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TEXS: in-vacuum tender X-ray emission spectrometer with 11 Johansson crystal analyzers

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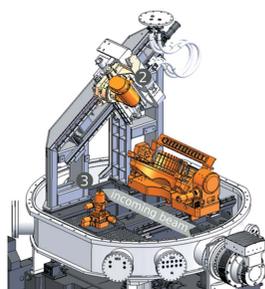
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The design and first results of a large-solid-angle X-ray emission spectrometer that is optimized for energies between 1.5 keV and 5.5 keV are presented. The spectrometer is based on an array of 11 cylindrically bent Johansson crystal analyzers arranged in a non-dispersive Rowland circle geometry. The smallest achievable energy bandwidth is smaller than the core hole lifetime broadening of the absorption edges in this energy range. Energy scanning is achieved using an innovative design, maintaining the Rowland circle conditions for all crystals with only four motor motions. The entire spectrometer is encased in a high-vacuum chamber that allocates a liquid helium cryostat and provides sufficient space for *in situ* cells and *operando* catalysis reactors.

1. Introduction

X-ray emission spectroscopy is attracting growing interest as a tool to characterize local electronic and atomic structure. We define emission spectroscopy as measuring the emitted X-rays from a fluorescence source with an energy bandwidth that is of the order of the core hole lifetime broadening. The spectroscopic techniques with such an instrument include non-resonant X-ray emission spectroscopy (XES), that does not require a monochromatic incoming beam to excite the analyte atom, as well as resonant inelastic X-ray scattering (RIXS) and high energy resolution fluorescence detected (HERFD) X-ray absorption near-edge structure (XANES) spectroscopy. A series of books and review papers describe the applications of XES, RIXS and HERFD-XANES in solid state physics, materials science, coordination chemistry and biology (Meisel *et al.*, 1989; Glatzel & Bergmann, 2005; Rueff & Shukla, 2013; Hayashi, 2000; Rovezzi & Glatzel, 2014; Bauer, 2014; Sa, 2014; DeBeer & Bergmann, 2016; Proux *et al.*, 2017). High-performance and user-friendly X-ray emission spectrometers at synchrotron radiation facilities and in the laboratory, combined with tools for theoretical interpretation of the data, have greatly helped the adoption of the techniques by a large community.

The X-ray energy range between 1.5 keV and 5.5 keV, the so-called 'tender' X-ray range, covers the *K* absorption edges of light elements (*e.g.* Al, S, Cl), the *L*-edges of 4*d* transition



metals and the M -edges of $5d$ transition metals and actinides. The chemical sensitivity of fluorescence lines measured in XES mode can be used to characterize the electronic structure and local coordination of a target element (Alonso Mori *et al.*, 2009; Mori *et al.*, 2010). It is very attractive for heavy elements to use absorption edges of shallow instead of deep core holes (e.g. L - instead of K -edge for $4d$ transition metals), because of the greatly reduced spectral broadening arising from the core hole lifetime. This has recently been exploited in high-pressure and magnetism research (Wilhelm *et al.*, 2016) and in chemistry and catalysis (Thompson *et al.*, 2015). The spectral broadening can be further reduced by using an X-ray emission spectrometer for recording the fluorescence lines instead of a conventional solid state detector. To date, this approach has been applied in the field of catalysis (Thomas *et al.*, 2015), Li-S batteries (Kavčič *et al.*, 2016), and actinides chemistry (Kvashnina *et al.*, 2013, 2019).

Despite its relevance, the tender X-ray range is rarely exploited under high energy resolution because of technical challenges. First of all, the low energies require vacuum conditions in order to minimize absorption by air. Furthermore, the high energy resolution can be achieved either with wavelength-dispersive optics or detectors that use materials in their superconducting state (Doriese *et al.*, 2017). Wavelength-dispersive optics can be realized using either gratings or perfect crystals. As the efficiency of gratings decreases rapidly towards higher energies, perfect crystals are generally used in tender X-ray spectrometers. Soft crystals with large d -spacing such as lithium fluoride (LiF), pentaerythritol (PET), thallium acid phthalate (KAP), Pb stearate and micas were employed for this energy range in some XES instruments. These crystals are not stable with time and when testing them we were not able to achieve the required energy resolution. Thus, standard high-quality hard crystals such as silicon (Si), germanium (Ge) and quartz (β -SiO₂) are preferred.

X-ray emission spectrometers can generally be grouped into non-dispersive (also referred to as ‘point-to-point focusing’) and dispersive geometries. The main difference is in the way the captured solid angle (*i.e.* the total crystal surface) is partitioned. A non-dispersive geometry minimizes the angular difference ($\Delta\theta = |\theta_i - \theta_B|$) between the Bragg angle at any point of the crystal (θ_i) with respect to the Bragg angle at the centre of the crystal (θ_B). This condition is satisfied with a bent optics along the diffraction direction. As a consequence, an emission spectrum is recorded by scanning the optics. In a dispersive set-up, the crystal surface is usually flat along the diffraction direction. The energy of the diffracted X-rays is directly related to the position on the detector. A prominent example is the von Hamos geometry (Hoszowska *et al.*, 1996; Dousse & Hoszowska, 2014). In this case, an emission spectrum is recorded in a stationary configuration with a position-sensitive detector. We note that there are also hybrid instruments working with the crystal off the Rowland circle and a position-sensitive detector (Welter *et al.*, 2005; Huotari *et al.*, 2006; Kavčič *et al.*, 2012; Holden *et al.*, 2017).

An important application for the instrument presented here is HERFD-XANES in samples with low analyte concentra-

tion. In this case, the captured solid angle must be used in the smallest possible energy window. Consequently, a non-dispersive geometry was chosen. The interested reader may refer to the seminal study by Wittry & Li (1993) for a quantitative comparison of scanning spectrometers *versus* dispersive set-ups.

Reviewing all existing instruments is well beyond the scope of this manuscript. We simply note that a multi-analyzer configuration is usually adopted to maximize the effective solid angle of detection. Whereas this strategy is well established for hard X-rays, it has not been realized yet for the tender X-ray energy range. In fact, existing instruments in this energy range use a single-crystal analyzer (Kavčič *et al.*, 2012; Abraham *et al.*, 2019).

The manuscript is organized as follows. In Section 2 the concept design is described. The mechanical design and description of the manufactured instrument are reported in Section 3. Finally, the results and performances obtained from the commissioning phase are reported and discussed in Section 4.

2. Concept design

The concept design of the spectrometer is based on the following specifications: (1) energy range between 1.5 keV and 5.5 keV, continuously covered with standard high quality crystals, e.g. Si or Ge and β -SiO₂; (2) energy bandwidth close to or below the core-hole lifetime broadening of the emission lines measured; (3) optimized solid angle per energy bandwidth, specifically a Rowland circle diameter ≤ 1 m and a multi-analyzer set-up; (4) windowless from the ultra-high vacuum of the host beamline up to the detector, in order to minimize X-ray attenuation.

Three sets of crystal cuts, β -SiO₂(100), Si(111) and Si(110), are chosen to continuously cover the 1.5–5.5 keV energy range. The Bragg angle (θ_B) ranges from 85° to 35°, as shown in Fig. 1. The elements and emission lines accessible in this range are also reported in the figure, where for simplicity only the $K\alpha_1$, $L\alpha_1$ and $M\alpha_1$ lines are shown.

The Rowland geometry (Rowland, 1882) that was adopted for the design of the spectrometer is shown in Fig. 2(a). The points representing the sample (O), centre of the crystal analyzer (C) and detector (D) define the Rowland circle with radius R . The plane containing the Rowland circle defines the meridional or dispersive direction. In symmetric Bragg reflections, the source-to-analyzer (OC) and the analyzer-to-detector (CD) distances are equal. The source volume is given by the point where the incoming X-rays impinge on the sample surface. The scattering geometry is important for anisotropic radiation emitted from the sample. This is the case for elastic, Compton and X-ray Raman scattering, which give rise to background in the energy range of the fluorescence lines. When light is polarized linearly in the horizontal plane (scattering plane, XY), it is thus advantageous to align the spectrometer normal to the incoming beam (X) and on the scattering plane. This explains why we chose to have the centre of the crystal analyzer at $Z = 0$ for all Bragg angles, as

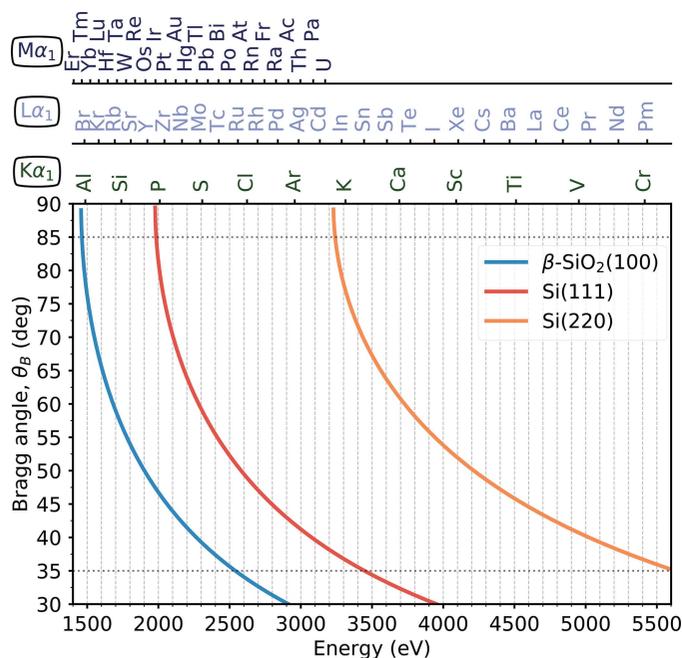


Figure 1
Bragg angular range required to continuously cover the tender X-ray range with β -SiO₂(100), Si(111) and Si(220) reflections. The elements and corresponding energies of three selected families of emission lines, namely $K\alpha_1$, $L\alpha_1$ and $M\alpha_1$, are indicated in the top axes. The horizontal lines indicate the angular range covered by the spectrometer.

