BRITISH STANDARD

BS EN 13925-3:2005

Non destructive testing — X ray diffraction from polycrystalline and amorphous materials —

Part 3: Instruments

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ICS 19.100

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Contents

Page

Foreword 3

Introduction 4

1 Scope 5

2 Normative references 5

3 Terms and definitions 5

4 Description of equipment 5
4.1 General 5
4.2 X-ray sources 6
4.2.1 General 6
4.2.2 Conventional X-ray sources (sealed tubes and rotating anode sources) 6
4.2.3 Synchrotron radiation sources 6
4.3 Incident and diffracted X-ray beam optics 7
4.3.1 General 7
4.3.2 Monochromators 7
4.3.3 Beam dimensions and geometry 10
4.4 Detectors 12
4.4.1 Types of detector 12
4.4.2 Spatial resolution of detectors 14
4.4.3 Energy resolution of detectors 14
4.5 Goniometers 14
4.5.1 General 14
4.5.2 Specimen positioning 16
4.6 Specimen stage 17
4.7 Data collection system 18

5 Characterisation of equipment components 18

6 Equipment alignment and calibration 23
6.1 General 23
6.2 Alignment 23
6.3 Calibration 23

7 Performance testing and monitoring 23

Annex A (informative) Relationship between the XRPD standards 25

Annex B (informative) Alignment of Bragg-Brentano diffractometers 26

Annex C (informative) Procedures for instrument performance characterisation 27
C.1 General 27
C.2 Position, intensity and breadth of a limited number of diffraction lines 27
C.3 Angular Deviation Curve 27
C.4 Line breadth 30
C.5 Intensity diagrams 30
C.6 Shape Analysis Curve 30
C.7 Lattice parameters 31
C.8 The use of the Fundamental Parameter Approach 31
C.9 Whole pattern fitting 32

Annex D (informative) Sample report forms for characterisation of instruments 33

Bibliography 40

Foreword

This document (EN 13925-3:2005) has been prepared by Technical Committee CEN/TC 138 "Non destructive testing", the secretariat of which is held by AFNOR.

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of an identical text or by endorsement, at the latest by November 2005, and conflicting national standards shall be withdrawn at the latest by November 2005.

This European Standard about "Non destructive testing - X-ray diffraction from polycrystalline and amorphous material" is composed of:

- prEN 1330-11, Terminology - Part 11: X-Ray Diffraction from Polycrystalline and Amorphous Materials
- EN 13925-1, Part 1:General principles
- EN 13925-2, Part 2: Procedures
- EN 13925-3 Part 3: Instruments
- WI 00138070, Reference Materials

In order to explain the relationship between the topics described in the different standards, a diagram illustrating typical operation involved in XRPD is given in Annex A.

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, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Introduction

X-ray powder diffraction (XRPD) is a powerful Non-Destructive Testing (NDT) method for determining a range of physical and chemical characteristics of materials. These include the type and quantities of phases present, the crystallographic unit cell and structure, crystallographic texture, macrostress, crystallite size and microstrain, and the electron radial distribution function.

This document aims to describe the general aspects of the XRPD technique and its applications but not to define a specific or detailed standard for each field of application or type of analysis.

The main purposes of the standard are therefore to provide:

- practical guidance, unified concepts and terminology for use of the XRPD technique in the area of Non-Destructive Testing with general information about its capabilities and limitations of relevance to laboratories working at different levels of sophistication, from routine testing to research;
- a basis for Quality Assurance in XRPD laboratories allowing performance testing and monitoring of instruments as well as the comparison of results from different instruments;
- a general basis (without imposing specifications) for further specific NDT product standards and related Quality Assurance applications, with aspects common to most fields of application.

In order to make the standard immediately usable in a wide range of laboratories and applications, diffractometers with Bragg-Brentano geometry are considered in more detail than other instruments.

Radiation Protection: Exposure of any part of the human body to X-rays can be injurious to health. It is therefore essential that whenever X-ray equipment is used, adequate precautions should be taken to protect the operator and any other person in the vicinity. Recommended practice for radiation protection as well as limits for the levels of X-radiation exposure are established by national legislation in each country. If there are no official regulations or recommendations in a country, the latest recommendations of the International Commission on Radiological Protection should be applied.

1 Scope

This document sets out the characteristics of instruments used for X-ray powder diffraction (“powder” as defined in EN 13925-1:2003, Clause 5) as a basis for their control and hence quality assurance of the measurements made by this technique. Performance testing indicators are given for diffractometer performance testing. Different types and makes of X-ray powder diffractometer vary considerably in their design and intended fields of application. This document attempts to cover as much of this range as possible by keeping to common principles. To make the standard more readily applicable, the Bragg-Brentano configuration is addressed in most detail because of its wide use. Additional considerations and adaptations may be necessary to cover some types of instruments or configuration and some fields of application. Some of these types of instrument are described in Annex B.

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 13925-2:2003, *Non-destructive testing – X-ray diffraction from polycrystalline and amorphous materials – Part 2: Procedures*

prEN 1330-11:2004, *Non-destructive testing – Terminology – Part 11: X-ray Diffraction from Polycrystalline and Amorphous Materials*

3 Terms and definitions

For the purposes of this document, the terms and definitions of prEN 1330-11:2004 apply.

4 Description of equipment

4.1 General

This description is particularly intended for instruments dedicated to the fields of application described in EN 13925-1. For other applications, additional considerations may be required.

A diffractometer generally comprises:

- goniometer;
- X-ray source;
- incident beam optics which may include monochromatisation or filtering, collimation and/or focusing or parallelism of the beam;
- diffracted beam optics which may include monochromatisation or filtering, collimation and/or focusing or parallelism of the beam;
- specimen stage;
- detector;
- data collection system.

These parts of the instrument are considered in more detail below. A data processing system is also required to produce measurements from the instrument. Data processing systems, whether manual or computerised, shall be included with the data processing procedures of EN 13925-2.

A well-controlled environment (temperature and pressure) is strongly recommended for analysis where reproducible measurement of line profile position, width and shape is required.

Humidity is may be important because compounds in the specimen may react with water or absorb it with a consequent change in their lattice constants, e.g. clay minerals.

The X-ray beam is partially scattered and attenuated by the air in the beam path with consequential effects on the detected diffraction pattern background and intensity. This effect has sometimes been minimised by use of an evacuated or helium filled beam path.

For all the items described in this clause the corresponding main characteristics to be controlled are given in Clause 5.

4.2 X-ray sources

4.2.1 General

There are several types of x-ray source that can be used for XRPD measurements ranging from conventional laboratory sources to intense and well-collimated synchrotron sources. Each source exhibits characteristics that make it more suitable for particular types of analysis. The main source types are described below.

4.2.2 Conventional X-ray sources (sealed tubes and rotating anode sources)

X-rays are obtained by bombarding a metal anode with electrons emitted by the thermoionic effect and accelerated in a strong electric field produced by a high-voltage generator. Most of the kinetic energy of the electrons is converted to heat, which limits the power of the tubes and requires efficient anode cooling. An increase of about two orders of magnitude in brilliance can be obtained using rotating anodes instead of sealed tubes. Microfocus sources operate at relatively low power settings but maintain brightness by electrostatically or magnetically steering the beam inside the X-ray tube onto the target. The spectrum emitted by a conventional X-ray source operating at sufficiently high voltage consists firstly of a continuous background of polychromatic radiation with a sharp cut off at short wavelengths determined by the maximum voltage applied. Upon this is superimposed a limited number of narrow characteristic lines whose wavelengths are characteristic of the anode material. The emitted radiation is not polarised.

The type of X-ray source and the electron emission current, and accelerating voltage applied to it by the high voltage generator have a marked effect on X-ray intensity and its energy distribution. The emission current and accelerating voltage of a conventional X-ray tube normally give reproducible adjustment of the X-ray beam intensity and energy spectrum on a time scale of days. However, experience has shown that the absolute X-ray intensity differs significantly for nominally equal sources and that it decreases with source age.

4.2.3 Synchrotron radiation sources

A beam of charged particles strongly accelerated in an electric field and deflected in a magnetic field emits a continuous spectrum of X-rays that is as much as 10^{13} times as brilliant as sealed X-ray tubes. It is called "synchrotron radiation". This increased brilliance relates to the total energy spectrum. Monochromatisation of the beam typically results in diffraction intensities one or two orders of magnitude greater than from conventional sources.

The main advantages of using synchrotron radiation for XRPD measurements are:

- nearly parallel-beam diffraction geometry;

- highly monochromatised and tunable radiation;

- very small and almost symmetric contribution of the instrument to the observed line shape that leads to simpler characterisation of line profiles and very good angular resolution.

This type of X-ray radiation source requires beam flux monitoring with time (the beam flux can decrease significantly during the experiment) and wavelength calibration. The emitted radiation is strongly polarised in the plane of deflection of the charged particles.

4.3 Incident and diffracted X-ray beam optics

4.3.1 General

The main characteristics of the incident and diffracted beams are their wavelength spectrum, their direction of propagation, their cross-sectional area and shape at the specimen as well as their degree of collimation (axial and equatorial divergence) and focusing. The items of equipment that determine these characteristics are called "beam optics". The effects of these items are referred to by the general term "beam conditioning".

The items of equipment described below are used to obtain different degrees of radiation purity and different geometries, i.e. a so-called "focused" beam, "monochromatised" beam, "collimated" beam, or "parallel" beam.

4.3.2 Monochromators

4.3.2.1 General

The wavelengths conventionally used with laboratory sources correspond to the characteristic spectral lines from specific anode materials.

