# Report by the Analytical Methods Committee

## Evaluation of Analytical Instrumentation. Part IV. Monochromators for Use in Emission Spectrometry with ICP Sources

**Analytical Methods Committee**
*Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN*

A method is provided for comparing the features of monochromators 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 (until July, 1985), Dr. L. Ebdon, Dr. E. J. Newman, Mr. D. Squirrell and Dr. P. Smith (until April, 1985) 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 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 fourth report of the Sub-Committee deals with monochromators 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 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 given 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: Monochromator 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 which can be distinguished as two spectral lines (normally separation at half height). Suitable lines pairs for this test are listed in the Appendix. | VI | In emission spectrometry it is essential to be able to resolve and measure a line of interest in a complex spectrum. | PS WF ST | | | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | | | |
|---|---|---|---|---|---|---|---|---|
| 2. *Wavelength range* | (*a*) The instrument *must* cover the spectral range which encompasses the lines of interest to the user. <br> (*b*) Score additionally for an extended range. | VI <br><br><br><br> NVI | Whilst it is obviously necessary for the user to be able to access the lines of interest, it is advantageous to be able to select other lines of interest, which may be used to alter sensitivity or avoid interferences. | PS <br> WF <br> ST | | | | |
| 3. *Scanning speed* (*for qualitative analysis*) | Score maximum for a wide range of scanning speeds, which will enable qualitative data to be obtained without the use of excessive amounts of sample. | I | Scanning speeds are important if qualitative information is required, as too slow a speed may require excessive amounts of sample solution, while unavailability of slow scanning rates may lead to loss of information. | PS <br> WF <br> ST | | | | |
| 4. *Measurement speed* | Select two lines near the extremes of the range of interest and measure the time required to obtain results at both lines with the required precision, including two pre-set background corrections; score accordingly. | I | This parameter defines the ultimate speed of analysis and will affect the amount of sample required and the economics of operation. | PS <br> WF <br> ST | | | | |
| 5. *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. Score accordingly. | VI | In routine use the photomultiplier tubes 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 <br> WF <br> ST | | | | |
| 6. *Stray light* | A low pressure mercury lamp should be used. The signal at 253.7 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 252.7 nm and 254.7 nm made at high gain. Score maximum for the minimum ratio of readings at the other wavelengths to those obtained at 253.7 nm. Other wavelengths, particularly short wavelengths, should be interrogated using high gain. | VI | As well as light loss, stray light produces unwanted and variable background readings. | PS <br> WF <br> ST | | | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | | | |
|---|---|---|---|---|---|---|---|---|
| 7. *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 $$\frac{BAS}{M}$$ where $B$ is the spectral radiance of the source (watts steradian$^{-1}$ cm$^{-2}$) and $S$ the spectral band width. The diaphragm should be closed until a very small net signal is obtained, the result being expressed as counts per watt. Score maximum for the highest value for this function. | I | The light gathering power of the monochromator will affect the sensitivity of the instrument (see Appendix). | PS WF ST | | | | |
| 8. *Wavelength search reproducibility* | Using a stable source, for example, a hollow cathode lamp or discharge lamp, use a normal analytical programme to search for appropriate lines. Repeat 10 times and record the mean signal and standard deviation. Repeat using the minimum scan rate and score maximum for closest agreement between two modes. | VI | Inaccurate wavelength settings will cause considerable reduction of analytical precision. | PS WF ST | | | | |
| 9. *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 monochromator is not stable, within acceptable limits, for short periods, it will not be possible to obtain useful quantitative results. | PS WF ST | | | | |
| 10. *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 | | | | |
|---|---|---|---|---|---|---|---|---|
| 11. *Slit geometry and selection* | Vertical rather than horizontal slits are more compatible with the plasma source geometry. Preference should be given to instruments with a selection of entrance and exit slits. | I | The region of maximum signal to background ratio in a plasma source is a small vertical region which is readily matched by vertical slits, minimising critical adjustment of the source. A choice of slit widths and heights is beneficial in selecting conditions to maximise signal to noise and background ratios to minimise interferences. | PS WF ST | | | | |
| 12. *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. | | | | | | | |
| 13. *Focal length* | The properties that are most affected by focal length, such as dispersion, stability, etc., have been dealt with under the appropriate headings. | | | | | | | |
| 14. *Computer compatibility* (*a*) Sophistication | Score maximum for the greatest extent to which the instrument is under computer control. Further score for ease of use and provision of high level language program access. | I | A compact, easily operable system which has high speed and capacity greatly assists the operator to obtain accurate results quickly, and also facilitates such items as inter-element corrections, background corrections and calibrations. | PS WF ST | | | | |
| (*b*) Output (*i*) High quality graphics (*ii*) Printer (*iii*) Report formatting (*iv*) Plotter | Score according to availability of each of these accessories and their degree of sophistication | I–VI depending on circum-stances | (i) Method development is often facilitated by visual-isation 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 systems and methods evaluation. | PS WF ST | | | | |
| 15. *Background correction modes* | Background correction is the compensation for extraneous radiation in the measured intensity of spectral lines such as continuum overlap and stray light. In a rapid scanning instrument it should be possible to correct for background by measurements on either side of the line of interest. Score maximum for systems with maximum versatility, *e.g.*, ability to correct using readings on either side of the line with varied weightings of the measurements or on one side only, and an ability individually | VI | Normally the best correction will be achieved by programming the computer to correct for background by subtracting the mean of the intensities on either side of the line. However, visual inspection using the graphics facility may indicate structured background and certain spectral features may make correction using only one wavelength or using a larger than normal wavelength shift advisable. | PS WF ST | | | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | | | |
|---|---|---|---|---|---|---|---|---|
| | to set the wavelengths for background correction. | | | | | | | |
| 16. *Dynamic range and mode of integration* | Maximum score should be given for digital integration, with the greatest linear dynamic range. | VI | For the stable signal produced by the ICP, digital integration following A–D conversion is the most accurate method. The source has a linear dynamic range of 5–6 orders of magnitude and the integrator should at least match this. | PS WF ST | | | | |
| 17. *Speed of quantitative analysis* | This is mainly determined by the "washout" time of 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 throughout for economic reasons. It is essential that any such required rate can be met by the instruments under consideration. | PS WF ST | | | | |
| 18. *Over-all performance* | A test procedure is outlined in the Appendix. It is appreciated that most users will only perform part of the exercise because of limitations of time. | VI | Evaluation of the over-all system is essential to ensure that performance of individual components is not degraded when they are integrated into a complete system. | PS WF ST | | | | |
| 19. *Amenities* (*a*) Bench/floor space/ weight (floor loading) | Self-explanatory. | Varies with users circum- stances but may be VI | 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. | PF WF ST | | | | |
| (*ii*) Electrical | Score maximum for compatibility with existing electrical supply, with regard to both 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*) Application 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 | | | | |

