

## Report by the Analytical Methods Committee Evaluation of Analytical Instrumentation.

### Part X Inductively Coupled Plasma Mass Spectrometers

#### Analytical Methods Committee

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#### A method is provided for comparing the features of inductively coupled plasma mass spectrometry instrumentation.

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), Mr. R. Brown, Dr. C. Burgess, Dr. K. E. Jarvis, Professor S. J. Hill, Dr. P. J. Potts 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 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.

The tenth report of the Sub-Committee deals with inductively coupled plasma mass spectrometer systems, 'ICP-MS'.

#### 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 a weighting factor according to their own needs.

Column 4. Here the Sub-Committee has given reasons for users to decide on 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 sum 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 obtained by multiplying PS by WF.

Inductively coupled plasma mass spectrometry is now a well established analytical technique with applications in many areas. An often bewildering range of instrumentation is available from well over a dozen different manufacturers. Systems range from relatively simple instruments, with a quadrupole detector and limited sample handling and data handling capabilities, to magnetic sector instruments with extensive data handling 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 Mass Spectrometer will also influence the sensitivity and selectivity of the assay. A number of alternative instruments may thus be suitable, although different sample preparation procedures may be required for the different techniques.

The first task in the selection of an instrument is to examine the range of analyses that it will be expected to perform. Care should be taken not to specify these requirements too closely as 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 (nebulizer) and MS type are outside the scope of these guidance notes but any specific requirements should be noted, such as high resolution or efficient use of small sample volumes.

With these requirements in mind, the user should then evaluate the instruments available on the market while bearing in mind the guidelines and any financial limitations. In many

instances it will quickly become clear that a number of different instruments could be satisfactory and non-instrumental criteria may then be important. However, in some specialized cases only one or two instruments will have the ability or necessary features to carry out the assay. The guidelines are intended to be used as a check list of features to be considered, mostly of the instrument itself, but some also of its service requirements and of the relationship of the user with the manufacturer. Their relative importance will depend on the installation requirements of the instrument as well as the uses to which it will be put. Therefore, to some extent, the selection process will inevitably be subjective, but if all the points have been considered it should be an informed choice.

Finally, as many laboratories are now working to quality protocols and standards such as GLP/UKAS(NAMAS)/ISO9000/FDA/EPA, some consideration should be given to third party recognition of the manufacturer to standards such as appropriate ISO 9000 series. Such accreditation should extend to the service organization, which is particularly important when working to UKAS (NAMAS) or GLP criteria.

### Previous Reports in this Series from the Analytical Methods Committee

#### Evaluation of Analytical Instrumentation

- Part 1. Atomic-absorption Spectrophotometers, Primarily for Use with Flames, *Anal. Proc.*, 1984, **21**, 45.  
 Part 2. Atomic-absorption Spectrophotometers, Primarily for Use with Electrothermal Atomizers, *Anal. Proc.*, 1985, **22**, 128.  
 Part 3. Polychromators for Use in Emission Spectrometry with ICP Sources, *Anal. Proc.*, 1986, **23**, 109.  
 Part 4. Monochromators for Use in Emission Spectrometry with ICP Sources, *Anal. Proc.*, 1987, **24**, 3.  
 Part 5. Inductively Coupled Plasma Sources for Use in Emission Spectrometry, *Anal. Proc.*, 1987, **24**, 266.  
 Part 6. Wavelength Dispersive X-ray Spectrometers, *Anal. Proc.*, 1990, **27**, 324.  
 Part 7. Energy Dispersive X-ray Spectrometers, *Anal. Proc.*, 1991, **28**, 312.  
 Part 8. Instrumentation for Gas-Liquid Chromatography, *Anal. Proc.*, 1993, **30**, 296.  
 Part 9. Instrumentation for High-performance Liquid Chromatography, *Analyst*, 1997, **122**, 387.

#### Instrument evaluation form. Subject: ICP-MS

| Manufacturer/Model number                |  |            |   |                |  |  |  |  |
|--|--|------------|---|----------------|--|--|--|--|
| Feature                                  | Definition and/or test procedures and guidance for assessment  | Importance | Reason  | Score          |  |  |  |  |
| <b>Non-instrumental criteria</b>         |  |            |   |                |  |  |  |  |
| <i>Selection of manufacturer</i>         |  |            |   |                |  |  |  |  |
|  | Laboratories in possession of other spectrometers should score highest for the manufacturer with the best past record based on the following sub-features: |            |   |                |  |  |  |  |
| (a) Previous instruments                 |  |            |   |                |  |  |  |  |
| (i) Innovation                           | Company's record for instruments with innovative features.   | I          | The manufacturer should be aware of new techniques in ICP-MS.   | PS<br>WF<br>ST |  |  |  |  |
| (ii) Reliability record                  | Company's record for instrument reliability.   | I          | Reflects the company's ability to employ good design and manufacturing practices.   | PS<br>WF<br>ST |  |  |  |  |
| (iii) Confidence in the supplier         | Confidence gained from past personal experience.   | I          | Good working relationship already in place.   | PS<br>WF<br>ST |  |  |  |  |
| (b) Servicing                            | Score according to manufacturer's claims and past record, judged by the sub-features (i) to (v) below:   |            |   |                |  |  |  |  |
| (i) Service contract                     | Availability of suitable service contracts from the supplier, agent or third party contractor.   | I/NVI      | Suggests long-term commitment to user. This often ensures preferential service and guarantees a specific response time to call-outs.          | PS<br>WF<br>ST |  |  |  |  |
| (ii) Availability and delivery of spares | Range of stock carried by, or quickly available to, the manufacturer/agent/contractor.   | (VI)       | Rapid delivery of spares reduces down time and operating cost.  | PS<br>WF<br>ST |  |  |  |  |
| (iii) Call-out time                      | Adequate service personnel readily available, minimising the call-out time.  | I(VI)      | Keeps laboratory in operation by reducing down time [see also (i)].   | PS<br>WF<br>ST |  |  |  |  |
| (iv) 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 reduce service cost. | PS<br>WF<br>ST |  |  |  |  |
| (v) Cost of call-out and spares          | Score for reasonable cost per hour and spares.   | I          | The proximity of the service centre may be a factor in travel costs.  | PS<br>WF<br>ST |  |  |  |  |