For many XRPD applications it is advantageous to eliminate all other spectral components emitted from the X-ray source or the specimen. When using the $K_{\alpha1,2}$ doublet is sometimes helpful to additionally suppress the $K_{\alpha2}$-line, i.e. to work with highly monochromatic $K_{\alpha1}$-radiation.

Monochromatisation devices can be used singly or in combination.

4.3.2.2 Filters and β filters

Partial monochromatisation can be obtained using K_β filters, i.e. foils made of a metal selected as having an absorption edge between the wavelengths of the K_α and K_β radiation emitted by the source.

Standard K_β filters are designed to reduce the K_β intensity to about two orders of magnitude less than the K_α intensity. Such a filter also attenuates the K_α doublet intensity, typically by a factor of 2, and reduces the polychromatic radiation from the source. Two filters are sometimes combined to form so-called "balanced filters" [1].

Spectral filters shall be used with caution because the absorption edges of the filter material cause significant steps in the background close to each of the observed diffraction lines. Such steps impede accurate analysis when the complete line profile(s) are used, for example, in line-broadening analysis.

In some cases it is useful to attenuate the incident or the diffracted beam. Then a foil is used that is made of a metal (often aluminium) selected as having no absorption edge near the radiation wavelength used.

4.3.2.3 Crystal Monochromators

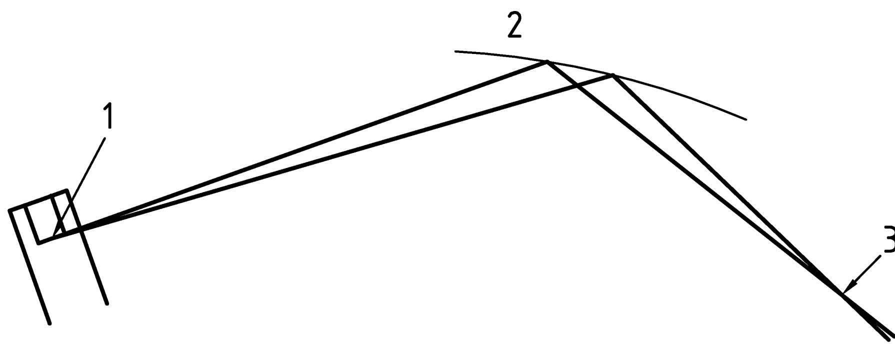
Monochromatisation of radiation is most often accomplished by diffraction from a crystal. We may distinguish:

a) a mosaic crystal. The relative energy or wavelength resolution ($\Delta E/E$ and $\Delta\lambda/\lambda$, respectively) is typically a few parts per hundred. Most of the K_β radiation and of the continuous polychromatic radiation is eliminated. The orientations of the coherently diffracting parts of the mosaic crystal (generally graphite) are spread over about 0,4 degrees for many commercially available monochromators. For such crystals more than 50 % of the incident intensity of the $K_{\alpha1,2}$ doublet can be retained. Mosaic crystal monochromators are usually installed in the diffracted beam. In this configuration, they also eliminate specimen fluorescence from all elements except the one that constitutes the anode.

b) a single crystal. The energy resolution is typically better than two parts per thousand. The two components of the $K_{\alpha1,2}$ doublet can be separated and the $K_{\alpha2}$ radiation eliminated. This type of monochromatisation causes a large loss in intensity as typically only about 15 % of the incident intensity of a spectral line is retained. Single crystal monochromators (usually almost perfect single crystals of quartz, silicon or germanium) are generally used on the primary beam often in a focusing arrangement. The intensity loss may be largely offset by the associated reduction in axial divergence of the beam, eliminating the need for one set of Soller slits (see 4.3.3.3.2).

Two or more crystals (e.g. [2]) may be combined to achieve much better resolution than one, but the use of multiple crystals may yield insufficient intensity for normal powder diffraction. Care shall be taken to ensure that the harmonics of the chosen wavelength are eliminated by the positioning of suitable apertures (slits) within the monochromator, or by other means.

These devices can be used in the incident and/or diffracted beams (see Figures 1 and 2).



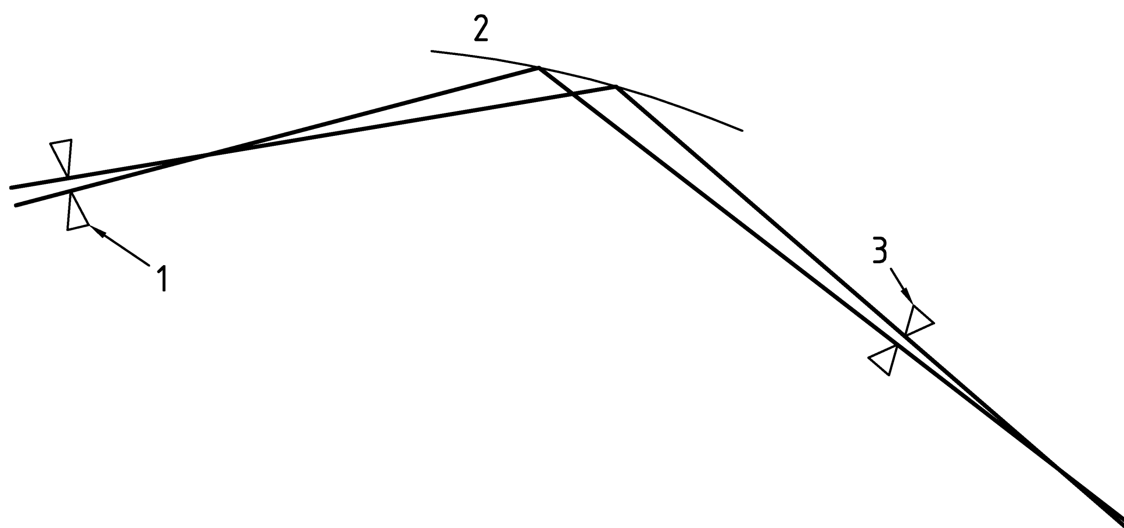
Key

1 Focus of X-ray tube

2 Monochromator

3 Apparent source (on the goniometer circle)

Figure 1 - Positioning the monochromator on the incident beam



Key

1 Receiving slit

2 Monochromator

3 Detector slit

Figure 2 - Positioning the monochromator on the diffraction beam

4.3.2.4 Electronic filters

Electronic filtering uses photon-counting detectors (see 4.4) and is often referred to as pulse height discrimination or “discrimination” or “energy discrimination”. It electronically selects the pulses arising from the photons of the radiation chosen for the experiment.

An effect similar to partial monochromatisation can be achieved by the use of a solid-state detector, e.g. Peltier-cooled. The relative energy resolution of these systems is of the same order as that of a mosaic crystal monochromator (about one part per 100), i.e. it is sufficient to eliminate the K_{β} component and most of the continuous background, but not to separate the $K_{\alpha 1,2}$ doublet. Detectors of this type typically have high counting efficiencies but are susceptible to dead time effects (prEN 1330-11). Such effects result in a non-linear response above about 10^4 counts per second, including all wavelengths registered by the detector, whether or not used for the measurement. Care shall therefore be taken to limit the maximum count rate observed to a level at which the detector function properly. If necessary an appropriate dead time correction shall be applied.

4.3.2.5 Multilayer mirrors

Multilayer mirrors usually consist of alternating thin layers of two elements (e.g. W and C) deposited onto an appropriately curved substrate. The layers have a thickness of the order of a few times the wavelength of the X-radiation used [3].

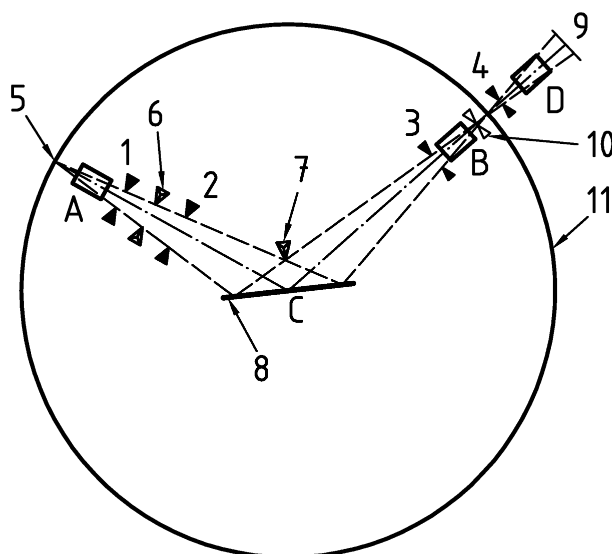
Multilayer mirrors for X-radiation are primarily used to reconfigure a divergent beam into an intense parallel or convergent beam (see 4.3.3.3.4). The mirror unit also acts as a monochromator by suppressing the K_{β} and polychromatic radiation from the source. The thickness of the layers deposited on the surface varies along the length of the mirror in such a way that Bragg’s law is satisfied over a range of beam divergence angles and the corresponding incidence angles at the mirror. These systems reach a reflectivity close to 100 % and thereby provide high intensity beams. A common configuration uses a parabolic graded mirror to transform the divergent incident radiation from the source into an intense nearly parallel beam. Elliptic graded mirrors may be used to transform the divergent radiation from the source into a convergent (focused) beam. For special applications several mirrors can be combined in the incident and/or diffracted beams.

4.3.3 Beam dimensions and geometry

4.3.3.1 General

The geometric dimensions of the incident and diffracted X-ray beams can be controlled using collimators and slits. The geometric dimensions may also be altered significantly by crystal monochromators and graded multilayer mirrors.

The items described below define the beam dimensions and geometry and are illustrated schematically in Figure 3.



