

Sampling and analysis of iron, steel and other ferrous metals —

Part 6: Guidelines on atomic absorption spectrometric techniques —

Section 6.1 Recommendations for the drafting of standard methods for the chemical analysis of iron and steel by flame atomic absorption spectrometry

Confirmed November 2008

Foreword

This Section of BS 6200 has been prepared under the direction of the Iron and Steel Standards Policy Committee. The text is identical with Information Circular No. 8 “*Chemical analysis of ferrous materials: Recommendations for the drafting of standard methods of analysis employing flame atomic absorption spectrometry for the chemical analysis of iron and steel*”, published by the Commission of the European Communities.

In the Synopsis on page 1, reference is made to a complementary Information Circular, No. 9, the text of which forms the basis for BS 6200-6.2. Both Information Circular No. 8 and Information Circular No. 9 were prepared by the European Committee ECISS/TC20 “*Methods of chemical analysis*” with the active participation and approval of the UK. The recommendations given in these documents have also been adopted by ISO/TC17/SC1, “*Steel — Methods of determination of chemical composition*”. Most of the European and ISO standards involving flame atomic absorption spectrometry produced by these two committees have been prepared in accordance with these recommendations. Many of these methods have been implemented as Subsections of BS 6200-3.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 20, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

Amendments issued since publication

Amd. No.	Date of issue	Comments

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Synopsis

Standard methods of chemical analysis have traditionally been based on the techniques of classical chemistry. Generally, by specification of quantities and purity of reagents, such methods may be described completely and thereafter followed exactly in any laboratory.

Today, however, the bulk of analysis is done by instrumental methods for which different laboratories may use instruments from various manufacturers with different configurations and operational settings. It becomes of pressing importance to consider how such methods may be specified in Standard documents with regard to both instrument quality and procedure.

The present document considers these matters for methods employing flame atomic absorption spectrometry and makes recommendations. These prescribe instrument quality in terms of limit of detection, curve linearity and precision.

Recommendations concerning the preparation of solutions, the calibration procedure and the expression of results are also included. Methods for the determination of calcium in steel and for cobalt in iron and steel are included as illustrative examples of the drafting recommendations.

NOTE Attention is also drawn to Information Circular No 9: Chemical analysis of ferrous materials; operational guidelines for the application of flame atomic absorption spectrometry in standard methods for the chemical analysis of iron and steel.

1 Introduction

An acceptable analytical procedure has to be written in such a form and in such detail that after faithful execution by a well trained analyst an unquestionable result will be obtained. Neither the individual analyst nor the make of apparatus used should have any influence on the final result. These requirements are particularly stringent in the formulation of standard methods used for reference purposes and for arbitration in cases of dispute.

Traditionally, Standard methods of analysis have been based on the techniques of classical chemistry. While technically sound, they do not reflect modern developments such as optical emission spectroscopy, X-Ray fluorescence and atomic absorption spectrometry, now in widespread use. New and revised standard procedures now in the course of preparation will increasingly embody these techniques and it becomes pressing important to consider how such methods may be specified.

With traditional chemical methods there was little problem. Generally, by specification of quantities and purities of reagents, the methods could be described completely and thereafter followed exactly in any laboratory. With instrumental methods, however, the situation is different. Different makes of instruments may be employed in the various laboratories, with different configurations or operational settings, and it becomes more difficult to specify the procedure precisely. Clearly, the standard should not refer to a particular make of instrument, to the implied exclusion of other satisfactory equipment, nor should it include operational settings or measurement times or solution concentrations which may be appropriate to a given instrument only.

On the other hand, if matters are left in the hands of the individual analyst just to "follow the manufacturer's instructions" the document can no longer be regarded as a Standard, nor is there any guarantee that the instrument employed will have a quality of performance suitable for the purpose.

The way forward is for the Standard document to specify instrument suitability in terms of fundamental performance criteria such as precision, limit of detection and linearity, according to agreed definitions. Individual manufacturers would then be free to meet these requirements in any way they choose. Also, since even a good instrument may deteriorate, the Standard should contain reference to practical procedures for the determination of these criteria, to ensure that the instrument meets the specification and continues to do so during its functional years. Other essential aspects of the Standard include instrument optimization, preparation of the test sample, calibration procedures, calculation of results and, where appropriate, how these should be related to the actual instrument used.

The present document considers these matters in relation to Standard methods of analysis employing flame atomic absorption spectrometry and makes recommendations for the drafting of such methods. Non-flame atomic absorption spectrometric methods involving instrumental parameters whose definitions and descriptions require further study are not included in the present document. The determination of calcium in steel for which performance data are available is included as an illustrative example of the drafting recommendations. A method for the determination of cobalt in steel covering a wide concentration range has also been included in order to illustrate dilution procedures, optimization for minimum matrix interference and correction procedures where cobalt may be present in the iron used for the calibration solutions.