| Feature                                 | Definition and/or test procedures and guidance for assessment  | Importance       | Reason   | Score          |  |  |  |  |
|---|--|------------------|--|----------------|--|--|--|--|
| (c) Technical support                   | As in (b) score in consideration of sub-features (i)–(iii) below.  | VI for new users |  |                |  |  |  |  |
| (i) Advice from applications department | The advice and training available from the manufacturers' applications department.   |                  | This helps in-house staff to maximize the use of the equipment and with problems on new applications.  | PS<br>WF<br>ST |  |  |  |  |
| (ii) Technical literature               | The range and quality of technical literature, including the operating manual.   | I                | Guidance on optimum use of instrument suggests manufacturer's awareness of applications.   | PS<br>WF<br>ST |  |  |  |  |
| (iii) 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<br>WF<br>ST |  |  |  |  |
| (iv) Customers maintenance              | Score for the ability of the user to perform routine maintenance such as cleaning and or replacing utility items, such as sampling cones and detectors.  | I                | Reduces call-out costs for simple maintenance procedures.  | PS<br>WF<br>ST |  |  |  |  |
| <b>Instrumental criteria</b>            |  |                  |  |                |  |  |  |  |
| 1. High frequency (Hf) generators       |  |                  |  |                |  |  |  |  |
| (a) Type of oscillator                  | The oscillators differ mainly in the method which is used to control the frequency of oscillation and are variously known as free running, crystal controlled, Huth–Kuhn and tuned-line oscillators. Scoring may be inappropriate (see reason).  | NVI              | The primary requirement of a generator is stability (see below). There is no scientifically credible evidence to show that any one type of generator offers superior performance for ICP-MS applications. This conclusion presupposes that any generator in question meets the requirements for stability demanded by the user, and complies with local and national regulations for Hf shielding and filtering. Newer types of generators based on solid-state devices have advantages in terms of physical size. |                |  |  |  |  |
| (b) Radiation shielding                 | All oscillators and torch boxes must be screened to prevent or minimise Hf leakage and such screening must be guaranteed to comply with the regulations of the country of operation. Score maximum for the minimum leakage, measured with a suitable meter.  | VI               | There are strict regulations in most, if not all, countries with regard to the amount of energy of specified frequencies that may be radiated from an oscillator. Stray radiation not only interferes with telecommunications, but may also affect the instrument's detector electronics and hence the signal output.  | PS<br>WF<br>ST |  |  |  |  |
| (c) Hf filtering                        | There should be adequate filtering of Hf signals on the power lines of the generator to prevent them from coupling with the power lines of any detection electronics. (There should be similar filters on the power lines of detector electronics.) Score accordingly for the presence of filters. | VI               | If any Hf leakage occurs within the generator unit, the power and earth lines can conduct Hf signals. These signals can then couple with the detector electronics and affect the background noise. This, in turn, will affect the limits of detection attainable. Leakage can readily couple with other local instrumentation and can modulate the signal, affecting performance of the instrument.  | PS<br>WF<br>ST |  |  |  |  |

| Feature  | Definition and/or test procedures and guidance for assessment   | Importance | Reason  | Score          |  |  |  |  |
|--|---|------------|---|----------------|--|--|--|--|
| (d) Frequency of operation                     | The usual frequency of operation of generators for ICP-MS instrumentation is 27 MHz, but some operate at higher frequencies. Scoring may be inappropriate. There is some evidence to suggest that lower frequency operation may offer some advantages in ICP-MS.                                | NVI        | In an ICP, the eddy currents induced by the magnetic field flow more closely to the outer portions of the plasma, known as the skin depth. This is defined as the depth at which the inductive current is $1/e$ of the surface value ( $e$ is the base of natural logarithms) and is inversely proportional to the square root of the frequency. The higher the frequency, the smaller the skin depth and consequently there is a decrease in the transfer of energy towards the central channel, which results in a lower temperature and a lower electron number density. Therefore the background emission will decrease, which is advantageous in emission as the limits of detection are usually improved, but is a disadvantage in ICP-MS as the dissociation of analyte oxide species is obviously more difficult at low temperatures. |                |  |  |  |  |
| (e) Power available                            | The power in kilowatts which can be developed in a plasma by the generator. Score according to application, bearing in mind that a high power generator may offer more flexibility if it can also be run at low power.  | I          | The power required will depend on the application. All commercial systems use a Fassel type torch and normally operate at around 1300 W, although higher powers of up to 1800 W may be required in the analysis of organic solvents to ensure adequate breakdown of solvent molecules.  | PS<br>WF<br>ST |  |  |  |  |
| (f) Selection and indication of power settings | The power developed in the plasma should be indicated by a meter or calibrated control. According to application, score maximum for the system which gives the most accurate and complete information. Score additionally for reproducibility and the ability to select several power settings. | I          | For comparison purposes in research work, as well as for method development, it is important to know the power developed in the plasma. For routine use, it is sufficient to know the power developed at the work coil and to set this reproducibly. Most generators have a reflected power meter, which gives the power into the impedance matched circuit. All meters and/or controls should have accompanying information which gives the power in the plasma from either calculation or calibration.  | PS<br>WF<br>ST |  |  |  |  |
| (g) Coupling efficiency                        | The fraction of power supplied to the coil which is transferred to the plasma. The power in the plasma can be determined directly by calorimetric measurement or indirectly by use of a dummy load and calorimetry. Score maximum for the highest efficiency.                                   | I          | For maximum efficiency, it is desirable to transfer the maximum amount of power available to the plasma.  | PS<br>WF<br>ST |  |  |  |  |
| (h) Power stability                            | The degree to which the power in the plasma varies from a set value. Score maximum for the highest degree of stability for a given mains variation. This figure should always be given by the manufacturer.   | VI         | Fluctuations are brought about by variations in line voltage and some form of feedback control should be incorporated in the generator. The number of ions produced is strongly dependent on the power delivered to the plasma. Short term fluctuations in power are, therefore, highly undesirable.  | PS<br>WF<br>ST |  |  |  |  |

