GENERAL PAPER

Analytical Methods Committee

Evaluation of analytical instrumentation. Part XVII. Instrumentation for inductively coupled plasma emission spectrometry

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

The Royal Society of Chemistry,
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Introduction

The following report was compiled by the above Sub-Committee of the Analytical Methods Committee (AMC), which consisted of Professor S. Greenfield (Chairman), Dr. M. Barnard, Dr. C. Burgess, Professor S.J. Hill, Dr. K.E. Jarvis, Dr. G. Lord, Dr. M. Sargent (the late), Mr. D.C.M. Squirrell, Dr. N. Walsh, and Dr. M. West with Mr. C.A. Watson as Honorary Secretary. The initial input of the features for consideration was undertaken by a working party comprising Professor S.J. Hill and Dr. N. Walsh to whom the committee expresses its thanks.

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

The overall object is to assist purchasers in obtaining the best instrument for their analytical requirements. It is also hoped that this evaluation will, to some extent, also help manufacturers to supply the instrument best suited to their customers' needs. It is perhaps pertinent to note that a number of teachers have found the reports to be of use as teaching aids.

No attempt has been made to lay down a specification. In fact, the Committee considers that it would be invidious to do so: rather it has tried to encourage the purchasers to make up their own minds as to the importance of the features that are on offer by the manufacturers.

The XVIIth report of the Sub-Committee deals with instrumentation for inductively coupled plasma emission spectrometry (ICP-AES).

Notes on the use of this document:

Column 1 The features of interest
Column 2 What the feature is and how it can be evaluated
Column 3 The Sub-Committee has indicated the relative importance of each feature and expects users to decide on a weighting factor according to their own application
Column 4 Here the Sub-Committee has given reasons for its opinion as to the importance of each feature
Column 5 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. Proportional scoring (PS). It will be assumed, unless otherwise stated, that the scoring of features will be by proportion (e.g. Worst/0 to Best/100).

2. Weighting factor (WF). This will depend on individual requirements. All features mentioned in the tables have some importance. If, in Sub-Committee's opinion, some features are considered to be of greater importance they are marked I. Those features of greatest importance are marked as VI (very important). A scale should be chosen for the weighting factor that allows the user to discriminate according to needs (e.g. $x1$–$x3$ or $x1$–$x10$). The factor could amount to the total exclusion of the instrument.

3. Sub-total (ST). Multiplying PS by WF obtains this.

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 checklist 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.

The Committee consider that, in general, instrumentation for ICP-AES is safe in normal use, but care should be taken to avoid exposure to UV radiation and when handling toxic chemicals and high voltages.

Finally, as many laboratories are now working to established quality standards, some consideration should be given to third party certification of the manufacturer to standards such as the ISO Guide 9000 series. Such certification should extend to the service organisation.

Other reports

The Analytical Methods Committee has published the following reports in the series:

Part I   Atomic absorption spectrophotometers, primarily for use with flames. Anal Proc (1984) 21:45. Revised in Analyst (1998) 123:1407.

Part II   Atomic absorption spectrophotometers, primarily for use with electrothermal atomizers. Anal Proc (1985) 22:128. Revised in Analyst (1998) 123:1415.

Part III   Polychromators for use in emission spectrometry with ICP sources. Anal Proc (1986) 23:109.

Part IV   Monochromators for use in emission spectrometry with ICP sources. Anal Proc (1987) 24:3.

Part V   Inductively coupled plasma sources for use in emission spectrometry. Anal Proc (1987) 24:266.

Part VI   Wavelength dispersive X-ray spectrometers. Anal Proc (1990) 27:324.

Part VII   Simultaneous wavelength dispersive X-ray spectrometers. Anal Proc (1991) 28:312.

Part VIII   Instrumentation for gas–liquid chromatography. Anal Proc (1993) 30:296.

Part IX   Instrumentation for high-performance liquid chromatography. Analyst (1997) 122:387.

Part X   Instrumentation for inductively coupled plasma mass spectrometry. Analyst (1997) 122:393.

Part XI   Instrumentation for molecular fluorescence spectrometry. Analyst (1998) 123:1649.

Part XII   Instrumentation for capillary electrophoresis. Analyst (2000) 125:361.

Part XIII   Instrumentation for UV-VIS-NIR spectrometry. Analyst (2000) 125:367.

Part XIV   Instrumentation for Fourier transform infrared spectrometry. Analyst (2000) 125:375.

Part XV   Instrumentation for gas chromatography-ion-trap mass spectrometry. Analyst (2001) 126:953.

Part XVI   Evaluation of general user NMR spectrometers. To be published.

Part XVII   Instrumentation for inductively coupled plasma emission spectrometers. To be published.

Part XVIII Differential scanning calorimetry. To be published.

Part XIX   CHNS analysers. To be published.

