17

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Steel and iron — Determination of manganese content — Flame atomic absorption spectrometric method

Aciers et fontes — Dosage du manganèse — Méthode par spectrométrie d'absorption atomique dans la flamme

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The main task of technical committees is to prepare International Standards, but in exceptional circumstances a technical committee may propose the publication of a Technical Report of one of the following types:

- type 1, when the required support cannot be obtained for the publication of an International Standard, despite repeated efforts;
- type 2, when the subject is still under technical development or where for any other reason there is the future but not immediate possibility of an agreement on an International Standard;
- type 3, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example).

Technical Reports of types 1 and 2 are subject to review within three years of publication, to decide whether they can be transformed into International Standards. Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.

ISO/TR 10281, which is a Technical Report of type 2, was prepared by Technical Committee ISO/TC 17, *Steel.*

Annex A forms an integral part of this Technical Report. Annexes B and C are for information only.

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Introduction

At the 10th ISO/TC 17/SC 1 meeting held in Chicago in 1984, WG 16 was created to develop a method for the determination of manganese content by flame atomic absorption spectrometry. Afterwards, in relation to this working group, three methods concerned with the determination of manganese were submitted for consideration. These were the ECSC/WG 20 working programme method (ECSC/WG 20 N 656), French standard method (NF A 08-331) and ASTM method (E 350), which were all similar. Coincidentally, at the 11th ISO/TC 17/SC 1 meeting held in Rome in 1986, delegates discussed whether the use of perchloric acid in the atomic absorption spectrometric technique was dangerous or not.

Taking into consideration the above position, the first working draft of WG 16 was therefore prepared as a method without using perchloric acid, based on the ECSC/WG 20 working programme. In accordance with the first working draft, an international co-operative experiment was conducted. The experimental results were reported at the 12th ISO/TC 17/SC 1 meeting held in Sydney in 1988.

That is to say, this method was developed at a time when there were grave doubts as to the safety of perchloric acid in the atomic absorption spectrometric technique and that the need to avoid its use had resulted in a relatively cumbersome method involving fusion.

However, by the time of the Sydney meeting, following further investigations, the use of perchloric acid had gained wider acceptance as the hazards associated with its use in atomic absorption spectrometric techniques became more clearly understood. It was agreed that perchloric acid could be used in atomic absorption spectrometric methods, provided that appropriate safety precautions were observed. In addition, it was suggested that coexisting silicon may interfere in the determination of manganese content. If this were the case, since perchloric acid attack could exclude silicon from the test solution, it would be better than hydrochloric/nitric acid attack which was used in the WG 16 experiments.

On the basis of the discussion described above, it was concluded at the 12th ISO/TC 17/SC 1 meeting that a new Working Group should be set up to develop a simpler method, of wider application, using perchloric acid in place of hydrochloric/nitric acid, thus avoiding the need for a fusion step, and to publish the present method in the form of a Technical Report, type 2.

Steel and iron — Determination of manganese content — Flame atomic absorption spectrometric method

1 Scope

This Technical Report specifies a flame atomic absorption spectrometric method for the determination of manganese content in non-alloy and low alloy steels and iron.

The method is applicable to manganese contents between 0,002 % (*m*/*m*) and 3,0 % (*m*/*m*).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Technical Report. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this Technical Report are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 377-2:1989, *Selection and preparation of samples and test pieces of wrought steels — Part 2: Samples for the determination of the chemical composition.*

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

3 Principle

Dissolution of a test portion in hydrochloric acid followed by oxidation with nitric acid. Ignition of the residue and removal of silica with hydrofluoric acid. Fusion of the residue with potassium hydrogen sulfate.

Determination of the manganese content by means of the spectrometric measurement of the atomic absorption of the 403,1 nm line emitted by a manganese hollow cathode lamp when the solution is sprayed into an air acetylene flame.

For low levels of manganese the more sensitive line of 279,5 nm may be used.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Pure iron, free from manganese.