| Feature  | Definition and/or test procedures and guidance for assessment  | Importance | Reason  | Score          |  |  |  |  |
|--|--|------------|---|----------------|--|--|--|--|
| (i) Tuning (for crystal controlled generators) | Crystal controlled generators require re-tuning if the impedance in the plasma changes. Re-tuning is accomplished by a 'match box' which should incorporate automatic tuning. Score maximum for the most rapid response to changes and the widest range over which this can be achieved with minimal overshoot.  | VI         | With crystal controlled generators, unless matching is automatic and rapid, the plasma will be extinguished. A wide tuning range will accommodate the greatest changes in impedance, permitting the use of the widest range of gases. Free running oscillators have their frequency fixed by the value of the components in the tank circuit. Any change in impedance will result in a small change in the frequency of oscillation, but no retuning is possible or necessary.                              | PS<br>WF<br>ST |  |  |  |  |
| (j) Cooling                                    | In most, if not all, plasma generators, the work coil and, in some cases, the oscillator valve, are water cooled. Score maximum for the system that requires the lowest flow and pressure of water and calls for the least treatment of the cooling water. Some generators are air, rather than water, cooled. In such instances, score maximum for the generator which achieves cooling with the lowest heat dissipation requirement. | I          | It is expensive to install high pressure mains supplies and to install water treatment in areas of hard water. Failure to treat water in such areas can lead to failure owing to blocking of work coils. Instruments designed with air cooling generators that have high power requirements for cooling, may be noisy and uneconomical.   | PS<br>WF<br>ST |  |  |  |  |
| (k) Interlocks                                 | The operator must not be able to gain access to the generator while the power is turned on whether the oscillator is producing Hf or not. Score zero if this interlock is not effective.   | VI         | The voltages and currents involved in Hf generation are dangerous!  | PS<br>WF<br>ST |  |  |  |  |
| <b>2. Torch boxes</b>                          |  |            |   |                |  |  |  |  |
| (a) Ease of access                             | Score according to the ease with which torches can be removed and refitted to the box and the ease with which load coils can be removed and refitted. Score additionally for ease of alignment of the torch within the coil.   | VI         | Breakage of torches can occur if it is difficult to remove or refit them. Water leakage resulting from difficulty in tightening connections on work coils can cause damage. It is essential to ensure that the torch tube is centrally placed in the coil if a good, well positioned plasma is to be obtained. Off-centre torches will cause off-axis plasmas and consequent melting of the torch tube.   | PS<br>WF<br>ST |  |  |  |  |
| (b) Ease of observation                        | It is desirable to be able to observe the plasma through an observation window which must be screened to suppress Hf leakage and equipped with UV filters. Score according to the degree of convenience offered.   | I          | This facility allows observation of any malfunction of the plasma torch, which can cause damage and will lead to unsatisfactory performance.  | PS<br>WF<br>ST |  |  |  |  |
| (c) Sampling depth                             | The distance between the load coil and the sampling cone. It is essential to be able to set the sampling depth in the plasma reproducibly. Score according to the ease with which this adjustment can be made.   | VI         | There is a significant spatial variation in the density of ions in the plasma. Incorrect positioning results in reduced sensitivity and increased interferences from refractory oxides and M(2+) species.   | PS<br>WF<br>ST |  |  |  |  |
| (d) Mounting of the plasma torch               | Score according to the ease with which the plasma torch can be held in position centrally within the work coil of the generator. Mounting devices with orthogonal adjustment consistent with accurate positioning are preferable.  | VI         | The region of maximum ion density in the plasma must be accurately aligned in relation to the sampling cone to maximise the analytical signal and minimise interfering signals. If the mounting device has many degrees of movement, it becomes very difficult to ensure that off-axis sampling does not occur. Most instruments in current production use a similar type of torch. However, other torches may have advantages in some circumstances and a mounting that permits their use is advantageous. | PS<br>WF<br>ST |  |  |  |  |

| Feature   | Definition and/or test procedures and guidance for assessment   | Importance | Reason  | Score          |  |  |  |  |
|---|---|------------|---|----------------|--|--|--|--|
| (e) Exhaust systems   | It is necessary for the torch box to be designed to remove all gases in a manner that will not disturb the plasma. Tests for gas flow and the presence of toxic substances should be augmented by visual observation of the plasma when the exhaust is turned on. Score maximum for the minimum observed movement when the extraction system is switched on.  | VI         | Hot and corrosive gases and toxic elements must be removed from the laboratory atmosphere; at the same time disturbance of the plasma should be avoided if high precision is to be maintained.  | PS<br>WF<br>ST |  |  |  |  |
| (f) Interlocks  | It must not be possible to gain access to the torch box while the Hf current is switched on, or to be able to switch on the Hf unless the water and gas supplies are on. The Hf must also switch off automatically in the event of the plasma being extinguished. Score zero if this interlock is not completely effective.   | VI         | The voltages and currents involved in plasma production are dangerous! These interlocks also prevent accidental damage to the torch and load coil in the event of failure of one of the supplies. Working interlocks are essential to ensure safe operation of the instrument.  | PS<br>WF<br>ST |  |  |  |  |
| 3. Gas supplies   |   |            |   |                |  |  |  |  |
| (a) Flow control  | A constant mass flow of, in particular, the nebuliser gas and, to a lesser degree, the coolant (outer) gas is highly desirable. Score highest for systems using electronic mass-flow controllers, less for spring-loaded mass flow controllers and less still for systems using restrictors and up-stream pressure gauges. There should be no interaction between the gas flows where supplies are taken from a common main. Score additionally for the accuracy of calibration.  | VI         | The distribution of ions in the plasma is very dependent on gas flows, particularly the nebuliser gas flow. It is, therefore, essential that these gas flows are accurately controlled. Any fluctuation in the nebuliser gas flow will affect the precision with which the analytical signal can be measured. Any interactions (cross-talk) caused by taking a relatively high gas flow for the coolant supply from the same source as the much lower nebuliser supply must be avoided. Alternative gas mixtures offer advantages in some applications in the avoidance of spectral interferences.  | PS<br>WF<br>ST |  |  |  |  |
| (b) Choice of gases   | The facility to add other gases to the argon supply may be useful in some applications. Score maximum for the facility to use the widest choice of gas mixtures and for ease of changeover.   | I          |   | PS<br>WF<br>ST |  |  |  |  |
| 4. Sample introduction  |   |            |   |                |  |  |  |  |
| (a) Liquid samples  |   |            |   |                |  |  |  |  |
| (i) Common nebulisers for liquids (concentric and crossflow, Babington-type, V-groove, conespray) | Various sample introduction devices are available for conveying the sample to be analysed into the plasma. Brief details of the more important of these devices are listed below for guidance. Score maximum for the instrument that offers the greatest choice of such devices, taking into account the intended application. Scoring of individual devices (summarised below) is inappropriate as performance depends on application.<br><br>Devices for converting a sample solution into an aerosol, which is then swept into the plasma by the nebuliser gas flow. The assembly normally comprises the nebuliser itself to create the aerosol coupled to a spray chamber to remove all but the smallest aerosol droplets. In some designs the solution supply to the nebuliser is regulated by a peristaltic pump, which must be used in the analysis of viscous solutions and can offer advantages in operating the nebuliser at a lower solution uptake rate. The spray chamber is thermostated, or cooled by a water jacket in some designs, to minimize drift and reduce the water load in the plasma. | VI         | Different sample introduction devices offer particular advantages, depending on the nature of the sample and the intended applications (see below).<br><br>Nebulisation is the usual way of injecting a sample solution into the plasma and is the standard sample introduction device fitted to ICP-MS instruments. Many designs of nebuliser and spray chamber are available, and whereas these show possible advantages in some applications of ICP-AES, the distinction is even less clear in ICP-MS where the total dissolved solid content, and acid strength of sample solutions, is normally restricted to lower values than ICP-AES. This restriction is related to the efficiency of the interface section of the instrument. | PS<br>WF<br>ST |  |  |  |  |

