INTERNATIONAL STANDARD

ISO 17054

First edition
2010-02-15

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

Reference number
ISO 17054:2010(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

COPYRIGHT PROTECTED DOCUMENT

© ISO 2010

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Copyright International Organization for Standardization
Provided by IHS under license with ISO
No reproduction or networking permitted without license from IHS
Not for Resale

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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*.

Contents

Page

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.

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 but 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'-Diquinolyl 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*

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).

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.

5.3 X-ray tube

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.

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$_l$
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.

11 Standardization

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.

13 ”Near by technique” method

13.1 Principle

Since this is a routine method, it is assumed that most users have their instrument already calibrated for steel (often optimized for in-house purposes). The concentration range given in Clause 1 represents a wide range of different steels. In order to eliminate the effect of not having a calibration that covers all different kinds of steel or to improve (minimize) the uncertainty in the reported values a ”Near by technique” method could be used.

By measuring the unknown sample together with a sample with known concentration (of the same steel grade), a correction of the calculated concentrations for the unknown sample can be done.

NOTE Be careful when using this method outside the calibrated range, but still within the range given in Clause 1. As an example, if the routine method is calibrated for a molybdenum concentration up to 3 % and an unknown sample with a concentration of 5 % is going to be measured, ensure that the detector is not saturated due to high intensities. If that is the case, a new calibration should be done covering that range.

13.2 Criteria for selecting CRMs

a) Use only CRMs from well recognized manufacturers;

NOTE A complete set of internationally recognized CRMs to cover all steel grades are not available today. Other CRMs could be used (e.g. in-house RM’s) if they are certified by referee procedures based on SI units, for those elements of interest.

b) if possible, the CRM should have the same metallurgical history (micro structure);

c) the certified values should be followed by a calculated uncertainty;

d) the closeness in composition between the unknown and the CRM is critical. As a rule of thumb, the following rules could be used:

   1) major elements (> 1 %): The CRM should not deviate more then ± 10 % relative;

   2) minor elements (< 1 %): The CRM should not deviate more than ± 50 % relative.

14 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. Full information of the CRM that has been used should be added;

b) the method used, by reference to this European Standard, i.e. EN 10315;

c) the results and the form in which they are expressed. Report the corrected values as shown in the following example:

EXAMPLE

Element	**Certified Reference Material “Target sample”**		**Difference∆ C**	**Unknown measured**	**Unknown corrected**
	Certified value	**Measured**			
Si	1,23	1,25	- 0,02	1,35	**1,33**
Mn	4,26	4,16	0,10	4,49	**4,59**
P	0,024	0,020	0,004	0,015	**0,019**

d) any unusual features noted during the determination;

e) any operation not specified in this European Standard or any optional operation which may have influenced the results.

A precision test was performed within ECISS/TC 20/WG 1 during 2001/2002 using the ”near by technique” method (NTM). Eleven laboratories from five countries participated in the test. Altogether one set of 15 unknown test samples and another 15 target samples were circulated between the participating laboratories, see Table A.1. During the statistical calculations those criteria formulated in 13.2 d), have been followed.

Annex A
(normative)

Precision

Table A.1 — Composition of test- and target samples, target samples in *italics*

Sample	C	Si	Mn	P	Cr	Ni	Mo	Cu	Co	V	Ti	Nb	N
SS9911	0,055	0,63	1,673	0,016	17,178	10,155	0,22	0,212	0,159	0,127	0,445		
SS9912	*0,062*	*0,48*	*1,219*	*0,031*	*17,207*	*9,350*	*0,21*	*0,282*	*0,149*	*0,065*	*0,509*		
SS9921	0,031	0,071	0,048	0,007	12,608	8,354	2,145	0,053	0,026		0,016		
SS9922	*0,035*	*0,091*	*0,062*	*0,008*	*12,604*	*8,315*	*2,236*	*0,042*	*0,038*		*0,050*		
SS9931	0,022	0,618	1,691	0,031	18,648	8,234	0,697	0,538	0,287	0,117			
SS9932	*0,063*	*0,447*	*1,739*	*0,025*	*18,240*	*8,456*	*0,348*	*0,259*	*0,122*	*0,045*			
SS9941	0,021	0,343	1,773	0,027	18,553	13,650	3,168	0,437	0,180	0,064			
SS9942	*0,020*	*0,496*	*1,843*	*0,024*	*18,249*	*13,547*	*3,255*	*0,313*	*0,085*	*0,077*			
SS0012	0,068	0,295	0,762	0,021	16,446	7,009	0,288	0,331	0,116	0,076	0,081	0,210	
SS0012	*0,075*	*0,385*	*0,821*	*0,024*	*16,417*	*7,089*	*0,433*	*0,410*	*0,107*	*0,122*	*0,075*	*0,170*	
SS0021	0,13	0,356	0,423	0,021	12,054	0,097		0,039	0,016	0,029			
SS0022	*0,05*	*0,604*	*0,416*	*0,018*	*12,387*	*0,229*		*0,035*	*0,018*	*0,033*			
SS0031	0,02	0,399	1,679	0,035	17,489	12,275	2,100	0,395	0,213	0,041			
SS0032	*0,06*	*0,741*	*1,461*	*0,031*	*17,179*	*10,077*	*2,042*	*0,342*	*0,161*	*0,126*			
WG1+1	0,02	1,501	1,62	0,026	18,32	4,89	2,68	0,062	0,029	0,035			
WG1+1RM	*0,02*	*1,660*	*1,46*	*0,020*	*18,32*	*4,95*	*2,69*	*0,038*	*0,024*	*0,060*			
WG1+2	0,02	0,160	4,67	0,009	25,00	22,07	2,130	0,031	0,022	0,022	0,051		
WG1+2RM	*0,02*	*0,210*	*4,61*	*0,008*	*25,14*	*21,84*	*2,110*	*0,081*	*0,028*	*0,023*	*0,070*		

