Report by the Analytical Methods Committee

Evaluation of Analytical Instrumentation. Part III. Polychromators for Use in Emission Spectrometry with ICP Sources

Analytical Methods Committee
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A method is provided for comparing the features of polychromators for use in emission spectrometry with ICP sources.

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), Professor E. Bishop, Mr. N. W. Barnett, Dr. L. Ebdon, Dr. E. J. Newman (from October, 1984), Mr. D. Squirrell, Dr. P. Smith (until April, 1985) and Mr. A. Westwell (until June, 1984) 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 to then 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 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 by manufacturers.

This third report of the Sub-Committee deals with polychromators for use in emission spectrometry with ICP sources.

Notes on the Use of this Document

Column 1. The feature 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 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 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.*, ×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.

INSTRUMENTAL CRITERIA SUB-COMMITTEE INSTRUMENT EVALUATION FORM

Type of Instrument: Polychromator for Use in Emission Spectrometry with ICP Source.

Manufacturer:								
Model No:								
Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
1. *Resolving Power* in the wavelength region of interest	Maximum score for highest values of $\lambda/\Delta\lambda$. $\Delta\lambda$ is the smallest difference between two wavelengths that can be distinguished as two spectral lines (normally separation at half height). Suitable line pairs for this test are listed in the Appendix.	VI	In emission spectroscopy it is essential to be able to measure a line of interest in a complex spectrum.	PS WF ST				
2. *Linear dispersion*	Maximum score for the highest value of $\Delta x/\Delta\lambda$. Δx is the distance between two spectral lines differing in wavelength by $\Delta\lambda$.	I	The linear dispersion will govern the number and proximity of exit slit/detector assemblies which can be mounted in the focal plane.	PS WF ST				

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
3. *Wavelength range*	(*a*) The instrument *must* cover the spectral range which encompasses the lines of interest to the user. (*b*) Score additionally for an extended range.	VI NVI	Whilst it is obviously necessary for the user to be able to select the principal lines of interest, it is advantageous to be able to select other lines of occasional interest.	PS WF ST				
4. *Number of channels*	Maximum score for the highest number that can be supplied by the manufacturer as standard.	I	The greater the number of channels the greater the versatility of the spectrometer, enabling the measurement of the widest range of lines. This permits measurements at both atom and ion lines and the selection of other suitable lines to minimise interferences.	PS WF ST				
5. *Ease of changing channel/line combinations*	Score maximum for the easiest and most economical method of changing channel/line combinations.	I	It is convenient to be able quickly and economically to change the suite of lines to meet changing requirements.	PS WF ST				
6. *Number of lines available for use*	Maximum score for the highest number of relevant lines available on the instrument.	I	The least desirable feature of emission spectroscopy is spectral interference. The greater the number of lines to choose from, the greater the chance of avoiding such interference.	PS WF ST				
7. *Effect of varying light levels*	Using a suitable source, *e.g.*, a hollow cathode lamp run at high current or an electrodeless discharge lamp, measure the signal resulting from this high intensity source. Insert a flag filter to reduce the intensity by a factor of 10 000 and repeat the measurement. This experiment should be repeated rapidly 20 times and the standard deviation and mean at each level calculated. Various sources should be used to cover the wavelength range of interest. There should be no statistically significant difference between the initial and final reading. [Analysis of co-variance (ANOCOV) table.] Score accordingly.	VI	In routine use the photomultiplier tubes of the polychromator will be subjected to rapidly changing light levels and this must not affect the response of the PMT to a given level if quantitative measurements are to be reliable.	PS WF ST				
8. *Stray light*	A He - Ne laser should be used. The signal at 632.8 nm should be substantial, so that a large amount of light enters the spectrometer. Measurements of this signal at minimum gain should be obtained, together with measurements at 631.8 and 633.8 nm made at high gain. Score maximum for the minimum ratio of readings at the other wavelengths to those obtained at 632.8 nm. Other channels, particularly at short	VI	As well as light loss, stray light produces unwanted and variable background readings.	PS WF ST				