| Feature                                | Definition and/or test procedures and guidance for assessment  | Importance | Reason  | Score          |  |  |  |  |
|--|--|------------|---|----------------|--|--|--|--|
| (ii) Ultrasonic nebulisation           | A device that substantially increases the efficiency of solution nebulisation by incorporating an ultrasonic frequency oscillator as the nebulisation medium. Such a device must be coupled to a desolvation unit. otherwise the low power plasma used in ICP-MS will be extinguished by the high load of solvent that is injected.  |            | Ultrasonic nebulisation increases the nebulisation efficiency to an extent that, in many cases, the limits of detection obtainable are improved by an order of magnitude over those obtainable by most common nebulisers. This device has the additional advantage that the aerosol production is independent of the carrier gas flow rate. It will not handle particulates and, unless removed, the high water loading will take power from the plasma and affect such properties as electron densities, ionisation and excitation temperatures. Also, a high water content, because of its oxygen content, leads to oxide formation. This water content can be reduced by desolvation (normally using either membrane separation or cryogenic cooling). | PS<br>WF<br>ST |  |  |  |  |
| (iii) Thermo-spray nebuliser           | In this device, the nebulisation is obtained by introducing the liquid sample into a heated capillary. The solvent boils near the outlet of the capillary and the vapour acts as a nebulising and carrier gas.   |            | This nebuliser is said to be as efficient as an ultrasonic nebuliser and the aerosol production is independent of the gas flow, but it also has a similar high solvent load.  | PS<br>WF<br>ST |  |  |  |  |
| (iv) Hydraulic high-pressure nebuliser | A high pressure pump is used to produce a constant flow of liquid sample through a nozzle having an orifice of 10–30 $\mu\text{m}$ . The jet of liquid partially disintegrates into an aerosol and is further converted into an aerosol cloud upon collision with an impact bead.  |            | The droplet generation is independent of the gas flow; however, the nebuliser will not tolerate particles because of the small orifice.   | PS<br>WF<br>ST |  |  |  |  |
| (v) The grid nebuliser                 | A gas stream is blown through two consecutive platinum grids. The upstream grid is wetted by the sample, which is blown off the grid as an aerosol. The downstream grid acts as a pulse damper. The glass frit nebuliser functions in a similar manner.  |            | Another nebuliser with a higher than average transport efficiency, but with the disadvantage of long washout times and sample carry-over  | PS<br>WF<br>ST |  |  |  |  |
| (vi) Flow injection                    | A facility which is normally used in conjunction with a solution nebuliser in which the sample solution is injected into the blank solution supplied to the nebuliser for a brief interval before reverting back to blank solution. Data acquisition must be capable of quantifying the transient analytical signal observed during flow injection.  |            | Flow injection offers the particular advantage of allowing the direct analysis of solutions of relatively high solids content, without preliminary dilution. The technique is particularly useful where preconcentration or matrix modification is desirable as these can be carried out on-line.   | PS<br>WF<br>ST |  |  |  |  |
| (vii) Electro-thermal vaporisation     | Electrothermal vaporisation involves heating a sample, normally injected onto a graphite rod, tantalum filament or into a graphite tube, using an electronic controller which permits the temperature to be increased in a programmed way in a similar manner to that used in graphite furnace atomic absorption spectrophotometry. In this way, samples may be dried, ashed and then volatilized with the volatilized fraction swept by carrier gas into the plasma. Data acquisition must be capable of quantifying a transient analytical signal observed during atomisation. |            | Electrothermal vaporisation offers some advantages including: (i) the highly efficient transfer of sample to plasma giving improved sensitivities; (ii) the capability of analysing very small sample volumes (down to a few $\mu\text{l}$ ); (iii) analysis of sample solutions containing complex matrices where the drying and ashing programmes can permit the elimination of specific interferences before measurement of the analyte signal during atomisation. The rapid release of hot gas from the volatilisation device can cause some disturbance of the plasma.   | PS<br>WF<br>ST |  |  |  |  |

| Feature                          | Definition and/or test procedures and guidance for assessment  | Importance | Reason   | Score          |  |  |  |  |
|----------------------------------|--|------------|--|----------------|--|--|--|--|
| (viii) Direct insertion          | In this technique, the sample is placed in the bored-out end of a graphite electrode, dried ashed and inserted axially into the plasma.  |            | Detection limits are said to be improved by an order of magnitude but the method is discontinuous.   | PS<br>WF<br>ST |  |  |  |  |
| (ix) Hydride generation          | An accessory which incorporates a reaction vessel in which the sample solution is reacted with a reagent such as sodium borohydride causing selected analytes to form volatile hydrides which are swept into the plasma for analysis.  |            | Hydride generation offers the advantage of significantly increasing the sensitivity and simultaneously reducing interference effects (in comparison with normal solution nebulisation) for elements which react to form volatile hydrides, including As, Bi, Cd, Ge, Pb, Se, Sb, Sn, Te. Other elements, including Hg, Os and I <sub>2</sub> can be determined by similar 'cold vapour' generating techniques.   | PS<br>WF<br>ST |  |  |  |  |
| (b) Solid samples                | Methods which involve the direct analysis of solid samples offer the advantages of no sample preparation, minimization of contamination effects ( <i>e.g.</i> , from reagents) and the capability of analysing very small sample masses. However, depending on the nature of the material, methods are likely to be inherently imprecise, and because of inhomogeneity effects, the small samples taken for analysis may not be representative of the bulk material. The availability of matrix-matched calibration samples may be restricted and selective volatilisation is also a problem for electrothermal vaporisation as well as for the direct insertion devices, details of which are summarised below. |            |  |                |  |  |  |  |
| (i) Electro-thermal vaporisation | Similar instrumentation to that described for the introduction of liquids can be used to introduce solids into the plasma.   |            | See 4(a)(vii)  | PS<br>WF<br>ST |  |  |  |  |
| (ii) Direct insertion            | As with liquids, solid material is introduced into the plasma by means of a bored-out electrode.   |            | Selective volatilisation can be a problem with this method.  | PS<br>WF<br>ST |  |  |  |  |
| (iii) Arc and spark ablation     | Aerosol generation using a dc/ac or an ac spark in a closed chamber. The aerosol produced is transported to the plasma by a flow of argon through connective tubing which can be a few centimetres or metres long.   |            | The material must be electrically conductive or made so by the addition of graphite.   | PS<br>WF<br>ST |  |  |  |  |
| (iv) Laser ablation              | A facility for the analysis of solid samples in which a selected area on the surface of the sample is ablated by the energy imparted by a laser. The ablated material is then swept into the plasma by the nebuliser carrier gas.  |            | Laser ablation offers the advantage of the direct analysis of solid samples. By use of a focused laser, spatially resolved information can be obtained of element distributions over the surface of the sample. Normal resolution is of the order of 100 µm, but 20 µm can be achieved with recently developed UV laser systems. In general, sensitivity follows an inverse relationship with the amount of material ablated, so that the smaller the laser beam, the worse the detection limits that can be achieved. Quantitative analysis can only be achieved if matrix-matched calibration samples are available. | PS<br>WF<br>ST |  |  |  |  |



