
Optična emisijska analiza malolegiranih jekel (rutinska metoda) – Metoda za določevanje C, Si, S, P, Mn, Cr, Ni in Cu

Optical emission analysis of low alloy steels (routine method) - Method for determination of C, Si, S, P, Mn, Cr, Ni and Cu

Optische Emissionsanalyse von niedriglegierten Stählen (Reihenanalyse) - Verfahren zur Bestimmung von C, Si, S, P, Mn, Cr, Ni und Cu

Analyse des aciers faiblement alliés par spectrométrie d'émission optique (méthode de routine) - Méthode de détermination de C, Si, S, P, Mn, Cr, Ni et Cu

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English version

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Method for determination of C, Si, S, P, Mn, Cr, Ni and Cu**

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d'émission optique (méthode de routine) - Méthode de
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(Reihenanalyse) - Verfahren zur Bestimmung von C, Si, S,
P, Mn, Cr, Ni und Cu

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

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Foreword

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CR 10320:2004 (E)**1 Scope**

This document specifies an optical emission spectrometry spark source routine standard method for multi-element analysis of unalloyed steel and iron.

2 Test sample preparation

Prepare reference materials, test samples and setting up samples, by grinding to provide a uniform flat surface. It is recommended a surface grinder with aluminium oxide, or zirconium oxide, abrasive to be employed with a coarse grit of 60 - 100.

3 Calibration of the instrument**3.1 Determination of calibration curve**

Analyse a series of reference materials (min. 5) for the element intensity/matrix intensity ratio according to the pattern shown in Figure 1.

Calculate the average intensity for each reference material.

NOTE In (Figure 1) the first group values into parentheses refers to odd ns.

Correlate the average intensity ratio with the concentration of test element.

$$c\% = \sum_{i=0}^n A_i I^i \quad \text{SIST-TP CEN/CR 10320:2004} \quad (1)$$

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where:

A_i means correlation constants;

I^i means unknown values (intensity ratio).

