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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

Chemische Analyse von Eisenwerkstoffen - Richtlinie für die Anwendung der Falmmen-Atomabsorptionsspektrometrie bei Standardverfahren der chemischen Analyse von Eisen und Stahl

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Analyse chimique des matériaux sidérurgiques - Recommandations pour la rédaction de méthodes d'analyse normalisées employant la spectrométrie d'absorption atomique dans la flamme pour l'analyse chimique des fontes et des aciers

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ICS

English version

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Chemische Analyse von Eisenwerkstoffen - Richtlinie für
die Anwendung der Flammen-
Atomabsorptionsspektrometrie bei Standardverfahren der
chemischen Analyse von Eisen und Stahl

This CEN Report was approved by CEN on 3 October 2001. It has been drawn up by the Technical Committee ECISS/TC 20.

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Foreword

This document (CR 10322:2003) has been prepared by Technical Committee CEN/TC 20 "Methods of chemical analysis of ferrous products", the secretariat of which is held by SIS.

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. This CEN Report considers the essential features of an atomic absorption system, identifies possible sources of error and gives verification procedures to ensure optimum performance. The Report is intended to be the work of reference during the performance of individual standard methods.

NOTE - Attention is also drawn to CR 10321, 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.

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CR 10322:2003 (E)**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 ensuring 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.

ECISS/TC 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. This Report 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 warning 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 Annex 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 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 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

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- 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;
 - (iii) Nitrous oxide cylinders should be fitted with an appliance to prevent excessive cooling and freezing of the regulator. Failure to do this could result in a decrease in gas flow, which in turn may lead to erroneous results or even a flash back.

2.3 The monochromator

Two adjustments are available – the slit width and the wavelength. For a correct setting of the instrument, the slit width should be set first and then the wavelength setting optimized until maximum light intensity is obtained. Over a period of time, a rise in temperature of the monochromator, as a result of flame radiation, may cause an alteration in the wavelength setting. This setting should therefore be checked and reset just before measurements are started. Suitable wavelengths are normally given in the manufacturer's manual and will be further specified in the standard method.

The slit width determines the spectral bandwidth (the section of the spectrum transmitted by the monochromator) as well as the quantity of radiation transmitted, and thereby the detection limit. It is therefore advantageous to select the largest possible slit width. However, the permissible slit width is limited by the presence of non-absorbing emission lines in the spectrum of the radiation source and possibly by interfering emissions from the flame, especially the nitrous oxide/acetylene flame.

The spectral bandwidths (or slit widths) recommended in the manufacturer's manual are usually based on the assumption that single element lamps are used. In the case of multi-element lamps, the resonance lines with the highest sensitivity are free from overlap from other lines in the more complex spectrum but this is not always the case for alternative lines. For this reason, it is necessary to use only the resonance lines of highest sensitivity or to scan the emission spectrum in the region of the relevant lines with a narrow slit and, if necessary, adopt a narrower slit width than prescribed.

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2.4 The detector, the signal processing system and the display

The radiation transmitted by the monochromator is converted by the detector into an electrical signal which is proportional to the intensity of the incident radiation. In the signal processing system, the output from the detector is transformed into a value T for the transmission (i.e. the ratio between transmitted and incident intensity) or into the absorbance A , where $A = \log T$.

With the advent of microprocessors, there are now many further possibilities for processing the signal. Such electronic devices have simplified the operating procedure and the reliability but for reasons explained later due caution must be exercised in having blind faith in the results obtained unless appropriate verification has been carried out beforehand. The following points are reviewed in some detail:

(a) Scale expansion

Essentially this implies electronic amplification of low absorbance signals or minor differences in absorbance. The read-out errors is reduced in this way and the sensitivity is apparently increased but the signal to noise ratio remains unchanged. Scale expansion changes the apparent signal, but the absorbance remains the same.

Scale expansion can be used until the noise observed is greater than the read-out error and is always recommended for absorbance below 0.1. If scale expansion has to be used and the instrument does not have the means to read the value of the scale expansion factor, the value can be calculated by measuring a suitable solution with and without scale expansion and simply dividing the signal obtained.

(b) Concentration read-out and curvature correction

For concentration read-out, the signal is amplified or reduced so that the numerical read-out value is equal to the concentration of the analyte in solution. This direct method can only be used if the calibration curve is linear. For non-linear calibrations, the curvature has to be corrected electronically so that for a limited range an apparently linear relationship is formed, which permits a correct concentration readout.