| Feature   | Definition and/or test procedures and guidance for assessment   | Importance | Reason  | Score          |  |  |  |  |
|---|---|------------|---|----------------|--|--|--|--|
| (v) Slurry nebulisation                               | The introduction of finely powdered material suspended in liquid media using a high solids nebuliser such as the V-groove type.   |            | Aqueous standards can be used if particles are small. However, it is not a general solution to the problem of solids introduction. The method may be prone to problems of density settling and consequent segregation, and the density of the liquid should be near that of the solid. In short, the particles should be very fine and uniform in size and the material under investigation should be homogeneous. Given these requirements, the physical preparation of samples ( <i>e.g.</i> , grinding) may not offer many advantages in comparison with dissolution procedures. | PS<br>WF<br>ST |  |  |  |  |
| (vi) Direct introduction of powders                   | Powders have been introduced into plasmas by means of direct injection from swirl chambers and fluidised beds, and by injection using pneumatic nebulisers. None of these methods have been successful quantitatively.  | VI         | These methods are prone to an inability to maintain a constant uniform feed of the powdered sample as well as segregation effects which can lead to inhomogeneity.  |                |  |  |  |  |
| 5. <i>Interface</i>                                   | Part of instrument between plasma (operated at atmospheric pressure) and mass spectrometer (operated at high vacuum). The interface section comprises differentially pumped stages through which plasma gases are transmitted to the mass spectrometer <i>via</i> sampling and skimmer orifices. All instruments are fitted with this device. |            | The interface is the key component of ICP-MS instrumentation for which design and manufacturing tolerances have a critical influence on the analytical performance of the instrument.   |                |  |  |  |  |
| (a) Choice of material for sampling and skimmer cones | Different materials (usually copper or nickel) are used, sometimes with a Pt insert. Score maximum for the most appropriate range of material, according to the application.  | I          | The material used for the manufacture of the sampling cone will contribute to the background spectrum. If nickel cones are used, a platinum insert is required to determine low levels of Ni.   | PS<br>WF<br>ST |  |  |  |  |
| (b) Ease of exchange of sampling and skimmer cones    | Score highly for a system which allows for easy removal and refitting of the cones.   | VI         | The cones must be removed for regular cleaning to remove build-up of material at the orifices. Erosion of the sampling orifice also necessitates removal for replacement.   | PS<br>WF<br>ST |  |  |  |  |
| (c) Cost of cones                                     | Score maximum for the availability of appropriate quality cones at the lowest cost.   | I          | The cost of replacing cones may account for a significant part of the instrument's consumables budget.  | PS<br>WF<br>ST |  |  |  |  |
| (d) Ion extraction lenses                             | Score maximum for easy accessibility to the ion lens assemblies.  | I          | These components require regular cleaning to avoid deterioration in the performance of the instrument and attention should be given to the ease of removal.   |                |  |  |  |  |
| 6. <i>Mass spectrometer</i>                           | Two types of mass spectrometer are available, quadrupole and magnetic sector. In addition, magnetic sector instruments are available with either single or multiple collector detectors. Score for the device with the most appropriate characteristics for the application (see below).  | VI         | Quadrupole instruments are very good general purpose instruments but in applications where serious polyatomic ion interferences are encountered, or very high precision isotopic ratio measurements are required, only magnetic sector instruments offer the higher mass resolution which may be necessary.   |                |  |  |  |  |

| Feature  | Definition and/or test procedures and guidance for assessment   | Importance | Reason  | Score          |  |  |  |  |
|--|---|------------|---|----------------|--|--|--|--|
| (a) Quadrupole instruments                         | Mass selection is achieved by applying radiofrequency and dc signals to four rods down the axis of which the ion beam is directed. The combination of Hf and dc fields created by the quadrupoles cause oscillations in ion trajectories, the magnitude of which depends on the mass to charge ( $m/z$ ) ratio. These fields may be adjusted so that only ions of interest have a trajectory that allows them to traverse the exit slits.   |            | Quadrupole instruments are.<br>Less expensive than magnetic sector instruments.<br>Offer unit mass resolution.<br>Have less stringent vacuum requirements.<br>Do not require baking out after changing a detector.<br>Offer a faster scan rate than current magnetic sector instruments (typically $\times 10$ ).<br>Are, therefore, more suitable for the detection of transient signals ( <i>e.g.</i> , when using electrothermal vaporisation).  | PS<br>WF<br>ST |  |  |  |  |
| (b) Single collector magnetic sector instruments   | Mass selection is achieved by subjecting the ion beam to a large magnetic field created by an electromagnet. Ions are deflected by this magnetic field in arcs of varying radii according to their $m/z$ ratio. Instrumentation is designed so that only the ions of interest are deflected by the magnetic sector to pass through the exit slits for detection by a single ion detector. Mass spectrum is scanned by varying the field created by the magnetic sector.                               |            | Single collector magnetic sector instruments are.<br>More expensive than quadrupoles.<br>Can operate at both low resolution ( $m/\Delta m = 400$ ) and high resolution ( $m/\Delta m = 5000-10\,000$ ). For example, in high resolution mode, the following mass interferences can be resolved: $^{28}\text{Si}$ from $^{14}\text{N}_2$ ( $m/\Delta m = 960$ ); $^{32}\text{S}$ from $^{16}\text{O}_2$ ( $m/\Delta m = 1802$ ); $^{31}\text{P}$ from $^{14}\text{N}^{16}\text{O}^1\text{H}$ ( $m/\Delta m = 966$ ); $^{56}\text{Fe}$ from $^{40}\text{Ar}^{16}\text{O}$ ( $m/\Delta m = 2504$ ); $^{51}\text{V}$ from $^{35}\text{Cl}^{16}\text{O}$ ( $m/\Delta m = 2572$ ).<br>Offer low background counts owing to the absence of photon transmission to the detector.<br>Offer, in consequence, better detection limits. | PS<br>WF<br>ST |  |  |  |  |
| (c) Multiple-collector magnetic sector instruments | Instrument design is similar to that described above, but the single exit slit and detector is replaced by multiple exit slits and multiple detectors, allowing simultaneous measurement of several adjacent mass peaks in the mass spectrum without having to change the strength of the magnetic sector. The most sophisticated (and expensive) instruments are fitted with a second electrostatic sector ( <i>i.e.</i> , double focusing instruments) to permit operation at very high resolution. |            | Multiple-collector magnetic sector instruments offer in addition to the characteristics of single collectors.<br>Very high price.<br>Very high precision suitable for isotope ratio determinations (including age dating).  | PS<br>WF<br>ST |  |  |  |  |
| 7. Vacuum system                                   | Score maximum for the fastest pump-down time. Score additionally for minimum water consumption (if water is required for cooling) and for vacuum pumps that require minimum maintenance.  | I          | Rapid pump-down times reduce instrument down time after routine maintenance. Turbo-molecular pumps, which may be air- or water-cooled, are used on most instruments.  | PS<br>WF<br>ST |  |  |  |  |
| 8. Ion detector                                    | Device used to measure the ion flux.  |            |   |                |  |  |  |  |
| (a) Type of detector                               | Three types are currently fitted to commercial instruments. In some cases, a choice is available either at the time of purchase, or subsequent to installation. Score highest for widest choice of detector types.  | I          | Characteristics of each detector type are different, particularly with respect to sensitivity and lifetime.   |                |  |  |  |  |
| (i) Continuous dynode electron multiplier          | Measures ion flux by conversion to electrons, which are multiplied by interaction with a continuous dynode. Can be vented to air without serious damage, although this action is likely to reduce the lifetime.   |            | This type of detector has a limited lifetime which is related to the total accumulated charge. The life-expired detector cannot normally be repaired. Cost is lower than the discrete dynode detector described next.   | PS<br>WF<br>ST |  |  |  |  |