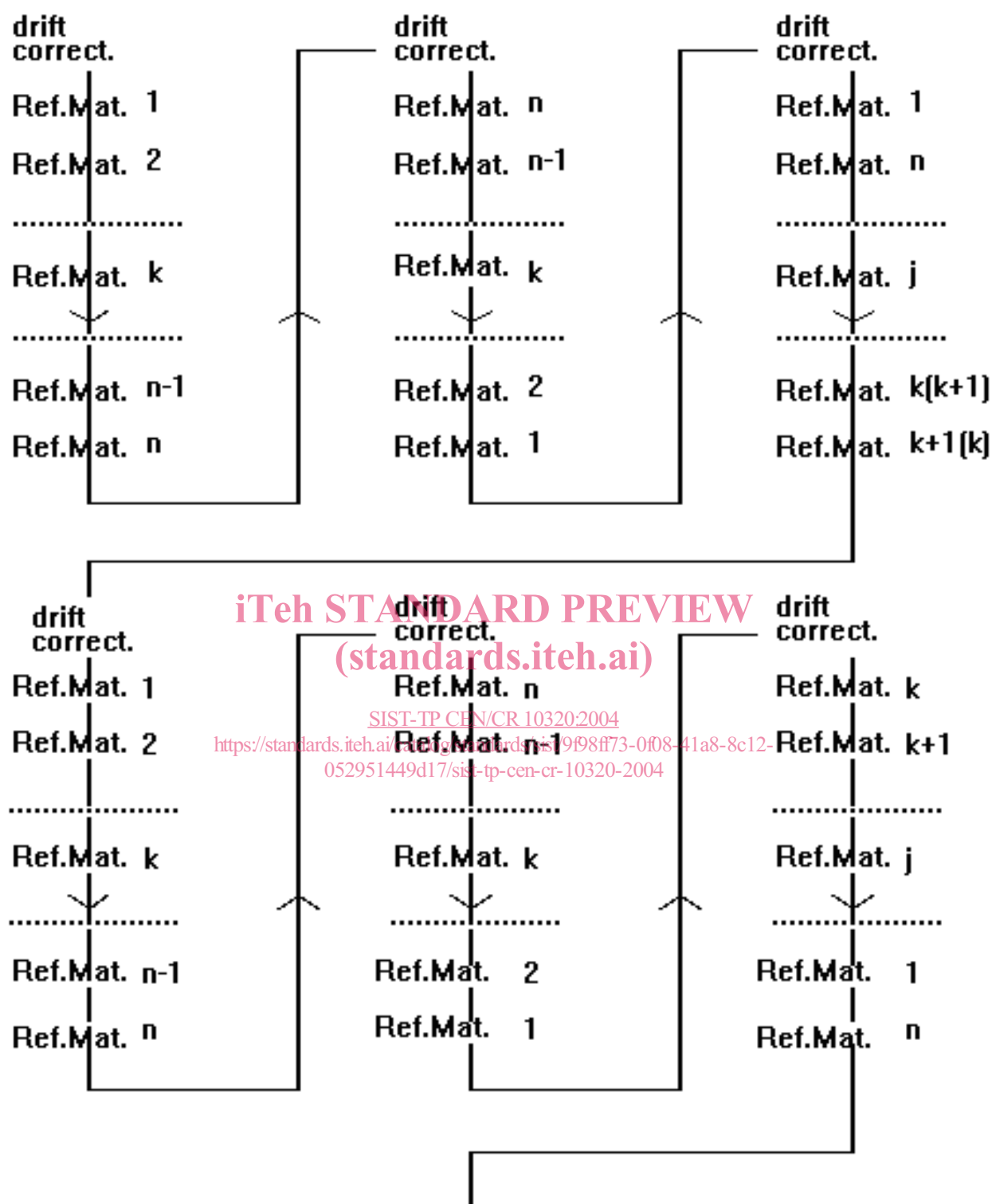


Figure 1

3.2 Linear correlation

For linear correlations, constants are calculated in the following way:

$$A_0 = y_m - A_1 x_m \quad (2)$$

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$$A_1 = \frac{\sum(xy)}{\sum(x)^2} \quad (3)$$

where:

\bar{x}_m and \bar{y}_m are average values ($\sum \bar{m}/n$);

n number of points;

x and y are intensity ratio readouts and concentrations, respectively, of test samples.

Besides correlation parameters, calculate the following:

$$r^2 = \frac{[n \sum xy - \sum x \sum y]^2}{[n \sum (x)^2 - (\sum x)^2] \times [n \sum (y)^2 - (\sum y)^2]} \quad (4)$$

where r is the correlation coefficient.

A_0 and A_1 may also be calculated by single values according to the following equations:

$$A_0 = \frac{\sum y \sum (x)^2 - \sum (xy) \sum x}{n \sum (x)^2 - (\sum x)^2} \quad (5)$$

$$A_0 = \frac{\sum y - A_1 (\sum x)}{n} \quad (6)$$

$$A_1 = \frac{n(\sum xy) - \sum x \sum y}{n \sum (x)^2 - (\sum x)^2} \quad (7)$$

3.3 Quadratic correlation

Calculate constants in the following way, by resolving the system:

$$A_0 \sum (x)^2 + A_1 \sum (x)^3 + A_2 \sum (x)^4 = \sum (x)^2 (y) \quad (8)$$

$$A_0 \sum x + A_1 \sum (x)^2 + A_2 \sum (x)^3 = \sum (xy) \quad (9)$$

$$A_0 n + A_1 \sum x + A_2 \sum (x)^2 = \sum y \quad (10)$$

where:

n is the number of tests.

$$r^2 = 1 - \frac{\sum (c_{it} - c_{ic})^2}{\sum (c_{it} - c_a)^2} \quad (11)$$

where:

c_{it} is the true value of the reference material i ;

c_{iC} is the value of the reference material i read on the calibration curve;

c_a is the average concentration of all the c_{iC}

3.4 Confidence limit (S_{yc}) and standard error (S_{yx}) in a linear correlation

Confidence limit indicates the area where the true value of y for a given x lies at 95 % of probability. In other words, it indicates the area including the regression range. The slope error is an evidence of the method sensitivity, in fact the wider x range the lower the slope error. The standard error in a correlation is the extent of the deviation around the regression line. Calculate the standard error in a linear correlation by the following formula:

$$S_{yx} = \sqrt{\frac{\sum (y)^2 - A_0 \sum y - A_1 \sum (xy)}{n-2}} \quad (12)$$

and the confidence limit:

$$S_{yc} = S_{yx} \times \sqrt{\frac{1}{n} + \frac{(x_i - x_m)^2}{\sum (x)^2}} \quad (13)$$