Sample	C	Si	Mn	P	Cr	Ni	Mo	Cu	Co	V	Ti	Nb	N
WG1+4	0,07	0,490	0,57	0,006	20,96	30,83			0,028	0,014	0,387		
NIST 1246	*0,08*	*0,180*	*0,91*	*0,018*	*20,10*	*30,80*			*0,076*	*(0,040)*	*0,320*		
WG1+5	0,01	0,470	1,72	0,019	19,99	25,01	4,53	1,51	0,062	0,056			
WG1+5RM	*0,02*	*0,420*	*1,76*	*0,017*	*19,51*	*24,40*	*4,00*	*1,48*	*0,045*	*0,046*			
WG1+6	0,05	0,411	1,589	0,022	16,76	12,04	2,531	0,199	0,089	(0,038)		(0,005)	
WG1+6RM	*0,04*	*0,72*	*1,541*	*0,024*	*16,93*	*11,00*	*2,732*	*0,182*	*0,139*	*0,074*		*0,023*	
AVEMO	0,01	0,27	0,47	0,015	20,12	17,96	6,23	0,71	0,034	0,04			0,2
WG1+8	*0,01*	*0,70*	*0,87*	*0,022*	*19,71*	*17,79*	*6,16*	*0,772*	*0,16*	*0,043*			*0,2*
WG1+9	0,04	0,41	1,24	0,020	19,52	9,75	0,115	0,076	0,034	0,054		0,55	
292-1	*0,04*	*0,40*	*1,74*	*0,018*	*18,00*	*10,09*	*0,046*	*0,039*	*0,026*			*0,57*	
18-10NB		0,41	1,28	0,022	19,35	9,75	0,170	0,15	0,07	0,051		0,71	
BAS 467/1	*0,08*	*0,52*	*0,79*	*0,018*	*18,09*	*9,21*						*0,99*	

Table A.2 — Precision – Silicon (smoothed value)

% Si	**0,05**	**0,1**	**0,2**	**0,5**	**1**	**1,5**
r	0,003 5	0,004 9	0,006 8	0,010 6	0,014 8	0,018 0
Rw	0,004 2	0,005 7	0,007 7	0,011 5	0,015 6	0,018 6
R	0,007 0	0,009 1	0,011 7	0,016 3	0,021 0	0,024 4
R (ISO 4829 [a])	0,008	0,012	0,018	0,032	0,049	No data
[a] Spectrophotometric method.						

Table A.3 — Precision – Manganese (smoothed value)

% Mn	**0,05**	**0,1**	**0,2**	**0,5**	**1**	**2**	**3**	**4**	**5**
r	0,003 4	0,003 1	0,004 0	0,005 7	0,007 5	0,009 8	0,011 4	0,012 8	0,013 9
Rw	0,002 5	0,003 3	0,004 3	0,006 3	0,008 3	0,011 0	0,013 0	0,014 6	0,015 9
R	0,004	0,005	0,007	0,010	0,013	0,018	0,021	0,024	0,026
R (EN ISO 10700 [a])	0,005	0,008	0,013	0,024	0,038	0,061	No data	No data	No data
[a] FAAS method.									

Table A.4 — Precision – Phosphorus (smoothed value)

% P	**0,005**	**0,010**	**0,020**	**0,030**	**0,040**	**0,050**
r	0,001 7	0,001 7	0,001 7	0,001 8	0,001 8	0,001 8
Rw	0,001 8	0,001 8	0,001 9	0,002 0	0,002 0	0,002 0
R [a]	0,001 5	0,001 9	0,002 5	0,002 8	0,003 1	0,003 3
R (EN ISO 10714 [b])	0,016	0,002 9	0,005 3	No data	No data	0,011 7
[a] Note, the correlation is bad (Figure B.3) but all values are below AIM CV(R)[1]. [b] Spectrophotometric method.						

Table A.5 — Precision – Chromium (smoothed value)

% Cr	**10**	**15**	**20**	**25**	**30**
r	0,028	0,044	0,060	0,077	0,095
Rw	0,026	0,047	0,071	0,097	0,126
R	0,042	0,082	0,133	0,192	0,261
R (ISO 4937 [a])	0,143	0,179	0,209	0,236	0,284
[a] Potentiometric titration method.					

---

[1] The AIM CV(R) value is a calculated figure based on the results of all precision studies performed within ISO TC17/SC 1. It is used as an upper limit for the reproducibility value to be accepted during a standardisation procedure.

Table A.6 — Precision – Nickel (smoothed value)

% Ni	0,1	0,5	1	5	10	15	20	25	30
r	0,003	0,008	0,012	0,029	0,043	0,054	0,064	0,073	0,081
Rw	0,004	0,009	0,014	0,033	0,049	0,061	0,072	0,082	0,090
R	0,004	0,011	0,018	0,056	0,091	0,120	0,147	0,171	0,195
R (ISO 4938 [a])	No data	0,025	0,030	0,071	0,123	0,174	0,226	0,278	0,329

[a] Gravimetric method.

Table A.7 — Precision – Molybdenum (smoothed value)

% Mo	0,05	0,1	0,2	0,5	1	2	5	10
r	0,001	0,001	0,002	0,003	0,005	0,008	0,014	0,023
Rw	0,001	0,001	0,002	0,003	0,005	0,009	0,018	0,030
R	0,002	0,003	0,004	0,007	0,010	0,015	0,025	0,037
R (ISO/TS 13899-1 [a])	0,008	0,013	0,021	0,041	0,067	0,11	0,21	0,35

[a] ICP, sandwich technique.