Equipment without a built-in microprocessor has been encountered which use correction methods which do not always lead to reliable results. Built-in microprocessors typically compute a mathematical function from the readings through a few calibration points only. In general, this gives better results but has the drawback of making even strongly curved calibration graphs seemingly usable, while in the upper part of the calibration graph, the slope may be so low that a minor error in the absorbance measurement can result in substantial deviations in the calculated concentrations. Errors in the preparation as well as in the measurement of the reference solutions have an additional and relatively large influence on the calculated calibration graph.

As the calibration graphs in atomic absorption spectrometry are usually not linear, the application of concentration read-out and curvature correction may give rise to errors in the ultimate results which are easily overlooked. Therefore these auxiliary procedures are only permissible for application in standard methods of iron and steel analysis if it has been explicitly verified that the results obtained do not deviate significantly from those obtained with a very carefully hand-drawn calibration graph of absorbance against concentration.

The following suggestions are helpful in drawing a correct (curved) calibration graph:

- (i) the curve should be drawn smoothly and without bends;
 - (ii) the data points should be spread evenly and at random around the drawn curve. By looking at grazing incidence along the graph paper, these two conditions can easily be checked;
 - (iii) for unknowns with low absorbance values, enlarging of the lower part of the calibration graph is advisable.
- (c) Damping/integration

Damping suppresses the noise but has the side effect of making the system respond slower to changes of the concentrations of solutions being measured. Integration means that the average signal is measured by integration over a pre-selected time. This averaging leads to a reduction of the random error in the final result. For convenience of operation, integration times less than 10 seconds are usually to be preferred, while times in excess of approximately 30 seconds are inadvisable because of the risk of drift. It is advisable to carry out two readings in order to be able to ensure that the signal has stabilized before the first integration period is initiated.

3 Systematic and random errors

As with all analytical measurements, the results obtained by AAS will deviate from the true value due to random and systematic errors. Random errors are made apparent by differences in results when the measurements are repeated. Averaging results reduces the random errors. Systematic errors are not reduced by repeating the measurement. The acceptable error in the final results depends on the purpose of the determination and the concentration of the element to be determined. In general, there is a tendency to keep the systematic error smaller than the random error. ECISS/TC 20 considers its task to be to formulate standard methods so that both types of error are within acceptable limits. Since the apparatus may have a major influence on the derived measurements and minor adjustments to the standard may be necessary with respect to the sample and the available instrument, it is important to have a clear understanding of the systematic and random errors which may occur.

3.1 Systematic errors

Since systematic errors are difficult to detect, much attention has to be given to this aspect in drafting and testing the standard methods. However, there are some sources of systematic errors which require particular attention.

3.1.1 Interferences

Subject to the composition of the solution, the following interferences or matrix effects may occur:

- (i) physical effects influencing the quantity of the element which reaches the flame;
- (ii) chemical interference influencing the number of atoms released in the flame;
- (iii) non-specific absorption by undissociated molecules in the flame;

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(iv) spectral line overlap, e.g. iron on zinc, although such effects are rare.

Physical effects

The quantity of the sample that is aspirated and the portion of it which reaches the flame for a given flow of the gas through the nebulizer, depends on the viscosity, surface tension, density and vapour pressure of the solution. It is therefore necessary to ensure that the physical properties of the sample and the calibration solutions are as similar as possible.

Chemical interferences

Chemical interferences are mostly due to reactions of the element of interest with other elements present in the flame. The effects may be very different and for this reason much attention will have been paid to avoiding and/or correcting these interferences during the drafting of the standard. Therefore it is undesirable to deviate from the standard method without a good reason. Since instances have been known an interference is peculiar to a particular instrument and not to others, the user is advised to check for these effects on his own instrument the first time at which that type of sample is analysed. A simple test is to add a known quantity of the element being determined to a portion of the sample and to check for complete recovery.

Non-specific absorption

Compounds present in the matrix may cause a decrease in the intensity of the resonance radiation reaching the detector. This is due to molecular absorption or scattering and it increases with decreasing wavelength. Using a flame, this interference only occurs at wavelengths below about 325 nm and with high salt concentrations in the solution. Solutions containing high concentration of iron (in excess of about 1 000 µg/ml) should always be checked for background absorption.

The occurrence of non-specific background absorption can easily be detected with the aid of the different devices available. These have to be used under the same conditions applied to the atomic absorption measurement. Simultaneous use of the atomic radiation source makes it possible to correct for background absorption automatically.

