for the instrument with the lowest installation and operating costs and laboratory space requirements commensurate with satisfactory analytical performance.	I	See item 1(*b*) above.	PS WF ST				

The following features need only be considered for the particular category of instrument selected by the above criteria.

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
2. *Excitation*								
(*a*) Generator								
(*i*) Conventional	These generators are based on vacuum tube technology and use relatively large and heavy transformers which require water cooling.		This item is only of significance if the physical size and/or weight or cooling water requirements limit application. Conventional generators are not normally used for low powered systems.	PS WF ST				
(*ii*) Solid state	These generators are based on solid-state circuits using higher frequency oscillators and smaller step-up transformers and are, therefore, more compact. Both types of generator are normally satisfactory and it may be inappropriate to score this item.		Whilst some higher powered instruments are fitted with this type of generator, they are standard items for low powered systems.	PS WF ST				

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
(*iii*) Stability	Score maximum for instruments with the best stability specification.	VI	The tube output in current and voltage is subject to both long term drift and short term fluctuations with mains voltage. Either source of instability will affect the frequency of recalibration and the over-all performance of the instrument.	PS WF ST				
(*b*) X-ray tubes								
(*i*) Type	End window tubes are standard for simultaneous instruments.		The geometry of simultaneous X-ray spectrometers precludes the use of side window tubes.					
(*ii*) Ease of replace-ment	Score maximum for convenient tube change procedure.	I	Tubes have a finite operating life and require replacement. Therefore, it is essential that this should not be excessively time consuming or difficult. Simultaneous instruments operate under compromise conditions and it is not necessary to change tube anode type in the course of an analytical programme (*cf.* sequential XRF instruments).	PS WF ST				
(*iii*) Cooling and water supplies (high powered instru-ments only)	Score maximum for minimum flow-rate and widest tolerance to temperature, supply pressure and dissolved salts without impairing cooling efficiency.	I	All tubes and some generators on high powered instruments require cooling water. A tight specification for hardness, temperature control and flow will increase installation and running costs. Low power instruments have internal recirculating cooling systems which are air cooled and do not require an external cooling water supply.	PS WF ST				
(*iv*) Maximum power	Within the category of instrument chosen, score maximum for the maximum power that can be delivered to the tube.	I	In general, higher power will increase sensitivity or reduce analysis times.	PS WF ST				
(*v*) Maximum voltage	Within the category of instrument chosen, score maximum for the highest voltage available for a tube with the anode of interest.	I	For higher atomic number elements, K lines are more efficiently excited by tubes operated at higher voltages.	PS WF ST				
(*c*) Safety interlocks								
(*i*) Operator protection	Safety interlocks are devices to prevent injury from ionizing radiation or hazardous voltages during stand-by, operation or maintenance of the instrument and must satisfy current national and international regulations and be guaranteed by the manufacturer. Failure to meet national safety standards would preclude legal operation of the instrument.	VI	Safety devices will include warning lights and appropriate safety switches and interlocks to prevent: (*i*), access to any potential source or area of ionizing radiation whilst the excitation power is switched on; (*ii*), access to high power cable connections or mains voltage whilst electrically energised; (*iii*), operation of the tube unless it is secured in its normal position within the instrument.	PS WF ST				