Overview of inductively coupled plasma emission spectrometry

Basic principles

ICP-AES is a process by which atoms or ions are excited to a higher energy state by inductively coupled plasma and, on de-excitation, these ions or atoms release their energy in the form of light. The wavelengths of this emitted light are specific to the elements that comprise the sample presented to the plasma. The quanta or amount of light emitted by the excited atoms or ions is proportional to their concentration in the sample, which may take the form of a solid, liquid or gas. The emitted light is dispersed (separated) into individual wavelengths by means of a grating contained within a spectrometer and appears as lines (images of the entrance slit) on a detector that is used to quantify the intensity of emitted radiation. The

ICP is formed in a silica tube, known as a torch, through which flows an easily ionised gas such as argon. This tube is placed within the coils of a high-frequency (HF) generator and kilowatts of electrical energy are induced in the ionised gas forming plasma at temperatures of several thousand degrees kelvin. The system can be likened to a transformer with the tube of ionised gas acting as a one-turn secondary. A second gas stream, injected through the plasma, forms an annulus, or tunnel, through which passes the sample, forming a long, flame-like tail. The sample is introduced by a number of different devices, the choice of which is determined by the physical state of the sample.

General instrument description and applications

The instrumentation for ICP-AES is basically comprised of:

– An HF (RF) generator with a water-cooled work coil
– An ICP torch with associated gas supplies
– A device for introducing the sample to the plasma
– An optical mechanism for selecting the wavelength of the light emitted from the plasma
– A detector (or detectors) for measuring the intensity of the light (both of these functions are usually performed by the spectrometer)
– A computer and associated software for controlling the instrument and analysing the spectral data acquired (not shown)

A typical schematic diagram is shown below:
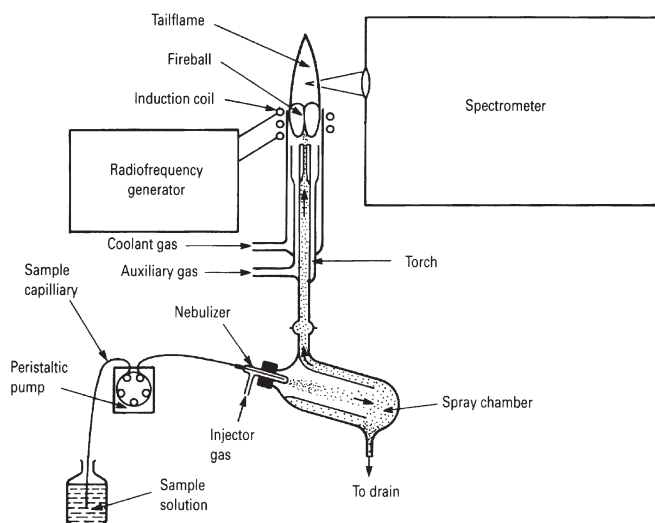
The important feature of ICP-AES is the use of the ICP to excite the sample atoms and ions. Because of the narrowness of the tail-flame of the plasma when viewed transversely there are fewer ground state atoms in the outer layers of the tail-flame to absorb the emitted light (i.e. it is optically thin). This absence of self-absorption coupled with the degree of excitation brought about by the high temperature of the plasma, results in high sensitivity and long linear dynamic range. Coupled with this is a *relative* freedom from the type of interference in emission spectrometry brought about by the formation of refractory compounds in, for instance, low-temperature excitation sources.

The high-temperature plasma will decompose most, if not all, refractory compounds and excite the majority of atoms in the periodic table and may be described as a simultaneous multi-element source that offers high sensitivity in optical emission measurements.

Techniques that can be compared with ICP-AES are inductively coupled plasma mass spectrometry (ICP-MS), graphite furnace atomic absorption (GFAA) and flame atomic absorption (FAA).

ICP-MS has limits of detection (LODs), some two orders of magnitude better than ICP-AES and has an equivalent linear dynamic range. It can be used for isotope analysis but is more sensitive to matrix effects than ICP-AES. It is a simultaneous multi-element system but the instrumentation is more expensive.

GFAA is comparable to ICP-AES in sensitivity but has a much shorter dynamic range than either of the systems incorporating a plasma and is subject to matrix interferences, at least as many as ICP-MS and more than ICP-AES. It is also a single-element technique and has a low sample throughput rate.

The LODs obtainable by FAA for many elements are not as low as can be obtained by ICP-AES and the technique has a much shorter dynamic range, it is also subject to more matrix effects, and is a single-element technique. The costs of the instruments mentioned are, in descending order, ICP-MS, ICP-AES, GFAA and FAA.