4.2 Potassium hydrogen sulfate ($KHSO_4$).

4.3 Hydrochloric acid, ρ about 1,19 g/ml.

4.4 Nitric acid, ρ about 1,40 g/ml.

4.5 Hydrofluoric acid, ρ about 1,15 g/ml.

4.6 Sulfuric acid, ρ about 1,84 g/ml.

4.7 Ammonia water, ρ about 0,88 g/ml.

4.8 Sulfuric acid, ρ about 1,84 g/ml, diluted 1 + 3.

To 75 ml of water add cautiously, with stirring, 25 ml of sulfuric acid (4.6).

4.9 Background solution.

Weigh, to the nearest 0,01 g, 10,00 g of pure iron (4.1). Place it in a 1 litre beaker and cover with a watch glass. Add 10 g of potassium hydrogen sulfate (4.2) and 150 ml of hydrochloric acid (4.3). Heat gently until the metal has dissolved. Oxidize with 30 ml of nitric acid (4.4) added in small portions. Boil to remove the oxides of nitrogen. Allow to cool, transfer the solution quantitatively to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.10 Manganese, standard stock solution, corresponding to 1 g of Mn per litre.

Weigh, to the nearest 0,001 g, 1,000 g of high purity manganese [purity > 99,9 % (*m*/*m*)]. Place it in a 250 ml beaker, add 40 ml of hydrochloric acid (4.3) and heat gently until the metal has dissolved. Cool and transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 1 mg of Mn.

5 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042 as appropriate.

Ordinary laboratory apparatus, and

5.1 Platinum capsule or crucible, of capacity 30 ml.

5.2 Atomic absorption spectrometer.

A manganese hollow cathode lamp; supplies of air and acetylene sufficiently pure to give a steady, clear fuel-lean flame, free from water and oil, and free from manganese.

The atomic absorption spectrometer used will be satisfactory if after optimization according to 7.3.5, the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and if it meets the precision criteria given in 5.2.1 to 5.2.3.

It is also desirable that the instrument should conform to the additional performance requirements given in 5.2.4.

5.2.1 Minimum precision (see clause A.2).

The standard deviation of 10 measurements of the absorbance of the most concentrated calibration solution shall not exceed 1,5 % of the mean absorbance.

The standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero member) shall not exceed 0,5 % of the mean absorbance of the most concentrated calibration solution.

5.2.2 Limit of detection (see clause A.3).

The limit of detection of manganese in a matrix similar to the final test portion solution shall be better than 0,2 µg of Mn per millilitre for the wavelength 403,1 nm and better than 0,02 µg of Mn per millilitre for the wavelength 279,5 nm.

5.2.3 Graph linearity (see clause A.4).

The slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 times the value of the slope for the bottom 20 % of the concentration range (expressed as a change in absorbance) determined in the same way.

For instruments with automatic calibration using two or more standard solutions, it shall be established prior to the analysis, by obtaining absorbance readings, that the above requirements for graph linearity are fulfilled.

5.2.4 Characteristic concentration (see clause A.5).

The characteristic concentration for manganese in a matrix similar to the final test portion solution shall be better than 1,0 µg of Mn per millilitre for the wavelength 403,1 nm and better than 0,1 µg of Mn per millilitre for the wavelength 279,5 nm.

5.3 Ancillary equipment.

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria in 5.2.1 to 5.2.3 and for all subsequent measurements.

Scale expansion can be used until the noise observed is greater than the read-out error and is always recommended for absorbances 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 both absorbances of a suitable solution with and without scale expansion, and simply dividing the signal obtained.

6 Sampling

Carry out sampling in accordance with ISO 377-2 or appropriate national standards for steel and iron.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,001 g, approximately 1,0 g of the test sample.

7.2 Blank test

With each analytical run, carry out a blank test in parallel with the test analysis using identical reagents, conditions, analytical procedures and dilutions throughout.

