Report by the Analytical Methods Committee

Evaluation of analytical instrumentation. Part II. Revised 1998. Atomic absorption spectrophotometers, primarily for use with ETA furnaces

Analytical Methods Committee

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A method is provided for comparing the features of atomic absorption spectrophotomers, primarily for use with furnaces.

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. M. Barnard, Dr. C. Burgess, Professor S. J. Hill, Dr. K. E. Jarvis and Mr. D. Squirrell, 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 that are not always easily comparable. The objective of the Instrumental Criteria Sub-Committee is 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 between instruments to be made.

The overall 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. It is perhaps pertinent to note that a number of teachers have found the reports to be of use as a teaching aid.

No attempt has been made to lay down a specification. In fact, the Committee considered 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 from manufacturers.

This report of the Sub-Committee, a revision of the report published in 1985, deals with instrumentation primarily designed for Furnace Atomic Absorption. There have been many advances since the first report: in particular, the use of computers and software to control instrument functions, to process data and provide data acquisition facilities. The automation has given large improvements in reproducibility and accuracy, since the first report was published. Use of boosted Hollow Cathode Lamps and the determination of a number of elements by hydride generation has also been included.

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 the users to decide a weighting factor according to their own needs.

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 will be indicated by the abbreviations 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.*, $\times 1$ to $\times 3$, or $\times 1$ to $\times 10$. The factor could amount to total exclusion of the instrument.
3. (ST) Sub-total. This is found by multiplying PS by WF.

Furnace ASS is now a very well established analytical technique with applications in many areas. Most of them are now routine, running on automatic machines. An often bewildering range of instrumentation is available from well over twenty manufacturers. Systems range from relatively simple instruments, with limited sample and data handling capabilities to powerful instruments with extensive data and automation capabilities.

Selection of a suitable instrument for purchase is, therefore, not an easy task and the purpose of these notes is to provide some guidance to areas which should be considered so that the choice is based on a full consideration of the available options. However, the performance of any instrument used for trace metal analysis depends primarily on the preparation conditions, and if test exercises are used in the evaluation a reliable method of preparation and presentation for the levels being examined must be available. The type of instrument will also influence the sensitivity, although selectivity varies very little. A number of instruments may thus be suitable, although different sample preparation procedures may be required for instruments sensitive to dissolved solids.

The first task in the selection of an instrument is to examine the range of analyses that it will be expected to perform. Care

uses change with time. The analytical scientist should also not try to envisage every potential application or the selection criteria may become too detailed.

The choice of the introduction device and the available built-in source supplies are outside the scope of these guidance notes but any specific requirements should be noted, such as the efficient use of small sample volumes.

With these requiremens in mind, the user should then evaluate the instruments available on the market while taking consideration of the guidelines and any financial limitations. In many instances it will quickly become clear that a number of different instruments could be satisfaa3ket while taking

Feature	Definition and/or test procedure and guidance for assessement	Importance	Reason	Score		
(*c*) Call-out time	Adequate service personnel readily available, minimizing the call-out time.	I/VI	Keeps laboratory in operation by reducing down time [see also (*a*)].	PS WF ST		
(*d*) Effectiveness of service engineers	The ability of the service engineers, as judged from previous experience and reports of others, including the carrying of adequate spares.	I	Ability to repair on-site avoids return visit or removal of equipment for off-site repair, so reducing down time, and may also reduce service costs.	PS WF ST		
(*e*) Costs of call-out and spares	Score for reasonable cost per hour and spares.	I	The proximity of the service center may be a factor in travel costs.	PS WF ST		
(3) Technical support	As in (2) score in consideration of sub-features (*a*) to (*d*) below:					
(*a*) Advice from Applications Laboratory	The advice and training available from the manufacturer's applications department is often very useful.	VI for new user	This helps in-house staff to maximize the use of the equipment and with problems on new applications.	PS WF ST		
(*b*) Technical literature	The range and quality of technical literature, including the operating manual.	VI	Guidance on optimum use of instrument suggests manufacturer's awareness of applications.	PS WF ST		
(*c*) Telephone assistance	Willingness of the manufacturer/ supplier/contractor to give advice over the telephone. This can normally be evaluated by reference to existing users.	I	Rapidly available technical help reduces the number of call-outs and enhances productivity.	PS WF ST		
(*d*) Customer's maintenance	Score for availability of facilities for the user to perform routine maintenance, *viz.* cleaning and replacing utility items, such as nebulizers and detectors.	I	Reduces call-out costs for simple maintenance procedures.	PS WF ST		
Instrumental criteria						
(1) Hollow cathode lamp supply						
(*a*) Number of lamp stations	Number of lamps under operating conditions should be commensurate with the analytical requirements, bearing in mind the possible use of multi-element lamps.	I	Economic (speed of analysis *versus* financial commitment).	PS WF ST		
(*b*) Modulation	Type and frequency—score high for electronic modulation at non-multiples of mains frequency and also for the highest frequency.	I	Suppression of unwanted dc signals, and rejection of mains noise and low frequency noise from the nebulizer and gas flows.	PS WF ST		
(*c*) Method of lamp alignment	Two-axis adjustment by accessible controls preferred. Score extra if this facility is automatic.	I	Accurate alignment of source on optical axis.	PS WF ST		
(*d*) Boosted hollow cathode lamp supply	An additional supply is required to run the boosted discharge lamps. Score maximum for best short and long term stability for a built-in unit.	I	A boosted lamp supply powers a secondary discharge to remove residual ground state atoms from the primary discharge. This results in narrower lines, which improves sensitivity, linearity and detection limit. They are particularly useful in the short ultraviolet region, where the increased brightness also improves the signal to noise ratio.	PS WF ST		
(2) Atomiser						
(*a*) Alignment	Maximum score for automatic stable, lateral, rotational and vertical adjustment with good accessibility.	VI	Alignment of furnaces critically affects reproducibility and sensitivity.	PS WF ST		
(*b*) Electrical contact	Score maximum for greatest area of contact compatible with robustness and simple replacement of tube.	VI	Consistent low contact resistance ensures reproducible heating cycles and increases lives of tube and furnace.	PS WF ST		

