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

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

Reference number
ISO 9647 : 1989 (E)

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 9647 was prepared by Technical Committee ISO/TC 17, *Steel*.

Annex C forms an integral part of this International Standard.

Annexes A and B are for information only.

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INTERNATIONAL STANDARD **ISO 9647 : 1989 (E)**

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

1 Scope

This International Standard specifies a flame atomic absorption spectrometric method for the determination of vanadium in steel and iron.

The method is applicable to vanadium contents between 0,005 % *(m/m)* and 1,0 % *(m/m)*, provided that the tungsten content in the test portion is not higher than 10 mg and/or the titanium content is not higher than 5 mg.

2 Normative references

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

ISO 377 : 1985, *Wrought steel — Selection and preparation of samples and test pieces.*

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, nitric and perchloric acids.

Addition of aluminium solution as spectrochemical buffer.

Spraying the solution into a dinitrogen monoxide-acetylene flame.

Spectrometric measurement of the atomic absorption of the 318,4 nm spectral line emitted by a vanadium hollow cathode lamp.

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, containing less than 0,000 5 % *(m/m)* of vanadium, or of low known vanadium content.

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

4.3 Nitric acid, ρ about 1,40 g/ml.

4.4 Perchloric acid, ρ about 1,67 g/ml.

4.5 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1 + 50.

4.6 Aluminium, solution, 20 g/l.

Dissolve 90 g of aluminium chloride hexahydrate $[AlCl_3 \cdot 6H_2O]$ in about 300 ml of water, add 5 ml of hydrochloric acid (4.2), dilute to 500 ml with water and mix.

4.7 Vanadium, standard solutions.

4.7.1 Stock solution, corresponding to 2 g of V per litre.

4.7.1.1 Preparation using vanadium metal

Weigh, to the nearest 0,001 g, 1,000 g of high purity vanadium [purity > 99,9 % *(m/m)*] and dissolve in 30 ml of aqua regia [mix three volumes of hydrochloric acid (4.2) with one volume of nitric acid (4.3)].

Heat to evaporate to just before dryness and add 20 ml of hydrochloric acid (4.2). Cool and transfer the solution quantitatively to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this solution contains 2 mg of V.

4.7.1.2 Preparation using ammonium metavanadate

Dry several grams of ammonium metavanadate (NH_4VO_3) [purity > 99,9 % (*m*/*m*)] in an air oven at 100 °C to 105 °C [see the note] for at least 1 h and cool to room temperature in a desiccator. Weigh 2,296 g of the dried product into a 800 ml beaker, add about 400 ml of hot water and gently simmer to dissolve. Cool, transfer to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this solution contains 2 mg of V.

NOTE — A drying temperature over 110 °C will cause decomposition of ammonium metavanadate. Keep strictly to the drying temperature specified.

4.7.2 Standard solution, corresponding to 0,08 g of V per litre.

Transfer 10,0 ml of the stock solution (4.7.1) into a 250 ml one-mark volumetric flask, dilute to the mark with water and mix. Prepare this standard solution immediately before use.

1 ml of this standard solution contains 0,08 mg of V.

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 Atomic absorption spectrometer

A vanadium hollow cathode lamp; supplies of dinitrogen monoxide and acetylene sufficiently pure to give a steady clear red-feather flame, free from water and oil, and free from vanadium.

The atomic absorption spectrometer used will be satisfactory if after optimization according to 7.3.4 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 5.1.1 to 5.1.3.

It is also desirable that the instrument should conform to the additional performance requirement given in 5.1.4.

5.1.1 Minimum precision (see clause C.1)

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

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

5.1.2 Limit of detection (see clause C.2)

This is defined as twice the standard deviation of 10 measurements of the absorbance of a solution containing the appropriate element of a concentration level selected to give an absorbance just above that of the zero member.

The limit of detection of vanadium in a matrix similar to the final test portion solution shall be better than 0,3 µg of V per millilitre.

5.1.3 Graph linearity (see clause C.3)

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 determined in the same way.

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

5.1.4 Characteristic concentration (see clause C.4)

The characteristic concentration for vanadium in a matrix similar to the final test portion solution shall be better than 1 µg of V per millilitre.

5.2 Ancillary equipment

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria of 5.1.1 to 5.1.3 and for all subsequent measurements.

Scale expansion can be used until the noise observed is greater than the readout 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 a suitable solution with and without scale expansion and simply dividing the signal obtained.

6 Sampling

Carry out sampling in accordance with ISO 377 or appropriate national standards for iron.

7 Procedure

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic material in general.