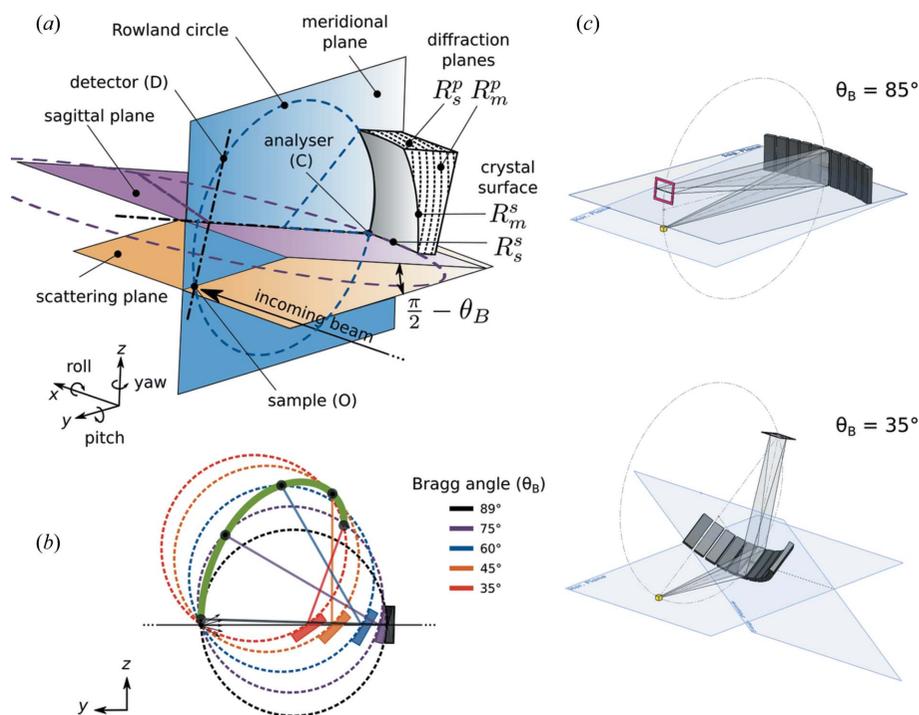


Figure 2
Rowland circle geometry employed for the instrument design [(a) and (b), dimensions not to scale]: a quarter section of a generic doubly bent diffractor; how the crystal analyzer and detector move on the Rowland circle when changing the Bragg angle (bottom). Cylindrical segmentation of the analyzer in the sagittal direction for a multi-analyzer configuration at the two extreme Bragg angles (c). The horizontal and sagittal planes are shown. For simplicity, the Rowland circle and rays volume are displayed only for the central analyzer.

shown in Fig. 2(b). In this configuration, OC stays on an axis (Y) and the detector follows a trajectory resulting from pivoting the Rowland circle around the sample during the Bragg scan [green line in Fig. 2(b)]. As a consequence, it minimizes the window opening required for sample environment set-ups, such as *in situ* and *operando* cells or cryostats.

The sagittal plane is perpendicular to the sample–detector axis (OD). It is inclined by $(\pi/2) - \theta_B$ with respect to the scattering plane. A rotation of the Rowland circle around the sample–detector axis describes a circle on the sagittal plane with radius $2R \sin(\theta_B)^2$, which we call the sagittal circle. Each point on this circle thus defines a Rowland circle containing points O and D and \widehat{OCD} angle $\pi - 2\theta_B$. This is the condition for dynamical sagittal focusing as it depends on the Bragg angle. This could be realized by dynamically bending a crystal wafer. However, this would lead to anticlastic bending in the meridional direction. The solution is a segmentation of the crystals in the sagittal direction [Fig. 2(c)]. The smaller the segments, the better the approximation to the correct sagittal bending radius. Our choice was to use an array of 11 cylindrical Johansson crystal analyzers with fixed shape and dynamically placed on the sagittal circle. This choice was governed by the availability of Johansson crystals and ultimately costs. The concept described in the following can be extended to more segments and/or smaller crystal bending radii.

The optimization of the performances for a generic doubly bent crystal analyzer is based on an analytical study (Wittry & Sun, 1990a,b, 1991, 1992). It consists of calculating analytically the $\Delta\theta(x,z)$ distribution over the area of the crystal analyzer as a function of the Bragg angle θ_B at the centre of the crystal. To achieve this purpose, the crystal analyzer is parametrized with four bending radii: R_m^s , R_m^p , R_s^s , R_s^p which are the bending radius of the surface (R^s) and crystal planes (R^p) in the meridional direction (R_m) or sagittal direction (R_s), as shown in Fig. 2(a). We included in the calculation only two types of crystal analyzers, based on well established production technologies [Fig. 3(a)]: (1) spherically bent crystal analyzers, SBCAs (Rovezzi *et al.*, 2017, and references therein); and (2) cylindrically bent Johansson crystal analyzers, CBJCAs (Johansson, 1933). SBCAs are widely used on hard X-ray instruments where it is possible to find a reflection to work in back-scattering conditions ($75^\circ < \theta_B < 90^\circ$). CBJCAs are mainly developed as X-ray optics for laboratory diffractometers with the goal of monochromatizing the X-ray tube source, *e.g.* selecting only the $K\alpha_1$ emission line, and usually working in grazing-incidence asymmetric Bragg

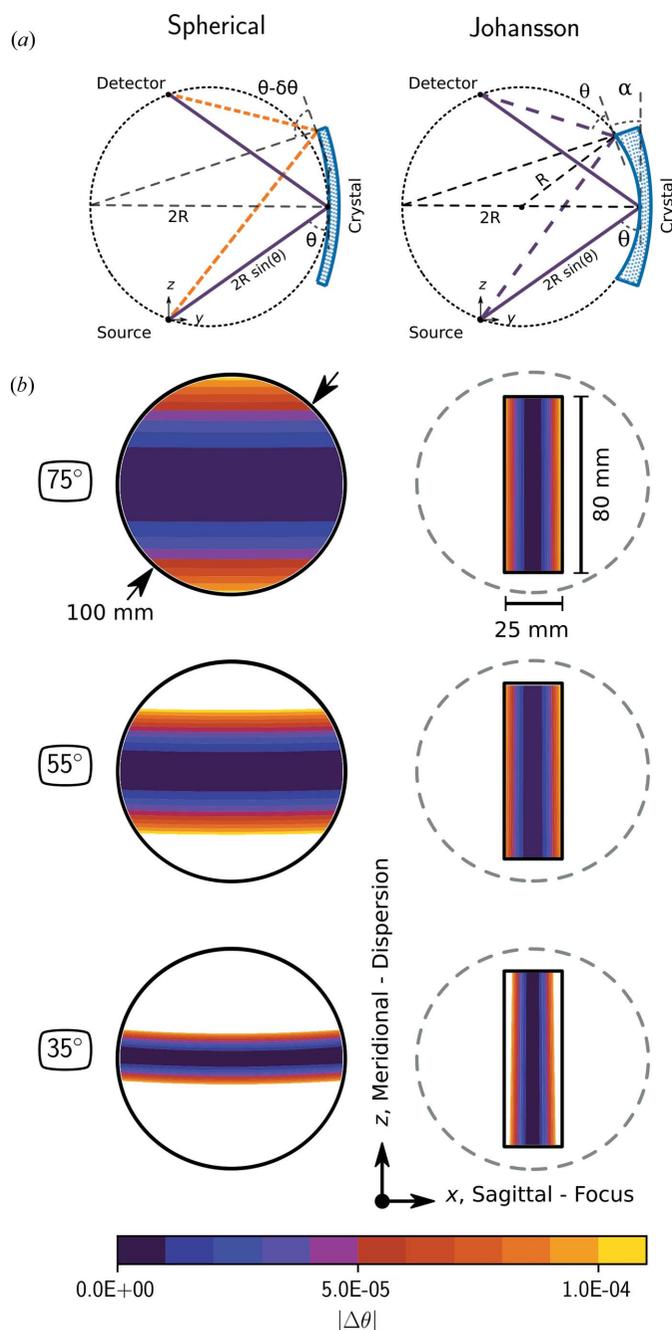


Figure 3 Spherical (left column) versus Johansson analyzer (right column). Summary of the geometry projected on the Bragg diffraction plane, YZ [(a), not to scale]. Effective scattering area plots (b) for Si(111) reflection with a bending radius of 1 m. The region of the crystal that reflects the 0.5 eV bandwidth at three Bragg angles, namely 75° , 55° and 35° , is shown with a colour scale representing the deviation from the Bragg angle at the centre of the crystal ($\Delta\theta$).