Feature	Definition and/or test procedure and guidance for assessement	Importance	Reason	Score
(*c*) Tube dimensions	Score highest for smallest tube with a sample capacity of 25 µl and with an ability to hold a platform with a sample capacity of at least 10 µl.	VI	Small tubes heat up rapidly, whereas large tubes simplify sample handling and give longer residence time. This recommendation is thought to be a reasonable compromise between conflicting requirements.	PS WF ST
(*d*) Accessibility for sample introduction	Score highest for furnace with ready access. Also see Section 10 for auto sample.	I	Facilitates manual sample introduction and may allow use of slurries and solid samples.	PS WF ST
(*e*) Purge gas entry	Score highest for gas entry at end of tube with exit in the middle.	I	Reduces non-specific absorption and fogging of windows, if fitted.	PS WF ST
(*f*) Ease of change to flame operation	Highest score for simplicity of change-over.	I	Self-explanatory.	PS WF ST
(*g*) Cooling system coatings	Score highest for most rapid cooling, with reasonable economy of gas or water.	I	Speeds up analysis and improves reproducibility of operating conditions and analytical results.	PS WF ST
(*h*) Tube composition and coatings available	Score highest for the widest range of materials.	I	Some coatings, *e.g.*, pyrolytic, increase sensitivity for some elements and reduce certain interference.	PS WF ST
(*i*) Tube replacement and ease of cleaning	Score highest for simple dismantling of tube and workhead.	I	Regular cleaning is required to prevent build up of contamination on tubes and furnace structure.	PS WF ST
(3) Atomiser power supply				
(*a*) Maximum temperature	Score highest for highest temperature attainable.	VI	Higher temperature facilitates the determination of refractory elements.	PS WF ST
(*b*) Maximum heating rates attainable	Score highest for fastest temperature rise time.	VI	Higher temperature rise rates increase sensitivity for some elements and minimise matrix interference.	PS WF ST