| Feature                                  | Definition and/or test procedures and guidance for assessment   | Importance | Reason  | Score          |  |  |  |  |
|--|---|------------|---|----------------|--|--|--|--|
| (ii) Discrete dynode electron multiplier | Measures ion flux by conversion to electrons, which are multiplied by interaction with a series of discrete dynodes in a manner similar to a photomultiplier tube. Excellent tolerance to venting to air.   |            | Long lifetime; individual dynodes can be replaced; initial cost is higher than the continuous dynode type.  | PS<br>WF<br>ST |  |  |  |  |
| (iii) Faraday cup                        | Measures ion flux <i>via</i> a cup-shaped metal electrode which has no intrinsic gain mechanism.  |            | This type of detector has a relatively low sensitivity and is usually used to extend the upper dynamic range of detection. This type of detector is not suitable for fast scan rates owing to the time taken to respond. The Faraday cup has a long life and does not normally require replacement in normal use.   | PS<br>WF<br>ST |  |  |  |  |
| (b) Detector lifetime                    | Score highest for the least sensitivity to deterioration after atmospheric exposure and to the total accumulated count rate history.  | I          | All detectors age with use, and they suffer varying amounts of damage either when exposed to the atmosphere during routine maintenance or high ion count rate usage.  | PS<br>WF<br>ST |  |  |  |  |
| (c) Cost of replacement                  | Cost of replacement depends on both the capital cost of a replacement detector together with its expected operational life. These factors vary according to the choice of detector, appropriate to a particular application. Score according to the anticipated running cost. | I          | The replacement cost of detectors can make a significant contribution to the running costs of an instrument: more specific details are listed under 8 (i).  | PS<br>WF<br>ST |  |  |  |  |
| (d) Detector characteristics             |   |            |   |                |  |  |  |  |
| (i) Linear dynamic range                 | Score maximum for the detection system ( <i>i.e.</i> , detector and electronics) offering the widest linear dynamic range.  | I          | Permits the measurement of the widest range of concentration of analytes.   | PS<br>WF<br>ST |  |  |  |  |
| (ii) Dead time                           | Score maximum for the detection system with the shortest dead time (in the case of electron multiplier detectors) or the shortest time constant (in the case of Faraday cup detectors).   | I          | For any ion counting system, the detection system requires a finite time to measure and record an ion. During this dead time, subsequent ions cannot be detected, leading to dead time losses. All instruments employing electron multiplier detectors incorporate a numeric correction to account for these dead time losses. However, the shorter the dead time of the counting system, the higher the count rate that can be detected before the response of the counting system become saturated and uncertainties in the dead time corrected data become excessive. For Faraday cup detectors, the response time will depend on the time constants used in the ion current measurement circuits. | PS<br>WF<br>ST |  |  |  |  |
| (iii) Detector background noise          | Score maximum for the detection system offering the lowest figure.  | I          | All noise decreases the signal-to-noise ratio and, therefore, degrades the detection limit.   | PS<br>WF<br>ST |  |  |  |  |
| (iv) Detector overload protection        | Score zero if this feature is absent from detectors other than the Faraday cup.   | I          | Overload of the detector and associated electronic circuits by exposure to an excessively high ion count rate can reduce the operating life of some detector types, particularly electron multiplier detectors. Furthermore, in these circumstances, the detector may take some time to recover its normal operating characteristics.   | PS<br>WF<br>ST |  |  |  |  |

| Feature                                     | Definition and/or test procedures and guidance for assessment  | Importance | Reason  | Score          |  |  |  |  |
|---|--|------------|---|----------------|--|--|--|--|
| (v) Operation at reduced sensitivity        | Reduced sensitivity may be achieved by operating electron multiplier detectors in analogue mode, switching to a Faraday cup detector or reducing the ion transmission characteristics of the ion extraction lenses. Score zero if this facility is absent.   | I          | This facility extends the linear dynamic range of the instrument, allowing analytes at higher concentrations to be measured.  | PS<br>WF<br>ST |  |  |  |  |
| 9. <i>Computer control and monitoring</i>   |  |            |   |                |  |  |  |  |
| (a) Instrument functions                    | Many manual controls on earlier instruments can now be set from the computer. In addition, safety interlocks can be monitored by the computer. Score highest for the comprehensiveness of computer automation, ease of use, clarity of operation and quality of display.   | I          | Optimisation of instrument functions should be more reproducible and interlocks more reliably monitored with computer automation.   | PS<br>WF<br>ST |  |  |  |  |
| (b) On-line diagnostics                     | Capability of the instrument control computer to monitor the operating status of the instrument and to log faults and deviations from operating specification. Score for the availability of a user-friendly diagnostic information. Score additionally for the ability to connect the instrument by modem to the manufacturer's service department to enable remote interrogation of instrument faults to be carried out. | I          | Downtime is kept to a minimum if faults can be diagnosed quickly. The availability of reliable diagnostic information may make an engineer's visit more effective or even unnecessary.  | PS<br>WF<br>ST |  |  |  |  |
| 10. <i>Data acquisition</i>                 |  |            |   |                |  |  |  |  |
| (a) Scan rate of the mass spectrometer      | Atomic mass units (amu) per second. Score highest for instruments with the highest scan rate applicable over the entire mass range (6–240 $m/z$ ). This feature is not relevant to instruments fitted with multi-collector detectors.  | VI         | Transient signals from electrothermal vaporisation or coupled chromatography require fast scanning. Fast scan rates generally improve precision in isotope ratio determinations where data are accumulated by repetitively scanning over a restricted region of the mass spectrum.  | PS<br>WF<br>ST |  |  |  |  |
| (b) Peak jumping                            | The capability of acquiring data by repetitively monitoring a number of mass peaks selected by the operator anywhere within the instrument's mass response range. Intermediate regions of the mass spectrum are scanned at maximum rate without acquiring data. Score zero if this feature is absent.  | VI         | Operation in this mode maximises the rate of data acquisition on mass peaks of interest, and prevents detector overload and ageing by avoiding regions of the mass spectrum containing intense mass peaks.  | PS<br>WF<br>ST |  |  |  |  |
| (c) Integration                             | The capability of summing data for a complete mass peak or, alternatively, a selected number of the channels of an individual mass peak acquired in scanning mode. Score for the availability of this feature and additionally if it is possible to re-integrate stored spectra by selecting a different range of channels.  | VI         | Integrating the channels of a peak adjacent to the peak maximum ( <i>e.g.</i> , $\pm 0.35 m/z$ ) is claimed to improve precision compared with integrating the whole peak area, particularly for measurements made at low count rates, because this method excludes data from the wings of the peak which contain a larger proportion of noise. | PS<br>WF<br>ST |  |  |  |  |
| 11. <i>Data correction and manipulation</i> |  |            |   |                |  |  |  |  |
| (a) Data processing                         | Ability to process raw data and implement quality control procedures. Facilities available should include recalibration, use of internal standards, external drift correction and interference correction. Score maximum if all are present.   | VI         | These facilities are necessary to apply the appropriate correction ( <i>e.g.</i> , for drift in instrument response, suppression of enhancement caused by sample matrix effects and spectrum overlap interference) to the raw analytical signal.  | PS<br>WF<br>ST |  |  |  |  |