Calculate the slope error (S_b) as follows:

$$S_b = \frac{S_{yx}}{\sqrt{\sum (x)^2}} \quad (14)$$

3.5 Confidence limit (S_{yc}) and standard error (S_{yx}) in a quadratic correlation

Calculate the standard error in a quadratic correlation by the following formula:

$$S_{yx} = \sqrt{\frac{\sum (y)^2 - A_0 \sum y - A_1 \sum (xy) - A_2 \sum (x^2 y)}{n-2}} \quad (15)$$

and the confidence limit:

$$S_{yc} = S_{yx} \times \sqrt{\frac{1}{n} + \frac{(x_i - x_m)^2}{\sum (x)^2}} \quad (16)$$

Calculate the slope error (S_b) as follows:

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$$Sb = \frac{S_{yx}}{\sqrt{\sum (x)^2}} \quad (17)$$

3.6 Correlation accuracy

Among reference standards, either secondary or tertiary, select a low, a medium and a high standard and determine their repeatability both in concentration and intensity ratio. The resulting values indicate the method accuracy index at the specific concentration (intensity ratio).

If *RSD* is correlated with concentration, a change in repeatability is obtained with respect to concentration.

4 Calculation of interferences

4.1 Spectral interferences

In the line intensity/matrix ratio, analyse at least 5 reference materials on the interference line with a variable concentration of the interfering element but possibly free from the interfered element. Analyses should be repeated at least four times after performing the drift correction, according to the Figure 2 scheme. Calculate the average intensity ratio for each reference material and compute the corresponding concentration of interfered element.