2 Instrumental criteria

In the past, attempts have been made to specify instrument performance in a variety of different ways under such headings as minimum sensitivity, curve linearity and minimum stability. It is important that terms used in Standard documents should be in accordance with agreed definitions. The term “minimum sensitivity”, for example, has been used to imply a stipulation that the absorbance of the most concentrated calibration solution measured in a flame path length of 10 cm must be at least 0.3. Useful as this requirement may be as a practical guide, it is not the accepted definition of sensitivity in instrumental analysis which is, more properly, the change in instrument reading for unit change in concentration (dx/dc), or the slope of the analytical curve at a given concentration. In atomic absorption spectroscopy, the term “sensitivity” has also been used very widely in manufacturers’ literature and elsewhere to imply the concentration of the analyte which will produce a change in the absorbance reading, compared with that of pure solvent, of 0.0044, i.e. 1 % net absorption. The IUPAC Commission has drawn attention to this misuse of the term sensitivity and while recognizing the usefulness of the value it represents, has suggested replacement of the name by the term characteristic concentration.

The present document recommends that instrument suitability as specified in a given Standard document should be based on three performance criteria, according to agreed definitions — limit of detection, acceptable curvature of the calibration graph and precision.

2.1 Limit of detection

The limit of detection is the smallest concentration in solution of the element of interest which may be detected with confidence. It is obtained from the calibration graph and is generally taken in instrumental analysis as that value on the concentration axis which corresponds to an instrument reading of two or three times the standard deviation above the mean reading of the blank (analytical background).

The IUPAC proposals recommend that this background measurement should be derived from a sufficient number of replicate determinations on the blank solution. Purely to facilitate the practical measurements, the present report suggests a minor modification, i.e. that the measurement should be based on a concentration value selected to give an absorbance of just above the zero and that the standard deviation should be calculated on the basis of 10 replicate determinations. In taking these measurements, as with all other measurements, it is very important that the instrument should be fully optimized. It is not sufficient that it should be adjusted merely to meet the detection limit quoted in the standard. Instrument optimization is considered in some detail in Information Circular No 9.

It is not unusual for the experimentally derived limit of detection to be a few times higher than that quoted by the manufacturer because the latter will have been derived, in all probability, from a new instrument under particularly carefully controlled conditions using pure solutions. If the discrepancy is large, however, the instrument should be overhauled.

The value placed on this detection limit in the standard should be specified with reference to the lowest concentration of the element of interest likely to be encountered in the application envisaged. In the ideal case, the specified limit of detection should be less than one-tenth of the lowest concentration level to be determined and should be measured in the same matrix. The analysis of drinking water which is subject to legal requirements provides a convenient example of this doctrine. If, for example, the maximum legally permitted concentration of lead in potable water were, say, 0.05 ppm Pb (mg/l) and a result very close to this were obtained, it would be necessary to know what confidence could be placed on the result. It would be little comfort to the analyst to feel that his instrument was working at the very limit of its capabilities. Since the limit of detection of many flame atomic absorption spectrometers is only of the order of 0.01 to 0.02 mg/l Pb, special techniques would be required to give the necessary confidence when operating near the statutory limit. In the case of manganese in potable water, on the other hand, for which the maximum permitted concentration is of the same order, the flame atomic absorption spectrometric technique is very sensitive (limit of detection typically 0.005 mg/l or better), thus meeting the criterion mentioned above and being eminently suitable for direct application.

It is of course recognized that there may be situations where flame atomic absorption spectrometry might still be the method of choice even though the above requirements could not be met. Such situations might exist where the technology does not require residual element determination with a high degree of precision, and a much higher limit of detection relative to the concentration being determined would be acceptable. In this sense, each analytical requirement could be considered on its own merits. Nevertheless, for a standard referee method, as distinct from a routine procedure, specification of a limit of detection of less than one-tenth of the lowest concentration to be determined is a useful guideline. The exception would be if, despite not meeting this requirement the method were still the most accurate one available.

2.2 Curvature of the calibration graph

It is widely accepted in instrumental analysis that the ideal analytical curve is one which is linear throughout the concentration range of interest. Not only does this situation imply that the measurement system is showing its highest sensitivity but the graph is easy to locate accurately either by a line drawn manually through all the points or by a simple linear "least squares" mathematical treatment. Most practising analysts feel instinctively that best results are obtained under these conditions.