7.1 Test portion

Weigh a test portion according to the presumed vanadium content as follows:

a) for vanadium contents from 0,005 % (*m*/*m*) to less than 0,2 % (*m*/*m*), a test portion of approximately 1,00 g, to the nearest 0,001 g;

b) for vanadium contents from 0,2 % (m/m) to 1,0 % (m/m), a test portion of approximately 0,20 g, to the nearest 0,000 2 g.

7.2 Blank test

Parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents including the pure iron (4.1).

7.3 Determination

7.3.1 Preparation of the test solution

Place the test portion (7.1) in a 250 ml beaker. Add 10 ml of hydrochloric acid (4.2) and 4 ml of nitric acid (4.3) and cover the beaker with a watch-glass. After effervescence ceases, add 10 ml of perchloric acid (4.4) and evaporate the solution until fumes of perchloric acid are visible, remove the watch-glass and evaporate until no more fumes come out of the beaker.

Allow to cool, add 10 ml of hydrochloric acid (4.2) and 20 ml of water, and heat gently to dissolve the salts. Filter through a medium texture filter paper into a 100 ml one-mark volumetric flask. Wash with warm hydrochloric acid (4.5), and add the washings to the flask. Cool, add 10,0 ml of aluminium solution (4.6), dilute to the mark with water and mix.

7.3.2 Preparation of the calibration solutions

7.3.2.1 Vanadium content < 0,2 % (m/m)

Introduce into a series of seven 250 ml beakers (1,00 ± 0,01) g of the pure iron (4.1), add 10 ml of hydrochloric acid (4.2) and 4 ml of nitric acid (4.3) to each beaker and cover them with watch-glasses. After effervescence ceases, cool, then respectively add, using a burette, the volumes of vanadium standard solution (4.7.2) indicated in table 1.

Table 1

Volume of vanadium standard solution (4.7.2) ml	Corresponding mass of vanadium mg
0*)	0
2,5	0,20
5,0	0,40
10,0	0,80
15,0	1,20
20,0	1,60
25,0	2,00

*) Zero member.

Proceed as specified in 7.3.1 from "add 10 ml of perchloric acid (4.4)..." (2nd sentence of 1st paragraph) to the end.

7.3.2.2 Vanadium content between 0,2 % (m/m) and 1,0 % (m/m)

Introduce into a series of seven 250 ml beakers (0,20 ± 0,01) g of the pure iron (4.1), add 10 ml of hydrochloric acid (4.2) and 4 ml of nitric acid (4.3) to each beaker and cover them with watch-glasses. After effervescence ceases, cool, then respectively add, using a burette, the volumes of vanadium standard solution (4.7.2) indicated in table 1. Proceed as specified in 7.3.1 from "add 10 ml of perchloric acid (4.4)..." (2nd sentence of 1st paragraph) to the end.

7.3.3 Adjustment of atomic absorption spectrometer

See table 2.

Table 2

Type of lamp	Vanadium hollow cathode
Wavelength	318,4 nm
Flame	Dinitrogen monoxide-acetylene red-feather flame adjusted for maximum vanadium response
Lamp current	Follow manufacturer's recommendations
Bandwidth	Follow manufacturer's recommendations

NOTE — 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 because a badly clogged burner may cause a flashback;

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

7.3.4 Optimizing the atomic absorption spectrometer settings

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

When 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 stabilized.

Set the absorbance value at zero using the zero member (7.3.2).

Choose a damping setting or integration time to give a signal steady enough to fulfil the precision criteria of 5.1.1 to 5.1.3.

Adjust the flame to a red feather and the observation height in the flame to about 20 mm. Spraying 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 5.1.1 to 5.1.3 and the additional performance requirement of 5.1.4 to ensure that the instrument is suitable for the determination.

7.3.5 Spectrometric measurements

Set the scale expansion so that the calibration solution of highest concentration gives nearly full scale deflection. Spray the calibration solutions in ascending order repetitively until each gives the specified precision, thus showing that the instrument has achieved stability. 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 (see the note).

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 analysed 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.

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

NOTE — The following safety precautions shall be taken when perchloric acid is used:

a) spray all solutions for the shortest practical period;

b) always spray distilled water between the test solutions, blank solutions and/or calibration solutions. Minimize the spraying of air;

c) clean the burner frequently, never allow the burner to clog, and wash it thoroughly both inside and out.

Ensure that all safety covers are in position, and wear approved ear protectors and safety glasses.

7.4 Plotting the calibration graph

It is necessary to prepare a new calibration graph for each series of determinations, and for the range of vanadium contents expected.

If pure metals and reagents have been used, the zero member should have a negligibly small absorbance. In this case, prepare a calibration graph by plotting the mean absorbance values of the calibration solutions against micrograms of vanadium per millilitre. Refer the mean test solution absorbances and the absorbances of the two adjacent calibration solutions to the graph.