Key

1, 2	Possible position of divergence anti-scatter slit
3, 4	Possible position of receiving anti-scatter slit
5	Source
6	Divergence slit
7	Knife edge
8	Specimen surface
9	Detector window
10	Receiving slit
11	Goniometer circle
A, B, D	Possible position of Soller slit
C	Centre of specimen surface and of the goniometer circle

Figure 3 — Schematic arrangement of the devices for control of beam dimension and geometry with respect to the centre of the goniometer circle (C)

4.3.3.2 Slits

4.3.3.2.1 General

Different types of slit can be placed in the incident and diffracted beam paths, usually to limit their equatorial and axial (see 4.5.1) divergence. Slits can also serve to reduce parasitic scattering, to define the radius of the focusing circle and to control the angular resolution. They are often made of a metal with high X-ray attenuation. Orthogonal slit pairs are used for some measurements (e.g. for crystallographic texture measurements) to control the equatorial and axial beam divergence. In 4.3.3.2.2 to 4.3.3.2.7 only slits will be dealt with, because in XRPD slits are far more widely used than other apertures.

A useful quantitative geometric treatment of slits for Bragg-Brentano diffractometers is described in [4].

4.3.3.2.2 Variable aperture slits

Mechanically or computer controlled slits can be applied as variable divergence, antiscatter and receiving slits.

A variable aperture slit is most often used in diffractometers with Bragg-Brentano geometry to maintain a constant irradiated surface area of the specimen while the angle between the incident beam and the specimen surface is varied. As a consequence, the irradiated specimen volume varies during the 2θ scan.

A matched variable anti-scatter slit may be used in conjunction with a variable divergence slit. This can be particularly effective in minimising parasitic scattering at low 2θ angles.

4.3.3.2.3 Divergence slits

Divergence slits between the X-ray tube and the specimen. They limit the equatorial divergence of the incident beam.

4.3.3.2.4 Antiscatter slits

Antiscatter slits reduce parasitic scattering caused by the interaction of the incident and diffracted beams with the air, the specimen stage and the components of the optical system. They are placed in the path of the X-ray beams directly before or after the specimen or after the receiving slit. They may be used singly or in combination. If properly aligned they do not restrict the incident or diffracted beams and they do not change the diffraction geometry.

4.3.3.2.5 Knife edge

The so-called "knife edge" can be used for flat specimens. It is a flat blade or wedge with a straight edge positioned close to the specimen surface, parallel to the specimen surface and the goniometer axis. A knife edge reduces the parasitic scattering by limiting the irradiated area of the specimen. It has the same function as the divergence and the antiscatter slits. The position of the knife edge can be stationary or variable, and it can be mechanically or computer controlled.

4.3.3.2.6 Receiving slits

A receiving slit serves to select the radiation seen by the detector at the angular position sampled. It is placed in the diffracted beam, in front of the detector or in front of the diffracted beam monochromator, if present.

For Bragg-Brentano geometry, the receiving slit shall be placed on the focusing circle (see 4.5.1). Its size is an important factor in determining the angular resolution. It is sometimes called a “focusing slit”, or “resolution slit”.

4.3.3.2.7 Detector slits

A detector slit selects the radiation diffracted by the specimen that is allowed to enter the detector. It prevents parasitic radiation from entering the detector, e.g. radiation scattered by components of the instrument, or K_β radiation when the monochromator is tuned to K_α radiation. The receiving slit often serves as detector slit.

If a monochromator is used in the diffracted beam, a detector slit can be placed in the diffracted beam between the monochromator and the detector and is often incorporated in the monochromator housing. For (para)focusing monochromators it is usually positioned at the focusing point of the radiation diffracted by the monochromator.

4.3.3.3 Collimators and related components

4.3.3.3.1 General

A collimator is a device intended to render the X-ray beam more nearly parallel, accomplishing this by restricting the beam dimensions and / or the divergence of the beam. It should be constructed in such a way that the stray radiation produced from the slits or diaphragms used for this task is excluded as completely as possible from the diffraction pattern of the specimen registered by the detector. The design of collimators may differ considerably and depends on the diffractometer configuration and the diffraction geometry used. They are often made of a metal with high X-ray attenuation. Simple slits, crystal monochromators and graded multi-layer mirrors are normally not regarded to be collimators, although some of their functions may be similar.

4.3.3.3.2 Parallel plate collimators (Soller slits)

A parallel plate collimator (or set of Soller slits) comprises an array of parallel thin plates (foils) that limit the beam divergence, in the direction perpendicular to the foils. They can be used in the incident and/or diffracted beams and they can be used to limit the divergence in the axial and/or equatorial direction.

4.3.3.3.3 Tube collimators

A tube collimator is a tube with diaphragms or sets of slits at each end to control the dimensions and the divergence of the beam.

4.3.3.3.4 Capillary optics

Capillary optics are formed from hollow optical fibres that guide the radiation by total reflection on their inner walls. Placed in the incident beam, they typically limit its divergence to about 0,3 degrees and suppress short wavelength radiation while increasing the intensity at the specimen. A single capillary produces a beam with a very small cross-section. An assembly made from a large number of parallel fibres bundled together produces a large cross-section beam with low divergence and reduced short wavelength radiation [5].

Micromirrors are monocapillaries with a shaped inner surface, normally parabolic and gold coated. The curvature changes with position along the mirror so that a convergent (focused) X-ray beam is formed by single bounce total reflection (see 4.3.2.4).

4.4 Detectors

4.4.1 Types of detector

Detectors used in XRPD may be very different in type, size, shape (curvature) and in the physical principles by which they function. They include photographic films, gas ionisation counters (Geiger-Müller and proportional), solid-state detectors (scintillators or semiconductors), fluorescent screens and image plates. Detectors can be categorised by considering:

a) physical principle of radiation detection:

— integrating detectors: photographic films, image plates and charge coupled devices (CCD). These detectors accumulate X-rays over a time interval and with intrinsic spatial resolution. They have a limited dynamic range (total number of X-rays per angular interval) and low energy resolution. Electronic readout of data from these detectors is required for reproducible measurements;

— photon counting detectors: Geiger-Müller counters, proportional counters, scintillation counters and semi-conductor detectors. They have, in principle, an unlimited dynamic range, when counts are summed into a computer memory. However, they have a limited linear response range for count rates;

b) position sensitivity of the detector:

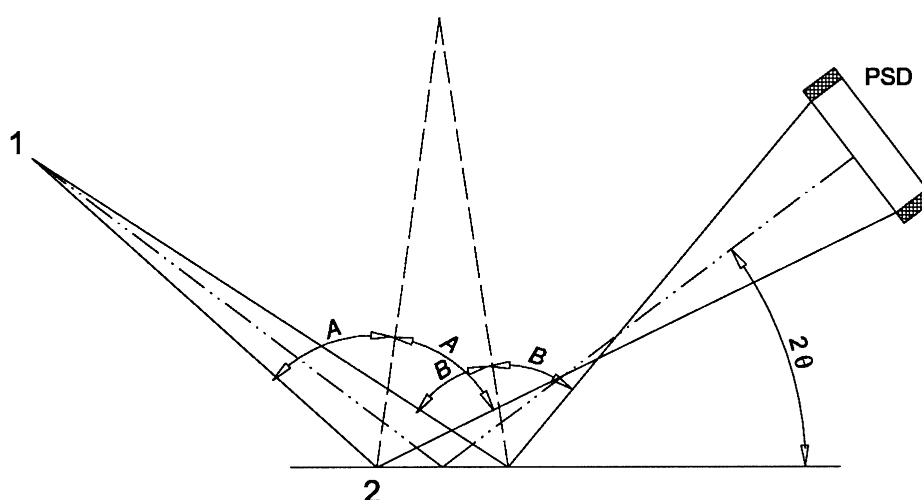
— "spot" counters such as Geiger-Müller counters, proportional counters, scintillation counters and semi-conductor detectors, that only register the number of the detected X-ray photon;

— linear position sensitive detectors (also called one-dimensional PSDs), such as proportional counters where the position at which the detected X-ray photons strike the device can be read out in addition to their number;

— area detectors (also called two-dimensional PSDs), such as two dimensional position sensitive proportional counters, photographic films, image plates, photo-luminescence tubes (as used in TV cameras), and charge coupled devices (CCD).

The physical principle of radiation detection is important in XRPD, because it is related to the statistical counting error in an observation as well as the detection efficiency. For photon counting detectors the variance in the number of photons detected during a given time interval is equal to the number of photons detected (Poisson statistics). Such a simple relation does not exist for integrating detectors.

The primary function of a position sensitive detector is to make simultaneous observations of count rate over a range of positions and thus improve the efficiency of data collection. In many diffraction geometries, e.g. Bragg-Brentano geometry and Seeman-Bohlin geometry, there is a degradation of the focusing or parafocusing condition that should be taken into account. This results in a shifting and broadening of diffraction-line profiles that strongly depends on diffraction angle. When a PSD is used, crystallites with orientations spread over half the range of diffraction angles covered by the detector contribute to the diffracted intensity, thereby increasing the apparent randomness of orientation (see Figure 4).



Key

1 Source

2 Specimen

A = $\pi/2 - \theta_{min}$

B = $\pi/2 - \theta_{max}$

PSD Position Sensitive Detector

$\Delta\omega$ Maximum difference of the orientation of lattice planes (with identical spacing) that contribute simultaneously to the radiation detected by linear position sensitive detector

NOTE Technical characteristics of various types of detector can be found in references such as [6].

