

**Report from Consultancy Meeting on Current Developments of Laboratory Based
Instruments for XAS or XES**

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Executive summary

Over the last 20 years the Nuclear Science and Instrumentation Laboratory (NSIL) has played a leading role worldwide in the effective use of nuclear instrumentation and nuclear spectrometry techniques, including the development of X-ray fluorescence techniques, portable systems and analytical methodologies for materials characterization in Member States adaptive research priority areas. NSIL also operates a beam line in Institute Ruđer Bošković (Zagreb, Croatia) and an Ultra High Vacuum end-station at Elettra Synchrotrone (Trieste, Italy). The access to these facilities is provided to IAEA Member States investigators for experimental work and adaptive research via Coordinated Research Projects or other IAEA sponsored activities. Supplementing these research activities hundreds of fellows have been trained and technical assistance has been provided to numerous National and Regional Technical Cooperation projects.

X-ray absorption spectroscopy techniques are advanced techniques that are conventionally used to determine the local geometric and/or electronic structure of matter, thus allowing to provide insights on speciation of elements and distortions in lattice structures, among many other applications. These techniques have been conventionally implemented at beam lines in synchrotron x-ray light sources, thus bearing the constraints of limited access for many research groups.

During the last decades several important results have been obtained in developing laboratory-based spectrometers to implement x-ray absorption fine structure measurements (XAFS) and more recently, x-ray emission spectroscopy (XES).

The consultancy meeting was organized to discuss on main conceptual design for laboratory-based XAS and XES spectrometers, results of investigations carried out, future potential applications and their relevance for the IAEA program on Nuclear Applications.

The meeting was attended by three consultants: Prof. Gerald Seidler (university of Washington, Seattle, USA), Dr René Bes (University of Helsinki / Helsinki Institute of Physics, Finland) and Dr Christopher Schlesiger (Institute for Optics and Atomic Physics, Berlin, Germany). The Scientific Secretary was Mr. Roman Padilla Alvarez, NAPC, IAEA.

This report provides information on fundamentals of XAFS and XES techniques, their fitness for a variety of application studies, the main solutions to implement the techniques at laboratory scale and a list of institutions that have contributed to the implementation of novel instruments.

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Introduction

The report is divided in several sections: the analytical role of XAFS and XES that is enabled by the new technical developments and growing dissemination of laboratory-based spectrometers is summarized in section 1. Eight broad classes of applications of lab-based XAFS and XES with direct relevance for the United Nations Sustainable Development Goals (SDGs) of strongest interest to the mission of NSIL and the IAEA program on Nuclear Applications are described in this section as well. Next, the fundamentals of XAFS and XES methods is briefly explained, with some discussion of their operation when coupled to conventional x-ray tubes. This includes a comprehensive description of the present spectrometer designs being used in various laboratories and commercialization efforts. Further, the report provides contact information for the principal University scientists and commercial entities who are working on tender and hard x-ray lab-based XAFS and XES for analytical purposes. In Annex 1 rough cost estimates are provided for different approaches.

1. A new branch of analytical chemistry: Laboratory-based XAFS and XES

Analytical chemistry is the core discipline whose methods allow us to quantify the chemical content and characteristics of all materials relevant for life on earth. In this report, the consultants summarize a new development in analytical chemistry that has deep relevance for numerous Sustainable Development Goals (SDG's), specifically, the ability to routinely perform advanced x-ray spectroscopies in the laboratory setting with conventional x-ray tube sources whereas previously these methods were almost exclusively at synchrotron x-ray facilities. While the national-laboratory scale synchrotron facilities provide an ultimate standard in technical capability and scientific impact, they are poorly suited to the demands of analytical chemistry. The access model for synchrotron use is strongly aimed toward fundamental science, and beamtime access is highly competitive and scheduled many months in advance. Hence, while all measurements described in the present document can, from a technical perspective, certainly be performed at the synchrotron facilities, such effort has previously been limited to demonstration studies.

The purpose of the present document is therefore to provide an overview of the applications of x-ray spectroscopies to SDG-relevant analytical purposes that are now, only recently possible at a truly routine level due to the availability of laboratory-based advanced x-ray spectrometers.

