
**Soil quality — Screening soils
for selected elements by energy-
dispersive X-ray fluorescence
spectrometry using a handheld or
portable instrument**

*Qualité du sol — Analyse rapide d'une sélection d'éléments dans
les sols à l'aide d'un spectromètre de fluorescence X à dispersion
d'énergie portable ou portatif*



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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.

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 13196 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

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Introduction

X-ray fluorescence spectrometry (XRF) is a quick method for determination of total elemental compositions of soil samples. Unlike analyses by atomic absorption spectroscopy and inductively coupled plasma spectroscopy, XRF needs no digestion step to prepare a test solution to be analysed. Factory pre-set calibrations can be used. Consequently XRF is suitable for the rapid on-site determination of selected elements, mainly heavy metals in screening processes. Typical elements that can be analysed are Cr, As, Se, Cd, Hg and Pb, depending on the instrument. For *in situ* or abbreviated preparation analyses at a site, a battery-powered handheld or portable XRF equipment is required.

When performing analyses at a site, it might be important to have information on the presence of an element and also obtain semiquantitative results. It is often impracticable to carry out calibration using reference materials at the site to be investigated. In these situations, factory pre-set calibrations should be used.

This International Standard describes rapid methods for the on-site analysis of selected elements, including heavy metals, using battery-powered handheld or portable energy-dispersive XRF (ED-XRF).

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Soil quality — Screening soils for selected elements by energy-dispersive X-ray fluorescence spectrometry using a handheld or portable instrument

WARNING — Soil samples may contain toxic contaminants. Avoid direct contact of soil samples with exposed parts of the body. Appropriate measures shall be taken to avoid ingestion and inhalation.

Exposure to X-rays may give rise to dermal and haematological diseases. X-ray fluorescence spectrometers shall comply with national regulations relevant to radiation protection. At least one person involved in X-ray fluorescence analysis shall qualify for managing or supervising the operation of X-ray apparatus according to national regulations.

1 Scope

This International Standard specifies the procedure for screening soils and soil-like materials for selected elements when handheld or portable energy-dispersive XRF spectrometers are used. This quick method is assumed to be applied on-site to obtain qualitative or semiquantitative data that assists decisions on further sampling strategy for assessing soil quality. The higher the efforts for pretreatment used on soil samples, the better the analytical results can be expected (see e.g. Reference⁴).

This International Standard does not explicitly specify elements for which it is applicable, since the applicability depends on the performance of the apparatus and the objective of the screening. The elements which can be determined are limited by the performance of the instruments used, the concentration of the element present in the soil, and the requirements of the investigation (e.g. guideline value).

For Hg, Cd, Co, Mo, V and Sb, a majority of instruments are not sensitive enough to reach sufficiently low limits of quantification (LOQ) to meet the requirements (limit or threshold values) set in the ordinances of different countries. In this case, other methods need to be employed to measure these low concentrations. Usually, wet chemical methods are used, based on *aqua regia* extracts, in combination with optical or mass spectrometric (MS) methods like atomic absorption spectrometry (AAS), inductively coupled plasma–optical emission spectrometry (ICP–OES) or ICP–MS.

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.

ISO 12404, *Soil quality — Guidance on the selection and application of screening methods*

EN 15309, *Characterization of waste and soil — Determination of elemental composition by X-ray fluorescence*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

fundamental parameter approach

method to obtain element composition through successive approximation of the theoretical X-ray fluorescence intensities to the measured X-ray fluorescence intensities

Note 1 to entry: The calculation of the theoretical X-ray fluorescence intensities is carried out based on assumed element composition, theoretical parameters and pre-determined sensitivity coefficients of the X-ray fluorescence spectrometer.

3.2

handheld XRF spectrometer

XRF spectrometer which can be used for in-situ analysis by handheld operation

3.3

portable XRF spectrometer

XRF spectrometer for samples taken out of a site, which can be carried to the site by hand

4 Principle

The concentration of selected elements in soil is determined using a handheld or portable XRF in the field. Element concentrations are measured after sampling and limited pretreatment or directly *in situ*.

5 Apparatus

5.1 X-ray fluorescence spectrometer (XRF)

Appropriate battery-powered handheld or portable energy-dispersive X-ray fluorescence spectrometer (ED-XRF).

5.2 Container for sampling and preparation

A plastic cup or tray that can accommodate a sufficient amount of soil sample. The plastic material shall be strong enough to hold aggregates while crushing them by pressing.