Evaluation of overall performance

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

The items for consideration can be summarised as: precision, sensitivity (detection limit, related to sensitivity and precision), accuracy (comparison of subsequent readings with a reference value), drift (calibration shift), freedom from spectral interferences (resolution), linear dynamic range and analytical range. Ideally, the instrument should be evaluated over its full wavelength working range and the following experiment is designed to permit this evaluation. However, in practice this may be too time consuming or impractical. It is recognised that only a limited number of wavelengths can be tested. If

such a truncated experiment is envisaged, it is essential that it be applied equally to all instruments under evaluation.

Experimental

For each wavelength/element to be tested, prepare five standard solutions; the lowest (S_1) should have a concentration corresponding to about one order of magnitude above the detection limit. The other four (S_2–S_5) should be prepared so that a total of five orders of magnitude are covered. The preparation of such a series of solutions is facilitated by the use of a suitable automatic diluter. The above solutions should be aspirated, in accordance with a randomised sequence, with a blank, S_0, in between each standard and the sequence repeated to give a replication of six readings for each of S_1–S_5. The sample order should be randomised.

An example of a randomised sequence is (reading left to right and top to bottom):

S_0 S_1 S_0 S_4 S_0 S_5 S_0 S_2 S_0 S_3
S_0 S_2 S_0 S_3 S_0 S_5 S_0 S_1 S_0 S_4
S_0 S_5 S_0 S_4 S_0 S_3 S_0 S_2 S_0 S_1
S_0 S_5 S_0 S_1 S_0 S_4 S_0 S_3 S_0 S_2
S_0 S_3 S_0 S_2 S_0 S_4 S_0 S_5 S_0 S_1
S_0 S_4 S_0 S_3 S_0 S_5 S_0 S_2 S_0 S_1

Set up the data system to record the intensities for the 60 sets of readings. Each set of readings should comprise six individual measurements for which the mean and standard deviation are calculated. The data system should be set to calculate the corrected signal ($x-b$) and x/b (total signal-to-noise ratio). The blank value (b) should be the mean of the S_0 mean values bracketing the test solution to compensate for baseline shifts. Ideally this experiment should be repeated over a number of days in order to assess reproducibility and not just repeatability.

Resolution should be checked at several points in the spectrum by recording the spectrum of a combination of elements with closely spaced lines. This test can only be carried out on instruments with a profiling facility. Suitable sets of lines include the following (in nm).

Element	nm	Element	nm
Al(II)	167.001	Pb(I)	283.306
P(I)	177.499	Sn(I)	283.999
P(I)	178.280	Cr(II)	284.325
As(I)	189.042	V(II)	292.402
Sn(I)	189.989	Fe(I)	302.064
Bi(II)	190.241	Al(I)	309.278
Ba(II)	193.400	Al(II)	309.284
As(I)	193.696	V (II)	309.311
Hg(II)	194.227	Ti(II)	310.623
Se(I)	196.090	V(II)	311.071
Mo(II)	202.030	Be(II)	313.042
Zn(II)	202.548	Be(II)	313.107
Mo(II)	202.800	Hg(I)	313.155
Se(I)	203.985	Hg(I)	313.188
Mo(II)	204.598	Ca(II)	315.887
Be(I)	205.601	Ca(II)	317.933
Zn(II)	206.200	Ti(II)	319.080
Sb(I)	206.833	Ti(I)	319.200
Al(I)	208.215	Y(II)	324.221
B(I)	208.893	Pd(II)	324.270
B(I)	208.959	Cu(I)	324.754
Cu(II)	213.598	Cu(I)	327.396
Zn(II)	213.856	Ag(I)	328.068
Cd(II)	214.438	Na(I)	330.298

Element	nm	Element	nm
P(II)	214.914	Ti(I)	334.500
Pb(I)	216.999	Ti(II)	334.904
Sb(I)	217.581	Ti(II)	334.941
Pb(II)	220.353	Ti(II)	336.121
Ni(II)	221.643	Ti(I)	338.289
Cu(II)	224.700	Pd(I)	340.500
Ag(II)	224.874	Ni(I)	341.476
Cd(II)	226.502	Ni(I)	344.476
Co(II)	228.616	Pd(II)	348.892
Cd(I)	228.802	Y(II)	360.073
Sb(I)	231.147	Y(II)	371.030
Ni(II)	231.604	Fe(II)	371.670
Ni(I)	232.003	Fe(I)	371.849
Al(I)	237.312	Fe(I)	371.994
Al(II)	237.335	Fe(I)	372.256
Fe(II)	238.204	Ce(II)	393.081
Ca(II)	238.892	Ca(I)	393.365
Fe(II)	239.562	Al(I)	396.152
Sn(I)	242.170	Ca(II)	396.847
Au(II)	243.779	Hg(I)	404.656
Pd(II)	248.892	K(I)	404.721
B(I)	249.678	Li(I)	413.256
B(II)	249.773	Ce(II)	413.380
Sb(I)	252.852	Ce(II)	418.660
Hg(I)	253.652	Ca(I)	422.673
Mn(II)	257.373	Hg(I)	435.835
Al(I)	257.510	Ba(II)	455.403
Mn(I)	257.610	Cs(I)	455.531
Fe(II)	259.940	Cs(I)	459.300
Pb(II)	261.418	Li(I)	460.286
Ge(I)	265.118	Ti(II)	552.430
Ge(I)	266.158	Na(I)	588.995
Cr(II)	267.716	Na(I)	589.592
Mn(I)	279.482	Li(II)	610.362
Mg(II)	279.553	Li(I)	670.784
Mg(II)	280.270	K(I)	766.490
Mo(II)	281.615		