In practice, however, non-linear calibration graphs are commonplace in atomic absorption spectrometry, even though the inherent curvature may in some cases be concealed by electronic manipulation of the signal before display, i.e. with inherently slightly curved calibration graphs there is the risk that a linear graph is forced through the calibration points which clearly introduces errors. Potential risks associated with a heavily curved region of calibration are that absorbance measurements are insensitive and there may be problems in defining the shape of the curve on the basis of relatively few points in the curved region. It is therefore necessary to consider what constraints should be written into the standard to safeguard analytical accuracy under the conditions of non-linear calibration graphs.

It has been proposed that the slope of the calibration curve covering the top 20 % concentration range (expressed as a change in absorbance) shall not be less than 0.7 of the value of the slope for the bottom 20 % concentration range determined in the same way. It is recognized that this criterion is not a fundamental requirement in the same sense as an adequate precision. It is quite possible that an instrument just failing to comply with the maximum permitted curvature requirement would give a satisfactory performance if the precision were adequate. Indeed, precision, being a function of sensitivity, curvature, and signal to noise ratio, and the basis on which limit of detection is calculated, is a fundamental performance criterion which, in effect, renders the others redundant. Ringbom plots have shown that acceptable precision can be obtained at absorption values considerably greater than those commonly recommended. Detailed study of such plots enable an analyst to decide on a working range for his instrument which will be appropriate to the precision requirements of his particular application.

However, bearing in mind that accuracy presupposes not only an adequate precision but also freedom from bias and likewise bearing in mind possible difficulties in locating exactly the position of a curved graph, i.e. where departure from linearity becomes significant and how the ensuing shape may be accurately described manually or mathematically in the absence of an inordinately large number of calibration solutions, it is recommended that the above requirement defining the maximum permitted curvature be incorporated in the Standard as a guideline.

It is also recommended that information on curvature of the calibration graph should be available for inspection at a point before data processing takes place. While modern developments are welcomed, it is important to ensure that curve straighteners and other electronic devices should not be operating on poor quality input information such as a near horizontal part of the curve, with possibly misleading results for the less experienced analyst.

Recent work has shown that if curvature is due to stray light, linearity requirements will be met if the mid-point calibration absorbance does not exceed 0.55 times full scale absorbance. This provides a particularly convenient and practical way of judging an acceptable linearity.

2.3 Precision

As mentioned in previous sections, precision is a performance criterion of fundamental significance. A value of precision stated in the Standard provides a requirement which proposed instrumentation must meet if it is to be considered suitable for operation of the Standard. It provides an assurance against inadvertent use of poor quality equipment.

In some methods, the acceptable precision of measurement at the two ends of the calibration curve has been defined as a stated proportion of the standard deviation of the absorbance of the most concentrated calibration solution.

Typical wording is "the standard deviation of the absorbance of the most concentrated calibration solution, and the standard deviation of the absorbance of the zero calibration solution, each being calculated from a sufficient number of repetitive measurements, shall be less than 1.5 % and 0.5 % respectively, of the mean value of the absorbance of the most concentrated calibration solution".

Although perhaps somewhat obscure at first sight, the recommendation has the advantage of relating the required precision to the concentration being determined. Thus assuming for a moment a linear calibration, the precision called for over the concentration range 0.0 % to 1 % of a given element in the above example would be 0.005 % and 0.015 % respectively or, at the 95 % confidence level (2σ), 0.01 and 0.03 % respectively. The introduction of precision limits based on absorbance measurements in this way also has the advantage of eliminating poor quality equipment at an early stage. The reproducibility of the entire method in terms of concentration units will, however, be affected by other factors, for example curvature of the calibration graph.

The exact values placed on these relative precisions (0.5 % and 1.5 % in the example given above) may well vary from element to element or from Standard document to Standard document. These values must take account of the purpose of the analysis, i.e. the technical or commercial implications, but will be limited ultimately by the capabilities of the instrument.

Obviously, specified instrumental precisions should not be so generous that the method is incapable of yielding the requisite technical information but it would be equally pointless to set limits in excess of requirements which no instrument is capable of meeting. A comparison of these values with what is available by alternative chemical means will be an important factor in assessing the acceptability of the AAS procedures for standard referee purposes. This point may well be illustrated by reference to some earlier work concerned with the determination of low levels of titanium in steel. It was found that with the instruments at that time available, the precision attainable at low concentrations of titanium was so inferior to the performance of an alternative spectrophotometric procedure as to rule out flame atomic absorption spectrometry for referee purposes, in this particular case.

Two modifications to the above precision requirements may be recommended. Firstly, the number of replicate measurements on which the precision is based should be specified. For consistency with the proposed definition of lower limit of detection, 10 replicate determinations are recommended. Secondly, it is suggested that the second precision measurement should be taken on the lowest calibration standard, instead of on the zero solution. In this way, distortion of the measurement by instrument noise may be minimized. The calibration procedure recommended in Section 5, taken in conjunction with the above precision requirements provides a warning of instrument drift.