5.3 Spoon

A non-metal spoon (e.g. plastic, ceramic) to take soil samples from sites and to disaggregate the sample.

5.4 Sieve (optional)

A sieve of size 2 mm.

5.5 Sample cup for portable XRF

A plastic cup, which is suitable for the XRF-equipment to be used, having a window at its bottom made of polypropylene or polyethylene terephthalate. Alternatively, for heavy metals a plastic bag may be used. The concentration of target elements in the cup or plastic bag material shall be negligible.

5.6 Sample container for handheld XRF

Plastic container suitable for simple sample pretreatment and direct XRF measurement. The concentration of target elements in the container shall be negligible.

5.7 Drying device (optional)

A portable electric drying oven, hot plate etc. that are powered by batteries, a portable generator or a heater driven by exothermic chemical reactions, e.g. hydration of calcium oxide.

6 Procedure

6.1 General

Handheld XRF instruments can be used for direct *in situ* soil measurement to receive qualitative results. Handheld and portable XRF instruments in combination with limited sample pretreatment will give semiquantitative results.

If quantitative results are needed, a complete set of sample pretreatment with homogenization and particle size reduction is necessary (see EN 15309).

Before starting calibration and measurements, define the parameters to be analysed. Check if the level of concentration to be measured is within the working range of your instrument. Use the manufacturer's instructions and perform tests with samples of known composition.

For further details of sampling and measurement concepts, see ISO 12404.

6.2 Performance check of instrument

Before analysis, follow the instrument manufacturer's instructions for setup, conditioning, preparation and maintenance. Additionally, the performance control of the instrument has to be carried out at least once a day to ensure the stability of the instrument.

X-ray fluorescence spectrometry would have spectral overlap interferences. In order to confirm the performance of the instrument and interference-correction software, it is recommended that the instrument be tested by using multi-element reference samples having elemental compositions similar to those of actual soils.

6.3 Calibration

Usually, calibration is not necessary and the pre-installed manufacturer's calibration is sufficient. If specific calibration is needed, follow the manufacturer's instructions.

If site-specific calibration graphs are to be used, measurement shall be done under the same operation and sample conditions that were employed in the calibration. For samples having large or unknown matrix effects, a fundamental parameter approach is recommended.

6.4 *In situ* measurement

6.4.1 Preparation of the measuring spot

Remove extraneous materials from the targeted spot and smooth the surface with a non-metal scoop or spoon.

6.4.2 Spot or surface measurement

Start up the handheld XRF spectrometer following the manufacturer's instructions.

Hold and apply the XRF spectrometer to the levelled ground surface.

Carry out measurement, and read elemental composition of the target elements. Besides the qualitative information estimated, concentration levels can be obtained.

NOTE Be aware that basically elements on the surface and the outermost soil layer can be measured.

6.5 Analysis of soil with sampling

6.5.1 Preparation of samples

Take a sufficient mass of soil sample to ensure acceptable repeatability (e.g. 10 g to 10 000 g). Where a large sample is taken, a subsample will need to be taken to give a representative test portion. Remove extraneous materials from the sample and crush the aggregates to fine soil particles by pressing them with a spoon.

Remove particles larger than about 2 mm e.g. by sieving. Homogenize the sample in the container e.g. by stirring.

Pack a sample cup/clear polyethylene bag with the pretreated soil sample. Tap the sample cup on a clean flat surface several times to ensure close packing of the soil particles. For clay or moist samples, press the material into the sample cup using the spoon. If there are visible voids on the film at the bottom of the sample cup, re-pack the soil sample or repeat tapping until the soil sample uniformly fills the entire surface of the film. Depending on the type of soil, a compression of the sample to reduce the voids is necessary to improve the results.

If using a plastic bag in place of a sample cup, the bag needs to be shaken or moulded to create a flat, smooth surface. Shake the bag to transfer the fines to the bottom of the bag. Ensure that there is no airspace in the bag and fold the bag over to tightly enclose the sample. The thickness of the soil sample shall be not less than 5 mm.

A high moisture content of the sample leads to underestimation. Drying of samples improves the accuracy of the results. If the sample is moist, i.e. the water content is higher than 10 %, spread part of the sorted and homogenized sample over a plastic plate and allow it to dry. Samples can be dried more efficiently with a portable drying device. Repeat the measurement after drying.