Table A.8 — Precision – Cobalt (smoothed value)

% Co	0,010	0,020	0,050	0,100	0,200	0,500
R	0,002 1	0,002 5	0,003 0	0,003 5	0,004 1	0,005 1
Rw	0,002 2	0,002 6	0,003 1	0,003 7	0,004 2	0,005 2
R	0,002 5	0,003 3	0,004 7	0,006 1	0,007 9	0,011 2
R (ISO 11652 [a])	0,001 5	0,002 6	0,005 4	0,009 3	0,016	0,033

[a] FAAS method.

Table A.9 — Precision – Vanadium (smoothed value)

% V	0,10	0,020	0,050	0,100	0,200
r	0,001 6	0,001 8	0,002 0	0,002 3	0,002 5
Rw	0,001 9	0,002 0	0,002 4	0,002 7	0,003 0
R[a]	0,001 1	0,001 8	0,003 4	0,005 5	0,009 0
R (ISO 4942 [b])	0,003 2	0,004 9	0,008 7	0,013 4	0,020 7

[a] Note, the correlation is bad (Figure B.9) but all values are below AIM CV(R)2).

[b] Spectrophotometric method.

---

2) The AIM CV(R) value is a calculated figure based on the results of all precision studies performed within ISO TC17/SC 1. It is used as an upper limit for the reproducibility value to be accepted during a standardisation procedure.

Table A.10 — Precision – Cupper (smoothed value)

% Cu	0,05	0,1	0,2	0,5	1	2
r	0,005	0,006	0,006	0,006	0,007	0,007
Rw	0,003	0,004	0,005	0,007	0,009	0,012
R	0,004	0,006	0,007	0,011	0,014	0,018
R (ISO 4946 [a])	0,006	0,009 6	0,015	0,290	0,046	0,073

[a] Spectrophotometric method.

Table A.11 — Precision – Titanium (smoothed value)

% Ti	0,010	0,025	0,050	0,100	0,250	0,500
r	0,001 9	0,002 3	0,002 6	0,003 1	0,003 7	0,004 3
Rw	0,002 4	0,003 0	0,003 7	0,004 5	0,005 8	0,007 0
R	0,003 7	0,005 4	0,007 2	0,009 5	0,013 7	0,018 1
R (EN ISO 10280 [a])	0,002	0,003 3	0,004 8	0,007 1	0,011 9	0,017 5

[a] Spectrophotometric method.

Table A.12 — Precision – Niobium (smoothed value)

% Nb	0,010	0,020	0,050	0,100	0,200	0,500	1,00
r	0,001 1	0,001 5	0,002 1	0,002 8	0,003 8	0,005 5	0,007 3
Rw	0,001 2	0,001 6	0,002 4	0,003 2	0,004 4	0,006 5	0,008 9
R	0,003 2	0,004 0	0,005 2	0,006 4	0,007 9	0,010 4	0,012 8
R (ISO 9441 [a])	0,003 4	0,005 5	0,010 2	0,016 4	0,026 4	0,049 3	0,079 1

[a] Spectrophotometric method.

The trueness has not been studied in this test, but it will strongly depend on the uncertainty of the corresponding CRM.

Using the NTM, the total measurement uncertainty can be calculated by the following equation:

$$U_{\exp} = 2 \times \sqrt{S_{RM}^2 + 2 \times S_r^2} \quad \text{or} \tag{1}$$

$$U_{\exp} = \sqrt{C_{95}^2 + 8 \times S_r^2} \tag{2}$$

where

U_{exp} is the expanded calculated measurement uncertainty (95 %);

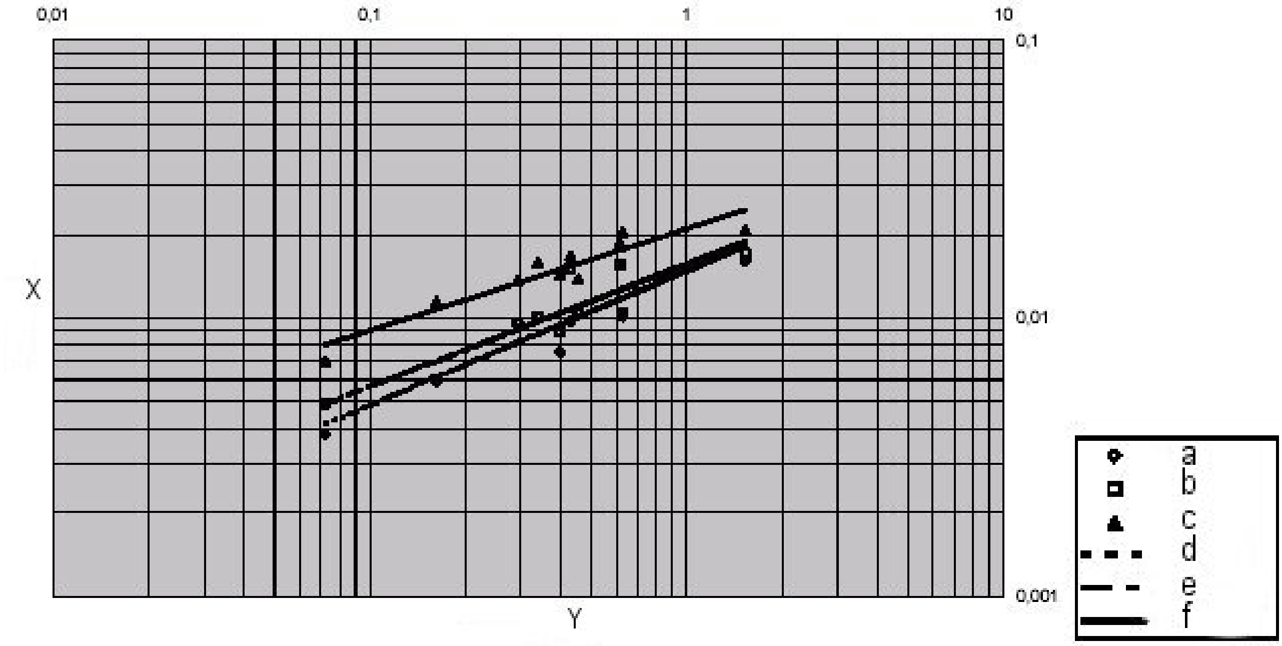
S_{RM} is the standard deviation of the certified value;

S_{r} is the standard deviation under repeatability conditions;

C_{95} is the half-width confidence interval (95 %), see ISO Guide 35:1989, Clause 4, given in the certificate of the CRM.