| Feature | Definition and/or test procedures and guidance for assessment | Importance | Reason | Score | | | | |
|---|---|---|---|---|---|---|---|---|
| (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 | | | | |
| 20. *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 various components of the instrument are evaluated individually it is desirable to make some evaluation of the over-all system performance. It is also appreciated that light gathering power (test 7) can be as easily tested by an evaluation of sensitivity as in this 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. A reasonable number of lines/elements should be evaluated and these should be selected to cover the normal range of the instrument. It is *essential* that the same lines should be evaluated for each instrument under evaluation.

## Experimental

1. For each wavelength 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. Preparation of such a series of solutions is facilitated by the use of a suitable automatic diluter.

2. The instrument should be set up to examine the appropriate analytical lines and the above solutions should be aspirated in turn with a blank between each solution. This would conveniently be carried out using an automatic sample changer.

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

N.B. Prior to commencing a series of measurements it is essential to ensure that the sample introduction system has reached a steady state.

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. Resolution should be checked at several points in the spectrum by recording the spectrum of suitable elements with closely spaced lines. Suitable sets of lines include the following (in nm).

Boron $\begin{cases} 208.893 \\ 208.959 \end{cases}$  Iron $\begin{cases} 309.997 \\ 310.030 \\ 310.067 \end{cases}$  Titanium $\begin{cases} 334.884 \\ 334.904 \\ 334.941 \end{cases}$

Aluminium $\begin{cases} 237.31 \\ 237.34 \end{cases}$  Beryllium $\begin{cases} 313.042 \\ 313.107 \end{cases}$  Iron $\begin{cases} 371.592 \\ 371.645 \end{cases}$

Boron $\begin{cases} 249.773 \\ 249.678 \end{cases}$  Mercury $\begin{cases} 313.155 \\ 313.183 \end{cases}$  Iron $\begin{cases} 371.841 \\ 371.994 \end{cases}$