6.5.2 Sample measurement and calculation

Set up the XRF spectrometer following the manufacturer's instructions.

Measure the samples prepared by the procedure described in [6.5.1](#), and read the elemental composition of the target elements. Besides the qualitative information, semiquantitative concentration levels can be obtained.

If site-specific calibration graphs are to be used, measurements shall be carried out under the same operating and sample conditions that were employed in the calibration. For the samples that have large or unknown matrix effects, the fundamental parameter approach is recommended.

NOTE Some XRF spectrometers are equipped with a CCD (Charge Coupled Device) camera to monitor the morphology of samples. It is useful to choose appropriate analytical points avoiding voids.

7 Quality control

7.1 Performance test by standard reference material

7.1.1 General performance

Periodically check the XRF spectrometer in accordance with the manufacturer's instructions. Use the reference material recommended by the manufacturer to confirm the normal condition of the XRF spectrometer.

When the test result is not in line with the manufacturer's specifications, carry out the energy calibration described in [7.2](#), and re-test the XRF spectrometer by using the same reference material.

7.1.2 Site-specific performance

Periodically check the XRF spectrometer using reference materials which have matrices similar to those of actual samples. The measurement protocol for the reference material shall be the same as that for the actual samples. If the results are not in line with the accuracy requirements of the investigation, repeat calibration and/or carry out an energy calibration.

7.2 Energy calibration

Periodically carry out the energy calibration in accordance with the manufacturer's instructions. Also perform an energy calibration when the performance check ([7.1](#)) failed.

8 Test report

The test report shall contain the following information:

- a) a reference to this International Standard;
- b) complete identification of the samples;
- c) identification of the mode of operation of the instrument;
- d) the results of the determination;
- e) any details not specified in this International Standard or which are optional, as well as any factor which may have affected the results.

Annex A (informative)

Precision data

A.1 Conclusion on the interlaboratory trial

An interlaboratory trial was organized by BAM Federal Institute for Materials Research and Testing, Berlin in 2011 with several international participants. The variety of instruments and other analytical conditions used conformed with the quality parameters specified in the method.

[Table A.1](#) shows typical concentration ranges for selected elements in soils derived from legislative documents from various countries.

Table A.1 — Selected typical contamination ranges

Element	mg/kg (dry matter)
As	25 to 200
Cd	0,5 to 60
Co	15 to 200
Cr	30 to 1000
Cu	20 to 1300
Hg	0,15 to 80
Mo	1 to 2
Ni	15 to 2000
Pb	40 to 2000
Sb	1 to 2
Sn	0,1 to 1
V	30 to 100
Zn	60 to 700

The statistical data of results evaluated according to ISO 5725-2 are presented in [Tables A.2](#) to [A.14](#).

Generally, all handheld or portable instruments are capable of determining important elements in homogeneous soil with sufficient precision and sensitivity. Results are produced with multi-elemental power in a short measurement time. They are flexible enough for quick on-site measurements showing sufficient accuracy at higher element levels to be used as a screening method in terms of this International Standard. However, basically, reference methods are required to obtain the exact concentration values of target elements besides the results from screening methods since the purpose of screening methods is to provide information on concentration levels of target elements or indications on whether the target element concentrations are over interesting specific limits.

For Hg, Cd, Co, Mo, V and Sb, a majority of instruments is not sensitive enough to reach sufficiently low limits of quantification (LOQ) to meet the requirements (limit or threshold values) set in ordinances of different countries. In this case, other methods need to be employed to measure these low concentrations. Usually, wet chemical methods are used, based on *aqua regia* extracts, in combination with optical or mass spectrometric methods like AAS, ICP-OES or ICP-MS.

Reproducibility and repeatability are worse, if element contents are near LOQ levels. If element contents are higher and the homogeneity based on grain sizes distribution is acceptable, instruments show

reproducible results. Measurement characteristics (measurement spots are a few mm in diameter) need sufficient fine material to produce results which are representative for the whole sample. Measurement of wet samples – compare results for soil 3 (dry) and soil 7 (wet) – give lower concentrations in soil. Moisture content could not be neglected and has to be corrected in any case to report reliable results.