Annex B
(normative)

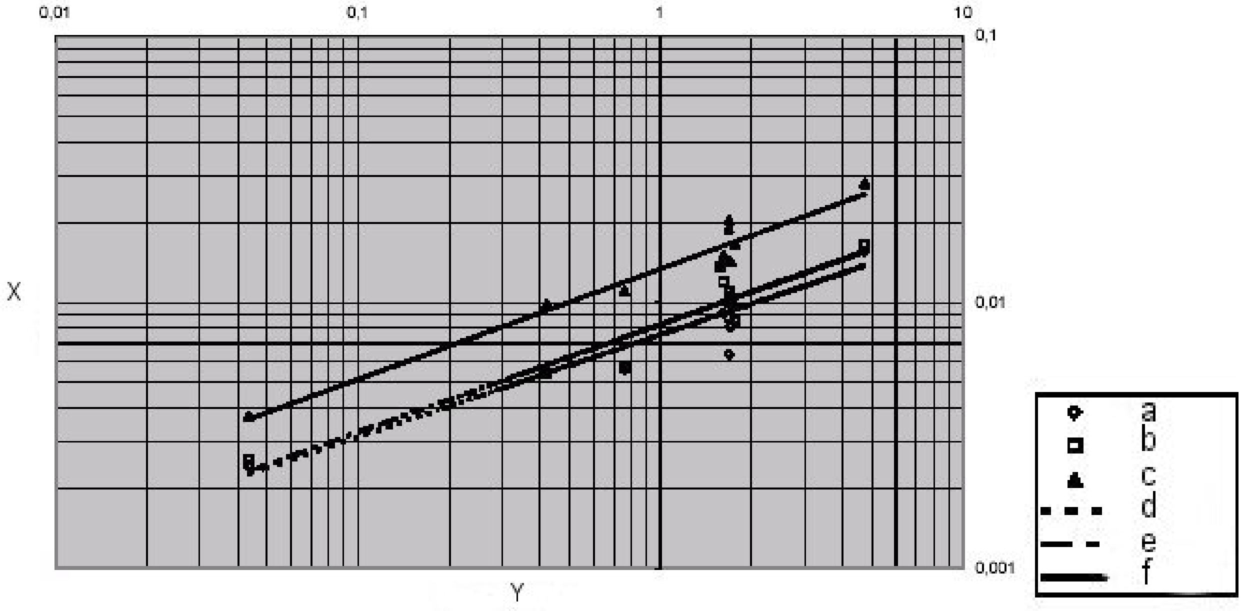
Graphical representation of precision data



Key

a	r
b	Rw
c	R
d	Power (r)
e	Power (Rw)
f	Power (R)

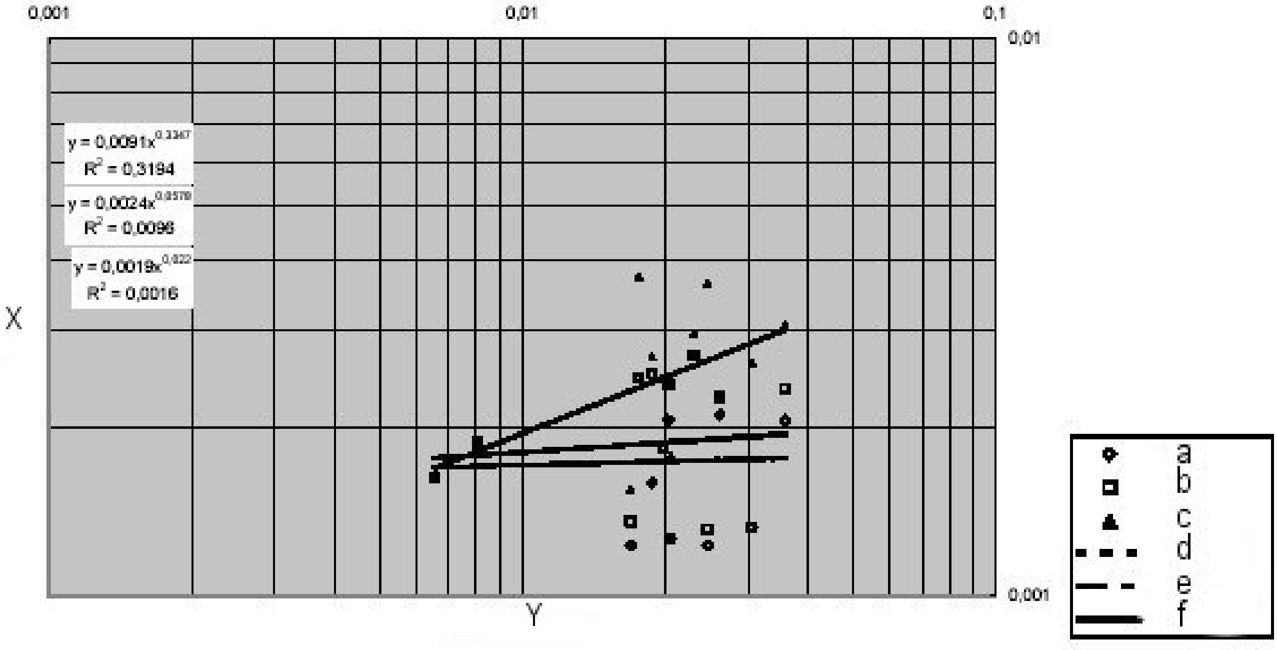
Figure B.1 — Silicon (log-log diagram)