Figure 4 — Simultaneous registration of crystallite orientations when using a linear Position Sensitive Detector (PSD)

4.4.2 Spatial resolution of detectors

The spatial resolution of a "spot" counter and of a detector that integrates over the area of its entrance window is normally determined by the size of the receiving slit situated in front of it. For linear and two-dimensional detectors, spatial resolution depends on the technical characteristics and electronic adjustment.

4.4.3 Energy resolution of detectors

The energy resolution of a detector depends on its technical characteristics and the electronic adjustment, including the upper and lower acceptance limits for energy discrimination.

4.5 Goniometers

4.5.1 General

The mechanical and electrical constituent parts of a diffractometer that are used to control the position of the diffractometer components in relation to the specimen are referred to as the goniometer.

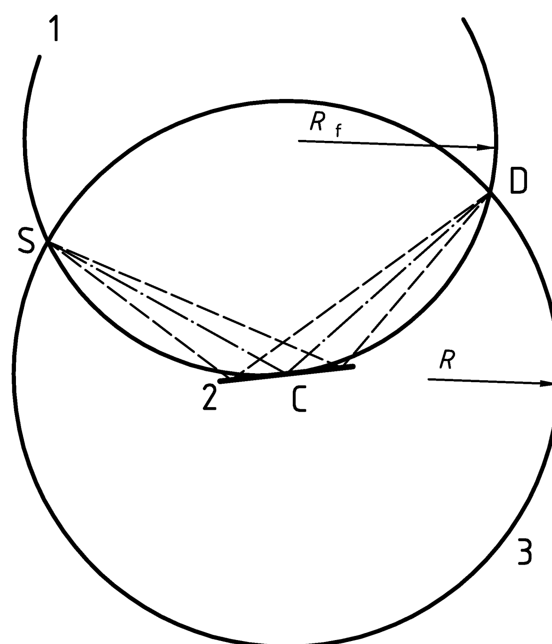
The plane containing the centres of the source (or apparent source if an incident beam monochromator is used), the specimen and the detector is known as the plane of diffraction.

The plane of diffraction is also named the equatorial plane. The direction perpendicular to this plane, and parallel to the goniometer axis, is known as the axial direction. For most standard powder diffraction measurements, the surface of a flat specimen shall lie perpendicular to the equatorial plane and shall contain the goniometer axis.

The measurement of the angle between the incident and diffracted beams is distinguished from the movement of the specimen itself.

In diffractometers that use focusing or parafocusing diffraction geometry the (apparent) X-ray source is positioned on the goniometer circle and the diffracted intensities are collected on the goniometer circle. When using a linear (or flat) position sensitive detector the diffracted intensity is collected in a plane tangent to the goniometer circle.

In Bragg-Brentano geometry the (apparent) source, the specimen and the receiving slit all lay on the focusing circle, which has a radius R_f. It is related to the diffraction angle 2θ and the radius R of the goniometer circle by $R_f = R / 2\sin\theta$ (see Figure 5). Seeman-Bohlin geometry differs from Bragg-Brentano geometry in that the goniometer circle is superimposed on the focusing circle so that, in Figure 5, $R_f = R$.



Key

1 Focusing circle

2 Specimen surface

3 Goniometer circle

NOTE The equatorial plane is defined by the point (S) representing the radiation source and the coinciding θ and 2θ axes. [C is the point where the coinciding θ and 2θ axes intersect the equatorial plane.] The point (D) representing the detector is situated in the equatorial plane at the same distance from the coinciding θ and 2θ axes as the point S. The line through C and parallel to SD represents the specimen surface. The circle defined by the points S, C, and D and by the radius R_f is called the focusing circle. In all powder diffractometers the plane of diffraction coincides with the equatorial plane. In a real Bragg-Brentano parafocusing diffractometer the goniometer axis coincides with the θ and 2θ axes, S is the centre of the "line" shaped radiation source that is perpendicular to the equatorial plane, and D is the centre of the area that is exposed to the radiation to be detected and that resembles the radiation source in size and shape. The goniometer circle passes through the centre of the "line" shaped radiation source and through the centre of the area that is exposed to the radiation to be detected. The goniometer axis passes through the centre of the goniometer circle.

Figure 5 — Arrangement of the focusing circle and the goniometer circle in the parafocusing configuration (Bragg-Brentano geometry)

The diffraction pattern is usually recorded by scanning rotationally around the goniometer circle with a "spot" detector or with a position-sensitive detector placed tangent to the goniometer circle. Parts of the diffraction pattern can be recorded by placing a stationary one- or two-dimensional detector tangent to the goniometer circle at a fixed diffraction angle.

Many diffractometers (e.g. Bragg-Brentano and Seeman-Bohlin) can be distinguished with respect to the orientation of their goniometer axis as:

— 'horizontal': horizontal goniometer circle, the goniometer axisis vertical. The specimen surface contains the goniometer axis and tilts about it (i.e. the equatorial plane lies horizontally and the axial direction is vertical); or

— 'vertical': vertical goniometer circle, the goniometer axis is horizontal. The specimen surface contains the goniometer axisand tilts about it (i.e. the equatorial plane lies vertically and the axial direction is horizontal). If the specimen surface is flat, it is usually arranged to face upwards.

Such diffractometers can also be distinguished with respect to the functioning of their goniometer axis as:

— θ–2θ when the flat specimen surface is tilted to remain at half the angle between source and receiving slit (or detector) during data collection. Conventionally, the source remains stationary and the detector is rotated at twice the speed of the specimen;

or

- θ–θ when the flat specimen surface remains static during a data collection. Conventionally it is placed horizontally and fixed to this position during data collection. The X-ray source and the detector are then rotated simultaneously at the same speed and in opposite directions.

4.5.2 Specimen positioning

4.5.2.1 General

The specimen is positioned using a specimen stage (see 4.6).

Diffractometer geometries are generally optimised for flat or rod-shaped specimens. The specimen shape should therefore correspond as closely as possible to this design criterion. The required positional precision depends on the instrument and its configuration. It is typically in the range of a few microns for flat specimens or tens of microns for rod-shaped specimens.

4.5.2.2 Rod-shaped specimens (capillary, fibre)

A rod-shaped specimen (capillary, fibre) shall have its axis coinciding with the goniometer axis. The specimen has no movement synchronised with the 2θ-scan, although it is usually rotated around the rod axis to improve the statistical randomness of crystallite orientation. With step-counting diffractometers this rotation shall be timed to avoid possible periodic anomalies in the collected data arising from any variation in diffracted intensities through a rotation cycle, e.g. by use of an integer number of rotations for each data point collected.

4.5.2.3 Flat specimens

For a flat specimen most measurements require the specimen to be mounted so that its surface contains the goniometer axis. In addition to the basic θ and 2θ movements of Bragg-Brentano geometry, some type of analysis (e.g. texture, stress) also require the following rotations (illustrated in Figure 6),

— Omega (ω), the angle between incident beam and the specimen surface, often coinciding with Theta (θ), half the diffraction angle (2θ):

  - $\omega = \theta$ when the goniometer is used in a Bragg-Brentano parafocusing system, i.e. with incident and diffracted beams symmetrically at angle θ to the specimen surface;

  - ω may be different from θ, e.g. fixed, especially:

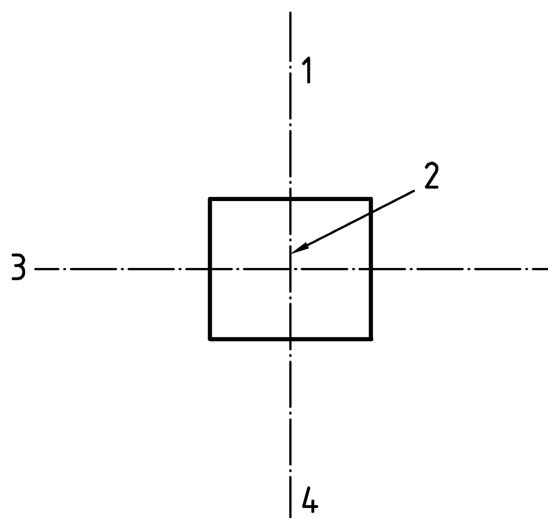
    - if it is required that the specimen depth probed is constant at different values of the diffraction angle, e.g. if surface-sensitive techniques are applied, or

    - if one- or two-dimensional position-sensitive detectors are applied.

— Phi (ϕ) is used to position a flat specimen by rotating it in its plane, a rotation, at a rate of one or more revolutions per data collection step, is often used to improve the crystallite statistics.

— Chi (χ) is used to orientate the specimen surface around the axis lying in the equatorial plane and normal to the goniometer axis.

The angles omega (ω) and chi (χ) are often called psi (ψ), depending on the geometry of the goniometer. These angles are mainly relevant to texture and residual stress measurements. The associated movements are normally controlled using special attachments or specialised diffractometers (Eulerian cradle, Kappa goniometer, etc.).



Key

1 Goniometer axis
2 In plane of specimen surface
3 ψ, χ Axis
4 θ axis, 2θ axis, ω axis

psi (ψ), chi (χ): axes are perpendicular to the goniometer axis

θ, 2θ, omega (ω): axes coincide with the goniometer axis

phi (ϕ) axis is perpendicular to the specimen surface

NOTE The sense of rotation around the θ, 2θ and ω axes is equivalent and related to the mounting of the flat specimen in the Bragg-Brentano diffractometer.

Figure 6 — Identification of the θ, 2θ, ϕ, χ, ψ and, ω axes independent of diffraction geometry.

For very large immobile specimens, specialised diffractometers have been made that allow all the required movements of the diffractometer components around a stationary specimen.