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Feature	Definition and/or test procedure and guidance for assessement	Importance	Reason	Score				
(*d*) Slits	Score minimum for fixed slits, intermediate for stepwise adjustment and highest for continuously variable. Score additionally for height adjustment.	I	Spectral discrimination and control of luminous flux.	PS WF ST				
(*e*) Grating, mount and blaze	Modified Czerny–Turner mount, generally preferred to Ebert or Littrow, as stray light characteristics are better. Score highest for blaze angle nearest to the wavelengths of most interest.	I	Suitable blaze angle required to ensure adequate radiation throughput throughout the range of interest. The useful working range is approximately from two to three times the blaze wavelength, the fall of efficiency being particularly sharp near to the short wavelength limit.	PS WF ST				
(*f*) Wavelength								
(*i*) Read-out precision	Four-figure digital read-out preferred for manual instruments.	I	Ease of re-setting instrument if it is not automatic.	PS WF ST				
(*ii*) Repeatability	Score highest for smallest range of transmission readings following re-setting to a previously located line.	I	Ability to locate analytical wavelength consistently.	PS WF ST				
(*g*) Number of reflective and refractive elements	Score highest for minimum number of optical elements. Score additionally for quartz coated optics.	I	Maximum energy throughput with minimum scatter. Coated optics increase the life of the instrument.	PS WF ST				
(*h*) Background correction	Score highest for widest wavelength range for which background can be corrected. Score additionally for ease of replacement of source, if present. (See Note *ii*)	I	Particularly important if ETA is to be used, or when samples with very high solids content are analysed using a flame.	PS WF ST				
(*i*) Dispersion, resolution and resolving power	Score highest for small angular deviation and high angular dispersion, also small reciprocal linear dispersion, high resolution and high resolving power.	NVI	Normally adequate for AAS, but many performance parameters are improved by the use of high quality optical components.	PS WF ST				
(*j*) Slewing speed	Score highest for maximum speed. For automatic instruments score maximum for speed and accuracy and ability to identify lines unambiguously.	NVI	The speed of analysis for automatic instruments will be higher if time is not wasted by slow slewing rates.	PS WF ST				
(*k*) Single or double	Double beam preferred for long continuous sample runs. Single beam for lower cost and better sensitivity.	NVI	Double beam eliminates any residual drift resulting from the source. This is only of importance when extended long continuous sample runs are contemplated, *e.g.*, auto-sampling. Single beam systems may be preferred for lower costs and minimum detection limits.	PS WF ST				
(5) Gas control system								
(*a*) Gas stop mode	Score for availability.	VI	'Gas Stop' improves sensitivity for many elements as a result of longer resistance time of the atoms.	PS WF ST				
(*b*) Number of gas inlets	Score highest for highest number.	I	Additional gas inlets are required to handle inert gas and hydrogen (to improve sensitivity for some elements) and possibly oxygen to speed ashing.	PS WF ST				
(*c*) Flow rate indicators	Score highest for digital indication.	I	Repeating conditions of use can only be realized with accurate information.	PS WF ST				

Feature	Definition and/or test procedure and guidance for assessement	Importance	Reason	Score				
(6) Detectors	Score highest for the availability of a photomultiplier tube which meets most requirements, and score additionally for ease of interchange with alternative photomultipliers.	I	A suitable photomultiplier is required to cover the wavelength range for the lines of the elements of interest. Where one photomultiplier cannot give sufficient spectral range, ease of interchange is important. The ability of the readout to attain working stability, rapidly is also important.	PS WF ST				
(7) EHT supply								
(*a*) Voltage range	Score highest for widest range and digital readout of applied voltage.	I	A wide range of applied EHT allows for the flexibility of adjustment of other instrument parameters, while digital readout aids reproducible instrument operation.	PS WF ST				
(*b*) Means of adjustment	Adjustment by calibrated control preferred. Automatic adjustment of EHT is not desirable.	I	A consistent signal to noise ratio can only be achieved by operaiton at constant EHT.	PS WF ST				
(8) Amplifier								
(*a*) Type	Synchronously demodulated 'lock-in' normal; score highest for this type with largest number of attenuation ranges. The processing can be done almost completely in the digital mode, but if the signals and/or background are noisy, a fairly powerful computer will be required.	VI	Operational versatility and removal of any dc signals. Note: Some instruments use digital data processing. The known timing of the signals from sample, background and instrument zero permits the signal to be extracted from the noise and to be deconvoluted from the background without the need for a lock-in amplifier.	PS WF ST				
(*b*) Integration and peak retrieval facilities	Score for availability of both peak height and area modes. Score additionally for widest range and highest speed.	VI	Area measurements may reduce effects of variable matrices and improve accuracy. Providing the amplifier has sufficiently fast response, peak height retrieval gives the best precision.	PS WF ST				
(*c*) Time constants	Score highest for fastest response.	VI	Signal rise times and atom residence times are short when using ETA. Ability to measure rapidly changing signals is, therefore, essential.	PS WF ST				
(9) Output								
(*a*) Read-out type	Score highest for availability of analogue, digital, printer and graphics output.	VI	Digital read-out with printer is particularly suitable for quality control applications and measurement of small signals. Analogue and graphics outputs are beneficial when measuring transient peaks.	PS WF ST				
(*b*) Interface	Score highest for suitable interfaces.	I	Compatibility with available computers, printers or other data systems.	PS WF ST				
(*c*) Curve fitting software	Score highest for the availability of statistically valid procedures.	I	Least squares methods and hyperbolic or polynominal curve fitting allow the use of moderately curved calibration functions without significant loss of precision or accuracy.	PS WF ST				
(10) Amenities	These items will have varying importance to different users and should be scored and rated accordingly							
(*a*) Modular construction	Self explanatory.		Allows expansion of system to meet changing needs.	PS WF ST				