Milling of the sample to grain size $< 500 \mu\text{m}$ results in better repeatability, but measured mean values differ from results of soil $< 2 \text{ mm}$ grain size. Compare mean value results from two participants Thermo Fisher for identical samples soil 7- dry (milled to $< 500 \mu\text{m}$) with results of soil 3 ($< 2 \text{ mm}$). The accuracy (trueness) is still a problem of instruments available today. Comparison of the instruments used in this trial show unacceptable high reproducibility standard deviations of low level elements. This term is influenced by repeatability of measurement results (high $C_{V,r}$) as well as by deviating of mean values. Only for elements with higher concentrations and for a homogeneous material (soil 1 to soil 5) the results can be accepted, if they are below $C_{V,R}$ of 25 %. If reproducibility standard deviation $C_{V,R}$ is above 25 %, the performance of the method cannot be accepted as a reliable quantification method. This is obvious for elements in samples with lower concentration levels and larger grain sizes (soil 6).

Table A.2 — Precision data for arsenic

	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6	soil 7
l	4	6	6	4	6	5	6
n	17	31	31	18	31	13	30
N_{Lab}	6	6	6	6	6	6	6
$w(X)$	15,7	202,8	48,5	18,3	349,4	48,7	45,2
ref. value	16^a	150^b	46^b	17^b	359^b	—	46^b
s_R	8,4	28,6	5,6	5,4	38,1	28,3	5,5
$C_{V,R}$	53,3	14,1	11,5	29,7	10,9	58,2	12,2
s_r	3	27,2	4,1	2,8	28,7	17,8	4,5
$C_{V,r}$	19,1	13,4	8,4	15,1	8,2	36,6	9,9
^a total element mass fraction in mg/kg; ^b aqua regia extractable element mass fraction in mg/kg; $w(X)$ is the element mean value in mg/kg; s_R is the reproducibility standard deviation in mg/kg; s_r is the repeatability standard deviation, in mg/kg; $C_{V,R}$ is the relative reproducibility standard deviation in %; $C_{V,r}$ is the relative repeatability standard deviation in %; l is the number of laboratories after elimination of outliers; N_{Lab} is the total number of laboratories; n is the number of results.							

Table A.3 — Precision data for cadmium

	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6	soil 7
<i>l</i>	1	0	1	2	1	1	1
<i>n</i>	1	0	3	2	1	1	1
<i>N</i> _{Lab}	6	6	6	6	6	6	6
<i>w</i> (X)	10		8	22,4	2	11	2
ref. value	7,3^a	0,5^b	2^b	2^b	4^b	4^b	2^b
<i>s</i> _R				27,5			
<i>C</i> _{V,R}				122,5			
<i>s</i> _r							
<i>C</i> _{V,r}							

For an explanation of the footnotes and symbols see [Table A.2](#).

Table A.4 — Precision data for cobalt

	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6	soil 7
<i>l</i>	2	2	2	2	2	2	2
<i>n</i>	11	11	11	11	11	11	10
<i>N</i> _{Lab}	6	6	6	6	6	6	6
<i>w</i> (X)	189,5	196,3	297,7	246,1	151,6	104,1	208
ref. value	16,2^a	0,5^b	18^b	14^b	10^b	11^b	18^b
<i>s</i> _R	216,6	187,9	346,2	286,4	174,1	129,5	260,4
<i>C</i> _{V,R}	114,3	95,7	116,3	116,4	114,8	124,4	125,2
<i>s</i> _r	9,2	36,5	11,8	24	33,5	23,7	32,5
<i>C</i> _{V,r}	4,9	18,6	4,0	9,8	22,1	22,7	15,6

For an explanation of the footnotes and symbols see [Table A.2](#).

Table A.5 — Precision data for chromium

	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6	soil 7
<i>l</i>	6	3	5	6	6	5	6
<i>n</i>	31	14	26	28	31	29	22
<i>N</i> _{Lab}	6	6	6	6	6	6	6
<i>w</i> (X)	216	68,1	57,6	74,9	271,5	160,3	57
ref. value	230^a	10^b	36^b	39^b	104^b	62^b	36^b
<i>s</i> _R	58,4	29,3	38,2	29,9	80,2	59,7	36,9
<i>C</i> _{V,R}	27,1	43,0	66,2	39,9	29,5	37,3	64,8
<i>s</i> _r	13,8	17,3	13,4	16,2	65,5	24,8	9,7
<i>C</i> _{V,r}	6,4	25,4	23,3	21,6	24,1	15,5	17,1

For an explanation of the footnotes and symbols see [Table A.2](#).