3.1.2 Errors as a result of curvature of the calibration graph

The concentration of the sample solution is determined by comparison with calibration solutions used to plot the graph. The accuracy with which the graph can be established depends on the number of points and its shape. If the graph is a straight line, a reliable calibration can be easily calculated from a limited number of points. However, the calibration graph in atomic absorption spectrometry is usually not a straight line and there is not yet a general agreement about the best mathematical function which describes it. This does not mean that one is restricted to the linear part but that extreme care has to be exercised in plotting since an erroneously placed line will lead to systematic errors in the results.

The uncertainty in positioning the graph increases as the curvature increases and as the number of points decreases. Therefore an upper limit has to be set to the permissible curvature in each standard method. This limit is stated explicitly or it is taken into account when the maximum permissible absorbance or concentration are given. It must be emphasized that these considerations apply not only to manually plotted graphs but also for calibration calculated mathematically. Most modern atomic absorption spectrometry instruments are fitted with microprocessors which calculate the best fitting curve through a number of calibration points. This number is often very small and it may therefore not be possible to obtain the optimum result when the graph is curved. Unless it has been previously verified that reliable results are attainable, this facility should not be used for most accurate work.

When the graph is not a straight line, it is not permissible to subtract absorbances, for example of blank solutions, from the calibration solution or test solution absorbances directly. All measurements of calibration and analyte solutions should be carried out with reference to a solution which does not contain the elements of interest in measurable concentration (for instance pure water or other solvent). Only after conversion of the measured absorbances into concentration units may corrections be made for the reagent blank.

3.2 Random errors

In the first place, random errors are apparent from the fluctuations of the absorbance values when measurements are repeated and may be characterized by the relative standard deviation. For the analytical determination however, it is the relative standard deviation of the concentration which is important and this correlates with the relative standard deviation of absorbance via the slope of the calibration curve at the point concerned. The relative standard deviation of the absorbance measurement depends on the instrument used, damping/integration time, element, flame and the absorbance level. It is at a minimum of about 0,5 to 1,5 % at an absorbance value of about 0.5. At greater absorbances the relative standard deviation of the concentration increases, either as a result of increased variability of the measurements or decreased slope of the graphs. In practice it appears that above absorbance values of 0,8 to 2,0 depending on the instrument, the setting and the element, the relative standard deviation of the concentration is too high to be acceptable for most purposes.

Generally the usable part of the calibration graph is limited by the desired relative standard deviation (coefficient of variation) in the concentration. If a large working range is required (e.g. when analysing batches of samples to avoid unnecessary dilutions), then its acceptable limits should be determined in concentration units for each selected combination of measurements conditions.

ECISS/TC 20, aiming to formulate the best standard method for a single sample, has opted for a simpler procedure, where for each standard method the upper limit of the measurement range is restricted in terms of absorbance, or concentration, the permissible curvature of the calibration graph is limited (3.1.2) and the allowable standard deviations at the top and the bottom of the working range are defined in absorbance units. Thus a check on the suitability of the instrument can be made (at an early stage) without performing the whole calibration procedure.

If the specified standard deviations are exceeded then the setting and operation of the instrument should be checked. If they are still exceeded, it may be possible to achieve them by reducing the working range. If not, the instrument is not suitable for the method.

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As noted above, the corresponding relative standard deviations in concentration units will be affected by graph curvature. When required, these may be determined by following the procedure given in Annex D3.

4 Setting and checking of the atomic absorption spectrometer

Instructions for the setting of and measurements with the spectrometer are given in Annex A. During the setting procedure, two properties of the instrument – sensitivity and detection limit – are determined. An explanation of these terms is given below, while directions for their determination are given in Appendices D1 and D2 respectively. Annex B gives a survey of the instrument parameters and settings which have to be defined and which may be stated in an Annex to the analysis report. Annex C deals with the safety aspects which should be observed.

4.1 Sensitivity

The sensitivity of a relative analytical method is defined as the slope of the calibration graph i.e. the relationship between concentration and signal. In atomic absorption spectrometry, sensitivity depends not only on the element but also on the instrument and on its settings.

The variations in sensitivity, combined with maximum permissible absorbance or concentration specified in the standard method make it necessary to adjust the concentrations of calibration solutions and dilution of the sample solutions to suit the particular instrument used.

Each standard method should include performance criteria that the instrument must meet, as described in CR 10321. As a check for correct functioning of the instrument, however, it is useful to compare achieved sensitivity with that quoted by the manufacturers. Practically all manufacturer's state the sensitivity which can be achieved for the various elements under defined operational conditions. With careful settings, it should be possible to approximate to these given values, i.e. within a margin of about 25 %, and this requirement should be met in the application of standard methods. If in spite of careful setting, however, deviations are greater, it has to be