reflections. Furthermore, to take into account the limited bandwidth of the fluorescence line of interest, ΔE , a θ_B -dependent threshold in $\Delta\theta$ is established using the differential form of the Bragg equation, $|\Delta E/E| = \Delta\theta/\tan\theta$. For example, sulfur $K\alpha_1$ has an intrinsic line width $\Delta E = 0.61$ eV at $E = 2307.8$ eV, as tabulated in *XRAYLIB* (Schoonjans *et al.*, 2011). With Si(111) this energy corresponds to $\theta = 58.95^\circ$. The angular width of this line is then $\Delta\theta = 4.3 \times 10^{-4}$ rad. We

chose a ΔE threshold of 0.5 eV to determine the area of the crystal diffracting such bandwidth. The results are shown in Fig. 3(b). An ‘effective solid angle per energy bandwidth’ as a function of the Bragg angle and for a given type of crystal analyzer was calculated.

The main differences between SBCAs and CBJCAs are shown in Fig. 3. We consider first the meridional/dispersive direction. SBCAs are built by bending a thin crystalline wafer (typically Si or Ge of ~ 100 μm) on a spherical substrate of circular shape (typically 100 mm diameter) and radius $2R$, the diameter of the Rowland circle. As a consequence, all four radii are equal, $R_m^s = R_m^p = 2R$. A chromatic aberration ($\delta\theta$) is introduced when moving out of the centre of the crystal. This aberration, also known as Johann error, scales with $\cot^2(\theta_B)$ and becomes prohibitive for small Bragg angles. Assuming a threshold of 0.5 eV, Fig. 3 shows that a smaller area of the analyzer contributes to the scattered amplitude for $\theta_B < 75^\circ$. This aberration is removed in CBJCAs. In fact, the Johansson analyzer is manufactured via a bending plus grinding process (Section 4.1). It results in $R_m^p = 2R$ and $R_m^s = R$. This condition ensures identical Bragg angle over the crystal surface in the meridional direction because the crystal planes have a variable miscut angle $\alpha = (1/2) \arcsin(l/R)$, where l is the distance from the centre of the analyzer. Without chromatic aberration, the CBJCAs efficiently diffract the X-rays for Bragg angles below 75° .

Regarding the sagittal direction, the ideal condition would require $R_s^s = R_s^p = 2R \sin^2(\theta_B)$. SBCAs are superior to CBJCAs because of the double bending. In fact, CBJCAs are flat in this direction ($R_s^s = R_s^p = \infty$) and for this reason suffer a chromatic aberration that has a second-order dependency on the Bragg angle. For a point source,

$$\Delta\theta = \tan\theta \left\{ 1 / \left[1 + \left(\frac{w}{4R \sin\theta} \right)^2 \right]^{1/2} - 1 \right\},$$

where w is the width of the flat side. This disadvantage can be corrected relatively easily by reducing the size of each analyzer in the sagittal direction and increasing the number of analyzers in the spectrometer. With the given threshold of 0.5 eV, it is found that a width of 25 mm keeps the full efficiency of the analyzer in the whole angular range. For those applications requiring better energy resolution, it may be beneficial to further reduce the width of the flat side with a rectangular mask, especially at low Bragg angles. Considering the current limitations in the production of CBJCAs from wafers of 100 mm diameter, the size in the meridional direction is reduced to 80 mm, allowing two analyzers per wafer.

Two additional non-negligible factors that contribute to the energy broadening are: (1) the finite source size, given by the footprint of the exciting radiation (X-rays or particles) on the sample; and (2) the strain and defects introduced in the analyzer crystal lattice by the bending and grinding. To correctly take into account these two effects, the previous analytical study was complemented by ray-tracing calculations. The simulations were carried out using the *SHADOW3* (Sanchez del Rio *et al.*, 2011) code for a cylindrically bent

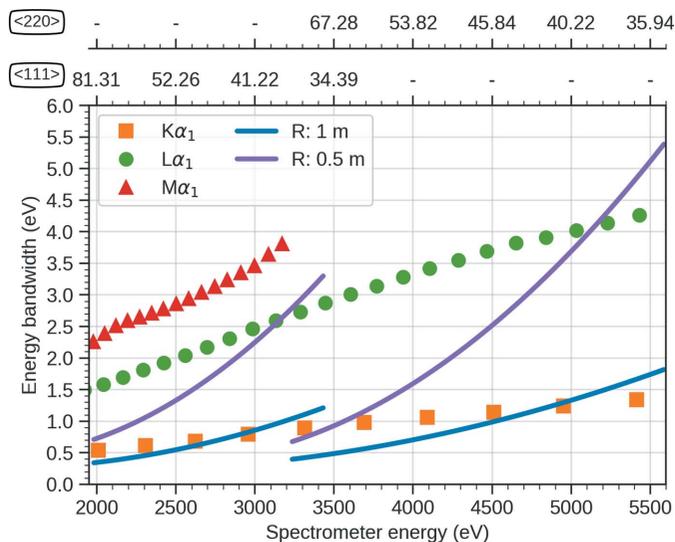


Figure 4 Results of the ray-tracing study for a Si CBJCA of 25 mm × 80 mm size plus an elliptical fluorescence source size of 0.1 mm × 0.5 mm. The tabulated width of the emission lines for all the elements accessible in the given energy range are shown for comparison (symbols). The top scales give the corresponding Bragg angle for Si(111) and Si(220) reflections.

Johansson-type crystal analyzer with rectangular shape of 25 mm (sagittal) and 80 mm (meridional). Two bending radii, 1 m and 0.5 m, were considered for each of the Si(111) and Si(110) analyzers. The simulations assumed an elliptical source of 0.1 mm (vertical, Z) and 0.5 mm (horizontal, X) and also considered the distortion of the crystal planes by the strain resulting from the bending using the multilamellar model (Sanchez del Rio *et al.*, 2015). The tabulated energy widths of the $K\alpha_1$ ($K-L_3$), $L\alpha_1$ (L_3-M_5) and $M\alpha_1$ (M_5-N_6) lines for all elements accessible in the covered energy range are plotted in Fig. 4 and compared with the expected performances from ray tracing. When studying L - or M -edges, both 0.5 m and 1 m configurations offer an experimental energy broadening below the width of the emission lines. For the K -edges of light elements, or when the highest energy resolution is required, a

configuration with 1 m bending radius is preferred. In fact, to collect HERFD-XANES spectra with sharper spectral features it may be necessary to reduce the experimental bandwidth to as low as ~ 0.5 eV, even for L - and M -edges. Nonetheless, for applications aiming to perform XANES spectroscopy on trace elements with dilution levels below 10 parts per million and complex matrices, the gain in collected solid angle provided by the 0.5 m bending radius configuration would be an asset.

A schematic view of the final concept design with 11 analyzers is shown in Fig. 2(c) for the two extreme angular positions of the spectrometer, namely 85° and 35° . The Rowland circle geometry of Fig. 2(a) is used: the sample and the incoming beam are lying on the horizontal plane, whereas the analyzers reside on the sagittal plane, their inclination depending on the Bragg angle. The 11 analyzers at $2R = 0.5$ m cover a solid angle ranging from 50 millirad ($\theta_B = 35^\circ$) up to 87 millirad ($\theta_B = 85^\circ$). The solid angle is about four times smaller when $2R = 1$ m.

3. Mechanical design and production

This section presents the mechanical design of the spectrometer as built and installed in the first experimental hutch of beamline ID26 at the ESRF. The instrument was manufactured, assembled and tested by the company Added Value Solutions (Spain).