4.5.2.4 Irregularly shaped specimens

For specimens with rough or curved surfaces, diffractometer configurations with parallel beam geometry have distinct advantages. The position of the specimen surface relative to the goniometer axis is much less critical than with the other diffraction geometries for accurate registration of diffraction angles (see 4.2.3, 4.3.2.4 and Annex B).

4.6 Specimen stage

The specimen stage is a device to contain and position the specimen. It can be completely open to the environment or a volume separated from the environment to accommodate atmospheres other than air (e.g. accommodate to control relative humidity), or accessories for applying cooling and/or heating and/or high pressure to the specimen. Unless the specimen is self-supporting and suitably shaped, it shall be contained in a specimen holder and mounted on the specimen stage in a position appropriate to transmission or reflection measurements.

Specimen holders are often constructed to allow specimen rotation around the appropriate axis (ϕ in 4.5.2.3).

4.7 Data collection system

The data collection system collects the X-ray data from the detector along with the corresponding data on the position and/or orientation of the specimen, the X-ray source and the detector; the collection system transforms these data into the format required for the data files of the data processing/evaluation system.

5 Characterisation of equipment components

The following Tables list the values of instrument characteristics that shall be traceable and made available as required.

Nominal or measured values (specified as such) shall be provided by the manufacturer of new equipment, or new components added to existing equipment, and recorded by the user. For existing equipment, as much of this information as possible shall be recorded by the user.

Table 1 — Instrument characteristics to be provided by the manufacturer

Component type	Component	Nominal or measured values
X-ray sources	High voltage generator	— accuracy of voltage and current, — long and short time stability of voltage and current, — ripple, specified for 50 Hz, 100 Hz and frequency of switched power supply (if applicable), — Voltage and current range or settings.
	Sealed tubes, microfocus tubes and continuously pumped sources	— material of anode, (Ag, Co, Cr, Cu, Fe, Mo, W, etc.) and its characteristic spectral purity when manufactured, — maximum electron emission current (mA) and recommended value for normal XRPD use, — maximum electron acceleration voltage (kV) and recommended value for normal XRPD use, — for microfocus tube: static or dynamic electron beam conditioning — the shape and dimensions, usually the length and width, of the anode area emitting X-rays, — material and thickness of tube window or window transmission,
	Recommended operational characteristics for normal use of XRD	— take-off angle of the X-rays from the anode, — anode coolant temperature range and stability, — apparent shape ("point focus" or "line focus") of the X-ray source at the recommended take-off angle, — electron current and electron acceleration voltage
	Synchrotron sources	See facility specifications
Monochromators	Filters	— material and thickness of filter(s), — material and thickness of attenuation filter(s) and attenuation for the wavelength(s) specified.
	Crystal monochromators and analysers	— material of monochromator crystal and lattice spacing used, — type of focusing and focal lengths, — any means of suppressing harmonics of the wavelength transmitted, — energy or wavelength resolution.
	Electronic filters	— type of electronic filter (counter). See detection systems
	Multilayer mirrors	— type of multilayer mirror(s) (layer materials used, grading applied when available), — type of curvature of the mirror(s) and the values of the characteristic parameters of curvature.
	Pre-configured combination of monochromating devices	— types and arrangement of devices.

Table 2 (*continued*)

Component type	Component	Nominal or measured values
Beam dimensions and geometry	Slits	for all divergence slits, variable aperture slits, antiscatter slits, knife edges and receiving slits used: — geometric dimensions, — position(s) in the diffractometer, — divergences accepted or produced, — geometric dimensions.
	Parallel plate collimators (Soller slits)	— number, thickness, material of foils, length and mutual distance of foils or the resulting divergence, — position(s) in the incident and/or diffracted beams, — maximum divergence in the direction parallel to the foils, — intensity attenuation.
	Tube collimators	— geometric dimensions, — position(s) in the incident and/or diffracted beams, — divergence accepted or produced,
	Capillary optics	— geometric dimensions, — position(s) in the diffractometer, — divergence accepted and divergence/convergence produced, — number of capillaries, — focal length.
Detection systems		— type of detection systems and electronic discrimination, — spatial resolution of the detector (for position-sensitive detectors), — dead time, — dark current of background count rate, or noise (depending on type of detector), — dynamic range, — maximum acceptable counting rate, — counting efficiency at specified energies or wavelengths, — energy resolution obtainable, — energy detection limit, — recommended gas composition and recommended pressure.

Table 3 (*concluded*)

Component type	Component	Nominal or measured values
Goniometers		— the type of goniometer the number and orientation of goniometer axes, — the range of available radii of the goniometer circle, — the minimum step size, repeatability and reproducibility of detector positioning — the minimum step size, repeatability and reproducibility of source positioning (θ-θ geometry), — the minimum step size, repeatability and reproducibility of specimen orientation (θ-2θ geometry), — the linearity of movement, — the minimum angular displacement step possible, — maximum scan speed, — minimum and maximum accessible 2θ angles (positive and negative).
Specimen stage		— the type of specimen stage, and its suitability for reflection or transmission measurements, — the method for mounting and/or exchanging the specimen, — the method for positioning the specimen surface, — the ability to rotate or oscillate the specimen in its plane or around an axis in its plane, — the ability to control the atmosphere composition, temperature and pressure that surrounds the specimen.

The following Table lists the equipment configuration characteristics that shall be traceable and made available by the user as required. For each experiment performed, the corresponding configuration shall be recorded or referred to.

Table 4 — Instrument characteristics to be provided by the user

Configuration aspect	Characteristic
Geometry type	e.g. Bragg-Brentano, Seemann-Bohlin, Guinier, etc.
X-ray source	— source type e.g. sealed tube, rotating anodes, synchrotron (*) etc. — material of anode (Ag, Co, Cr, Cu, Fe, Mo, W , etc.), — the shape and dimensions, usually the length and width, of the anode area emitting X-rays, — apparent shape ("point focus" or "line focus") of the X-ray source, — take-off angle of the X-rays from the anode.
Goniometer	— type of goniometer, — the number and orientation of goniometer axes, — the radius of the goniometer circle, — the distance from the “apparent” source to the centre of the goniometer, — the distance from the centre of the goniometer to the detector or the receiving slits.
Monochromator(s)	— position(s) with respect to the beam(s) concerned, — type of focusing and focal lengths (if focusing is applied), — filter(s) used, position(s), materials and thicknesses, — type of electronic filter(s) (see detection systems), — nominal wavelength or range of wavelengths.
Multilayer mirrors	— type of multilayer mirror(s), position(s), curvature(s), focal length(s) (where relevant), — types and arrangement of optical monochromating devices.
Slits and collimators	— type(s), position(s), size(s), shape(s) and orientation(s) if different from standard values.
Capillary optics	— position(s) when different from standard.
Detection systems	— type(s) of detector, — energy discriminator window, — PSD angular window, — type of electronic filter, dead time correction, energy or wavelength window (where relevant).
Specimen stage	— type, position and movement, — specimen holder dimensions, — specimen environment where applicable (e.g. temperature, gas, pressure.

(*) The synchrotron source characteristics depend on the configuration and time of use and shall therefore be specified in each analysis result report form. It is recommended that at least the following items are reported: the synchrotron source name, the beam line name and configuration, the operating energy, the wavelength used, the spectral purity ($\Delta\lambda/\lambda$), the method for determining the wavelength used and the monochromator used, the means of monitoring the beam intensity with time, any intensity normalisation applied to the data, the time, date and duration of the measurement.

6 Equipment alignment and calibration

6.1 General

The powder diffraction technique is expected to measure line positions 2θ, intensities (line profile maximum and/or integrated intensities) and diffraction line shape parameters (e.g. full width at half-maximum FWHM) with an accuracy and uncertainty that completely meet the requirements of the specific application.

In order to accomplish this, the equipment shall be properly aligned and, where required by the application, calibrated. Special attention shall be paid to environmental conditions, particularly temperature and pressure.

6.2 Alignment

Goniometers and the corresponding incident and diffracted X-ray beam optics have many mechanical parts that need adjustment. The degree of alignment or misalignment directly influences the accuracy and reproducibility of the results of an XRPD investigation. The different components of the diffractometer shall therefore be adjusted carefully (by optical, mechanical or other means) to adequately minimise systematic errors, while optimising the intensities received by the detector. Roughly speaking: a misalignment of 5 micrometers of any component in commercial Bragg-Brentano diffractometers will have an observable effect on the collected data.

Many different diffractometer configurations have been constructed and each manufacturer's equipment requires specific alignment procedures. Specific tools may be provided to check the correct positioning of the goniometer with respect to the X-ray source, the specimen and its holder, the detector, etc. It is not intended to describe such procedures in detail in this document. However, the main parameters needing to be controlled during alignment are listed in Annex B for Bragg-Brentano diffractometers, see [7].

The alignment shall be verified by collecting (part of) the diffraction pattern of an appropriate calibrant (see WI 138070). The procedures described in Annex C are recommended. C.2 is the simplest procedure and does not require additional information. Other procedures such as C.3, C.7, C.8 and C.9 can be adopted when necessary.

6.3 Calibration

Calibration allows the quantification of non-removable systematic effects of the experiment on the measurements. Calibration of an XRPD instrument is not always essential but recommended. When used, it allows for evaluation of the characteristic instrumental contribution to the diffraction signal. This contribution can affect the position, broadening and shape of the line profile.

The calibration shall be performed using an appropriate and preferably certified calibrant for determining each of the above mentioned effects.

Appropriate working standards can also be used as internal standards and for application-specific calibrations and instrument qualification.

Calibration shall be performed according to a written procedure. Those described in Annex C are recommended. The procedures from C.3 to C.9 may be used to produce “instrument parameter curves”. These curves are useful for estimating non-removable systematic deviation for interpretation of experimental data. They are also useful for performance testing and monitoring.