If, however, the zero member has a significant absorbance a more complicated procedure is required. In this case, the concentration of vanadium ϱ_z in the zero member can be calculated using the equation

$$\varrho_z = \varrho_{c1} \times \frac{A_z}{A_{c1} - A_z}$$

where

ϱ_{c1} is the concentration of vanadium, expressed in micrograms per millilitre, added to the first calibration solution;

A_z is the absorbance of the zero member;

A_{c1} is the absorbance of the first calibration solution.

The derived value ϱ_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 absorbance values of the calibration solutions against vanadium content, 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

The vanadium content, expressed as a percentage by mass, w_V (%) is given by the equation

$$w_V\,(\%) = \frac{(\varrho_0 - \varrho_1) \times 100}{10^6} \times \frac{100}{m} + C$$

$$= \frac{(\varrho_0 - \varrho_1)}{100\,m} + C$$

where

ϱ_0 is the concentration, expressed in micrograms per millilitre, of vanadium in the test solution derived from the calibration graph (7.4);

ϱ_1 is the concentration, expressed in micrograms per millilitre, of vanadium in the blank test (7.2);

C is the vanadium content, expressed as a percentage by mass, in the iron used in the blank test;

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

8.2 Precision

A planned trial of this method was carried out by 23 laboratories, at seven levels of vanadium, each laboratory making three determinations (see notes 1 and 2) of vanadium content at each level.

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

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

The data obtained showed a logarithmic relationship between vanadium content and repeatability (r) and reproducibility (R and R_w) of the test results (see note 3) as summarized in table 3. The graphical representation of the figures is given in annex B.

NOTES

1 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.

2 The third determination was carried out at a different time (on a different day) by the same operator as in note 1 using the same apparatus with a new calibration.

3 From the results obtained on Day 1 the repeatability (r) and 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 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 International Standard;

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 International Standard, or any optional operation which may have influenced the results.

Table 3

Vanadium content % (m/m)	Repeatability	Reproducibility	
	r	R	R_w
0,005	0,000 5	0,001 6	0,001 5
0,010	0,000 8	0,002 4	0,002 2
0,020	0,001 4	0,003 7	0,003 1
0,050	0,002 7	0,006 4	0,005 0
0,100	0,004 6	0,009 9	0,007 1
0,200	0,007 9	0,015 1	0,010 2
0,500	0,015 8	0,026 4	0,016 2
1,000	0,026 8	0,040 4	0,023 1

Annex A
(informative)

Additional information on the international co-operative tests

Table 3 was derived from the results of international analytical trials carried out in 1985 on six steel samples and one pig iron sample in ten countries involving 23 laboratories.

The results of the trials were reported in document 17/1 N 646, March 1986. The graphical representation of the precision data is given in annex B.

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

Table A.1

Sample	Vanadium content % (m/m)		
	Certified	Found	
		$\overline{w}_1$	$\overline{w}_2$
JSS 113-2 (Pig iron)	0,007	0,007 2	0,006 9
JSS 516-4 (Low alloy steel)	0,010	0,009 8	0,009 8
JSS 652-7 (Stainless steel)	0,038*)	0,038 0	0,037 8
JSS 152-8 (Low alloy steel)	0,10	0,106	0,106
JSS 153-7 (Low alloy steel)	0,21	0,215	0,214
JSS 604-7 (Tool steel)	0,51	0,516	0,516
CMIEC CE 058 (Low alloy steel)	0,75	0,748	0,751

*) : non-certified value

$\overline{w}_1$: general mean within a day

$\overline{w}_2$: general mean between days

CMIEC : Chemical Standard prepared by CHINA Metallurgical Import and Export Corporation.

Annex B
(informative)