X-ray attenuation by air and windows is strong in the tender energy range. 1 cm of air or 8 μm of Kapton absorb, respectively, 50% and 40% of X-rays at 2 keV. For this reason, a fully in-vacuum solution was adopted. The whole spectrometer mechanics and sample environment are encased in a vacuum vessel of ~ 4 m³, roughly a cylinder of 1.74 m diameter and 1.67 m height [Fig. 5(a)]. The dimension of the vessel is optimized for a complete movement on the scanning trajectories of the crystal analyzers with a bending radius comprised between 1020 mm and 480 mm and to accommodate the displacement of the X-ray detector. The vacuum level is high,

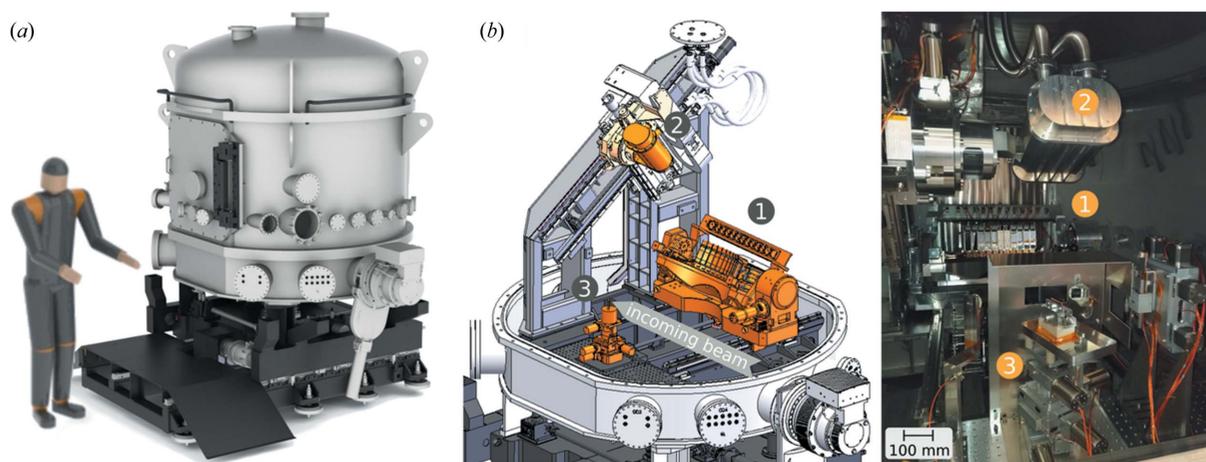


Figure 5 Mechanical layout of the spectrometer. Three dimensional (3D) rendering of the external view (a). Internal view (b) as 3D drawing (left, upper parts of the vacuum vessel are removed for clarity) and photograph (right), showing the spectrometer frame with the main sub-assemblies: analyzer table (1), detector (2) and sample environment (3). The incoming beam direction (X) is represented with a grey arrow.

with a pressure below 1×10^{-5} mbar. It allows connecting the spectrometer directly to the ultra-high vacuum of the host beamline – via a differential pumping system – and is sufficient for thermal insulation, allowing the use of a windowless liquid-helium cryostat (Section 3.3). The required vacuum level is obtained by introducing only high-vacuum-compatible components and avoiding trapped volumes. The obtained outgassing rate is 3×10^{-10} mbar L s⁻¹ cm⁻², comparable with unbaked stainless steel after 24 h of pumping. Primary and turbo pumps are mounted on a CF 250 port. The pumping capacity is 80 m³ h⁻¹ (Leybold Leyvac 80 dry compressing pump) and 2100 l s⁻¹ (Turbovac MagW 2200iP turbomolecular magnetically levitated pump). Via this system, the pumping time is less than 90 minutes to reach the low 10^{-5} mbar range. The spectrometer is operated in vacuum during the experiment and the change of sample is performed via a load lock system (Section 3.3). Installation of an *in situ* cell is possible by inverse vacuum set-ups and feedthroughs in the available chamber ports. Gas, liquid and electrical connections are possible.

The spectrometer counts a total of 52 motorized axes controlled by the *BLISS* software (Guijarro *et al.*, 2018) via IcePap stepper motor drivers. The exact Rowland circle tracking is achieved via a device server implemented in Python (Rovezzi, 2017). Critical motor axes are equipped with absolute encoders. The vacuum vessel is mounted on motorized long rails. It allows aligning the origin of the spectrometer along the *Y* direction, perpendicular to the incoming X-ray beam in the horizontal plane, and moving out the whole spectrometer in a ‘maintenance mode’, when disconnected from the beamline. The whole spectrometer is isolated from the vacuum vessel via an externally motorized four-point ball-screw lifting system plus three guiding columns connected to the vacuum chamber only via edge-welded bellows. This system allows aligning the spectrometer along the *Z* direction and avoids transmitting vibrations from the vacuum pumps to the mechanics. The vibrations from the ground are minimized by the internal damping factor of the cast iron *Y* carriage. The structural analysis performed via finite-element calculations confirms that the vibration modes do not act in the direction of interest, that is, along the pathway of the diffracted beam. The first main mode consists of a global lateral oscillation along *X* with a maximum displacement of 0.4 mm and a frequency of 16.3 Hz. This mode does not affect the energy resolution as the whole spectrometer oscillates around the incoming beam focal point.

The spectrometer frame consists of a welded stainless steel structure divided into three main sub-assemblies [Fig. 5(b)]: the crystal analyzer table (1), the detector arm (2) and the sample tower (3). These components are described in the following sub-sections.

3.1. Analyzer table

The 11 segments supporting the analyzer crystals must follow the motion of the sagittal circle as described previously. This can be achieved by two translations (*e.g.* along *Y* and *Z*)

and two rotations (*e.g.* θ and χ with rotation axes in and perpendicular to the Rowland circle). In previous multi-analyzer spectrometers, this was achieved by piling up multi-stages with each crystal (Moretti Sala *et al.*, 2018). We dismissed this solution because of space constraints and costs. Furthermore, the acceptable angular error of <10 μ rad in the meridional direction over the scan range is beyond the achievable mechanical specifications of the components, as the angular errors for each of the four components add up.

We conceived a new design for the displacement of the crystal analyzers that minimizes the angular errors and is, at the same time, less expensive than the above-described four-axes solution. All crystal analyzers are mounted on a custom-designed table [Fig. 6(a)]. The table translates along *Y* (*TY*) and rotates by θ_B around an axis that passes through the centre of the central analyzer. Ten out of the 11 analyzer crystals are mounted on each side of the central crystal on a chained mechanical system [bronze pieces shown in Fig. 6(b)], which is kept in contact with an underlying plate via three points that are held in place by magnets. The chained mechanics is actioned by two linear actuators via a ball-bearing accordion-like system. We call this mechanical system a ‘pantograph’ as it resembles a pantograph drawing tool. The underlying plate is made out of carbon steel (magnetic). It is rectified, polished and hardened via a surface nitridation process, ensuring minimal angular errors during the motion of the pantograph and resistance at friction with bronze. The measured flatness is below 6 μ m peak-to-valley over the whole surface of 0.15 m². The plate is parallel to the sagittal plane and thus ensures correct positioning of all crystals. This friction design mechanics allows obtaining the required dynamical sagittal focusing for all analyzers with only two motors.

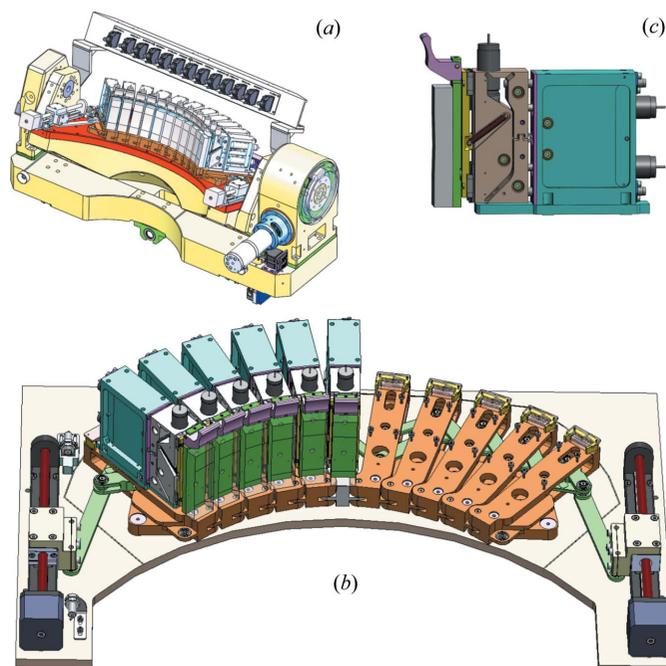


Figure 6 Components of the analyzer table (a): pantograph (b) and analyzer module (c).

An important property of this solution is that it can fit a larger number of crystals of different bending radii.

The analyzer table provides combined movements for the Rowland tracking (energy scan). Additional degrees of freedom are implemented per analyzer via a three-axis motorized module [Fig. 6(c)]. The module carrying the analyzer allows fine tuning the alignment of each analyzer with respect to the central one, taken as reference. It compensates for the defects introduced during the analyzer's production and the inevitable mis-alignment of the mechanics in the whole scanning range. The motorized axis is driven by three compact high-precision linear actuators, the ESRF fixed-head micro-jacks: (1) vertical adjustment of ± 2 mm stroke, (2 + 3) horizontal adjustment of ± 5 mm, and θ adjustment. The last two axes are obtained by driving the actuators either in the same or the opposite directions. We chose to have three motorized degrees of freedom for each analyzer for commissioning and validation of the concept. A simplified design would only require one angular adjustment in the meridional direction.

