
**Routine method for analysis of high alloy
steel by X-ray fluorescence spectrometry
(XRF) by using a near-by technique**

*Méthode de routine pour l'analyse des aciers fortement alliés par
spectrométrie de fluorescence de rayons X (FRX) à l'aide d'une
méthode de correction*

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Published in Switzerland

Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 17054 was prepared by the European Committee for Standardization (CEN) (as EN 10315:2006) and was adopted by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

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Foreword

This document (EN 10315:2006) has been prepared by Technical Committee ECISS/TC 20 “Methods of chemical analysis of ferrous products”, the secretariat of which is held by SIS.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by December 2006, and conflicting national standards shall be withdrawn at the latest by December 2006.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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EN 10315:2006 (E)

1 Scope

This European Standard specifies a procedure on how to improve the performance of a routine XRF method, already in use for analysis of high alloy steels, by using a "near by technique".

The "near by technique" requires at least one target sample (preferable a CRM) of a similar composition as the unknown sample.

The method is applicable to elements within the concentration ranges according to Table 1:

Table 1 — Concentration ranges

Element	Concentration range, % (m/m) ^a
Si	0,05 to 1,5
Mn	0,05 to 5,0
P	0,005 to 0,035
Cr	10 to 25
Ni	0,1 to 30
Mo	0,1 to 6,5
Cu	0,02 to 1,5
Co	0,015 to 0,30
V	0,015 to 0,15
Ti	0,015 to 0,50
Nb	0,05 to 1,0
^a The concentration ranges specified, represents those ranges studied during the precision test. The procedure has the potential to be used outside those ranges <u>but</u> it needs to be validated by each laboratory in every case.	

The method is applicable to analysis of either chill-cast or wrought samples having a diameter of at least 25 mm and with a carbon concentration of less than 0,3 % (see NOTE). Other elements should have a concentration below 0,2 %.

NOTE High carbon concentrations, in combination with high Mo and Cr concentrations, could have undesirable structural effects on the sample and could affect the determination of phosphorus and chromium, in particular.

Matrix effects exist between the elements listed. To compensate for those inter-element effects, mathematical corrections shall be applied. A variety of computer programs for corrections is commonly used and included in the software package from the manufacturers.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 10280, *Steel and iron — Determination of titanium content — Diantipyrylmethane spectrophotometric method (ISO 10280:1991)*

EN ISO 10700, *Steel and iron — Determination of manganese content — Flame atomic spectrometric method (ISO 10700:1994)*

EN ISO 10714, *Steel and iron — Determination of phosphorus content — Phosphovanadomolybdate spectrophotometric method (ISO 10714:1992)*

EN ISO 14284, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition (ISO 14284:1996)*

CR 10299, *Guidelines for the preparation of standard routine methods with wavelength-dispersive X-ray fluorescence spectrometry*

ISO 4829-1, *Steel and cast iron — Determination of total silicon content — Reduced molybdosilicate spectrophotometric method — Part 1: Silicon contents between 0,05 and 1,0 %*

ISO 4829-2, *Steel and iron — Determination of total silicon content — Reduced molybdosilicate spectrophotometric method — Part 2: Silicon contents between 0,01 and 0,05 %*

ISO 4937, *Steel and iron — Determination of chromium content — Potentiometric or visual titration method*

ISO 4938, *Steel and iron — Determination of nickel content — Gravimetric or titrimetric method*

ISO 4942, *Steel and iron — Determination of vanadium content — N-BPHA spectrophotometric method*

ISO 4946, *Steel and cast iron — Determination of copper content — 2,2'-DiquinolyI spectrophotometric method*

ISO 9441, *Steel — Determination of niobium content — PAR spectrophotometric method*

ISO 11652, *Steel and iron — Determination of cobalt content — Flame atomic absorption spectrometric method*

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ISO/TS 13899-1, *Steel — Determination of Mo, Nb and W contents in alloyed steel — Inductively coupled plasma atomic emission spectrometric method — Part 1: Determination of Mo content*