Germanium $\begin{cases} 265.12 \\ 265.16 \end{cases}$  Titanium $\begin{cases} 319.08 \\ 319.20 \end{cases}$  Iron $\begin{cases} 372.256 \\ 372.438 \end{cases}$

Aluminium $\begin{cases} 257.41 \\ 257.44 \end{cases}$  Sodium $\begin{cases} 330.23 \\ 330.30 \end{cases}$  Iron $\begin{cases} 390.648 \\ 390.794 \end{cases}$

Aluminium $\begin{cases} 309.27 \\ 309.28 \end{cases}$  Titanium $\begin{cases} 522.430 \\ 522.493 \end{cases}$

## 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. Data should not be presented or analysed in the form of log - log graphs, as 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
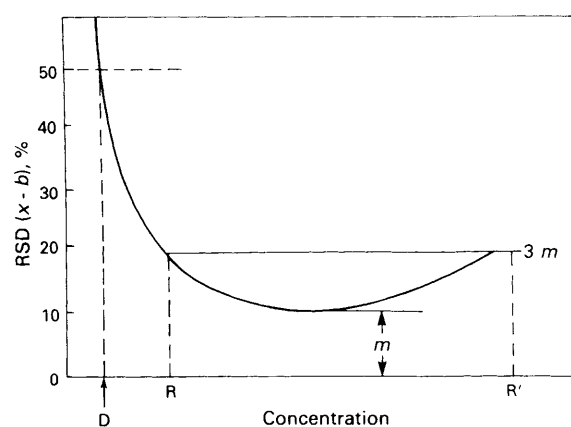


**Fig. 1.** Graph of relative standard deviation $(x - b)$ *versus* concentration (log $x/b$)

be compared by means of 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 plot of RSD *versus* $\log x/b$ will provide a graph from which the analytical range and the detection limit can be computed. The detection limit $(D, 2\sigma)$ is, by 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 consistently 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.

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## GORDON F. KIRKBRIGHT BURSARY FUND

This fund was established in 1985 as a memorial to Gordon Kirkbright and his contributions to analytical spectroscopy and analytical science in general. The aim is to enable promising young analytical scientists of any nation to visit a recognised scientific meeting or place of learning in order to further their education.

### Applications are invited for the Award of the Gordon F. Kirkbright Bursary

While there are no formal age restrictions on the award it is expected that the successful applicant will either be undertaking research towards a PhD or be in his or her first postdoctoral position.

Please write for an application form to Dr. N. W. Barnett (Vice-Chairman of the Association of British Spectroscopists), Department of Environmental Sciences, Plymouth Polytechnic, Plymouth, Devon PL4 8AA. The form must be completed and returned to the above address not later than **March 31st**, 1987.

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## RSC ELECTROANALYTICAL GROUP

### 6th International Symposium on Electroanalysis and Sensors in Biomedical, Environmental and Industrial Sciences

### UWIST, Cardiff, April 6–9, 1987

The Plenary and Keynote Lectures to be presented at this Symposium will include the following: A. G. Fogg (Loughborough, UK), "Electrochemical Pre-treatment and Chemical Modification of Electrodes"; G. G. Guilbault (New Orleans, USA) "Enzymes and Biosensors"; W. R. Heineman (Cincinnati, USA), "Immunoassay with Electrochemical Detection"; J. Janata (Utah, USA) "Integrated Solid-state Electrochemical Sensors"; H. J. Marsoner (Graz, Austria), "Quality Control and Standardisation for ISE Analysis in Clinical Practice"; C. Tran Minh (St. Etienne, France), "Biosensors for Electrochemical Analysis of Enzyme Inhibitors"; M. Otto (Freiberg, GDR), "Chemometric Principles in Electrochemical Analysis"; E. Pungor (Budapest, Hungary), "Education and Training of Non-chemist Users of Electrochemical Sensors"; and J. Wang (New Mexico, USA) "Recent Advances in Adsorptive Stripping Voltammetry".

Contributed papers will be presented as lectures or posters. Some additional contributions may be accommodated. There will be an exhibition of commercial equipment.

Further information and registration details can be obtained from the Short Courses Section (Electroanalysis Symposium), UWIST, P.O. Box 68, Cardiff CF1 3XA. Tel. (0222) 42588, Ex. 2213.