Each analyzer module with its motorized degrees of freedom is mounted on the pantograph with an additional degree of freedom that allows the fine angular alignment in the sagittal direction. This alignment is performed manually with a laser (Section 4.2). The crystal analyzers are mounted separately with wax or glue on holders that are held in place by three magnets.

3.2. Multi-wire gas detector

The second core component of the spectrometer is the detector. The first step in defining the required specifications was to simulate, via ray tracing, the focal image of the 11

cylindrical Johansson analyzers. The detector is centred on the YZ plane facing the centre of the analyzer table. The configuration with $2R = 0.5$ m and at $\theta_B = 35^\circ$ is shown in Fig. 7(a). This is the configuration where the focus spreads the most. The focal image has a butterfly-like shape because each analyzer contributes to a line focus 50 mm long (twice the size of the flat side) and approximately 0.1 mm thick (vertical size of the source). The focal image of the central analyzer is a horizontal line whereas the focal images of the side analyzers are tilted. The tilting angle depends on the χ angle. For the highest tilt configuration [Fig. 7(a)] the total height of the combined focal image is approximately 40 mm. Furthermore, and as expected from Fig. 3 and shown in Fig. 7(a), the focal image has an energy dispersion in the horizontal direction, starting from the centre. This implies that a detector with spatial resolution along the horizontal direction will enable us to perform an in-focus energy correction. The ray-tracing simulations with a source size of $0.1 \text{ mm} \times 0.5 \text{ mm}$ show that the energy spread along the horizontal direction does not significantly change within 5 mm. Thus, an in-focus energy correction can be applied even when using a detector with a coarse position sensitivity of the order of a few millimetres.

The main specifications required for the detector are the following: (1) active area of $50 \text{ mm} \times 40 \text{ mm}$. This is obtained from the analysis of the simulated focal images. (2) Overall quantum efficiency (sensor absorption and electronic threshold) $\geq 80\%$ from 1.5 keV to 5.5 keV. (3) Electronic noise without X-rays ≤ 1 event in 10 s over the whole area at the minimum photon energy discriminator's threshold. This requirement is dictated by the fact that we would like to be able to detect rare events with count rates of only a few counts per second and therefore we want low electronic noise signal within the counting interval. (4) $\leq 10\%$ non-linearity at 1 MHz

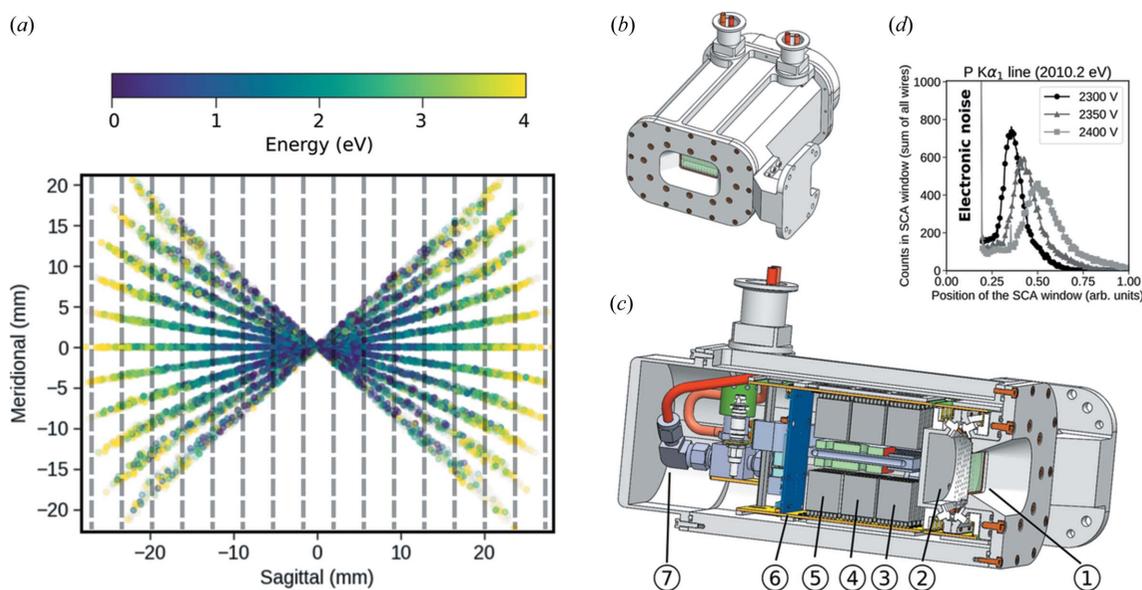


Figure 7

Multi-wire gas detector. Ray tracing simulation (a) of the focal image from the 11 analyzers at 500 mm bending radius and 35° Bragg angle. The overlay grey dashed lines represent the chosen wires distribution. Inverse vacuum chamber (b). Main components (c) of the detector: entrance X-ray window (1); gas chamber with 16 wires (2); charge-sensitive pre-amplifier (3); baseline restore amplifier (4); Gaussian shaper (5); single-channel analyzer board (6); gas and cooling pipes (7). Spectral response (energy distribution) as a function of the applied potential (d) for a P $K\alpha_1$ emission line.

counting rate over the whole area. In fact, assuming a negligible background signal, our target statistics is 10^{-3} . (5) Continuous data read-out with ≤ 2 ms delay. The read-out dead-time during continuous scans of the monochromator should be kept as low as possible. In fact, for radiation-sensitive samples, the XANES scans ideally last less than 5 s with acquisition times of a few milliseconds per data point. (6) Vacuum compatibility. (7) Weight not to exceed 8 kg. The detector must be mounted on moving stages covering an area of almost 1 m^2 .

According to these specifications, we surveyed the commercial solutions during the design phase. The conclusion was that the detector fulfilling all specifications was not available ‘off the shelf’ at the time or within our budget (see Section S1 of the supporting information). For these reasons, we designed and built a multi-wire gas flow proportional counter at the ESRF. The reader interested in more details about gas detectors may refer to the book by Knoll (Knoll, 2000) or the didactic work of Winkler *et al.* (2015). Proportional counters are frequently used in the detection and spectroscopy of low-energy X-ray radiation. This is because of their low noise and an energy resolution below 20% of the measured energy. Historically, flow proportional counters were mounted in wavelength-dispersive spectrometers for micro-analysis at electron microscopy stations [see, for example, Wuhler & Moran (2018) for a recent overview].

We developed the 16-wires flow proportional counter shown in Figs. 7(b) and 7(c). The wires are gold-coated tungsten of $50 \mu\text{m}$ diameter mounted vertically (along the meridional direction, Y) with a horizontal spacing of 4 mm (along the sagittal direction, X). The choice of a multi-wire configuration has two advantages: (1) to increase the detector linearity; (2) to obtain a spatial resolution in the sagittal direction. A 90% linearity per wire is measured at approximately 50 kHz (counts s^{-1}), as shown in Fig. S5 of the supporting information. The 16 wires provide an overall linearity up to 1 MHz count-rate as the cylindrical crystals distribute the intensity homogeneously in the sagittal direction. The spatial sampling of the horizontal direction gives access to the energy-dispersion correction within the focal image, improving the energy resolution of the instrument. Furthermore, it allows controlling the spectrometer alignment. In fact, in case of mis-alignment not all line foci will cross the central wires, showing a signal drifting to the side wires. The data analysis presented in Section 4.3 makes use of such information. The naming convention used for the commissioning and the distribution of the wires within the geometry of the spectrometer is given in Fig. S1.

The gas chamber plus the electronics are encased in an ‘inverse vacuum’ chamber, where the vacuum is outside and the atmospheric pressure inside. The chamber is mounted on the detector arm, consisting of one rotation and two translation stages. This allows positioning the detector on all required points in the Rowland tracking space, as shown in Fig. S2, while always facing the central analyzer crystal. The detector chamber is connected to the outside of the vacuum vessel via two highly flexible, annular corrugated metallic hoses

(Witzenmann GmbH, model RS 321). The choice of these specific hoses was made after building a dedicated prototype for measuring the forces acting on the detector during the movement (Fig. S3). The hoses allow carrying the gas and cooling pipes plus the power, Ethernet and signal cables. The dimensions of the gas chamber are $113 \text{ mm} \times 50 \text{ mm} \times 40 \text{ mm}$ (width \times height \times depth). It is filled with a gas mixture composed of 15% carbon dioxide (CO_2) in argon (Ar). The 40 mm path results in an efficiency of $\geq 90\%$, decreasing to 60% before the Ar K -edge (3205.9 eV) (Fig. S4). An X-ray window separates the gas chamber from the spectrometer vacuum. The window (MOXTEK ProLINE 20) is composed of an ultra-thin polymer of $0.6 \mu\text{m}$ thickness coated with 45 nm of Al and deposited on a metal support grid. It can hold 1.2 atm differential pressure sustaining hundreds of cycles, and has a total (including the metal support grid) X-ray transmission of $>90\%$ above 1 keV .