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
	wavelengths, should be interrogated using high gain.							
9. *Light gathering power*	This is the minimum amount of energy that can be detected at a suitable selection of wavelengths covering the instrument's range. Use a calibrated tungsten lamp at the normal source position of the spectrometer, focused by the spectrometer lens on the slit. An iris diaphragm, suitably positioned, will determine the useful solid angle, *S*, subtended by the source. If the area of the slit is *A* and the magnification of this image, *M*, the energy passing into the spectrometer is $\frac{BAS\,\Delta\lambda}{M}$ where *B* is the spectral radiance of the source (watts steradian^{-1} cm^{-2}) and $\Delta\lambda$ the spectral band width. The diaphragm should be closed until a very small net signal is obtained, the result being expressed as counts W^{-1}. Score maximum for the highest value for this function.	I	The light gathering power of the polychromator will affect the sensitivity of the instrument (see Appendix).	PS WF ST				
10. *Short term stability*	Using a stabilised light source, such as a hollow cathode lamp or low pressure mercury lamp, produce a series of readings at one per minute for 30 min. This should be repeated using suitable attenuation to cover the dynamic range of the instrument. The system should be allowed to stabilise between each set of measurements. Score maximum for the lowest standard deviations. Drift should be essentially absent over the period of the measurements.	VI	If the polychromator is not stable, within acceptable limits, for short periods it will not be possible to obtain useful quantitative results.	PS WF ST				
11. *Long term stability*	Using conditions similar to those for the middle of the dynamic range used in test 10, produce a set of readings at a rate of two per hour for 24 h, or if this is impracticable, over 2 consecutive working days. Score maximum for lowest standard deviation and minimum drift.	VI	If the instrument is to be used in conjunction with an automatic sample changer, long-term stability is essential. Long-term use of stored calibration functions also calls for long-term stability.	PS WF ST				
12. *Temperature stability*	Maximum score for the widest range of ambient temperatures over which the stabilities as determined above can be guaranteed by the supplier/ manufacturer.	VI	The shorter the temperature range over which the instrument will function at full efficiency, the more complex and expensive will be the required laboratory temperature control system.	PS WF ST				

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
13. *Slit geometry and selection*	Vertical rather than horizontal slits are more compatible with the plasma source geometry. Curved slits are claimed to be preferable to straight slits. Preference should be given to instruments with a selection of entrance and exit slits.	I	The region of maximum signal to background in a plasma source is a small vertical region which is readily matched by vertical slits, minimising critical adjustment of the source. The image of the entrance slits at at the Rowland Circle is curved and theoretically light losses are minimised by compensating for this by using curved slits. A choice of slit widths and heights is beneficial in selecting conditions to maximise signal to noise and background ratios and minimise interferences. This choice may be made by the manufacturers.	PS WF ST				
14. *Grating*	The properties that are affected by such considerations as ruled or holographic gratings, blaze angle, etc., are light gathering power and stray light, and these have been dealt with under the appropriate headings.			PS WF ST				
15. *Focal length*	The properties that are most affected by focal length, such as dispersion, stability, and light gathering power, have been dealt with under the appropriate headings.			PS WF ST				
16. *Computer compatibility* (*a*) Sophistication	Score maximum for the greatest extent to which the instrument is under computer control. Further score for ease and provision of high level language programme access.	I	A compact, easily operable system, which has speed and high capacity, greatly assists the operator to obtain accurate results quickly; it also facilitates such items as inter-element corrections, background corrections and calibrations.					
(*b*) Ouput (*i*) High quality graphics (*ii*) High speed printer (*iii*) Report for-matting (*iv*) Plotter	Score according to availability of each of these accessories and their degree of sophistication.	Will vary with user circum-stances	(*i*) Method development is often facilitated by visualisation of spectral profiles. (*ii*) Quality Control requires provision of hard copy. (*iii*) Very useful in conjunction with management systems. (*iv*) Complements graphics output for investigation of interferences and for systems and methods evaluation.	PS WF ST				
17. *Background correction (inter-element correction)*	Background correction is the compensation for extraneous radiation in the intensity of spectral lines, such as continuum overlap and stray	VI	It is possible to store blank intensities in the computer for each channel and to subtract these from the sample intensities. Although this	PS WF ST				