7.3 Determination

7.3.1 Preparation of the test solution

Place the test portion (7.1) in a 250 ml beaker. Add 15 ml of hydrochloric acid (4.3). Cover the beaker with a watch glass and heat gently until the reaction ceases. Oxidize with 3 ml of nitric acid (4.4) added drop by drop. Boil the solution for 1 min to remove the oxides of nitrogen. Cool the solution, add approximately 15 ml of water and filter the solution through a paper pulp pad into a 100 ml one-mark volumetric flask, washing with water. Leave sufficient room (about 20 ml) in the flask to accept the acid insoluble fraction (see 9.1).

Place the pad containing the insoluble residue in a platinum capsule or crucible (5.1). Ignite at a low temperature to remove the organic matter, then maintain at 800 °C for 15 min. Allow to cool, add two drops of sulfuric acid (4.8) and approximately 2 ml of hydrofluoric acid (4.5). Place on a hot plate and evaporate to dryness. Add 1 g of potassium hydrogen sulfate (4.2), heat gently over a bunsen burner until the crystals have melted, and then heat more strongly until the residue has dissolved (see 9.2). Cool the crucible, place it in a 250 ml beaker, add 10 ml of water and 2 ml of hydrochloric acid (4.3), and heat gently until the fusion products have dissolved. Cool, add to the original filtrate and dilute to the mark with water to give a test solution S.

7.3.2 Treatment of the test solution S (see note 1)

Set up the instrument as described in 7.3.6. Test the solution S at various approximate dilutions to find the dilution factor D that brings the solution near the midway of the optimum working range of the instrument, for example 0,25 absorbance unit to 0,45 absorbance unit. Accurately dilute the solution with water by factor D to give a test solution t (see note 2).

NOTES

1 This procedure, designed as a reference for single samples, could be adopted for batch analysis by adding extra background solution (4.9) as the samples are diluted, and having standards with the matrix level of the original test solutions.

2 Where high precision is required, test solution volumes of less than 5 ml should not be taken for dilution.

7.3.3 Precision of the calibration solution (see note 1)

If the test solution t gives an absorbance above 0,25, accurately dilute the manganese standard stock solution (4.10) to give a stock solution approximately 600 times the characteristic concentration. Using a burette, transfer 0 (zero member); 5,0 ml; 10,0 ml; 15,0 ml and 20,0 ml of this manganese standard solution to 100 ml one-mark volumetric flasks. Add 25 × 1/D of background solution (4.9) to each, dilute to the mark with water and mix. (D is the dilution factor of the test solution).

If the test solution t gives an absorbance below 0,25, make two solutions each containing 25,0 ml of background solution (4.9) per 100 ml, one containing 5 µg/ml of manganese and the other no added manganese. Using these, a rough estimate of the manganese in the test solution can be made. Accurately dilute the manganese standard stock solution (4.10) to give a stock solution with 10 times the manganese concentration of the test solution, as estimated above. Using a burette, transfer 0 (zero member); 5,0 ml; 10,0 ml; 15,0 ml and 20,0 ml of the manganese standard stock solution to 100 ml one-mark volumetric flasks. Add 25,0 ml of background solution (4.9) to each, dilute to the mark with water and mix.

For very low levels of manganese, the top standard solution should contain sufficient manganese to give full scale deflection when using maximum scale expansion compatible with an acceptable noise level. For low levels of manganese, e.g. below 0,020 % (m/m) Mn in the steel, the wavelength of 279,5 nm may be superior.

7.3.4 Adjustment of atomic absorption spectrometer

See table 1.

Table 1

Element	Characteristic
Type of lamp	Manganese hollow cathode
Wavelength	Manganese content less than 0,020 % (*m/m*): 279,5 nm Manganese content greater than 0,020 % (*m/m*): 403,1 nm
Flame	Air acetylene fuel-lean flame adjusted for maximum manganese response
Lamp current	Follow manufacturer's recommendations
Bandwidth	Follow manufacturer's recommendations

WARNING — The manufacturer's recommendations should be closely followed and particular attention is drawn to the following safety points:

a) the explosive nature of acetylene, and regulations concerning its use;

b) the need to shield the eyes of the operator from ultraviolet radiation by means of tinted glass;

c) the need to keep the burner head clear of deposits. A badly clogged burner may cause a flashback;

d) the need to ensure that the liquid trap is filled with water.