| Feature                       | Definition and/or test procedures and guidance for assessment   | Importance | Reason  | Score          |  |  |  |  |
|-------------------------------|---|------------|---|----------------|--|--|--|--|
| (b) Isotope ratio measurement | The ability to measure the abundance of one isotope relative to another isotope of either the same, or a different element. Score for the availability of this feature. If relevant to the type of instrument and application, score additionally for the availability of specialised software that allows data to be acquired and processed to maximise precision. | I/VI       | In some applications, isotope ratios must be measured rather than elemental abundances. Quadrupole instruments acquire data in a sequential manner and can achieve precisions of typically 0.1% RSD. If very precise measurements are required ( <i>e.g.</i> , 0.001% RSD), so that small differences in isotopic composition can be distinguished with confidence, special considerations apply. Measurements must be made on a magnetic sector instrument fitted with multiple collectors. Special procedures are then required to acquire and analyse data in a way that maximises the precision of the measurement. | PS<br>WF<br>ST |  |  |  |  |
| (c) Reporting formats         | Choice of hard copy formats for the output of raw data and/or analytical results. Score for a choice of output formats that suit the application. Score additionally for the option for the user to design customised formats.  | I          | Specific hard copy formats may be required to satisfy existing quality systems. Further manipulation of data may require formatting output so that it can be read by third party software. ASCII files are particularly useful.   | PS<br>WF<br>ST |  |  |  |  |
| (d) Operating system          | System under which the manufacturer's software operates. Score if the operating system is compatible with software that already exists in the user's laboratory.  | I          | Raw and processed data files may need to be transferred to other computers for off-line manipulation. Initial training is also simpler if operators are already familiar with the operating system.   | PS<br>WF<br>ST |  |  |  |  |
| 12. Calibration               | Data can be quantified using one of several procedures (summarised below). Score zero if the procedure(s) relevant to the proposed application(s) are not available.  | VI         | Different matrices and different analytical problems require different calibration approaches.  |                |  |  |  |  |
| (a) External calibration      | The calibration of an instrument by comparing the response of sample solutions with standard solutions of the analytes of interest.   |            | The 'standard' method of calibrating instruments for the analysis of sample solutions at low total dissolved salts content and low acid concentration.  | PS<br>WF<br>ST |  |  |  |  |
| (b) Standard additions        | The calibration of an instrument by comparing the response on sample solutions with that from the same sample solution, which has been 'spiked' with a known concentration of a standard solution of the analyte(s) of interest.  |            | Appropriate for the analysis of 'difficult' sample solutions that fall outside the above criteria because the sample and spiked solutions have essentially matched matrices.  | PS<br>WF<br>ST |  |  |  |  |
| (c) Isotope dilution          | The calibration of an instrument by 'spiking' the sample solution with a known mass of an isotopically enriched solution of the element of interest. The ratio of two specified isotopes of the analyte are then measured to very high precision and the concentration calculated from these data and a knowledge of the natural and spike isotopic abundance.      |            | Use of isotope dilution is a calibration technique that is the least susceptible to bias. However, measurements are relatively time consuming and cannot be applied to monoisotopic elements.   | PS<br>WF<br>ST |  |  |  |  |
| (d) Surrogate calibration     | The capability to calibrate an instrument for the determination of an isotope by external calibration using standard solutions that do not contain the analyte of interest.   |            | This calibration procedure can be used when a standard solution of the analyte is not available. Calibration is undertaken by comparison with a standard solution containing (normally) an adjacent element in the mass spectrum, account being taken of differences in natural isotopic composition, and sometimes the mass response of the instrument.  | PS<br>WF<br>ST |  |  |  |  |

| Feature                                 | Definition and/or test procedures and guidance for assessment   | Importance | Reason  | Score          |  |  |  |  |
|---|---|------------|---|----------------|--|--|--|--|
| (e) Semi-quantitative analysis          | Calibration is achieved by measuring the instrument response from a single multi-element standard solution selected to contain a range of elements that cover the full mass range of interest, though not necessarily containing the specific analytes of interest.   |            | By measuring the instrument response as a function of mass, the concentration of any analyte can be interpolated from data from a single standard solution allowing rapid multi-element analysis. Results are semiquantitative because of differences in the matrix of standard and sample solutions and because of uncertainties in characterising the mass response function from a limited number of elements. | PS<br>WF<br>ST |  |  |  |  |
| 13. Overall performance characteristics | Parameters most relevant to making a judgement on the overall analytical suitability of the instrument for the intended purpose, as summarised below.   | VI         | Users cannot normally test the performance of individual components in isolation from the rest of the instrument and indeed it would not normally be sensible to do this because of the way all components interact with one another.   |                |  |  |  |  |
| (a) Sensitivity                         | Counts per unit concentration at a specified mass. The response from a solution containing a range of elements across the mass range should be used to evaluate relative sensitivity. Score maximum for the instrument demonstrating the highest sensitivity, taking into account the proposed application. In multi-element applications, score additionally for a uniformly high sensitivity across the entire mass range.  | I          | High sensitivity coupled with a low and stable background will result in the lowest detection limit. A relatively uniform mass response is useful for applications requiring multi-element determinations, particularly if semi-quantitative calibration procedures are to be used.   | PS<br>WF<br>ST |  |  |  |  |
| (b) Instrument stability                | The stability of response over both short (e.g., 5–10 min) and long (e.g., 4 h) term operation. One way of measuring instrument stability is to make periodic measurements on a single sample solution at suitable intervals throughout the chosen test period (typically 4 h). The sample solution should contain relevant elements covering the mass range of interest and each measurement should consist of six sequential measurements, using an integration time of typically 1 min. The sequence of analyses should be repeated as many times as practicable, taking into account the total amount of data that will be acquired. For each set of six measurements, calculate the mean signal and its standard deviation. Long-term instrument stability can be assessed from: (i) the standard deviation calculated from the means of each set of replicate measurements (the smaller this value the better); (ii) by examining the trend with time of the magnitude of the replicate means (a small progressive drift is acceptable, significant jumps in instrument response are undesirable); (iii) by examining the magnitude and range of standard deviation values calculated from each set of replicate measurements (the smaller range and the lower the magnitude of the mean standard deviation the better). Stability over a short time scale may also be assessed from the mean standard deviation obtained in (iii). Score maximum for the instrument that shows best overall performance. | I          | Any drift in instrument response will degrade the quality of analytical results. Significant drift will necessitate frequent recalibration.   | PS<br>WF<br>ST |  |  |  |  |