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
	light. Score maximum for systems which employ moveable entrance slits or refractor plates in addition to fixed slit routines.		procedure is rapid and easy to use, illconditioning can occur, resulting in error when a general elevation of background occurs. Therefore, it is more accurate to use off-peak methods. This latter method is slower but more reliable than the former.					
18. *Qualitative information*	Identification of elements other than those for which there are channels on the Polychromator. Score maximum for systems having an in-built scanning monochromator or equivalent device.	I	The ability to analyse elements (spectral lines) not programmed in the polychromator is desirable. The provision of an $n + 1$ channel permits an intensity readout from regions of the spectrum not covered by the fixed channels. Automatic scanning over user-selected spectral regions for qualitative analysis can be undertaken.	PS WF ST				
19. *Dynamic range and mode of integration*	Maximum score should be given for digital integration, however, in the absence of such a system score highly for capacitative integration using high quality polystyrene feed-back capacitors. "Cascade" methods of capacitative integration are not recommended.	VI	For the stable signal produced by the ICP, digital integration following A–D conversion is the most accurate method. However, for multi-channel instruments this approach is not currently used because of the excessive cost of the integrating A–D convertors. It is thought that current methods of signal detection and integration will always have a linear dynamic range, which will exceed the requirements imposed by the nature of the ICP source (which, in practice, does not exceed 5 orders of magnitude).	PS WF ST				
20. *Speed of analysis*	This is mainly determined by the "washout" time of the the nebuliser/spray chamber employed. This can be evaluated by measuring the time for the signal for 1000 p.p.m. of manganese or other suitable element, to decay to a level at which it has no statistically significant effect upon the precision or accuracy of the measurement of a 1 p.p.m. solution. This parameter must be used with caution as the use of a different nebuliser/spray chamber may significantly change the assessment.	I	Instruments for routine use may require a high sample throughput for economic reasons. It is important that any such required rate can be met by the instruments under consideration.	PS WF ST				
21. *Over-all performance*	A test procedure is outlined in in the Appendix. It is appreciated that most users will only perform part of the exerise	VI	Evaluation of the over-all system is essential to ensure that performance of individual components is not degraded	PS WF ST				

Feature	Definition and/or test procedures and guidance for assessment	Importance	Reason	Score				
	due to limitations of time.		when they are integrated into a complete system.					
22. *Amenities* (*a*) Bench/floor space/ weight (floor loading)	Self-explanatory.	Varies with users circum-stances.	The instrument must be laboratory compatible or else expensive alterations will be required.	PS WF ST				
(*b*) Services (*i*) Environmental control	Score maximum for minimum requirements for environmental control (room temperature and humidity) necessary to enable the instrument to operate within its specification.	VI	Additional installation costs may be considerable, if close control of environmental factors is required.	PS WF ST				
(*ii*) Electrical	Score maximum for compatibility with existing electrical supply, both with regard to loading and stability.	Varies with users circum-stances.	Additional power requirements may significantly increase installation costs.	PS WF ST				
(*c*) Servicing and spares	Enquire in detail as to local arrangements and score accordingly.	VI	Cost of spares, servicing and downtime may severely alter over-all running costs.	PS WF ST				
(*d*) Applications support	Enquire as to availability of applications support in field(s) of interest and score accordingly.	I	Time and facilities for method development may add significant costs, especially if training facilities are scant.	PS WF ST				
(*e*) Availability of major accessories and updates	Enquire about manufacturers' policy on updating software and compatibility of present and future accessories, score accordingly.	I	Future analytical requirements.	PS WF ST				
(*f*) Training facilities and documentation	Enquire as to local arrangements for operator training and available documentation and score accordingly.	I	Availability of efficient programme and good documentation can greatly reduce commissioning time for a new instrument.	PS WF ST				
				Sum of sub-totals				
23. *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 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				

APPENDIX

EVALUATION OF OVER-ALL PERFORMANCE

Although the performance of each component of the instrument is evaluated individually it is desirable to make some evaluation of the over-all system performance. It is also appreciated that light gathering power (test 9) can be as easily tested by an evaluation of sensitivity as part of a test of over-all performance.

The items for consideration can be summarised as: precision; sensitivity (detection limit, related to sensitivity and precision); accuracy (comparison of subsequent readings with calibration value); drift (calibration shift); freedom from spectral interference (resolution); linear dynamic range and analytical range. Ideally, every channel of the instrument should be evaluated over its full working range and the following experiment is designed to permit this evaluation. However, in practice this may be too time-consuming or impractical. It is recognised that only a limited number of channels can be tested. If such a truncated experiment is envisaged, it is *essential* that it is applied equally to each of the instruments under evaluation.