The wires are connected directly to an application-specific integrated circuit (ASIC) composed of a primary analog stage and a secondary digital part based on a field-programmable gate array (FPGA). The analog electronics implements an RC reset scheme of $100 \mu\text{s}$ damping time. The signal is amplified with a charge-sensitive pre-amplifier, then transformed to Gaussian pulse via a shaper amplifier of 500 ns and baseline restore. The ASIC allocates commercially available amplifiers that can be easily replaced in case of failure or performance loss. Currently, the charge-sensitive amplifiers are provided by Cremat Inc. The digital electronics implements a single-channel analyzer (SCA) for the signal of each wire and outputs 16 NIM-type signals transferred to the control computer via a differential line. Having the analogical signal processed close to the wires allows reducing the electronic noise. Furthermore, the whole electronics is water-cooled. All detector settings are remotely controlled via an Ethernet connection to a local embedded ARM computer (Qseven).

The spectral response of the detector and separation from the electronic noise is visible in Fig. 7(d), obtained by scanning the level of a small window in the SCA. The fluorescence peak of the P $K\alpha_1$ line at 2010.2 eV is well separated from the electronic noise peak at a voltage of 2300 V . Increasing the voltage up to 2400 eV shifts the fluorescence signal peak to higher threshold values. At this voltage, the Si $K\alpha$ lines ($\sim 1739 \text{ eV}$) can be clearly separated from the electronic noise peak (not shown). The low energy threshold of the SCA is set to cut the electronic noise below the acceptable level of 1 count per 10 s over the entire detector area. The high energy threshold allows reducing the signal arising from cosmic rays and possible background from fluorescence lines that are excited by higher harmonics of the incident beam energy. Events arising from cosmic rays are very short and can thus easily be identified as spikes in single data points. The affected data points are removed during the data processing.

3.3. Sample environment

The vacuum vessel allocates a versatile sample environment volume approximately 500 mm wide (Fig. S6). At the base of

this volume, a breadboard allows mounting all required equipment. The standard configuration is composed of a four-axis goniometer, which provides X, Y, Z translations plus a rotation around the Z axis. The goniometer allows aligning the sample on the beam with micro-metric precision. A stroke of 40 mm is available on each translation axis, whereas the rotation could in principle perform 360° unless the sample environment constrains the motion.

A thick aluminium shielding positioned around the sample prevents the direct fluorescence from reaching the detector or the X-ray scattering background from reaching the crystal analyzers or the vacuum vessel walls. A set of photo-diodes are employed to measure the total fluorescence yield. An incoming X-ray beam monitor with horizontal and vertical slits is mounted upstream of the sample. The beam monitor consists of a four-quadrant diode with a hole, reading the back-scattering signal from a thin calcium-free Kapton foil ($<8 \mu\text{m}$ thickness).

The vacuum vessel has two large doors of square shape with a side of 700 mm in front of the sample area [Fig. S6(a)] and in the back of the analyzer table. During maintenance mode, the sample environment volume and the detector are accessible via the front door. Four flanges mounted on the front door are dedicated to: (1) a load-lock system for quick sample change; (2) a solid state detector for partial fluorescence yield analysis; (3) a pressure gauge; (4) a glass window for visual inspection.

The core components of the sample environment routinely available for users are the load lock set-up and the liquid He cryostat. In addition, two experimental cells were built: one for studying *operando* gas sensors (Fig. S8) and another for *in situ* catalytic reactions.

The load lock set-up was initially built at the ESRF with a simple rod design. However, it turned out to be not suited for user operation. The current design is a commercial solution (Ferrovac GmbH) featuring a fast entry load lock with a quick-access door and a CF40 single shaft sample transport rod of 750 mm linear travel. The transfer rod head is customized for inserting a multi-sample holder of 45 mm length and 30 mm height into the sample receptacle. The sample transfer chamber of ~ 0.7 l volume is pumped from ambient pressure down to 10^{-5} mbar in less than a minute thanks to a combination of pre-pumping by a small primary pump and a turbo pump unit, which are connected by a three-way valve ensuring continuous operation of the system. This quick sample load is crucial to transfer frozen samples (*e.g.* frozen solutions) from a liquid-nitrogen tank into the cold sample receptacle.

The standard sample holders are made of copper (Fig. S7) and designed to receive either three 13 mm pellets or eight 5 mm pellets (two rows of four) with a base plate having a locking mechanism for the sample transfer system. Thermal contact is further enhanced with a frame screwed on the surface of the copper holder. Samples presenting safety risks (*e.g.* toxic, radioactive) can be sealed by inserting a thin Kapton foil in between the copper pieces.

The transfer system puts the sample holder in mechanical contact with the copper body of the sample receptacle, which is connected via a flexible copper braid to the cold head of a

liquid-He cryostat mounted directly on the spectrometer chamber on a CF63 flange. Thermal isolation from the goniometer is realized by a polyether ether ketone (PEEK) interface block supporting the sample receptacle. The required freedom in motion for the sample and necessary large optical access lead to thermal losses over the length of the copper braid limiting the working sample temperature to a minimum of approximately 22 K with the cold head staying at 12 K. The initial cool-down time for the cryostat is approximately three hours but after a sample transfer the base temperature is recovered within ten minutes.

4. Commissioning results

The commissioning of the spectrometer was performed at beamline ID26 of the ESRF during multiple experimental sessions. The beamline was equipped with a cryogenically cooled double Si(111) monochromator, giving a resolving power $E/\Delta E \simeq 7000$, that is, an energy bandwidth of 0.3 eV at 2 keV. Harmonic rejection was achieved by three Si mirrors working in total reflection. The beam was focused to $90 \mu\text{m}$ vertical by $350 \mu\text{m}$ horizontal. The incoming beam was monitored as previously described.

4.1. Johansson crystal analyzers

The performance of the spectrometer critically depends on the quality of the Johansson crystals. At the early stage of the design phase we tested commercially available crystals from Saint-Gobain (France), Rigaku (USA), AlpyX (France), and compared them with those fabricated at the ESRF. The performance of one commercial crystal was close to theoretical simulations (Fig. S9), demonstrating the feasibility of producing high-quality crystals. This test validated the concept of the non-dispersive geometry, for which the energy bandwidth crucially depends on the optical quality of the crystals, in contrast to the dispersive geometry. A full set of high-quality crystals could not be manufactured yet, therefore the results presented here do not represent the optimal performance of the instrument. We report in Section 4.3 the results obtained with Si(111) and Si(110) crystals of $25 \text{ mm} \times 80 \text{ mm}$ surface area and 1 m bending radius produced at the ESRF.

We followed two manufacturing processes, a single machining and a double machining. A schematic view is reported in Fig. S10. The single machining process consists of bending the crystal wafer on a cylindrical substrate of radius $2R$ and machining the surface to a radius R . This approach is relatively simple and results in an analyzer thicker at the borders than at the centre, thus requiring to bend a thick crystal. The second approach consists of machining the two sides of a crystal to a thin meniscus ($150\text{--}250 \mu\text{m}$) of radius $2R$, and bending it afterwards on a substrate of radius R . Although more time-consuming, this procedure provides uniformly thin crystals. The double machining process is the method of choice for reaching $R \leq 500 \text{ mm}$, as plastic deformation methods would be needed to bend a single machined crystal.

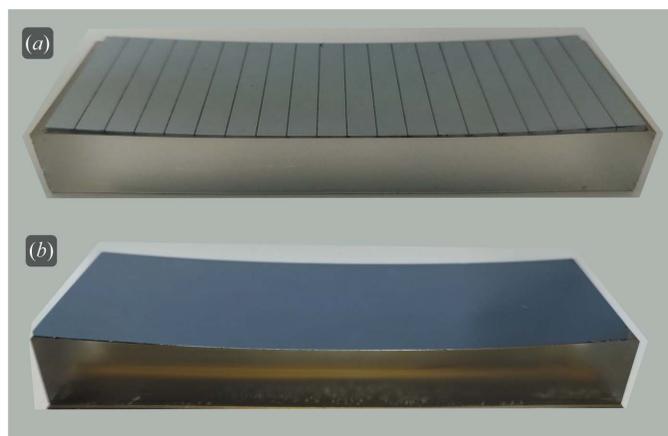


Figure 8
Johansson cylindrical crystal analyzers of 25 mm × 80 mm size and 1 m bending radius as produced at the ESRF: single-machined (a) and double-machined (b).