7 Performance testing and monitoring

Different instrument configurations and performance levels are required depending on the type of analysis to be performed. Therefore, the performance needed shall be defined for each type of analysis. This level of performance shall be monitored. Equipment performance monitoring shall take the form of one or more suitable test procedures conducted to a defined time schedule.

The frequency of monitoring instrument performance will depend on the stability of the instrument configuration, the field of application and the circumstances of the laboratory. The aim is to ensure that all measurements are carried out under sufficiently well defined equipment and environmental conditions. A suitable frequency may be established by initial high frequency monitoring, using this data to establish an acceptable, less frequent monitoring

interval. The monitoring interval should be chosen recognising that a failure to meet the set level of performance shall require re-evaluation of the data produced since the last accepted monitoring measurement. In practice, many laboratories find that weekly monitoring of an instrument is sufficient. Test procedures for the overall diffractometer performance can be at different levels of sophistication. The results of such a test procedure may lead to testing of individual parts of the equipment.

Annex C gives several approaches to instrument performance testing at increasing levels of sophistication.

Proposed parameters to be monitored for each procedure given in Annex C are:

a) positioning error or mean absolute positioning error, intensity and FWHM of a specified number of diffraction peaks, (procedure C.2);

b) positioning error as a function of 2θ, (procedure C.3);

c) FWHM as a function of 2θ, (procedure C.4);

d) normalised intensity as a function of 2θ,(procedure C.5);

e) analytical profile function parameters as a function of 2θ, (procedure C.6);

f) refined lattice parameters or Smith and Snyder Figures of Merit (FOMs) or refined zero point correction, (procedure C.7);

g) fundamental parameters as described in [8], [15] and the derived parameters e.g. Δ2θ, FWHM, intensity, shape, (procedure C.8);

h) when a complete refinement of profile is made (procedure C.9) one or several of the following elements can be monitored:

- the scale factor S (relating measured and calculated intensities on an absolute scale, which can be used to monitor X-ray tube ageing and to verify the correct alignment of the optical system after diffractometer adjustment);

- the ratio $I_{K\alpha 2}/I_{K\alpha 1}$ (to verify the stability of monochromator optics and absence of time–dependent tube window contamination, e.g. by tungsten);

- specimen offset Δh (for monitoring the reproducibility of specimen positioning, e.g. when an automatic specimen changer is used);

- the lattice parameters (to verify the accuracy and precision of line positions measurements), parameters describing the 2θ-dependence of line profiles;

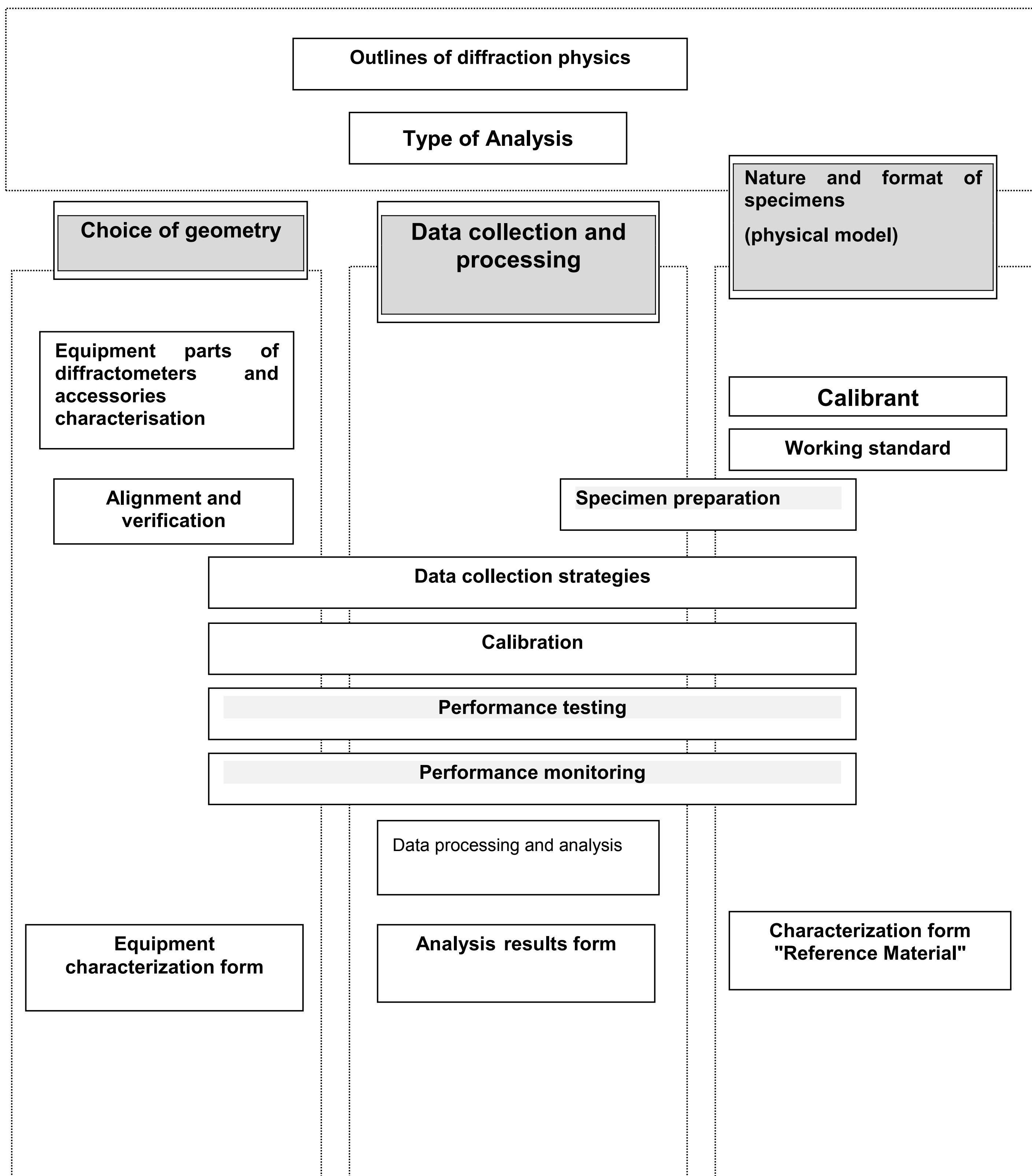
- the figures of merit for Rietveld refinement (R_{wp}, χ^2, etc.) (as a measure of the internal consistency of diffraction data).

Although the procedure C.9 is more complicated to apply than the other methods, it extracts more information from the diffraction pattern.

Annex A
(informative)

Relationship between the XRPD standards

(Linking of the topics within the standards)



Annex B
(informative)

Alignment of Bragg-Brentano diffractometers

For typical diffractometers working in Bragg-Brentano geometry, the following list gives the minimum set of actions that are recommended in order to achieve reproducible results from standard samples:

— assess radius of the goniometer circle and adjust the position of the receiving slit;

— centre the incident beam on the goniometer axis;

— centre the specimen surface reference plane on the goniometer axis;

— adjust the parallelism of the line source, slit system and specimen surface to the goniometer axis;

— align the Soller slits (incident and diffracted beam);

— adjust the zero points for ω or θ and 2θ circles.

Annex C
(informative)

Procedures for instrument performance characterisation

C.1 General

This annex describes procedures to characterise and assess the performance of a diffractometer as it is used in an XRPD experiment for a particular analysis.

All procedures can be used as calibration procedures if a certified calibrant is used. These procedures have different levels of sophistication and can be used for testing the instrument performance.

C.2 Position, intensity and breadth of a limited number of diffraction lines

The accuracy and/or the consistency of line position (e.g. at peak maximum), intensity (e.g. integrated intensity) and breadth (e.g. FWHM) can be readily measured for a specified set of diffraction lines. Differences in observed and reference values of line positions (e.g. as mean absolute errors) indicate any errors in the 2θ scale. Line intensity measurements are useful in assessing the overall performance and consistency of the X-ray source, alignment of optical components, and the detector efficiency. Breadth values are indicative of the instrument angular resolution and the state of instrument alignment.

C.3 Angular Deviation Curve

C.3.1 General

It is recommended that this procedure is used in combination with C.4 and C.5.

The angular deviation curve also known as an "angular calibration curve" is derived from a diffraction pattern obtained from a calibrant (WI 00138070) over a specified angular range by evaluating the residual line shifts after alignment. An accurate alignment is usually required to minimise the residual misalignment, i.e. the differences between the observed and the theoretical diffraction angle $2\theta^{theo}$, to within 0,02° over the whole pattern (see Figure C.1). For older instruments it may be higher. The most significant causes of line shift and their dependence on $2\theta^{theo}$ are given in Table C.1. The contributions of all individual causes (named also aberrations) to the line shift ($\Delta 2\theta$) are additive:

$$\Delta 2\theta(2\theta) = \sum_I A_I(2\theta) \tag{C.1}$$

where A_i is the coefficient of an instrument or specimen contribution to line shift with a characteristic dependence on $2\theta^{theo}$ [9]. Depending on the accuracy the number “I” ranges from 0 to 5 (see Table C.1) or more [10], and their values depend on the configuration and the optics applied and on the specimen. Wilson has given the values of A_i in terms of geometrical and physical quantities [7]. The diagram that shows the observed line shift $\Delta 2\theta$ as a function of $2\theta^{theo}$ of the calibrant, is called the “Angular Deviation Curve”.