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
(*ii*) Instrument protection	The flow of internal coolant and/or external cooling water must be monitored and facilities provided for automatic safe shut-down in the event of supply failure. Score additionally if the system also monitors water temperature and, where applicable, conductivity of the deionized water supply.	VI	Efficient cooling is essential to prevent tube deterioration and/or burn-out. A rise in water temperature will give early warning of partial blockage in supply lines or malfunction of heat exchanger in a recirculatory system. A rise in conductivity indicates loss of efficiency of the deionizer which, if allowed to continue, could lead to insulation break-down by high voltages present in the end-window tube.	PS WF ST				
3. *Sample changer and presentation*								
(*a*) Number of samples								
(*i*) Internal sample changer	Score maximum for provision of an internal sample changer.	I	If at least two positions are available on an internal sample changer, pump down time is reduced, improving sample throughput rate.	PS WF ST				
(*ii*) External sample changer	Score maximum for the sample changer which can accommodate the maximum number of samples that are likely to be encountered in an analytical program. Score additionally if the sample changer can be retrofitted.	I	An external sample changer is often needed to give flexible and efficient operation. If a decision is taken to retrofit this device, substantial expense could be incurred if instrument design is incompatible.	PS WF ST				
(*iii*) Sample identification	Score maximum for a system of automatic identification which enables samples to be identified positively and the analytical sequence defined flexibly.	VI	Essential if instrument is to be used for routine analysis, particularly if unattended operation is envisaged.	PS WF ST				
(*b*) Vacuum system								
(*i*) Reproducibility	Providing a level of less than 1 torr can be reached, scoring is inappropriate.	VI	Adequate vacuum within the spectrometer is essential to avoid attenuation of low energy fluorescence X-rays in the determination of light elements ($z \leq 20$, Ca).					
(*ii*) Pre-analysis pump-down	In the absence of a pre-analysis evacuation compartment, score maximum for the minimum pump-down time for sample exchange.	I	If an instrument is not designed with a pre-analysis evacuation compartment, pump-down time must be added to sample counting time when calculating total analysis time. Pump-down time may be further extended if delays are encountered in achieving an operating vacuum owing to outgassing from the sample.	PS WF ST				
(*iii*) Helium path option	If downward facing sample geometry is employed, permitting the analysis of liquids and loose powders, score for the provision of a facility to change to an atmosphere of helium within the sample chamber/spectrometer as an alternative to vacuum. Score additionally for economical use of helium.	Depends on sample type.	This option is essential if light elements are to be analysed in either liquid samples or finely divided loose powders.	PS WF ST				
(*c*) Positioning and alignment of sample	Score maximum for the best precision for locating samples in the excitation position for each position of the sample changer and in each sample holder.	VI	This feature will affect the precision of measurements as very small errors in the position of the sample with respect to the X-ray tube will change the excitation efficiency.	PS WF ST				

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
(*d*) Sample spinning	Score for the provision of a facility to rotate the sample continuously during the analysis period.	I	Averaging the excitation induced at the sample surface will compensate for effects caused by minor sample inhomogeneity and surface defects.	PS WF ST				
(*e*) Sample area irradiated and masking								
(*i*) Sample holder	Score maximum for the largest proportion of the sample area which can be excited.	I	Maximizing the area on a sample from which fluorescence radiation is detected by the spectrometer will reduce sample inhomogeneity effects and enhance detected count rates.	PS WF ST				
(*ii*) Materials and design of sample holders	Score maximum for the availability of sample holders constructed in the widest range of materials and designs.	Varies according to sample types to be analysed.	Sample holders may also yield a fluorescence signal, particularly if liquid or thin film samples are analysed. Selection of holder from a wide range of materials will enable the user to avoid such interferences. A range of sample holder designs is also required if non-standard small samples are to be analysed.	PS WF ST				
(*iii*) Masking	Score maximum for the availability of suitable masks or apertures to match each sample size that may be used.	I	The use of suitable masks to restrict excitation to the sample itself will minimize scattered radiation and unwanted fluorescence from the sample holder. Masking is particularly important when analysing small samples to avoid excitation of the sample support.	PS WF ST				
4. *Spectrometer*								
(*a*) Number of channels	Within the category of instrument selected (see 1 above), score maximum for the highest number of channels that can be fitted.	I	Flexibility of application and the capacity to fit additional channels beyond the current analytical requirements.	PS WF ST				
(*b*) Range of mono-chromators available	Score maximum for the availability of the widest range of monochromators comprising the optimum combinations of diffracting crystal and X-ray counter that cover lines of all elements that are of interest.	VI	The availability of a wide range of monochromators will enable the selection of an instrument that will maximize analytical performance in the selected application. As discussed more fully under sequential XRF instruments, a range of diffracting crystals is available in XRF together with a range of X-ray detectors (including flow proportional counters, sealed proportional counters and scintillation counters). Selection from a full list of these components will allow the instrument to give maximum detection performance for the element line selected for analysis.	PS WF ST				
(*c*) Ease of change of channel	Score maximum for the easiest and most economical method of changing channel combinations.	I	It is convenient to be able to change quickly and economically the suite of channels to meet changing requirements.	PS WF ST				
(*d*) Scanning channel	If this feature is required, score for the availability of a scanning channel which can be substituted for the minimum number of fixed channels.	I	This feature allows some instrumental flexibility when non-routine analyses are required and also provides a qualitative analysis capability.	PS WF ST				