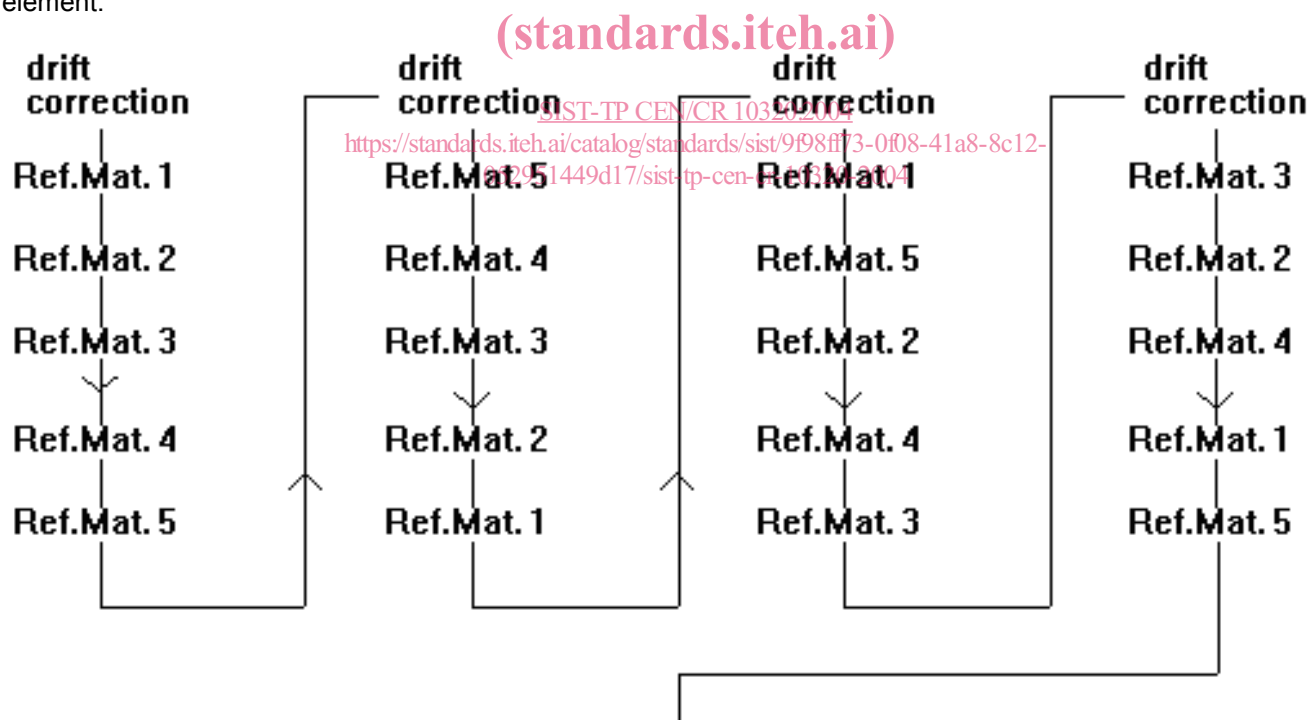


Figure 2

Correlate the resulting concentrations to the concentration of the interfering element by the method of least squares. The following equation is obtained:

$$c\% = \sum_{i=0}^n A_i c_i^i \quad (18)$$

where:

$c\%$ is the concentration of the interfered element;

c_i is the concentration of the interfering element;

A_i is the correlation constants (it is advisable to calculate a straight line).

The angle coefficient of the straight line (A_1) is the factor of spectral interference of the element interfering over the analyte.

This factor is nonlinear only rarely and for wide concentration ranges of the interfering and/or interfered elements. In this case it is advisable to work with analyte families and limit concentration ranges.

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The following equation calculates the analyte concentration:

$$c^0\% = \sum_{i=0}^n A_i I^i + \sum_{j=0}^k f_j c_j \quad (19)$$

where:

f_j means the factor of spectral interference of element j over the analyte;

c_j means its concentration.

It is possible to calculate interference factors in intensity. In this case correlations must be made with intensities. The following formula is used to calculate f_j easier and when only one interfering element has been detected:

$$c^0\% = \sum_{i=0}^n A_i I^i + f_1 c_1 \quad (20)$$

$$f_1 = \frac{c^0\% - \sum_{i=0}^n A_i I^i}{c_1} \quad (21)$$

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Suitable reference materials must be selected that have a variable concentration of the interfering element and that have already been analysed during the calibration curve construction.

4.2 Matrix interferences

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Having established that matrix interferences are minimized by subdividing test samples into spectral families, it is however possible to calculate them by selecting at least 5 reference materials with a composition as close as possible to the matrix, the interfering and the interfered element in variable concentration. Analyse materials according to the previous scheme and calculate interference factors by the following equation:

$$c^0\% = \sum_{i=0}^n A_i I^i \left(1 + \sum_{t=0}^k f_t c_t \right) \quad (22)$$

where:

f_t is the interference factor of element t over the analyte;

c_t is its concentration.

4.3 Calculation of an interfered element due to either matrix effect or spectral interference

The concentration of an interfered element, due to either matrix effect or line overlap, is calculated by the following formula:

$$c^0\% = \sum_{i=0}^n A_i I^i \left(1 + \sum_{t=0}^k f_t c_t \right) + \sum_{j=0}^s f_j c_j \text{ for } t \neq j \quad (23)$$

5 Determination of performance criteria

5.1 Determination of background equivalent concentration *BEC*

The background equivalent concentration corresponds to a net intensity whose value is equal to background intensity. It is calculated as follows:

- Calculate calibration curve;
- Determine background intensity, i.e. the intensity corresponding to the intercept between curve and axis of abscissas (I_0);
- Multiply I_0 by 2 ($I_0 \times 2 = I_B$);
- With correlation parameters, calculate the concentration equivalent to I_B . The resulting value corresponds to the *BEC* of the test element.

In a linear concentration, *BEC* is equal to the known term multiplied by -1.