Key

a	r
b	Rw
c	R
d	Power (r)
e	Power (Rw)
f	Power (R)

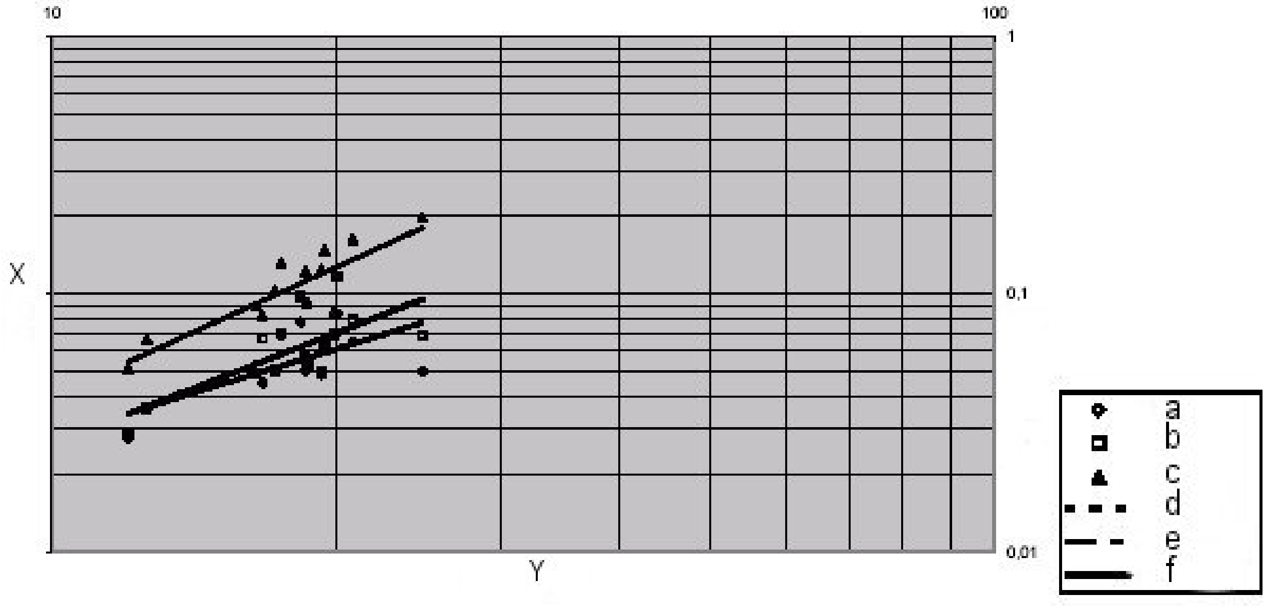
Figure B.2 — Manganese (log-log diagram)



Key

a r
b Rw
c R
d Power (r)
e Power (Rw)
f Power (R)

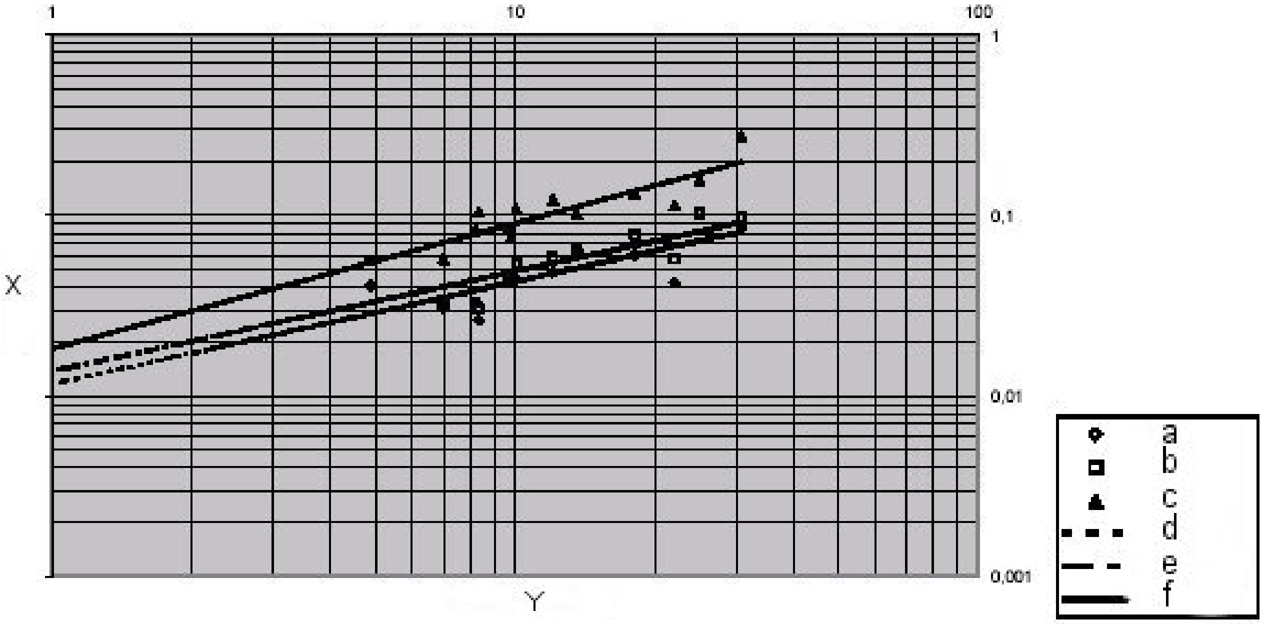
Figure B.3 — Phosphorus (log-log diagram)