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
5. *Electronics*								
General comment: Pulse processing electronics are replicated on each channel fitted to a simultaneous XRF spectrometer. Since a single set of excitation conditions must normally be used, it is important that the count rate response of channels is adequate for the very high count rates likely to be encountered in the measurement of matrix elements, as well as the low count rates that may be encountered simultaneously in other channels in the measurement of minor and trace elements.								
(*a*) Pulse processing								
(*i*) Window selection	Electronic windows are selected to limit the acceptance of X-ray pulses from the detection system. Providing this facility is available on each channel, it may be inappropriate to score this feature.	VI	A minimum voltage threshold must be set to exclude electronic noise. It is beneficial to set an upper threshold to exclude pulses that originate from higher order diffractions that will contribute to the background count rate.					
(*ii*) Pulse height depression	Score for the provision of effective electronic compensation for change of pulse height distribution as a function of count rate. Providing this facility is available on each channel, it may be inappropriate to score this feature.	VI	Pulse-height depression occurs progressively at count rates above about 10^4 counts per second owing to changes in electric fields within gas proportional counters. The depression, if uncorrected, may cause the analytical signal to drift out of the electronic window set by the pulse height analyser when samples of varying count rate are measured.					
(*iii*) Maximum usable count rate	Score maximum for the highest count rate for which individual channels will yield a linear response.	VI	Provided detection systems retain a linear response over a wide dynamic range, a wide range of elemental concentrations can be measured under fixed excitation conditions. Analysis times are then minimized as excitation conditions do not need to be compromised by the need to constrain count rates on channels measuring matrix elements.	PS WF ST				
(*iv*) Dead-time correction and linearity	Score highly for accurate dead-time correction up to the maximum usable count rate. The accuracy of the dead-time correction may be tested by measuring the count rate response of individual channels with variations in tube current (providing the response of the tube generator is linear).	VI	Dead time time arises from the ability of the counter to respond to a second X-ray event detected a short time after the first and the inability of the amplifier to distinguish between two events occurring within the resolving time of the electronic circuits fitted to individual channels. Both of these effects could lead to systematically low measurements at high count rates, unless the appropriate correction is made.	PS WF ST				
(*v*) Total count capacity	Score maximum for the maximum number of counts that can be registered by individual channels.	VI	The limitation on the maximum number of events that can be accumulated in any individual channel used to measure matrix elements may reduce precision in the determination of minor or trace elements being measured concurrently by other channels. This limitation arises because of the necessity to reduce count times to those appropriate to the channels with the highest count rate.	PS WF ST				