Graphical representation of precision data

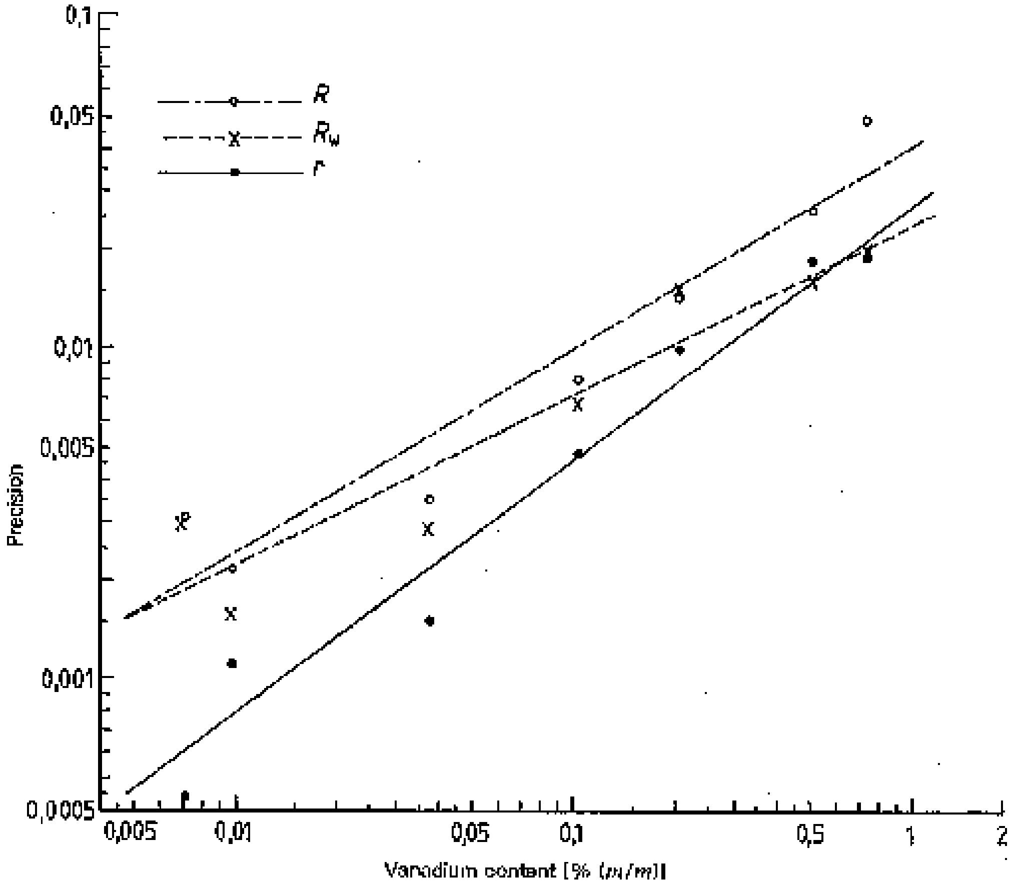


Figure B.1 — Logarithmic relationship between vanadium content [% (*m*/*m*)] and repeatability, *r*, or reproducibility, *R* and R_w

Annex C
(normative)

Procedures for the determination of instrumental criteria

C.1 Determination of minimum precision

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

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

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

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

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

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

C.2 Determination of limit of detection ϱ_{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' µg/ml to give an absorbance A' of approximately 0,01;
- matrix blank to give an absorbance A_0.

Spray the ϱ' and blank solutions ten 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 $\overline{A}'$ and $\overline{A}_0$.

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

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

where

A'_i is the individual measured absorbance reading;

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

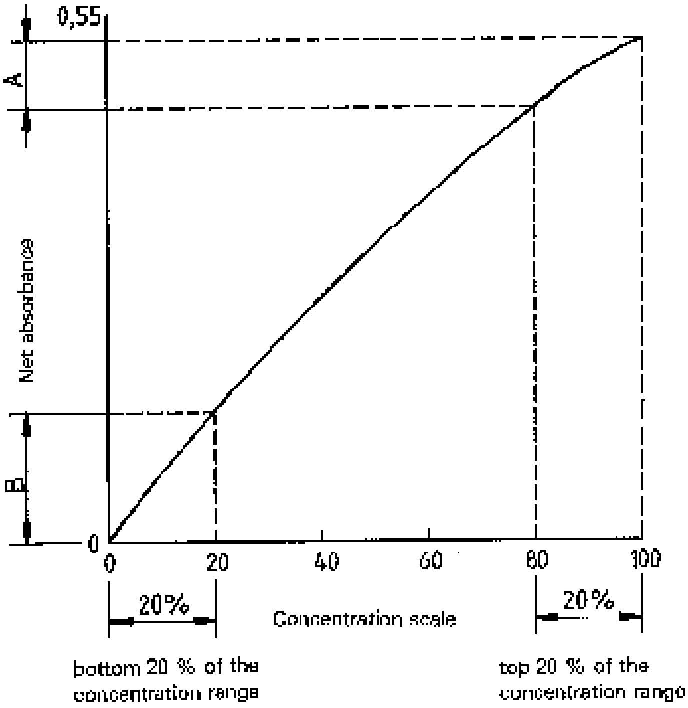
The limit of detection ϱ_{min} is given by the equation

$$\varrho_{min} = \frac{\varrho' \times s_{A'} \times k}{\overline{A}' - \overline{A}_0}$$

(k is normally taken as 2)

C.3 Criterion for graph linearity

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



C.4 Determination of characteristic concentration ϱ_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 µg/ml to give an absorbance A of approximately 0,1.

Spray the ϱ and the blank solutions without scale expansion and measure the absorbances A and A_0. The characteristic concentration ϱ_k is given by:

$$\varrho_k = \frac{\varrho \times 0{,}004\,4}{A - A_0}$$

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

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