3 Principle

The sample is finished to a clean uniform surface and then irradiated by an X-ray beam of high energy. The secondary X-rays produced are dispersed by means of crystals and the intensities are measured by detectors at selected characteristic wavelengths. The measuring time is set to reach below a specified counting statistical error. Preliminary concentrations of the elements are determined by relating the measured intensities of unknown samples to analytical curves prepared from reference materials, CRM or RM, of known compositions. The final concentrations are calculated by using the results obtained by measuring a CRM of the same grade. The correction is made for the elements of interest by using the difference between the certified value and the value obtained during the measurement of the CRM (the "near by technique"). A fixed channel or a sequential system may be used to provide simultaneous or sequential determinations of element concentrations.

4 Reagents

4.1 P10 gas (90 % argon mixed with 10 % methane) for the gas-flow proportional detector.

4.2 A set of Certified Reference Materials (CRM). All reference material used for calibration or calibration verification shall be certified by internationally recognized bodies (see NOTE).

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NOTE A complete set of internationally recognised CRMs to cover all elements at all concentration levels may not be available. Other CRMs could be used if the material is certified by referee procedures based on SI units.

4.3 Reference materials used for standardization or for statistical process control (SPC samples) of the method need not to be certified, but adequate homogeneity data shall be available. Select the standardization samples in such a way that they cover at least the low and top end of the concentration range for each element.

4.4 Pure ethanol.

5 Apparatus**5.1 Sample preparation equipment**

For the final preparation, use a surface grinder with 180-grit or finer **aluminium oxide** (see NOTE) belts or discs. Other preparation procedures are also possible (turning, for example). But in each case, the surfaces of CRMs, RMs and samples shall be prepared under the same conditions.

NOTE Paper made of silicon carbide will disable Si determinations and paper made of zirconium oxide will disable Zr determinations, and aluminium determinations also sometimes as zirconium oxide is often contaminated by aluminium oxide.

5.2 X-ray fluorescence spectrometer

A simultaneous or sequential wavelength dispersive spectrometer. This test method is written for use with commercially available instruments. (standards.iteh.ai)

5.3 X-ray tube

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Tube with a high-purity element target. Rhodium is recommended for analysis of steel.

5.4 Analysing crystals

To cover all elements specified in this method, flat or curved crystals made of LiF(200) and PE (for light elements, atom no. approximately < 22) are required. Crystals made of LiF(220) and Ge or other crystals optimized for individual elements may also be used.

5.5 Collimators

For sequential instruments, a two collimator system is necessary: a coarse collimator for light elements (atom no. approximately < 22) and a fine collimator for heavy elements.

5.6 Detectors

One scintillation detector for heavy elements and one gas-flow proportional detector for light elements (atom no. approximately < 22). Sealed proportional detectors may also be used. The combination of detectors and how to use them, in single or dual mode, depends on the equipment used. See the operation manual for the equipment in question.

5.7 Vacuum system

A vacuum system capable of keeping the pressure at a constant level below at least 40 Pa during the measurement.

5.8 Measuring system

An electronic circuit capable of amplifying and integrating pulses received from the detectors.

A computer system with an adequate software package for the calculation of concentrations based on the measured intensities.

6 Safety precautions

They shall be in accordance with national regulations for X-ray equipment.

X-ray equipment shall be used only under the guidance and supervision of a responsible, qualified person.

7 Sampling

Carry out sampling in accordance with EN ISO 14284 or appropriate national standards for iron and steel.

8 Final sample preparation

8.1 Preparation of CRM's and test samples

Grind the samples on a surface grinder (see 5.1) or turn them until the surface is flat and has a uniform finish. The minimum sample size is approximately 25 mm in diameter and with a thickness of at least 5 mm. Before measurement, clean the surface with pure ethanol to avoid dust on the exposed sample surface.

If the samples have been stored in air for more than a day, always prepare the surface before the measurement.

8.2 Preparation of standardization samples and check samples

Samples used as standardization samples or used for checking the instrument performance should be prepared in the same way as were done during the calibration of the routine method. It is recommended that those samples should have a mirror like surface in order to avoid any influence from the sample preparation. The samples should be stored in a desiccator between measurements. Clean the surface before measurement with pure ethanol.