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
6. *Computer*								
(*a*) Automation								
(*i*) Instrument control	Score maximum for the greatest number of instrument functions that are under computer control.	VI	Computer control of instrumental parameters ensures reliable and reproducible operation of the instrument by well-trained, but non-expert operators. This prevents instrumental errors (*e.g.*, conflicting settings) which could lead to instrumental malfunction, or even damage. Furthermore, computer control is essential to facilitate operation for extended periods, even when a number of parameters need resetting during such a period of automatic operation.	PS WF ST				
(*ii*) Operating programme	Score maximum for a user friendly operating system which permits the user to develop versatile analytical programmes tailored to the application.	I	Difficult or repetitive interaction and complex access codes can lead to errors. The use of 'soft' keys or other devices for reducing setting up times minimizes training requirements.	PS WF ST				
(*iii*) Instrument	Score maximum for the most comprehensive display of instrument status parameters and alarm functions that monitor whether the instrument is operating within its design envelope.	I	A comprehensive display of instrument parameters will confirm to the operator that the required analytical programme is being followed. Effective monitoring of instrument status will give early warning of malfunction.	PS WF ST				
(*b*) Data processing								
(*i*) Quantitative	Score maximum 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 fundamental parameter procedures; (3), facilities to output and store results for further processing and comparison, as well as editing data into a report format; (4), the facility to transfer data files in computer format to an external compatible device; (5), statistical process control software for quality control applications.	VI	Raw data can rarely be used to calculate quantitative analyses directly. In quality control applications, statistical treatment of sets of measurements is normally essential before these data can be interpreted meaningfully.	PS WF ST				
(*ii*) Qualitative analysis	Score, if appropriate to the application, for the maximum wavelength range that can be scanned and for effective display, peak identification and hard copy facilities for the interpretation of spectral data.	May be I, depending on application.	Qualitative analysis is not normally performed on simultaneous X-ray fluorescence instruments. However, when available, the capability of qualitative scans is valuable for trouble shooting (*e.g.*, the assessment of unsuspected spectrum overlap interferences) and in the determination of 'extra' elements for which there is no fixed channel and for qualitative identification of non-routine samples.	PS WF ST				

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
7. *Installation and services*								
(*a*) Instrument footprint	The bench and/or floor space and the floor loading required for the instrument.	Varies with location but may be VI.	The instrument must be laboratory/plant compatible to avoid expensive alterations.	PS WF ST				
(*b*) Services								
(*i*) Environ-mental control	Score maximum for minimum requirements for environmental control (temperature, humidity, vibration, *etc.*) necessary to enable the instrument to operate within its design specification.	VI	Additional costs may be considerable in providing services to control environmental requirements. Service specifications may be particularly important if the instrument is to be operated in a plant environment.	PS WF ST				
(*ii*) Electrical	Score maximum for compatibility with existing electrical supplies with regard to loading, stability, phase requirements, earth specification and tolerance to transients.	May be I.	Provision of alternative power supplies may significantly increase installation costs.	PS WF ST				
(*iii*) Cooling water	Evaluate costs for the provision of a cooling water supply and score maximum for lowest costs.	I	Requirements for large volumes of cooling water or the installation of a recirculating cooling water system can significantly increase running costs.	PS WF ST				
(*c*) Service and spares	Enquire as to local arrangements and score accordingly.	VI	Cost of consumables and spares and the availability of service may affect down-time and running costs.	PS WF ST				
(*d*) Training facilities, effective documen-tation and technical support	Enquire as to local arrangements and score accordingly.	I	Good technical support can reduce commissioning time and improve the analytical efficacy of the instrument.	PS WF ST				
8. *Safety considerations*	In the UK, construction of instrumentation and all safety interlocks must comply with the appropriate legislation including the Ionising Radiations Regulations 1985. Other countries have similar National Regulations with which instrument design and construction must comply.	VI	Apart from the obvious hazard, operation of instrumentation in contravention of statutory regulations is illegal.					
9. *Extraneous leakage of radiation*	The lowest possible extraneous leakage of radiation from instrumentation should be aimed for. Score additionally for extra features that minimize extraneous radiation.	VI	Exposure to any X-ray radiation is undesirable and legally enforceable limits apply in most countries.	PS WF ST				
				Sum of sub-totals				
10. *Value for money* (Points per £)	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.	I	'Simple' instruments are often good value for money, whereas those with unnecessary refinements are often more costly.	PS WF ST				
				Grand Total				