

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

Part 6: Guidelines on atomic absorption spectrometric techniques —

Section 6.2 Recommendations for the application of flame atomic absorption spectrometry in standard methods for the chemical analysis of iron and steel

Confirmed November 2008

Foreword

This Section of BS 6200 has been prepared under the direction of the Iron and Steel Standards Policy Committee. It is based on Information Circular No. 9 “Chemical analysis of ferrous materials: Operational guidelines for the application of flame absorption spectrometry in standard methods for the chemical analysis of iron and steel”, published by the Commission of the European Communities. An additional appendix, Appendix E, provides further details and recommendations relating to the use of perchloric acid in flame atomic absorption spectrometric methods of analysis. The information in Appendix E is a result of investigations undertaken since Information Circular No. 9 was published.

In the Synopsis on page 1, reference is made to a complementary Information Circular, No. 8, the text of which has been adopted unchanged in BS 6200-6.1. 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.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 14, 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.

This British Standard, having been prepared under the direction of the Iron and Steel Standards Policy Committee, was published under the authority of the Board of BSI and comes into effect on 28 September 1990

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Contents

	Page
Foreword	Inside front cover
1 Introduction	1
2 Equipment	1
2.1 Radiation source	1
2.2 Atomization of the sample	2
2.2.1 Nebulization	2
2.2.2 Atomization with a flame	2
2.3 The monochromator	3
2.4 The detector, signal processing system and display	3
3 Systematic and random errors	4
3.1 Systematic errors	4
3.1.1 Interferences	4
3.1.2 Errors as a result of curvature of the calibration graph	5
3.2 Random errors	5
4 Setting and checking of the atomic absorption spectrometer	6
4.1 Sensitivity	6
4.2 Detection limit	6
5 Literature	7
Appendix A Instrumental settings and optimization of the Atomic Absorption Spectrometer	8
Appendix B Reporting of results	9
Appendix C Safety	10
Appendix D Directions for the determination of some instrument parameters	11
Appendix E The use of perchloric acid in flame atomic absorption spectrometry	12
Publications referred to	Inside back cover

Synopsis

Flame atomic absorption spectrometry is playing an increasingly important role in the analysis of iron and steel. However, the quality of results attainable, including the sensitivity, the detection limit and the precision depends not only on the instrument used but also, and markedly, on its optimization. The present report considers the essential features of an atomic absorption system, identifies possible sources of error and gives verification procedures to ensure optimum performance. This document is intended to be the work of reference during the performance of individual standard methods.

NOTE Attention is also drawn to 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.

1 Introduction

The introduction of flame atomic absorption spectrometry into the analysis of iron and steel has greatly facilitated the determination of many of the elements. Indeed, some determinations which were scarcely practicable by the older methods and subject to serious inaccuracies may now be determined with relative ease. Understandably, atomic absorption spectrometry is being increasingly adopted as the preferred procedure for many future standard methods of analysis.

As in the case of molecular absorption spectrophotometry, atomic absorption spectrometry is a relative method of analysis which depends on a comparison of absorbance values with those obtained from a series of calibration solutions. Whereas in spectrophotometric methods, absorbance values are relatively independent of the instrument used and the settings are not very critical, in atomic absorption spectrometry absorbances are influenced by many factors. Not only the slope of the calibration graph but also its curvature, the random and systematic errors, the detection limit and the occurrences of interferences are dependent on the instrument and on its many variables. This means that sample and calibration solutions have to be measured under identical conditions and that much care has to be exercised in the correct setting and regular checking of the instrument. The successful application of atomic absorption spectrometry in standard methods therefore depends on defining the operational parameters and achieving them in practice.

The differences between available instruments implies that specific operational settings may vary from one to another. In order to meet the precision requirements of the Standard methods, however, the equipment will have to satisfy certain performance criteria. These criteria and the appropriate adjustable variables of the equipment are discussed in the ensuing sections of this document. Parts of the spectrometer are also discussed where it is felt that unfamiliarity with certain aspects may give rise to erroneous results. For general aspects of atomic absorption spectrometry, reference is made to ISO 6955:1982, ISO/DIS 6956:1981, and to the literature mentioned in section 5.

ECSC Working Group 20 is of the opinion that operational parameters cannot as yet be sufficiently well defined and controlled for flameless atomic absorption spectrometry to warrant its use in Standard methods. The present document is therefore confined to consideration of the flame technique.

2 Equipment

2.1 The radiation source

For most elements, hollow cathode lamps are available as radiation sources of sufficient intensity, stability and life. In general, separate single element lamps are preferable and the manufacturer's literature often includes a recommended lamp current. When multi-element lamps are employed, a higher current may be required to ensure sufficient intensity of the resonance line and a sufficiently low detection limit.