9 Procedure

9.1 Preparation of apparatus

Prepare the instrument for operation according to the manufacturer's instructions. Since most of the instruments are used for routine analyses, it is assumed that they are running and in most cases also already are calibrated for steel. If the instrument has been turned off for a long period (several hours), ensure that the conditions have stabilized before starting the measurements, e.g. temperature and vacuum. Verify the calibration status by analysing the SPC samples or CRMs.

EN 10315:2006 (E)**9.2 Measurements****9.2.1 "Near by technique" method**

Select a Certified Reference Material (CRM) with a composition close to the composition of the unknown sample. The required closeness in composition of the CRM is specified in 13.2. Load and measure the unknown sample and the CRM in a close sequence according to the instrument user's manual. Be sure that the sample is properly fixed in the sample cup.

It is assumed that the instrument is equipped with a sample spinner in order to avoid effects from grinding striations. If that is not the case, orient the sample in such a way that the relation between the X-ray beam and the grinding striations are always the same from measurement to measurement.

Calculate the concentrations according to Clause 14. The precision data is given in Annex A and B.

10 Calibration

The calibration is done when the instrument is installed, after major repairs are made, or as indicated by SPC data. To compensate for the instrumental day to day drift, standardization or recalibration procedures are used.

If a new calibration is going to be prepared, follow the calibration strategy according to CR 10299. Typical operating conditions for analysis of steel are given in Table 2.

Measure the calibration samples together with the standardization samples according to the instrument user's manual.

Make the regression calculations and store the coefficients.

Verify the calibration by measuring a set of CRMs not used in the calibration and that covers at least the low, mid and top points of the calibration range for each element.

Table 2 — Typical operating conditions and line interferences (Rh-tube)

Element	Line	Crystal	Angle 2θ	Voltage KV	Current mA	Time (s)	Line overlap
Si	Kα	PE	109,21	60	40	40	
Mn	Kα	LiF200 ^a	62,97	60	40	30	CrKβ
P	Kα	PE	89,57	60	40	40	MoL _I
Cr	Kα	LiF200	69,36	60	40	30	
Ni	Kα	LiF200	48,67	60	40	30	
Mo	Kα	LiF200	20,33	60	40	20	
Co	Kα	LiF200	52,80	60	40	40	FeKβ
V	Kα	LiF200	76,93	60	40	40	TiKβ
Ti	Kα	LiF200	86,14	60	40	40	
Cu	Kα	LiF200	45,03	60	40	30	NiKβ
Nb	Kα	LiF200	21,40	60	40	20	
Fe ^b	Kβ	LiF200	51,73	60	40	10	

^a LiF220 may be used instead, to resolve MnKα and CrKβ.

^b Fe is measured for line overlap correction on Co.

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11 Standardization

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To correct for day-to-day variations, a ~~standardization~~ (reference measurement) procedure is used. Standardization actions are based preferably on the result of SPC samples for checking the instrument performance (sample preparation eliminated). Instrument performance should be checked at least every 6 h to 8 h or before and after the measurement of a set of unknown samples.

If the calibration is still outside the control limits after a new standardization (reference measurement), a recalibration or calibration procedure is necessary.

12 Statistical Process Control (SPC) parameters

It is common practice to establish SPC diagrams (control charts) in order to check both the instrument and method performance.

Instrument performance is checked by measuring the same SPC samples, without new sample preparation, at regular time intervals or whenever it could be expected that measuring conditions have been changed. The results are plotted in control charts and further actions (start measuring unknowns, standardization or recalibration) are based on comparison with the specified control limits.

The control limits, upper and lower warning limits (± 2 s) and upper and lower action limits (± 3 s) are calculated from a set of measurements (> 25) of the check samples. The measurements should have been performed under reproducibility conditions within laboratory (same instrument, same sample, different sample cups, different operators, and different days).

Control charts for checking method performance are built up in the same way but the check samples are treated as unknown samples, e.g. sample preparation is included.