7.3.5 Optimization of the atomic absorption spectrometer settings

Follow the manufacturer's instructions for preparing the instrument for use.

After the current to the lamp, the wavelength and the flow of gas have been adjusted and the burner lit, spray water until the indication has been stabilized.

Set the absorbance value to zero using water.

Choose a damping setting or integration time to give a signal steady enough to fulfil the precision criteria of 5.2.1 to 5.2.3.

Adjust the flame to be just off luminous and the burner height to about 1 cm below the light path. Spray, alternately, the calibration solution of highest concentration and the zero member. Adjust the gas flow and burner position (horizontally, vertically and rotationally) until the difference in absorbance between the calibration solutions is at a maximum. Check that the spectrometer is set accurately on the required wavelength.

Evaluate the criteria of 5.2.1 to 5.2.3 and the additional performance requirement of 5.2.4 to ensure that the instrument is suitable for the determination of manganese.

7.3.6 Spectrometric measurements

Set the scale expansion so that the calibration solution of highest concentration gives nearly full scale deflection. After the instrument has achieved stability in accordance with the precision criterion given in 5.2.1, select two calibration solutions, one having an absorbance just lower than the test portion solution and one just higher. Spray these first in ascending order, then in descending order, with the test solution as the middle solution, in each case measuring the absorption in relation to water. Spray the complete range of calibration solutions again.

It is recognized that these procedures cannot be followed with automatic instruments which accept two calibration solutions only. In this case, it is suggested that the two "sandwiching" solutions should not be used for the primary calibration but should be analyzed alternately with the test solution.

Spray calibration solutions at frequent intervals during the measurement of a batch of determinations. Clean the burner if the results show loss of precision caused by clogging.

Obtain the absorbance of each calibration solution.

Obtain the absorbance of the test solution and the mean absorbance of the blank test.

7.4 Plotting the calibration graph

It is necessary to prepare a new calibration graph for each series of determinations.

If the zero member has a significant absorbance, the concentration of manganese $\rho_{\mathrm{Mn,z}}$ in the zero member can be calculated using the equation

$$\rho_{\mathrm{Mn,z}} = \rho_{\mathrm{Mn},c_1} \times \frac{A_{\mathrm{z}}}{A_{\mathrm{Mn},c_1} - A_{\mathrm{z}}}$$

where

ρ_{Mn,c_1} is the concentration of manganese, expressed in micrograms per millilitre, added to the first calibration solution;

A_{z} is the absorbance of the zero member;

A_{Mn,c_1} is the absorbance of the first calibration solution.

The derived value $\rho_{\mathrm{Mn,z}}$ is then added to each of the nominal calibration concentrations in order to obtain a mean calibration graph passing through the origin. Refer the absorbances of the blank solution, the test solution and the two adjacent calibration solutions to this graph. Subtract the concentration of the blank solution from the other concentrations.

Prepare a calibration graph by plotting the mean absorbance values of the calibration solutions against manganese contents, expressed in micrograms per millilitre. Refer the absorbances of the two adjacent calibration solutions to the graph. If these two calibration readings do not deviate from the graph by more than the permitted precision criteria, then the test solution readings are also acceptable.

8 Expression of results

8.1 Method of calculation

Convert the absorbances of the test solution and of the blank solution to micrograms of Mn per millilitre by means of the calibration graph (7.4).

The manganese content, expressed as a percentage by mass, w_{Mn}, is given by the equation

$$w_{\text{Mn}} = \frac{(\rho_{\text{Mn},1} - \rho_{\text{Mn},0}) \times D \times 100}{10^6} \times \frac{100}{m}$$

$$= \frac{(\rho_{\text{Mn},1} - \rho_{\text{Mn},0}) \times D}{100m}$$

where

$\rho_{\text{Mn},0}$ is the concentration, expressed in micrograms per millilitre, of manganese in the blank test (7.2);

$\rho_{\text{Mn},1}$ is the concentration, expressed in micrograms per millilitre, of manganese in the test solution derived from the calibration graph (7.4);

D is the dilution factor applied in 7.3.3;

m is the mass, in grams, of the test portion.