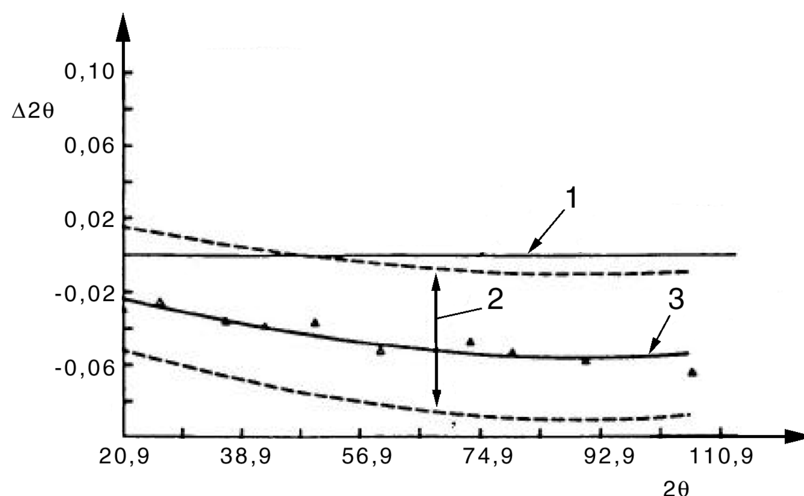
Table C.1 — Most significant contributions of instrument and specimen to line shift

i	Sources of contributions	Magnitude of contributions (deviations from the expected Bragg angle)
1	Error of the angle 2θ = 0 (zero shift)	A_0
2	Specimen surface displacement	$A_1 \cos \theta$
3	Specimen transparency	$A_2 \sin 2\theta$ (thick specimen, no X-rays transmitted) or $A_3 \cos \theta$ (thin specimen, most X-rays transmitted through specimen)
4	Flat specimen	$A_4 \cot \theta$
5	Axial divergence	$A_5 \cot 2\theta$ (two sets of narrow Soller slits) a
[a] For arrangement with none or one set of Soller slit refer to [7], [11].		

NOTE The magnitude of contributions included in this Table are intrinsically related to residual, not removable errors.

If the calibration process reveals the presence of unexpected contributions of misalignment, the alignment shall be performed again according to Clause 6.

In order to monitor the performance of diffractometers it is a good practice to prepare Angular Calibration Curves for one or more of the various aberrations. Figure C.1 shows the practical Angular Calibration Curve for a α-quartz specimen [12], where only the parameters A_2, A_4 and A_5 were taken into account.



Key

1 range of experimental 2θ
2 theoretical 2θ
3 practical 2θ

The line "theoretical 2θ" describes the ideal situation.

The "practical 2θ" curve is a predicted curve obtained by summing the contributions of the instrument and specimen, as calculated from the Wilson formulae [7], to line shift.

The experimental points for a quartz specimen are marked (▲).

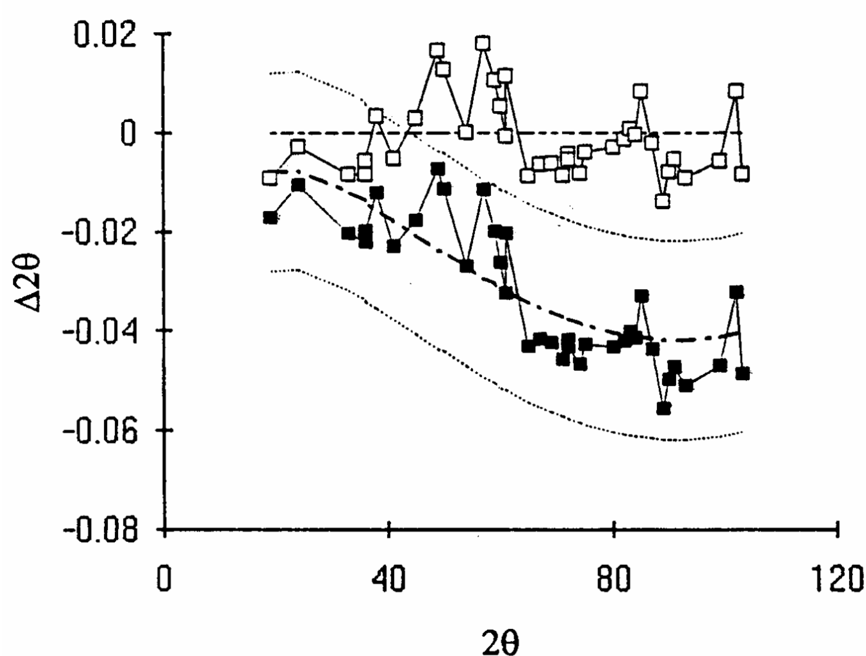
The “range of experimental 2θ” shows the acceptable experimental 2θ based on a tolerance of about ± 0,04° [12].

Figure C.1 — Practical Angular Calibration Curve

C.3.2 Example of the application of the angular deviation curve

The A_l coefficients can be estimated via an optimisation process and then the goodness of results evaluated against the theoretical ones. This approach is effective specially when a large number of patterns have to be compared (e.g. round robin tests or comparison of data coming from different laboratories and/or the same laboratory in different time).

This process gives the "effective values of A_i coefficient of Equation C.1" The optimised $\Delta 2\theta$ shall not differ by more than ± 0,02° from zero (see Figure C.2).



Key

The dashed line is the "theoretical $\Delta 2\theta$" being 0.

The point dashed line is the optimisation of model accounting for the Wilson formulae [7].

The "experimental" points (■) are obtained by processing the diffraction pattern of a quartz specimen according to the methods described in 6.3 of EN 13925-2:2003 "Procedures". Then the separation of the experimental points from the theoretical ones are calculated as the difference $2\theta^{theo}$-$2\theta^{exp}$, where: $2\theta^{exp}$ is the line position coming from fitting process of the diffraction pattern and $2\theta^{theo}$ is the expected diffraction line position.

The optimised points (□) still have residual shifts from the expected values. These shifts have arisen from random errors. The range shown of experimental 2θ is based on a tolerance of about ± 0,02°.

Figure C.2 — Optimised Angular Calibration Curve

In order to monitor the performance of a diffractometer, two or more angular deviation curves shall be taken at different times. They shall be compiled in one single diagram. If requested, the angular deviation curve and the monitoring diagrams of the single aberrations listed in Table C.1 shall also be provided to demonstrate the instrument performance.

C.4 Line breadth

It is recommended that this procedure be used in combination with C.3 and C.5.

The breadth curve is derived from a diffraction pattern obtained from a calibrant (WI 00138070) over a specified angular range, e.g. by evaluating the FWHM (Full Width Half Maximum) of a representative set of the diffraction lines present. Depending on the types of analysis and sophistication required, different plots of the variation of FWHM can be used:

a) "tan θ diagram". When a calibrant material is used, which has negligible strain and size broadening effects, the FWHMs of all the lines of the diffraction pattern are reported against tan θ. The dependence on tan θ is usually close to linear in the higher angular range with a fixed divergence slit

$$FWHM \approx A \tan\theta + B \tag{C.2}$$

A and B depend on the configuration, slits and other beam conditioning devices.

To monitor the performance of a diffractometer, the parameters A and B shall be monitored with time.

b) "IRF diagram". The plot of $FWHM^2$ (2θ) is called the Instrument Resolution Function (IRF) [13]:

$$FWHM^2 = A \tan^2\theta + B + C \cot^2\theta + D \sin^2\theta \tag{C.3}$$

The parameters A, B, C depend on the instrument geometry and dimensions, the spot size, the radiation used and the slit systems. D depends on specimen transparency. When a strongly absorbing calibrant is used, the term D in formula (C.3) may be zero [14].

To monitor the performance of a diffractometer the parameters A, B, and C shall be monitored with time or different Line Breadth Curves may be monitored with time.

C.5 Intensity diagrams

It is recommended that this procedure be used in combination with C.3 and C.4.

The intensity calibration is performed by comparing the experimental relative peak heights with those expected. These are either calculated or reported by one of the diffraction pattern databases available (the PDF of ICDD is currently widely used). The experimental values are either directly observed data or calculated by one of the methods described in 6.3 of EN 13925-2:2003 "Procedures". The intensities are expressed as a percentage of the strongest reflection (normalisation to the strongest line as 100). Corundum is widely used as the specimen to obtain such an Intensity Calibration Curve, although its anisotropy can lead to preferred orientation, making it imperfect for this purpose.

The observed intensity shall be monitored against 2θ and with time in a diagram reporting the intensity (either normalised or not) to check the overall performance of the diffractometer.

The integrated intensities (not normalised) of the strongest lines are often used to monitor the performance of the source and detection system (see C.2).

C.6 Shape Analysis Curve

It is recommended that this procedure be used in addition to other procedure in this Annex.

Depending on the precision and accuracy required, the instrumental contribution to the line profile may be required prior to determination of lattice parameters, line profile analysis, crystallographic texture, macrostress or crystal structure. A reference material based on LaB_6 is currently recommended as the calibrant specimen for this purpose (see WI 00138070).

The instrumental contribution is derived from a diffraction pattern obtained from the calibrant (WI 138070) over a specified angular range. The diffraction pattern of the calibrant is represented by one of the analytical functions: Gaussian, Lorentzian, Voigt, pseudo-Voigt, Pearson as described in Annex D of EN 13925-2:2003. These analytical functions are afterwards interpreted as an approximation to the instrument contribution. When Pearson VII, Voigt, or pseudo-Voigt are used, the “mixing parameter” (also called "shape parameter") adjusts the contribution of Lorentzian and Gaussian component. The value of the mixing parameter η shall be monitored, and possibly reported against $2\theta^{theo}$. The dependence on 2θ is sometimes linear, particularly for the pseudo-Voigt mixing parameter in fixed-slit Bragg Brentano geometry:

$$\eta = k_0 2\theta + k_1. \quad \text{(C.4)}$$

Deviations from linearity might reveal incorrect use of beam conditioning devices in the axial and equatorial plane (divergence slits, Soller slits, etc.). In such cases the alignment shall be verified.