Table A.6 — Precision data for copper

	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6	soil 7
l	5	6	5	5	6	6	6
n	31	31	31	31	29	31	30
N_{Lab}	6	6	6	6	6	6	6
$w(X)$	270,3	516,8	192,7	130,1	48,8	93,8	164,9
ref. value	263^a	600^b	183^b	111^b	38^b	110^b	183^b
s_R	34	69,4	8,6	13,2	6,2	25,2	19,6
$C_{V,R}$	12,6	13,4	4,5	10,1	12,8	26,9	11,9
s_r	7,6	57,5	5,9	3,6	5,9	14,7	10,2
$C_{V,r}$	2,8	11,1	3,1	2,8	12,0	15,6	6,2

For an explanation of the footnotes and symbols see [Table A.2](#).

Table A.7 — Precision data for mercury

	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6	soil 7
l	5	3	1	1	1	0	1
n	29	10	6	5	1	0	5
N_{Lab}	6	6	6	6	6	6	6
$w(X)$	52	12,6	15	4,6	4,6		14,1
ref. value	51,5^a	1^b	0,2^b	0,1^b	0,1^b	—	0,2^b
s_R	11,7	15					
$C_{V,R}$	22,5	119,3					
s_r	4,3	0,9					
$C_{V,r}$	8,2	6,9					

For an explanation of the footnotes and symbols see [Table A.2](#).

Table A.8 — Precision data for molybdenum

	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6	soil 7
l	4	5	2	0	0	1	0
n	6	26	4	0	0	1	0
N_{Lab}	6	6	6	6	6	6	6
$w(X)$	5,4	9	5,5			8,1	
ref. value	4^a	—	0,6^b	0,7^b	0,4^b	3,5^b	0,6^b
s_R	3,4	5,7	6,3				
$C_{V,R}$	62,9	63,2	116,3				
s_r	0,8	3,6	0,3				
$C_{V,r}$	14,9	39,7	5,2				

For an explanation of the footnotes and symbols see [Table A.2](#).

Table A.9 — Precision data for nickel

	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6	soil 7
<i>l</i>	5	2	3	3	4	3	3
<i>n</i>	26	6	14	11	21	21	19
<i>N</i> _{Lab}	6	6	6	6	6	6	6
<i>w</i> (X)	93,2	92,5	33,2	41,4	40,4	33,9	27,9
ref. value	101^a	20^b	27^b	30^b	33^b	40^b	27^b
<i>s</i> _R	14,2	69,3	21,4	36,6	15,6	12,1	13,2
<i>C</i> _{V,R}	15,2	74,9	64,6	88,4	38,5	35,5	47,5
<i>s</i> _r	4,4	6,4	8,8	8,7	10	4,6	7,6
<i>C</i> _{V,r}	4,8	6,9	26,6	20,9	24,7	13,6	27,2
For an explanation of the footnotes and symbols see Table A.2 .							

Table A.10 — Precision data for lead

	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6	soil 7
<i>l</i>	5	6	6	6	6	6	5
<i>n</i>	31	31	31	31	31	31	30
<i>N</i> _{Lab}	6	6	6	6	6	6	6
<i>w</i> (X)	195,8	310,2	105,3	237,1	878,9	1327,3	87,3
ref. value	197^a	200^b	96^b	224,4^b	876^b	1300^b	96^b
<i>s</i> _R	18,5	59,7	11,6	15,1	85,4	266,1	10,6
<i>C</i> _{V,R}	9,5	19,2	11,0	6,4	9,7	20,1	12,1
<i>s</i> _r	5,6	40,2	6,2	11,9	72,5	177,8	4,5
<i>C</i> _{V,r}	2,9	13,0	5,9	5,0	8,3	13,4	5,2
For an explanation of the footnotes and symbols see Table A.2 .							

Table A.11 — Precision data for antimony

	soil 1	soil 2	soil 3	soil 4	soil 5	soil 6	soil 7
<i>l</i>	0	3	1	0	4	0	0
<i>n</i>	0	4	1	0	19	0	0
<i>N</i> _{Lab}	6	6	6	6	6	6	6
<i>w</i> (X)		24,5	14		24,5		
ref. value	7^a	—	—	—	—	5^b	—
<i>s</i> _R		4,6			6,4		
<i>C</i> _{V,R}		18,8			26,3		
<i>s</i> _r		4,6			4,4		
<i>C</i> _{V,r}		18,8			18,1		
For an explanation of the footnotes and symbols see Table A.2 .							