8.2 Precision

A planned trial of this method was carried out by 16 laboratories, at 10 levels of manganese, each laboratory making three determinations (see notes 3 and 4) of manganese content at each level.

The test samples used are listed in table B.1.

The results obtained were treated statistically in accordance with ISO 5725.

The manganese content obtained showed logarithmic relationships with repeatability (r) and reproducibility (R and R_w) of the test results (see note 5) as summarized in table 2 and table 3 for wavelengths 279,5 nm and 403,1 nm respectively. The graphical representations of the figures are given in annex C.

Table 2

Manganese content	Repeatability	Reproducibility	
% (m/m)	r	R	R_w
0,0020	0,000 27	0,000 60	0,000 40
0,0050	0,000 37	0,001 17	0,000 69
0,010	0,000 48	0,001 94	0,001 04
0,020	0,000 61	0,003 23	0,001 57

Table 3

Manganese content	Repeatability	Reproducibility	
% (m/m)	r	R	R_w
0,020	0,001 34	0,003 91	0,001 16
0,050	0,002 48	0,007 18	0,002 75
0,10	0,003 94	0,011 4	0,005 29
0,20	0,006 28	0,018 0	0,010 2
0,50	0,011 6	0,033 0	0,024 1
1,00	0,018 4	0,052 3	0,046 3
2,00	0,029 4	0,082 9	0,089 0
3,00	0,038 5	0,108 4	0,130 5

NOTES

3 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725, i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period of time.

4 The third determination was carried out at a different time (on a different day) by the same operator as in note 3 above using the same apparatus with a new calibration.

5 From the results obtained on day 1 the repeatability (r) and the reproducibility (R) were calculated using the procedure specified in ISO 5725. From the first result obtained on day 1 and the result obtained on day 2, the within-laboratory reproducibility (R_w) was calculated.

9 Special case

9.1 Manganese is sometimes retained in the acid-insoluble residues of those samples which contain large amounts of acid-insoluble carbides. For many samples, however, the amount of manganese remaining on the pad may be insignificant and the fusion step may be omitted. If, after washing, only a small quantity of pale siliceous residue remains on the filter pad, the pad can be discarded and the fusion step omitted. In this case the potassium hydrogen sulfate should be omitted from the background solution (4.9).

9.2 For samples containing large amounts of chromium carbide, further heating may be necessary to fuse the residue. The potassium hydrogen sulfate can be regenerated by allowing the fusion products to cool, adding two drops of sulfuric acid (4.6) and repeating the fusion. This can be repeated until the residue has dissolved. The final fusion should be at a fairly low temperature to avoid the formation of chromium sulfate which is rather inert.

10 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis;

b) the method used by reference to this Technical Report;

c) the results, and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this Technical Report, or any optional operation which may have influenced the results.

Annex A
(normative)

Procedures for the determination of instrumental criteria

A.1 General

For the preparation of standard methods of analysis using flame atomic absorption spectrometry, these criteria should be decided by the working group in charge of inter-laboratory test results.

A.2 Determination of minimum precision

Spray the most concentrated calibration solution 10 times to obtain 10 individual absorbance readings A_{Ai} and calculate the mean value $\bar{A}_A$.

Spray the least concentrated calibration solution (excluding the zero member) 10 times to obtain 10 individual absorbance readings A_{Bi} and calculate the mean value $\bar{A}_B$.

The standard deviations s_A and s_B of the most and least concentrated calibration solutions respectively are obtained from the equations

$$s_A = \sqrt{\frac{\sum (A_{Ai} - \bar{A}_A)^2}{9}}$$

$$s_B = \sqrt{\frac{\sum (A_{Bi} - \bar{A}_B)^2}{9}}$$

The minimum precisions of the most and least concentrated calibration solutions are obtained from $s_A \times 100/\bar{A}_A$ and $s_B \times 100/\bar{A}_A$, respectively.