Feature	Definition and/or test procedure and guidance for assessement	Importance	Reason	Score
(*b*) Bench space required	Self explanatory.		The instrument must fit the laboratory or expensive modifications may be needed.	PS WF ST
(*c*) Services	Electrical, plumbing, drainage.		Installation of additional services (*e.g.*, 3 phase power) will increase the cost of installation.	PS WF ST
(*d*) Automation	Various items such as sample presentation, lamp selection, wavelength setting, slit setting, furnace and burner operation may be automated.		Items such as auto-samplers are essential for some users (*e.g.*, ETA), while other automation may be desirable if large numbers of samples are to be handled. Automation also reduces operator errors and invariably improves precision.	PS WF ST
(*e*) Availability of major accessories and updates	Enquire about manufacturer's policy on updates of software and compatibility of present and future accessories.		Future analytical requirements.	PS WF ST
(11) Program of operational parameters for furnaces				
(*a*) Stages in operational cycle	Number of independently programmable heating cycles, minimum requirement 'dry', 'ash', 'atomise' and 'clean' cycles. Score extra for additional 'ash' and 'dry' stages.	I	The four basic stages are essential for all matrices. Ability to vary drying and ashing stages in steps may greatly reduce matrix ef1Tj 0.5D (s4)Tj 4.5 TD to vary drying and ashing stages in	

Feature	Definition and/or test procedure and guidance for assessement	Importance	Reason	Score
(*d*) Range of sample sizes	Score highest for widest range of sample size without undue loss of precision, bearing in mind furnace capacity.	NVI	Flexibility and convenience.	PS WF ST
(*e*) Control system	Score highest if linked to the computer that controls furnace operation.	I	Improves degree of automation. Replication combined with on line statistics can ensure analysis is performed to present confidence limits.	PS WF ST
(13) Over-all performance				
(*a*) Base line stability (See Notes *ii, iii* and *iv*)	With the furnace in position, allow 30 min for spectrometer to warm up, then take readings at 2 min intervals for 1 h. Take a further 30 readings at 2 min intervals, each after injecting 10 μl of 1% sodium chloride solution using the following program: dry at 100 °C, 30 s ash at 800 °C and 2 s, atomise at 3000 °C, followed by 4 s clean at			

Feature	Definition and/or test procedure and guidance for assessement	Importance	Reason	Score				
(*v*) Curve correction	Use the curve correction facility to linearise the calibration function and analyse a solution with a known concentration which is independent of the calibration and a nominal absorbance of 1.2–1.5. Score highest for the nearest result to the given concentration.	I	Self explantory.	PS WF ST				
(14) Value for money Points per £	Sum of previous sub-totals divided by the purchase price of the instrument. Subject to proportional scoring and weighting factor as for previous features. Include ST in Grand Total.	I	Simple instruments are often good value for money, whereas those with many refinements are often costly.	PS WF ST				
				Grand Total				

Notes

(*i*) The efficiency of most background correction systems depends on the availability of equal time constants in both channels of the amplifier and the ability to match both size and intensity for both channels. Conventional background correction is effective for most situations, but is unable to deal with a structured background. Alternative systems, such as Zeeman or Smith–Hieftje, are now used routinely and do not require a separate source. A test of the efficiency can be made by evaluating the effect of a 1000-fold excess concentration of aluminium (as the chloride) on the analysis of a suitable level of arsenic at 193.7 nm. This is most easily performed using a direct graphics output, but satisfactory evalution can be made using a conventional output if the analysis is repeated in the absence and presence of aluminium.

(*ii*) Choice of test matrix
The user can employ any matrix of interest; the possibilities include, sea-water, urine, blood, aluminium chloride* and plant materials. However, the Sub-Committee suggests that convenience may lead to the choice of something more generally available, such as 1–5% sodium chloride solution for most tests.

(*iii*) Measurements can be made using a high speed recorder. Normally, they would be obtained as a digital readout from the instrument and printer, a digital interface, as a database on a floppy disk or a portable hard drive. In all cases, the peak retrieval facility and both results should be used and both results should be recorded.

(*iv*) Choice of test element. The user can employ any element(s) thought to be of importance. Some possibilities are as follows.

Arsenic at 193.7 nm: evaluates performance at the far ultraviolet end of the instrument's range.

Lead at 217.0 or 283.3 nm: a commonly analysed element, which is relatively volatile and which may be incompletely resolved from an inorganic matrix.

Cadmium at 228.3 nm: this element can be determined with high sensitivity, but can be difficult to measure in the presence of even simple matrices, such as sodium chloride.

Chromium at 357.9 nm: element with primary analytical line near the end of the range of the background correction for deuterium arc lamp systems.

(*v*) In the importance column I stands for important, VI for very important and NVI for not very important.

* Makes considerable demands on background correction facilities if a matrix such as aluminium chloride is used.

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