Experimental

1. For each channel to be tested, prepare five standard solutions; the lowest should have a concentration corresponding to about one order of magnitude above the detection limit. The other four should be prepared at intervals of about an order of magnitude so that a total of 5 orders of magnitude is covered. The preparation of such a series of solutions is facilitated by the use of a suitable automatic diluter.
2. The above solutions should be aspirated, in turn, with a blank between each solution. This can conveniently be carried out using an automatic sample changer. The measurements should, preferably, be repeated at least twice a day for a period of 2 or 3 days.

   The data system should be set to record the blank (b), the total signal (x) and the net signal ($x - b$). The values of x/b should also be computed and stored.

   N.B. It is essential to ensure that the signal has reached a steady state prior to commencing integration of the sample signal and that this signal is allowed to decay to a steady state before recording the background signal.
3. Measure the second solution in each series 30 times over a period of 1 h, then increase the instrument gain by a factor of two and repeat the measurements.
4. The interference ratio should be evaluated by spraying the strongest solution of a given element prepared as described above and recording the signal from each of the other channels. Elements particularly prone to cause interference across channels include calcium, magnesium, aluminium, iron and titanium. Comparison of results is facilitated by plotting them in the form of a histogram.
5. Resolution should be checked at several points in the spectrum by recording the spectrum of suitable elements with closely spaced lines. This test can only be carried out on instruments with a profiling facility. Suitable sets of lines include the following (in nm).

Boron	208.893 208.959	Iron	309.997 310.030 310.067	Titanium	334.884 334.904 334.941
Aluminium	237.31 237.34	Beryllium	313.042 313.107	Iron	371.592 371.645
Boron	249.773 249.678	Mercury	313.155 313.183	Iron	371.841 371.994
Germanium	265.12 265.16	Titanium	319.08 319.20	Iron	372.256 372.438
Aluminium	257.41 257.44	Sodium	330.23 330.30	Iron	390.648 390.794
Aluminium	309.27 309.28			Titanium	522.430 522.493

Treatment of Results

The first set of results should be used to establish the calibration function, x/b *versus* (concentration). This will permit a check on the linear dynamic range of the instrument. Statistical examination of the residuals will give additional information on the efficiency of the curve fitting programme. Subsequent sets of results should be compared with the initial set to provide information on instrument drift, which will affect accuracy, if the common practice of calibrating daily is envisaged. Non-superimposable plots will indicate drift. Data should not be presented or analysed in the form of log - log graphs, as quite large differences in signal show only as small shifts in the graphs. Individual points can be compared by calculating the standard deviation of the residuals of the replicates, while if desired the total plot of each set of data can be compared by means of a multi-tailed "F-test" (or analysis of co-variance) using the residuals.

Short-term precision should be evaluated by calculating the standard deviation of (x/b) for the second set of results. The mean of (x/b) for each set will give a measure of the accuracy if compared with the computed value from the first set of results.

A graph of RSD *versus* log x/b will provide a plot from which the analytical range and the detection limit can be computed.

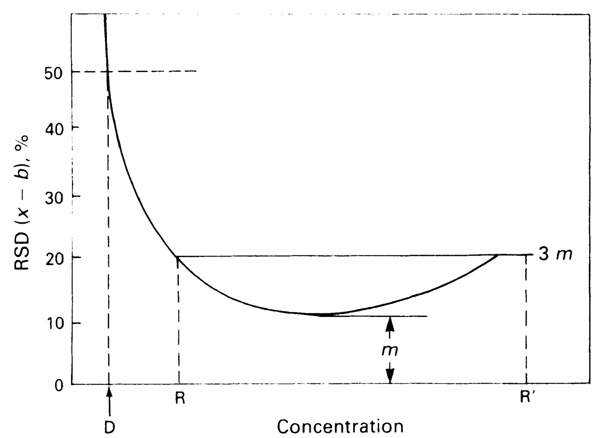

Fig. 1. Graph of relative standard deviation ($x - b$) *versus* concentration (log x/b)

The detection limit (D) is by popular definition the point at which the RSD of x/b = 50% and is accepted for the purposes of this document. However, the actual definition is unimportant, provided that it is consistantly applied. The analytical range R′−R is the range over which the function has values of less than, for instance, three times the minimum value, m. These values can be expressed in terms of log x/b, which is directly related to concentration. The lower the value of D and m and the greater the value of $R'-R$, the better the performance of the instrument.