A.3 Determination of limit of detection $\rho_{Mn,min}$

Prepare two solutions each containing the same matrix concentration as the sample solution, but with the element of interest at the following known concentrations:

- ρ'_{Mn} µg/ml to give an absorbance A' of approximately 0,01;
- matrix blank to give an absorbance A_0.

Spray the ρ'_{Mn} solution and blank solution 10 times each, recording each reading for about 10 s, and using sufficient scale expansion to make the fluctuations in signal clearly visible.

Obtain the mean absorbance readings $\bar{A}'$ and $\bar{A}_0$.

The standard deviation $s_{A'}$ is given by the equation

$$s_{A'} = \sqrt{\frac{\sum (A'_i - \bar{A}')^2}{9}}$$

where

A'_i is the individual measured absorbance reading;

$\bar{A}'$ is the mean value of A'_i.

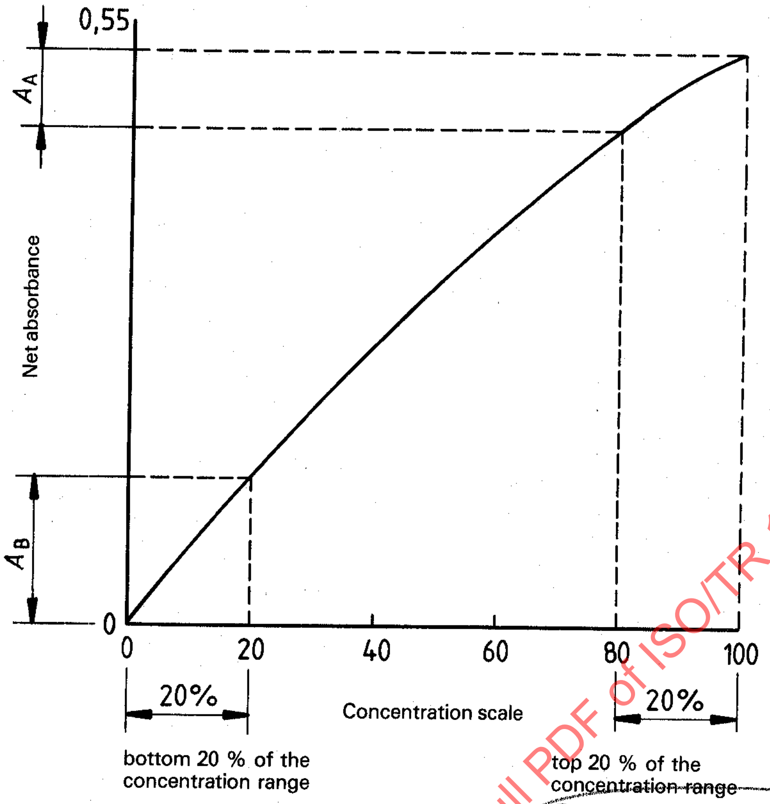
The limit of detection $\rho_{Mn,min}$ is given by the equation

$$\rho_{Mn,min} = \frac{\rho'_{Mn} \times s_{A'} \times k}{\bar{A}' - \bar{A}_0}$$

(k is normally taken as 2)

A.4 Criterion for graph linearity

After having established the calibration graph, before the application of any curve-straightening device, obtain the net absorbance value A_A corresponding to the top 20 % of the concentration range and the net absorbance value A_B corresponding to the bottom 20 % of the concentration range. Calculate A_A/A_B. This must not be less than 0,7.



See figure C.1

Figure A.1

A.5 Determination of characteristic concentration [illegible] $\varrho_{\mathrm{Mn},k}$

Prepare a solution containing the same matrix concentration as the sample solution, but with the element of interest at the following known concentration: ρ_{Mn} µg/ml to give an absorbance A of approximately 0,1.

Spray the ρ_{Mn} solution and blank solution without scale expansion and measure the absorbances A and A_0. The characteristic concentration [illegible] is given by the equation

$$[illegible] = \frac{\rho_{\mathrm{Mn}} \times 0{,}004\ 4}{A - A_0}$$

(+2) H $\varrho_{\mathrm{Mn},k}$

because ϱ_k is the symbol for a density.