Fig. 8 shows the two types of 1 m bending radius analyzers produced at the ESRF. For the single machined one, the starting wafer has a thickness of 1.2 mm and is cut into stripes of 4 mm along the short side, with a groove of 1 mm height (incomplete cuts). Then, the Si wafer is bent on a borosilicate glass substrate with a tested anodic bonding procedure (Rovezzi *et al.*, 2017). The grooves allow releasing part of the strain, resulting in a high-quality bending on the substrate. In the absence of grooves, the underlying substrate cracks after anodic bonding. The machining removes 0.8 mm at the centre of the analyzer. This is performed by grinding the wafer with a silicon carbide powder from 17 μm down to 1 μm in size. The strain and damage introduced by the grinding are released via etching in a solution of nitric and hydrofluoric acid (20:1) for 40 minutes. At the end, the surface is polished with a 1 μm diamond powder. For the double machined crystals, the process starts with a thick 3 mm Si wafer. The convex face of radius $2R = 1$ m is prepared first with a grinding plus etching and polishing steps, as described previously. This face is temporary glued with bee wax on a glass substrate of the same radius and the concave face is prepared with grinding and polishing. A meniscus of 250 μm in thickness is obtained and afterwards bonded to the borosilicate glass substrate of radius $R = 0.5$ m through anodic bonding. The final step is an etching plus polishing of the surface.

4.2. Initial spectrometer alignment

The first step of the spectrometer alignment consists of aligning all mechanical parts with a precision of ≤ 100 μm . This is performed once at the commissioning stage using a laser tracker, which gives an absolute precision in space (X , Y and Z) of 10 μm at best. The translation stages that move the entire spectrometer along Y and Z allow bringing the incoming X-ray beam into the source volume of the spectrometer. The alignment of the beam footprint on the sample along X is important to achieve the optimal performance, and is assured by carefully considering the dimensions of the

sample mount and sample thickness. We plan in a future upgrade to align the sample surface along X by an in-line optical system in which the focus coincides with the spectrometer source volume.

The θ rotation (TR) and all crystal analyzer mounts are calibrated at 90° with a precision below 5 μrad using an inclinometer. The centre of the detector window is positioned on the Rowland circle by introducing an offset in the control system representing the origin of the two inclined translation axes defining the trajectory space (DY, DZ). The χ angles of each crystal are aligned using a laser. This is performed only once, when mounting the analyzers modules on the pantograph.

The final alignment is performed with X-rays. Once a strong fluorescence line is excited, the spectrometer is driven to the tabulated emission energy and then the θ -angle of each crystal is scanned with the other crystals moved out of diffraction, to find the maximum intensity of the line. At the end of this procedure, each crystal has its own θ offset that is stored in a lookup table and kept constant during the emission scan of the spectrometer. We found that this is the only fine alignment that needs to be performed for each fluorescence line or group of lines. We did not find any benefit in fine tuning the vertical correction for each analyzer.

The bending radii of the crystals are not necessarily identical to those of the substrate. For a new set of analyzers, the actual bending radius is found by optimizing the diameter of the Rowland circle ($2R$). The procedure which we followed consists of measuring the emission line of an element against the $2R$ value of the Rowland circle for each analyzer. The width and height of the lines are extracted through peak fitting. The best $2R$ value is at the minimum of a quadratic fit. An example of this procedure applied to sulfur $K\alpha_{1,2}$ lines is shown in Fig. S13. For the same production series of analyzers, the optimized $2R$ is usually found with a variance below 5 mm, thus the average value is set in the control software for all analyzers and is kept fixed for all Bragg angles.

4.3. Instrumental energy resolution

The figure of merit of the spectrometer performance is the instrumental energy broadening as a function of the Bragg angle. It can be obtained with two Gaussian deconvolution methods, either from elastic peak scans (1) or from the emission lines (2). The first method is usually employed for high energy at synchrotron radiation facilities, where a scanning monochromatic beam is readily available, as we have adopted previously (Rovezzi *et al.*, 2017). The second method was historically applied to laboratory-based instruments. Nowadays there is a re-gained interest in laboratory spectrometers, thus it is worth harmonizing the procedure employed. In the tender X-ray range and for the chosen 90° scattering geometry, the elastic scattering is weak. Furthermore, the incoming beam double Si(111) monochromator has a relatively large bandwidth (e.g. 0.3 eV at 2 keV). For these reasons we adopt the following procedure.

First, one measures an emission spectrum, composed of a single or multiple lines. The spectrum is fitted with Voigt profiles, that is, a convolution of Gaussian and Lorentzian profiles, accounting for the instrumental and intrinsic broadening, respectively. The instrumental/Gaussian width, w_G , is taken from the full width at half-maximum (FWHM) of the Voigt profile, w_V , using the modified Whiting relation (Olivero & Longbothum, 1977),

$$w_V \simeq 0.5346w_L + (0.2169w_L^2 + w_G^2)^{1/2},$$

where the intrinsic/Lorentzian width, w_L , is kept fixed at the tabulated value. If the measured emission spectrum contains two lines (e.g. $K\alpha_{1,2}$, $L\alpha_{1,2}$), the energy separation and peak ratio of the two lines are kept fixed at tabulated values, not fitted. The peak-fitting was performed with the *Lmfit* code (Newville *et al.*, 2019) and the signal of each wire was taken separately. The details of the procedure are reported in Section S11 of the supporting information. The assumption made in the peak fitting for the Lorentzian component results in negligible error bars on the fitted variables. Nevertheless, a systematic error is introduced assuming a Gaussian profile for the spectrometer response function. Furthermore, the overall energy alignment of the 11 analyzers may not be perfect. For these reasons we decided to report as error bars the standard deviation of the results obtained for each wire signal and for each analyzer crystal mounted on the 11 holders [Fig. S12(c)].

The results of the fits are shown in Fig. 9 and reported in Table 1. A series of emission lines from *K*-, *L*- and *M*-edges were measured with Si(111) and Si(110) crystals, sampling the entire angular range. The averaged data are shown in Fig. S11. Metallic foils were used as samples, when available. Otherwise, the emission lines from simple compounds (e.g. oxides) were used. The broadening reported here may be larger than the

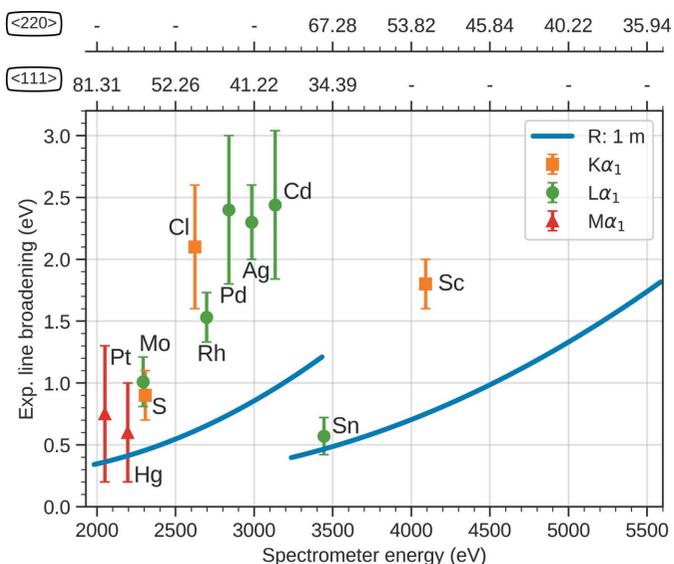


Figure 9
Spectrometer resolution function de-convoluted from the measured emission lines (symbols) and compared with the expected performances simulated with ray tracing (lines).

Table 1

Peak-fitting results for a series of emission lines covering the whole Bragg angular range (θ_B), partially shown in Fig. 9.

The analyzers without a label are single-machined, whereas those double-machined are labelled by the provider: commercial (C) or ESRF (E). The samples consist of powders (compound or metal) pressed into pellets or metallic foils. The last two columns report, respectively, the intrinsic broadening of the line (w_L) and the experimental contribution (w_G). The error bar on the last digit is reported in parentheses.