The linearity and sometimes the slope of the calibration graph usually increase if a slightly lower lamp current is chosen, especially for volatile elements such as cadmium, lead and zinc. This has the added advantage of extending the life of the lamp. When the emphasis is on the attainment of low detection limits, a relatively high lamp current, within the specified maximum, will have to be chosen.

The quality of the hollow cathode lamp should be regularly checked by scanning the emission spectrum in the vicinity of the wavelength used under the normal conditions of lamp current and slit width. The background signal on each side of the line should be less than 2 % of the maximum intensity. The intensity is considered zero when the light path is blocked.

Some of the more volatile elements are less suitable for hollow cathode lamps and a better intensity is obtained by the use of electrodeless discharge lamps. These, however, require a special high frequency power supply.

After the manufacturer's prescribed warming up time, the signal from each radiation source should not deviate by more than 0.5 % from the maximum value (equivalent to 0.002 absorbance units) over a period of 15 minutes. Many different devices are available to correct for any non specific absorbances (background correction).

2.2 Atomization of the sample

2.2.1 Nebulization

The quantity of the element reaching the flame per unit of time, and thus the absorbance measured, depends on the rate of aspiration and the fraction of the nebulized sample which is carried forward into the flame. Consequently, all the physical properties involved, such as density, vapour pressure, surface tension, viscosity (and thus also temperature) should be identical as far as possible for the calibration and analyte solutions. This will be taken into account in the drafting of the standard method. It must also be realized by the analyst should he be forced to make minor adjustments in the execution of the method.

Most nebulizers have an adjustment device to optimize the setting. The optimum setting depends on the solvent (water, alcohol etc.) so that re-adjustment is required for each new solvent or mixture, in order to obtain the maximum signal to noise ratio.

The main effect of the nebulizer setting is on the fraction of the nebulized sample reaching the flame. With some types the fuel gas/oxidant ratio will also be influenced. For a given solvent, it is advisable to adjust the nebulizer with the aid of an element which is not sensitive to the gas ratio (such as silver, magnesium, copper) and to do so only with an air-acetylene flame. The manufacturer's instructions, however, should always be followed. Corrosion and wear of the nebulizer may lead to a decrease in efficiency and increasing instability, as well as a deterioration in the characteristic concentration (4.1), the limit of detection (4.2) and the relative standard deviation (3.2).

2.2.2 Atomization with a flame

On reaching the flame, part of the fine sample mist, the aerosol, is converted into atoms. The extent of the atomization which differs for each element depends on the temperature, the oxidizing or reducing properties of the flame and the measuring height above the burner head. These factors may also influence the effect which other components in the solution have on the atomization — the matrix effect.

The gas mixture consists of an oxidant (air or nitrous oxide) for burning the fuel gas which is usually acetylene. The temperature and the nature of the flame is determined by the ratio of the two gases. While the components of the gas mixture can be specified in a standard method, the composition and the measuring height can only be indicated and the optimum conditions have to be determined. After optimizing the equipment, all solutions including the calibration solutions, the test solution and the blank should be measured in one series, without interruptions or intermediate adjustment of the flame.

Safety regulations (see also Appendix C) must be strictly followed. Nitrous oxide/acetylene flames require special care.

The nitrous oxide/acetylene flame has a much higher burning velocity than the air/acetylene flame which means that either the overall gas rate has to be increased or a special burner with a slot length of about 5 cm has to be used to avoid flashback. This "nitrous oxide" burner may also be used for air/acetylene but gives a lower absorption than the usual 10 cm long air/acetylene burner.

Use of a too strongly reducing nitrous oxide/acetylene flame may cause the formation of soot-like encrustation on the burner slot and undesired changes in the absorbance measurements. Similarly, when solutions with high salt concentrations are aspirated, various types of burner head may become gradually blocked due to deposition of salts in the slot. This results in undesired changes in measurements, and may be the cause of flash back of the flame, especially when using solutions containing perchloric acid or its compounds. Such deposits may be minimized by frequent aspiration of pure solvent between measurements.

After the ignition of the air/acetylene flame and also after switching to the nitrous oxide/acetylene flame, sufficient time must be allowed for the burner head temperature to stabilize before measurements are started.

The gases are subject to the following requirements:

- i) the acetylene must be sufficiently pure to burn with a clear blue transparent flame. In some countries a "phosphine-free" grade is sold which meets these requirements. The pressure in the acetylene cylinder should not be allowed to fall below 600 kPa (approximately 6 bar) or as otherwise recommended by the manufacturers in order to avoid risk of contamination with acetone;
- ii) the air supply should be compressed air of high purity;