Multiple shape analysis curves can be plotted in a single diagram to monitor the performance of a diffractometer with time.

C.7 Lattice parameters

This procedure is only intended to give an overall indication of the angular performance. It should be used in conjunction with other procedures in this annex.

This involves monitoring changes in calculated lattice parameters refined on the basis of a wide angular range of the diffraction pattern of a reference material.

FOMs M_{20} and F_{30} as defined in Annex E of EN 13925-2:2003, $<|\Delta 2\theta|>$, and the 2θ-calibration curve $|(2\theta_{observed})_i - (2\theta_{calculated})_i| = f(2\theta)$ are all indicators of diffractometer alignment in terms of angular position and can be used for stability monitoring as function of time.

Special attention should be paid to the temperature dependence of lattice parameters.

C.8 The use of the Fundamental Parameter Approach

The Fundamental Parameters Approach to X-ray diffraction-line profile fitting combines a:

— function that describes the diffraction-line shape inherent to the material of the specimen;

— function that describes the instrumental line shape in terms of the geometric parameters of the instrument;

— mathematical function describing the spectral distribution of the X-ray beam [15], [16], [17], [18].

The observed profile is the convolution of the instrument contribution and structural specimen contribution. The contribution of an ideal specimen is negligible so a standard specimen should provide a diffraction pattern giving a reliable approximation of the instrument contribution.

For the purpose of the evaluation of the instrument performance, the Fundamental Parameter Approach uses parameters related to the spectral distribution of the X-ray beam, the dimension of the diffractometer, the receiving slit width, the receiving slit length, the X-ray source size, the divergence of the incident beam, etc. In addition other physical properties of the specimen can be incorporated (e.g. the attenuation coefficient, the surface roughness).

When all the optical devices in a diffractometer are well known and well aligned, the observed profile can be synthesised and fitted using instrumental parameter values close to the directly measured values.

When the diffraction pattern is obtained from a specimen free from defects and the calculated diffraction pattern differs significantly from the measured patterns, this indicates changes in diffractometer settings. Details of the present approach are reported by [16].

C.9 Whole pattern fitting

A comprehensive analysis ([19], [20], [21]) of a diffraction pattern is carried out by minimisation of differences between calculated and observed patterns and changes in the most relevant refined parameters are monitored. In practice (see e.g. [21], [22]), the complete diffraction pattern of a suitable specimen, e.g. a fine-grained quartz plate or a reference material like corundum powder is recorded periodically. The data are refined by the Rietveld method that provides the optimised parameters and their standard deviations. By monitoring the variation of these parameters as prescribed throughout this Annex, instrument deviations as a function of time can be detected.

Annex D
(informative)

Sample report forms for characterisation of instruments

Instruments and accessories used in the experiment shall be characterised according to the characteristics mentioned in Table 1 of Clause 5 and Table 2 of Clause 5. Sample Tables are given here. They have been subdivided between Parts A and B to clarify the information to be provided by the manufacturer and by the user respectively.

Instrument Characterisation Form - Part A
(normally to be provided by the manufacturer on instrument delivery)

Sheet 1 (manufacturer)		Nominal (N)or measured (M) values. Specify which.	
X-ray sources			Component
	H. V. Generator		accuracy of voltage and current
			long and short time stability of voltage and current
			Voltage range or settings
			Current range or settings
			ripple, specified for 50 Hz, 100 Hz
			frequency of switched power supply (if applicable)
	Sealed tubes and rotating anode sources		material of anode (Ag, Co, Cr, Cu, Fe, Mo, W, etc.)
			characteristic spectral purity (when available)
			maximum electron emission current (mA)
			maximum electron acceleration voltage (kV)
			Static or dynamic electron beam conditioning (microfocus tube)
			shape and dimensions (length and width) of the anode area emitting X-rays
			material and thickness of tube window
			window transmission
			take-off angle of the X-rays from the anode
			recommended anode coolant temperature and its range
	Recommended operational characteristics for normal XRPD use		stability
			apparent shape ("point focus" or "line focus") of the X-ray source at the recommended take-off angle
			electron emission current
			electron acceleration voltage

Signatures	Manufacturer's Representative:	Date:

Sheet 2 **(manufacturer)**		**Nominal (N) or measured (M) values. Specify which.**	
Monochromators			**Component**
	Filters (for each filter used)		material and thickness
			attenuation for the wavelength (s) specified
	Crystal monochromators and analysers		the type and reflection plane of the monochromator crystal
			type of focusing and focal lengths
			any means of suppressing harmonics of the wavelength transmitted
			energy resolution or wavelength resolution
	Electronic filters		maximum acceptable count rate
			Dead time of electronic filter
	Multilayer mirrors		type of multilayer mirror(s) layer materials used
			grading applied (when available)
			type of curvature of the mirror(s)
			the values of the characteristic parameters of curvature
			types and arrangement of optical monochromating devices

Signatures	Manufacturer's Representative:	Date:

Sheet 3 **(manufacturer)**		**Nominal (N)or measured (M) values. Specify which.**	
Beam dimension and geometry		Da= Dp= W= L=	**Component**
	Slits		For all the divergence slit mention the types: variable (or fixed) aperture slits
			antiscatter slits
			knife edges
			receiving slits
			For each type specify: their positions in the diffractometer (p=…) the divergences accepted (Da = ….)
			the divergence produced (Dp =…)
			the geometric width and length (W =…, L=…)
			position(s) in the incident and/or diffracted beams
	Parallel plate collimators (Soller slits)		number
			thickness
			material of foils
			length
			spacing of foils or the resulting divergence
			maximum divergence in the direction parallel to the foils
			intensity attenuation
			positions in the incident and/or diffracted beams
	Tube collimators		divergences accepted or produced
			geometric dimensions
			position in the diffractometer
	Capillary optics		divergence accepted and divergence/convergence produced
			geometric dimensions
			number of capillaries
			focal length

Signatures	Manufacturer's Representative:	Date:

Sheet 4 (manufacturer)	Nominal (N)or measured (M) values. Specify which.	
		Component
Detection systems		type of detection systems and electronic discriminator
		spatial resolution of the detector (for position-sensitive detectors)
		dead time
		dark current, or noise (depending on type of detector)
		dynamic range
		energy resolution obtainable
		maximum acceptable count rate
		counting efficiency at the specified energies and/or wavelength
		energy detection limit
		life expectancy (see 3.6)
Goniometers		the type of goniometer, the number and orientation of goniometer axes
		the range of available radii of the goniometer circle
		the dimension of the minimum sphere (sphere of confusion) enclosing the closest points of approach of the goniometer axes
		test of the repeatability and reproducibility of detector positioning
		test of the linearity of movement
		the smallest angular displacement step possible for each goniometer axis
		maximum scan speed
		accessible and inaccessible 2θ angle ranges
Specimen stage		the type of specimen stage, and if it should be used for reflection or transmission measurements
		the way of mounting and/or exchanging the specimen
		the way of positioning the specimen surface
		the possibilities to rotate or oscillate the specimen
		the possibilities to control the atmosphere, temperature and pressure that the surrounds the specimen.

Signatures	Manufacturer's Representative:	Date:

Instrument Characterisation Form - Part B

(to be provided by the instrument user)

Sheet 1 **Configuration aspect**	**Nominal (N)or measured (M) values. Specify which.**	**Effective values (*)**	**Description where relevant**
Geometry type			e.g. Bragg-Brentano, Seemann-Bohlin, Guinier, etc.
X-ray source			– Source type e.g. sealed tube, rotating anodes, synchrotron etc.
			– material of anode (Ag, Co, Cr, Cu, Fe, Mo, W, etc.)
			– the shape and dimensions, usually the length and width, of the anode area emitting X-rays
			– apparent shape ("point focus" or "line focus") of the X-ray source
			– take-off angle of the X-rays from the anode
Goniometer			– type of goniometer
			– number and orientation of the goniometer axis,
			– the radius of the goniometer circle
			– “apparent” source to centre of goniometer distance
			– centre of goniometer to detector or receiving slits
Monochromator(s) [one block for each monochromator]			– position(s) with respect to the beam(s) concerned
			– type of focusing and focal lengths
			– filter(s) used, position(s), material and thickness
			– type of electronic filter(s) (see detection system)
			– nominal wavelength on the range of wavelengths
(*) Effective values as they are obtained from the calibration process C.2 to C.9 of Annex C when and if used.			

Signatures	
Date:	Responsible X-Ray person:
Date:	Responsible Q.A. person :

Sheet 2 Configuration aspect	Nominal (N)or measured (M) values. Specify which.	Effective values (*)	Description where relevant
Multilayer mirrors [one block for each monochromator]			– type of multilayer mirror(s), position(s), curvature(s), focal length(s)
			– types and arrangement of optical monochromating devices
Slits and collimators [one block for each slit and collimator]			– type
			– position
			– size
			– shape
			– orientation
Capillary optics			– position(s) when different from standard
Detector(s) [one block for each detector]			– type(s) of detectors
			– energy discriminator windows
			– PSD angular window
			– type of electronic filter(s), dead time correction or wavelength windows (when relevant)
Specimen stage			– type, position and movement
(*) Effective values as they are obtained from the calibration process C.2 to C.9 of Annex C when and if used.			

Signatures	
Date:	Responsible X-Ray person:
Date:	Responsible Q.A. person :

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