Key

a	r
b	Rw
c	R
d	Power (r)
e	Power (Rw)
f	Power (R)

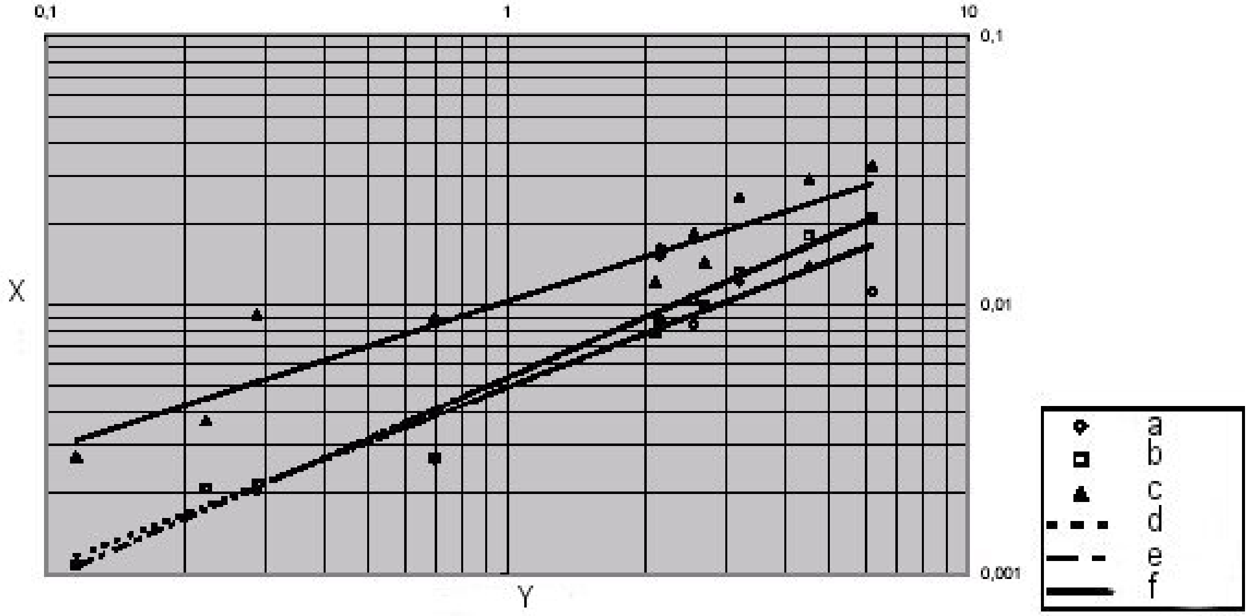
Figure B.4 — Chromium (log-log diagram)



Key

a r
b Rw
c R
d Power (r)
e Power (Rw)
f Power (R)

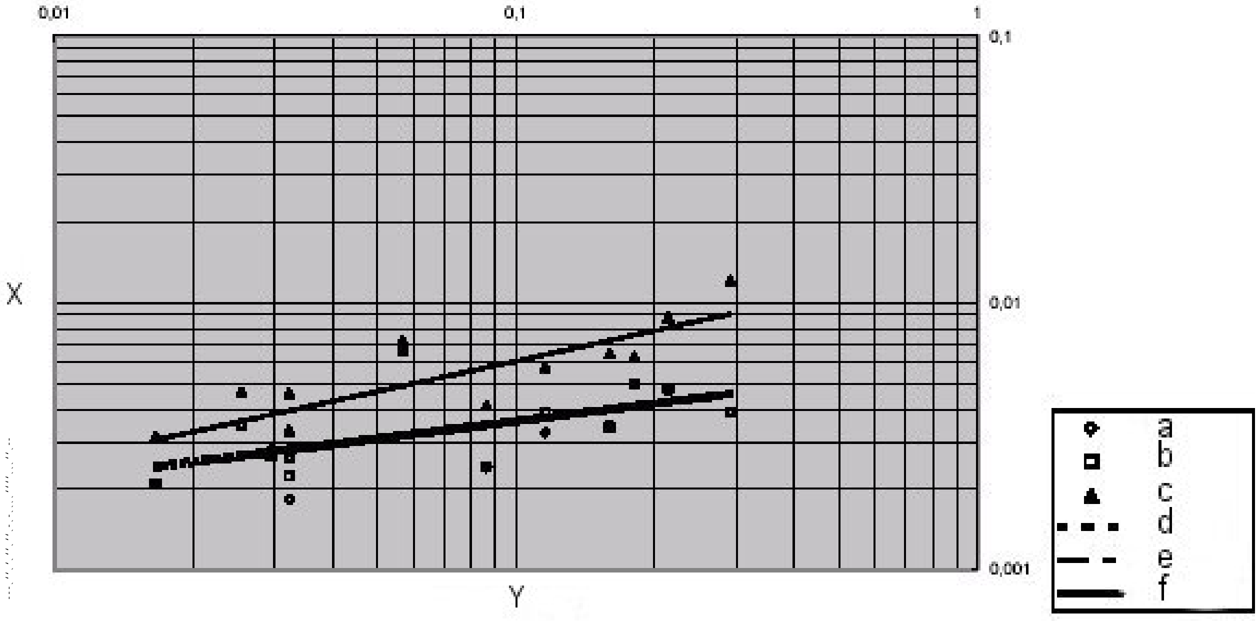
Figure B.5 — Nickel (log-log diagram)



Key

a	r
b	Rw
c	R
d	Power (r)
e	Power (Rw)
f	Power (R)