Line	Energy (eV)	analyzer mat(hkl)	θ_B (°)	Sample	w_L (eV)	w_G (eV)
Pt $M\alpha_1$	20500.0	Si(111)	74.667	Pt _{foil}	2.39	0.75(55)
Hg $M\alpha_1$	2195.0	Si(111)	64.250	HgSe	2.59	0.6(4)
Mo $L\alpha_1$	2293.2	Si(111)	59.550	Mo _{foil}	1.81	1.0(2)
S $K\alpha_1$	2307.8	Si(111)	58.945	ZnSO ₄	0.61	0.9(2)
S $K\alpha_1$	2307.8	Si(111) _C	58.945	ZnS	0.61	0.7(1)
Cl $K\alpha_1$	2622.4	Si(111)	48.929	KCl	0.68	2.1(5)
Rh $L\alpha_1$	2696.8	Si(111)	47.147	Rh _{met.}	2.17	1.7(2)
Pd $L\alpha_1$	2838.6	Si(111)	44.145	Pd _{foil}	2.31	2.4(6)
Ag $L\alpha_1$	2984.4	Si(111)	41.487	Ag _{foil}	2.45	2.3(3)
Cd $L\alpha_1$	3133.8	Si(111)	39.114	Cd _{foil}	2.58	2.4(6)
Sn $L\alpha_1$	3444.0	Si(111)	35.033	Sn _{met.}	2.87	3.6(6)
Sn $L\alpha_1$	3444.0	Si(220)	69.622	Sn _{met.}	2.87	0.6(2)
Sn $L\beta_3$	3750.3	Si(220)	59.413	Sn _{met.}	5.70	1.9(6)
Sc $K\alpha_1$	4090.6	Si(220)	52.115	Sc ₂ O ₃	1.06	1.8(2)
Cu $K\alpha_1$	8047.8	Si(444) _C	79.309	Cu _{foil}	2.10	0.96(40)
Cu $K\alpha_1$	8047.8	Si(444) _E	79.309	Cu _{foil}	2.10	1.3(2)
Cu $K\alpha_1$	8047.8	Si(333) _C	47.475	Cu _{foil}	2.10	1.83(40)
Cu $K\alpha_1$	8047.8	Si(333) _E	47.475	Cu _{foil}	2.10	3.3(3)

real instrumental broadening, because line splittings (e.g. multiplets) are not considered in the analysis.

The experimental line broadening increases from 0.5 eV to 2.5 eV as the Bragg angle decreases. Comparison of the experimental results with ray-tracing simulations (Section 2) shows that the angular dependence of the spectrometer resolution is reproduced in the simulations. The measured energy bandwidth is compatible with calculation down to a Bragg angle of 70°, but deviates from calculation at lower angles reaching approximately twice the simulated values at 35°. We attribute this discrepancy to the high residual strain in the single-machined crystals because of the thickness gradient. This was verified at high energy by measuring the Cu $K\alpha_{1,2}$ lines with two $R = 1$ m Si(111) analyzers produced via double machining, one from a commercial provider (C) and another from the ESRF (E), using the same experimental set-up. The Cu $K\alpha_{1,2}$ lines were measured with the Si(444) and Si(333) reflections at Bragg angles of 79.309° and 47.475°, respectively (Table 1). The ESRF and commercial analyzers performed equally well at high Bragg angle [1.3(2) eV *versus* 0.96(40) eV], whereas the ESRF one had a lower performance at low Bragg angle [3.3(3) eV *versus* 1.83(40) eV]. The reason for this discrepancy lies in the deviation between the crystal surface and substrate bending radius. The travel ranges of the spectrometer stages did not suffice to test the ESRF double-machined crystal at the optimal bending radius. However, the excellent performance of the commercial analyzer at high energy over the full Bragg angular range is not confirmed at low energy for sulfur [Si(111)_C in Table 1]. The energy bandwidth is 0.7(1) eV, which is more than 0.2 eV above the simulated value of 0.45 eV. We attribute this discrepancy to

the optical quality of the crystal surface. We think that the energy bandwidth can be further reduced by improving the machining process.

4.4. First results for HERFD-XANES

The non-dispersive geometry was chosen because an important application of the instrument is to perform HERFD-XANES spectroscopy. An example at the L_3 and L_1 edges of tin (Sn) is shown in Fig. 10. The experimental energy broadening obtained with the Si(110) crystals is 0.6(2) eV for the $L\alpha_1$ (L_3 - M_5) line and 1.9(6) eV for the $L\beta_3$ (L_1 - M_3) line. The natural bandwidths of these lines are 2.87 eV ($L\alpha_1$) and 5.7 eV ($L\beta_3$). This introduces a sharpening effect on the XANES features that is clearly visible when compared with the total fluorescence yield (TFY) measurements [Figs. 10(a) and 10(b)]. The additional spectral features that become visible provide important information when comparing the experimental data with quantum chemical calculations.

The gain in energy resolution provided by the spectrometer also allows one to suppress the parasitic fluorescence from elements in the sample having an absorption edge just below the edge of the target element, e.g. As K -edge parasitic fluorescence when measuring at the Au L_3 edge (Merkulova *et al.*, 2019). At low energy, the line separation can be used to measure the L_1 edge of an element without interference of the L_3 and L_2 signals. As an example, metallic Sn has the nominal

electronic configuration of $4d^{10}5s^25p^2$ and the highest oxidation state is 4^+ . This means that the $4d$ shell is formally always filled, thus the L_3 edge has little sensitivity to the Sn valence shells. Therefore, correlating the edge position to the nominal oxidation state is difficult at the L_3 edge [Fig. 10(c)]. In contrast, it is straightforward at the L_1 edge [Fig. 10(d)] because dipole transitions to the $5p$ orbitals directly probe their occupation and energy and thus the oxidation state. The L_3 edge probes the unoccupied s and d orbitals that are strongly sensitive to the ligand environment as shown by the rich spectral features in Fig. 10(c) with Sn and demonstrated previously for $5d^{10}$ in Hg (Manceau *et al.*, 2015). In general, probing several edges provides complementary information on the electronic structure and bonding environment, and is thus highly desirable. This is greatly facilitated using an emission spectrometer with high energy resolution covering a wide energy range in a single configuration.

5. Conclusions

We have presented the design and performances of a tender X-ray emission spectrometer based on an array of 11 cylindrically bent Johansson crystals in non-dispersive scanning geometry. This design ensures that the entire available solid angle (up to 87 millirad for 0.5 m bending radius) is used within the operating energy of the instrument, thereby achieving high detection efficiency for background-free and HERFD-XANES spectroscopy. An innovative mechanics for the table supporting the analyzer crystals allows optimizing the sagittal focusing dynamically with only two actuators. It can be adapted to a larger number of crystals and to different bending radii. A series of emission lines was measured to evaluate the performance of the instrument. Currently, the energy resolution is limited by the quality of the single-machined Johansson crystals produced at the ESRF. Higher resolution will be obtained in the near future with their replacement with double-machined crystals. The performance of the instrument in terms of detection rate and background noise will then be presented for such optimized optics. We have reported an example of application of HERFD-XANES at the L_3 and L_1 edges of Sn. During the commissioning phase, the spectrometer was successfully employed for recording full RIXS planes, valence-to-core XES and HERFD-XANES on all the elements reported in Table 1. Those measurements will be presented elsewhere.

6. Related literature

The following references, not cited in the main body of the paper, have been cited in the supporting information: Zhao & Sakurai (2017); Strüder (2000); Staerz *et al.* (2018); Safonova *et al.* (2005); Koziej *et al.* (2009); Klačková *et al.* (2019); Hübner *et al.* (2011); Holden *et al.* (2018); Haro *et al.* (2020); Hafizh *et al.* (2019); Donath *et al.* (2013); Doering *et al.* (2011); Degler *et al.* (2016); Degler (2018); Bufon *et al.* (2014); Barsan & Weimar (2003); Barsan *et al.* (2007).

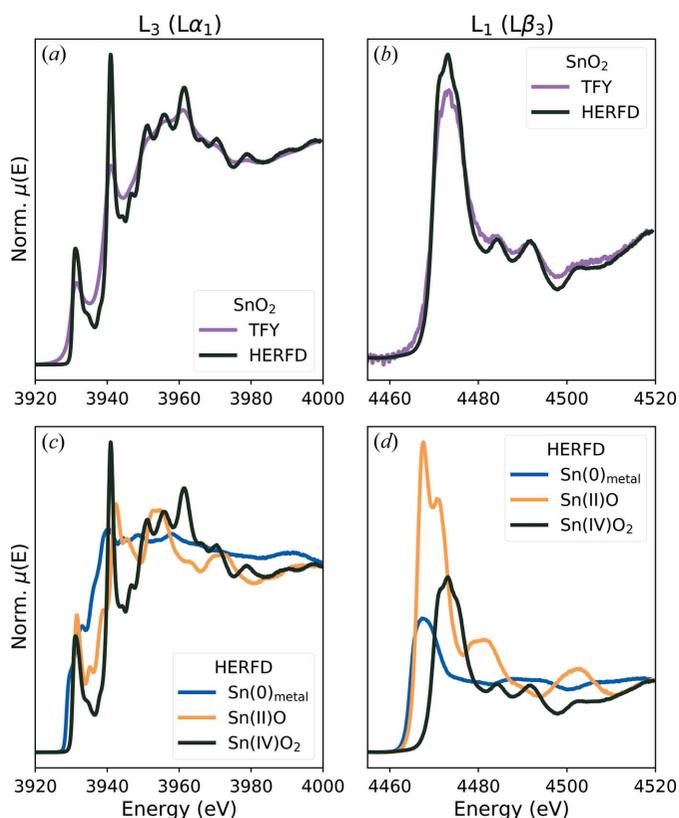


Figure 10 Example of collected data on Sn at the L_3 and L_1 edges: (a, b) HERFD compared with TFY for SnO_2 ; (c, d) HERFD spectra for three nominal oxidation states.

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