5.2 Determination of detection limit *DL*

The detection limit may be assessed in two different ways according to whether the instrument *DL* for a given analyte line or the method *DL* is to be calculated

5.2.1 Detection limit of the method

5.2.1.1 Base straight line curve

- Record the element intensity/matrix ratio for a series of reference materials (min. 4) in a matrix pattern as in the following example:

RefMat	1	2	3	4
Conc.	C ₁	C ₂	C ₃	C ₄
Int.	I ₁₁	I ₂₁	I ₃₁	I ₄₁
	I ₁₂	I ₂₂	I ₃₂	I ₄₂
.....				
	I ₁₆	I ₂₆	I ₃₆	I ₄₆

- Calculate:

RefMat	1	2	3	4
Conc.	C ₁	C ₂	C ₃	C ₄
Int.	I ₁₁	I ₂₁	I ₃₁	I ₄₁
	I ₁₂	I ₂₂	I ₃₂	I ₄₂
.....				
	I ₁₆	I ₂₆	I ₃₆	I ₄₆

Σ	Σ I _{1i}	Σ I _{2i}	Σ I _{3i}	Σ I _{4i}
mean	I _{1m}	I _{2m}	I _{3m}	I _{4m}
Σ (I _{ni}) ²	Σ (I _{1i}) ²	Σ (I _{2i}) ²	Σ (I _{3i}) ²	Σ (I _{4i}) ²

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c) Calculate Sp^2 (pooled estimate of standard deviation) according to the following formula:

$$Sp^2 = \frac{\sum (I_i)^2 - \left[\frac{(\sum I_1)^2}{n_1} + \frac{(\sum I_2)^2}{n_2} + \dots + \frac{(\sum I_k)^2}{n_k} \right]}{N - k} \quad (24)$$

where:

I_i represents all readings;

n_i is the number of readings for each reference material;

N is the total number of readings;

k is the number of test samples.

d) From the equation of the calibration curve

$$c\% = A_1 I + A_0 \quad (25)$$

calculate the DL for a discharge:

$$DL = A_1 \times t \times Sp \quad (26)$$

where:

t is the t of Student at 95 % for $N - k$ degrees of freedom.

If r discharges are struck during an analysis:

$$DLr = \frac{DL}{\sqrt{r}} \quad (27)$$

where DLr is the limit of determination.

5.2.1.2 Quadratic base curve

Calculate a straight line with the lowest 5 points in the curve and compute as per point 5.2.1.1.

5.2.2 Instrument detection limit DLi

Perform 10 analyses on a reference material with an analyte concentration equal to the background. Calculate the standard deviation of the resulting concentrations. DL is obtained from:

$$DLi = 3 \times \sqrt{2} \times s_0 \quad (28)$$

where:

s_0 is standard deviation of concentrations

5.3 Determination of repeatability as relative standard deviation *RSD*

Over a short time period, perform 10 analyses on a reference material without making any drift correction between an analysis and the other. The instrument repeatability *RSD*, with a 95 % confidence limit, is expressed by:

$$RSD = 2\sqrt{\frac{\sum (d_i)^2}{2(n-1)}} \quad (29)$$

where:

d_i is the difference between a given value (intensity or concentration) and the average value of it;

n is the number of analyses.

Calculate repeatability for at least 3 reference materials with low, medium and high concentration within the calibration curve validity range.

5.4 Determination of accuracy *SEA*

Perform at least 10 analyses, each time making a drift correction, with a reference material belonging to a specific analyte family that has not been used in the calibration curve construction. The spectrometer accuracy, with a 95 % confidence limit, is expressed by:

$$SEA = 2\sqrt{\frac{\sum (d_i)^2}{2(n-I-1)}} \quad (30)$$

where:

d_i is the difference between calculated and true concentration;

n is the number of analyses;

I is the degree of the calibration curve polynomial.

Calculate the instrument accuracy for at least 3 reference materials with low, medium and high concentration within the calibration curve validity range.

6 Performing analysis

Place the sample on the sample table and position the ground surface over the counter electrode.

Excite the sample. At the end of the instrument analysis cycle, record the reading (if the intensity ratio is read), or the concentration % m/m.

Reanalyze the sample, average the duplicate readings for each element.

Excite the samples in two opposite sides of the surface, half way between the center and the end of the grinded surface.