| Feature                               | Definition and/or test procedures and guidance for assessment   | Importance | Reason   | Score          |  |  |  |  |
|---------------------------------------|---|------------|--|----------------|--|--|--|--|
| (c) Background signal                 | Signal resulting from the detection of stray ions and photons. Test by measuring the signal from high purity water, analysed under relevant operating conditions at mass numbers 6–240 $m/z$ . Score highest for the smallest background signal at each mass number.  |            | The magnitude of and variations in the background signal will affect detection limits.   | PS<br>WF<br>ST |  |  |  |  |
| (d) Polyatomic ion interference       | The signal from specific molecular species formed from the plasma gas (Ar) and elements entrained either from air, or introduced <i>via</i> the sample solution ( <i>e.g.</i> , H, C, N, O, S, Cl). An example is $^{40}\text{Ar}^{16}\text{O}$ , which causes a background interference on Fe at 56 $m/z$ . Score highest for the smallest signal relative to an adjacent mass peak obtained during a full mass range scan. Some instruments now have special features or devices ( <i>e.g.</i> , shield torch) which reduce selectively certain polyatomic species; however, such features may also reduce the overall instrument sensitivity. Score for the presence of such features only if the application requires the determination at low levels of analytes that suffer polyatomic interferences that are reduced in severity by the feature. Measurements should be made using relevant operating conditions since the magnitude of this interference effect may change significantly at other operating conditions. |            | The presence of polyatomic ions results in a degradation in detection limits of analyte peaks that suffer overlap interference.                          | PS<br>WF<br>ST |  |  |  |  |
| (e) Refractory oxide ion interference | The signal from molecular ions formed from a major component of the sample combined with oxygen. An example is $^{90}\text{Zr}^{16}\text{O}$ , which causes an overlap interference on Pd at 106 $m/z$ . Score highest for the least overlap interference obtained during a full mass range scan under relevant operating conditions, measured using a sample solution containing the refractory element. The magnitude of this interference may change significantly with changes in instrument operating conditions.  |            | The presence of refractory oxide ions results in a degradation in detection limits of analyte peaks that suffer overlap interference.                    | PS<br>WF<br>ST |  |  |  |  |
| (f) Doubly charged ion interference   | Although most ions formed in the argon plasma are singly charged, those with a second ionisation energy lower than 15.8 eV (the first ionisation energy of argon) will form a proportion of doubly charged species. Doubly charged ions may be detected from elements such as Ba, Ca, Ce, Eu, Gd, La, Sc, Sm, Sr, Ti, Y, Zn, Zr. Score highest for the lowest intensity of doubly charged species measured relative to the singly charged parent for all elements from the above list relevant to the application. Use relevant operating conditions as the magnitude of this interference may change with instrument operating conditions.   |            | The presence of doubly charged ions results in a degradation in detection limits of any analyte species that suffer from a partial overlap interference. | PS<br>WF<br>ST |  |  |  |  |

| Feature                            | Definition and/or test procedures and guidance for assessment   | Importance | Reason  | Score          |  |  |  |  |
|------------------------------------|---|------------|---|----------------|--|--|--|--|
| (g) Resolution                     | The mass peak width at 10% of the peak maximum, which should be measured for a number of elements selected across the mass range of the instrument. On multi-element quadrupole instruments, the minimum acceptable resolution is one mass unit. Since all instruments are likely to achieve this level of performance, it may be inappropriate to score this feature. On high resolution magnetic sector instruments, there is a compromise between increasing the mass resolution and a corresponding reduction in the intensity of the transmitted ion beam.                               |            | On multi-element quadrupole instruments, it is essential that adjacent mass peaks may be distinguished and wing overlaps avoided. On magnetic sector instruments, an evaluation of resolution is usually related to the analytical strategy to be used in a specific application.   | PS<br>WF<br>ST |  |  |  |  |
| (h) Abundance sensitivity          | A parameter that measures the overlap interference from a specific mass peak of high intensity on an adjacent low intensity mass peak 1 amu away. In ICP-MS, abundance sensitivity can be measured as the ratio of concentrations between two adjacent isotopes where no significant interference effects from tailing can be detected. Score highest for the largest figure obtained from solutions of analytes of relevance to the intended application run under routine operating conditions. Note that the magnitude of this parameter will change with instrument operating conditions. |            | An example of where high abundance sensitivity is important is in the determination of an analyte mass peak situated 1 amu from an intense polyatomic ion interference. High abundance sensitivity is required to minimise interference on the analyte peak.  | PS<br>WF<br>ST |  |  |  |  |
| (i) Matrix effects                 | Effects derived from the sample matrix that suppress or enhance analyte sensitivity, causing differences in sensitivity when the signal from sample solutions are compared with simple aqueous standard solutions. These effects should be absent in dilute solutions and at a minimum in solutions of more complex matrices. Score highest for the least effect in the presence of a matrix typical of the intended application, run under relevant operating conditions. Note that the magnitude of this parameter may change with changes in instrument operating conditions.              |            | Calibration using simple aqueous standards is possible if suppression or enhancement effects are not significant, so avoiding the necessity of preparing matrix-matched calibration samples.  | PS<br>WF<br>ST |  |  |  |  |
| (j) Sample signal stability        | The change in the signal with time from a sample matrix representative of the application. Score highest for minimum drift.   |            | Drift in the analytical signal from complex matrices can be caused by deposition of undissociated sample material in the sampling cone so obstructing the orifice. This drift must be corrected during a run to avoid calibration errors. This test is complementary to the test for instrument stability (13b), which would normally be undertaken using a sample at high dilution, and so not detect drift problems that may occur when real samples are run. | PS<br>WF<br>ST |  |  |  |  |
| 14. 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<br>WF<br>ST |  |  |  |  |
|                                    |   |            |   | Grand Total    |  |  |  |  |