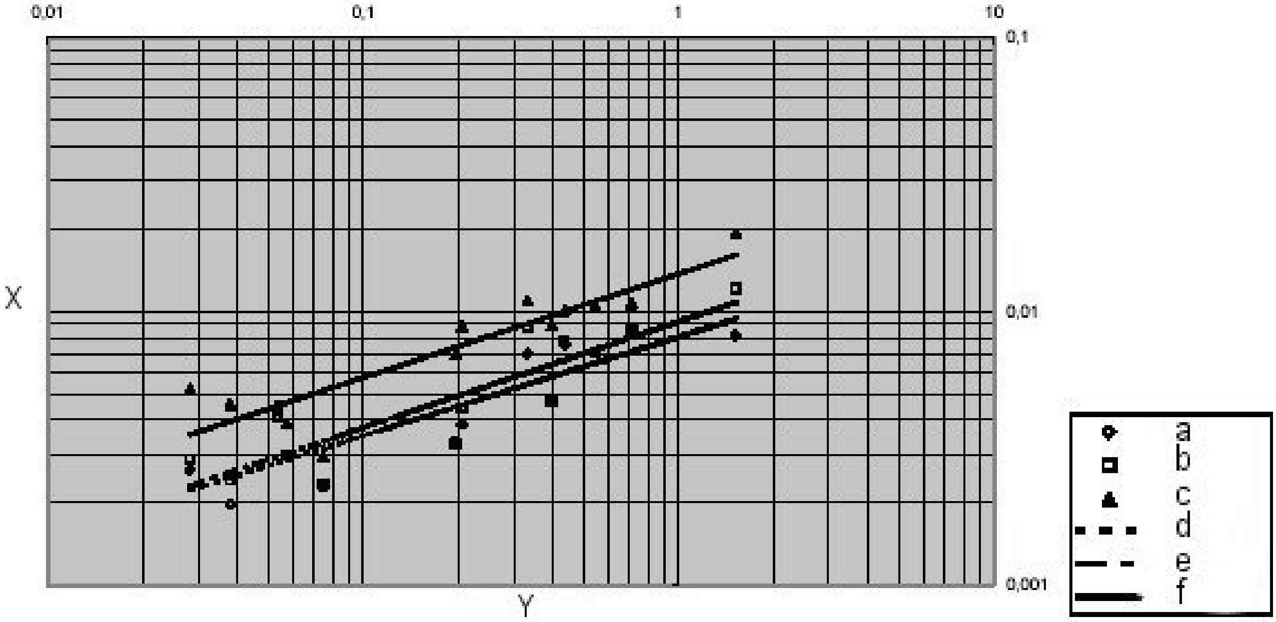
Figure B.6 — Molybdenum (log-log diagram)



Key

a r
b Rw
c R
d Power (r)
e Power (Rw)
f Power (R)

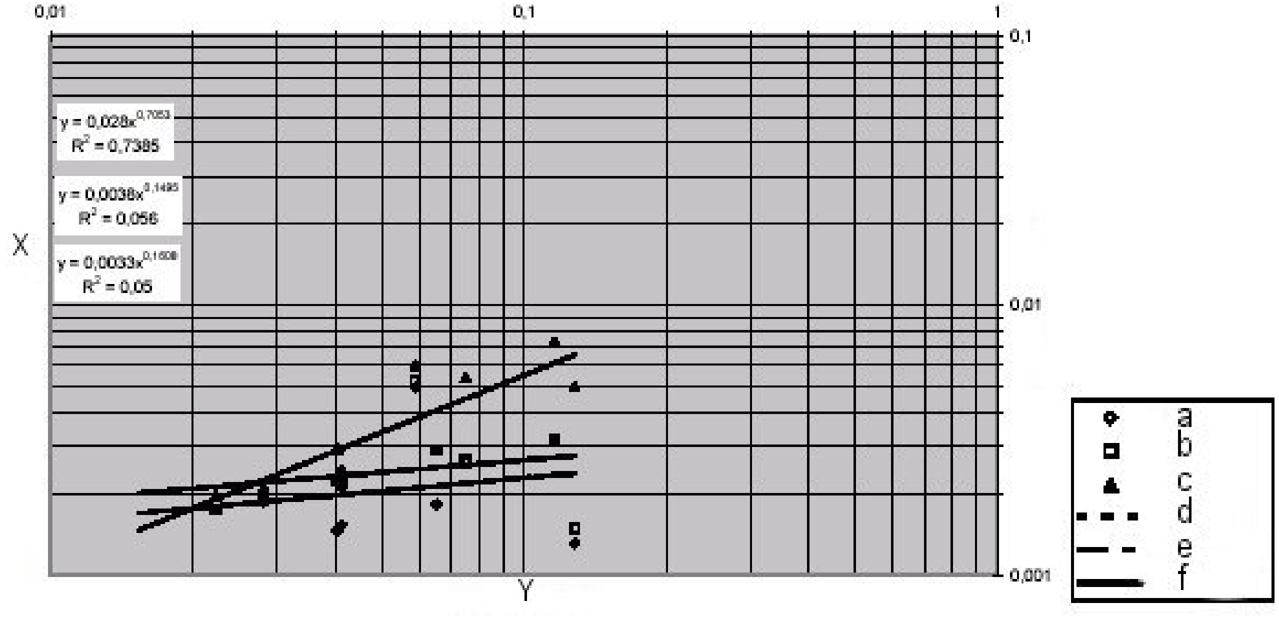
Figure B.7 — Cobalt (log-log diagram)



Key

a r
b Rw
c R
d Power (r)
e Power (Rw)
f Power (R)