Treatment of results

The first set of results should be used to establish the calibration function ($x-b$) versus concentration. This will permit a check on the linear dynamic range of the instrument. Statistical examination of the residuals will give additional information on the efficiency of the curve-fitting programme. Subsequent sets of results should be compared with the initial set to provide information on instrument drift, which will affect accuracy, if the common practice of calibrating daily is envisaged. Non-superimposable plots will indicate drift. A typical example is shown below:
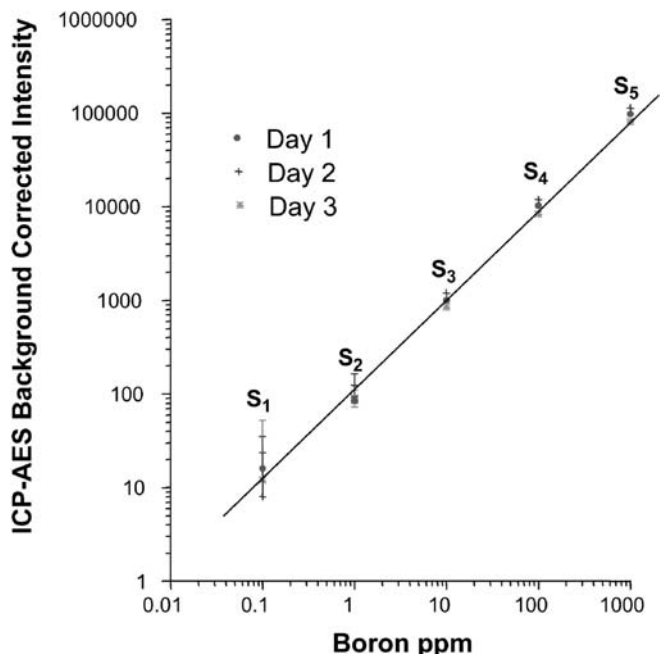
However, data should not only be presented or analysed in the form of log–log graphs, as quite large differences in signal show only as small shifts in the graphs. For example, the top standard intensity is useful in assessing drift. In the example below day 1 shows excellent freedom from drift whereas days 2 and 3 indicate significant problems over the 3-h total run time.
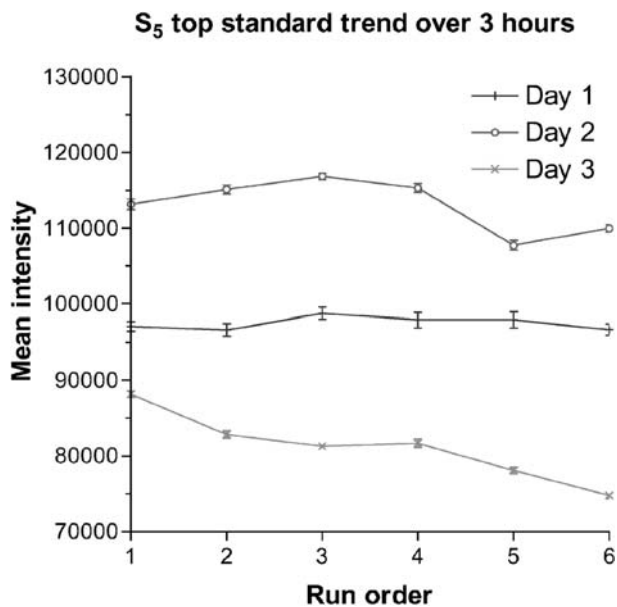
Individual points can be compared by calculating the standard deviation of the residuals of the replicates, while if desired the total plot of each set of data can be compared by means of a multi-tailed "F-test" (or analysis of covariance) using the residuals.

Short-term precision should be evaluated from the standard deviations of (x) for the six replicates comprising each data point. A graph of RSD of the corrected signal ($x-b$) versus log x/b will provide a plot from which the analytical range and detection limit can be estimated. The detection limit is the signal ($x-b$) which has a S/N ratio of about 3. The limit of quantitation is usually defined as a S/N ratio of about 10. However, the actual definitions are relatively unimportant, provided that they constantly applied for evaluation purposes. The analytical range R_1-R_2 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. The lower value of LOD and m and the greater the value of $R'-R$, the better the performance of the instrument.