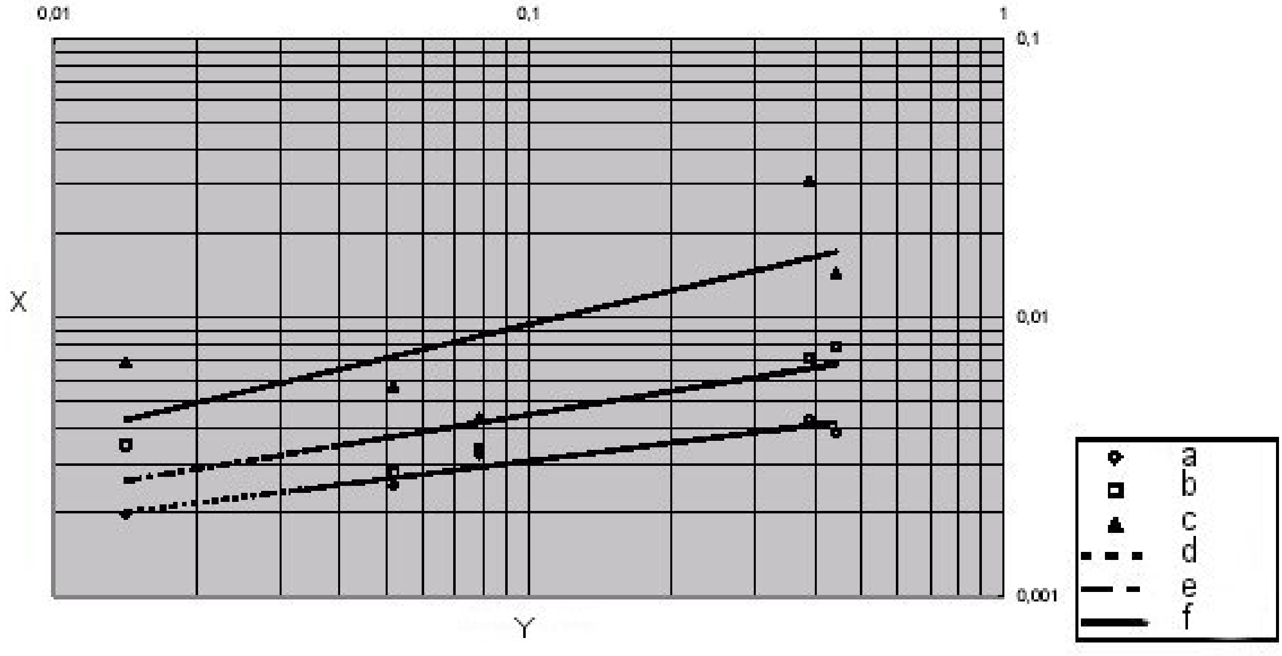
Figure B.8 — Cupper (log-log diagram)



Key

a	r
b	Rw
c	R
d	Power (r)
e	Power (Rw)
f	Power (R)

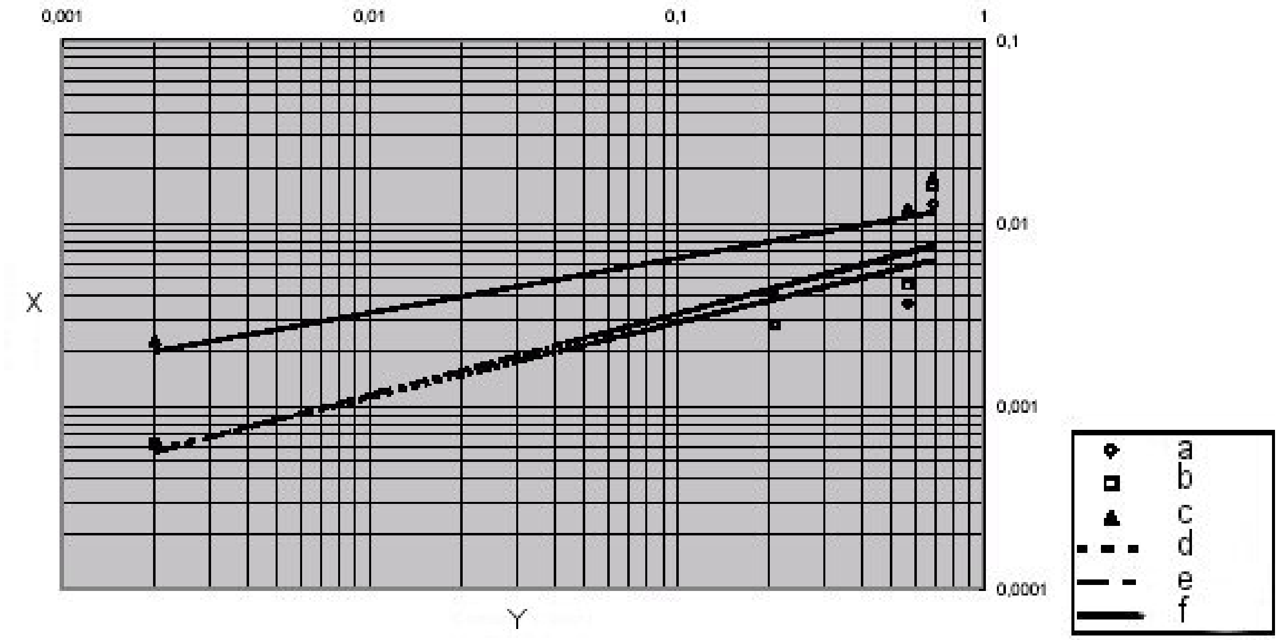
Figure B.9 — Vanadium (log-log diagram)



Key

a	r
b	Rw
c	R
d	Power (r)
e	Power (Rw)
f	Power (R)

Figure B.10 — Titanium (log-log diagram)



Key

a	r
b	Rw
c	R
d	Power (r)
e	Power (Rw)
f	Power (R)

Figure B.11 — Niobium (log-log diagram)

ICS 77.080.20

Price based on 24 pages