1.1. Analytical Applications of Laboratory-based X-ray Absorption Fine Structure (XAFS) and X-ray Emission Spectroscopy (XES)

Below, eight broad classes of application of laboratory-based XAFS and XES are summarized that have strong relevance for SDGs emphasized in the mission of the NSIL and the IAEA program on Nuclear Applications. This is not expected to be a comprehensive list. The applications are

selected not just for relevance, but also because it is the professional opinion of the consultancy panel that the technical feasibility of the proposed applications is either already demonstrated or else highly likely follow from already demonstrated efforts.

a. **Bioaccumulation of toxic elements:** Bioaccumulation of toxic elements in plants and animals (including humans) is a key consequence of ecosystem contamination, whether by resource extraction and processing, via occupational hazards in several industries, as an unwanted consequence of major civil engineering projects, as an unplanned byproduct of the massive growth in use of nanophases in consumer products, or from environmental contamination from industrial efforts, electrical power production, or nuclear incidents or accidents. Such issues arise under SDGs 3 (good health and well-being), 6 (clean water and sanitation), 14 (life below water) and 15 (life on land). While in some cases identification of the concentration of toxic element is itself technically enough, in many cases the determination of the oxidation state or even local chemical environment of the undesired contaminant element is needed for a more complete understanding and diagnosis of likely consequences. There have been numerous synchrotron XAFS studies on bioaccumulation in living things. While the low concentration of the contaminants will generally preclude laboratory XAFS, in many cases the desired speciation may be determined by XES. Examples may include As(III)/As(V) determination, such as in industrially contaminated lake sediments and the local ecosystem and its living things, and similar considerations for other transition metals and heavier elements. [Jahrman 2018, Jahrman 2019b]

b. **Industrial Mineral Extraction and Processing:** Industrial scale wastes associated with mineral extraction and processing present numerous examples having strong environmental, health, and financial impact on people and lands in many countries, and hence impacting SDG's 3 (good health and well-being), 6 (clean water and sanitation), 9 (industry, innovation and infrastructure), and 15 (life on land). For example, annual production of coal ash is in the scale of hundreds of millions of metric tons per year. Coal ash, blast furnace slag, and mine tailings (e.g., from phosphate extraction for fertilizer production or for metal extraction) exhibit similar issues for public health, safe water supply, and the environment due to the presence of varying concentrations and chemical forms of elements such as Cr, As, Se, Pb, and in some cases actinides as Technically Enhanced-Naturally Occurring Radioactive Materials (TE-NORM). Given the scale of production of these materials, there is also global effort to reprocess such wastes into value added products, such as by using coal ashes as additives to asphalt or cements. There are many examples of the use of synchrotron XAFS and XES to better understand the properties of such materials, their fitness for the intended purpose, and the long-term outcomes thereof. For problems of speciation and local structure investigations for concentrated systems (such as Cr(III)/Cr(VI) determination in mine tailings), lab-based XAFS may be an advantageous tool. More generally, lower concentration investigations of the oxidation state of many metals, S, and P are now possible with lab-based XES. [Jahrman 2018, Jahrman 2019b, Holden 2018, Stein 2018]

c. **Nuclear Wastes and Fuels:** Nuclear energy helps many countries in achieving SDG 7 (affordable and clean energy) and is globally-relevant for SDG 13 (climate action). However, one undesirable consequence is the production of nuclear wastes that must be disposed of for a few hundred to thousands of years, i.e. until the radiotoxicity is back down to natural radioactivity levels. Nuclear waste refers here in a large amount of materials ranging from reactor's structural activated materials (steels, alloys, cements) to spent nuclear fuels, as well as uranium mining side-products, fuel reprocessing effluents, medical radionuclides production and contaminated soils remediation. Safety then relies on the degree of prevention of radionuclides reaching the environment, water supply, biosphere and finally humans through the food chain. Therefore, a safe nuclear waste disposal, which relies on engineered and natural barriers, is directly related to SDGs 6 (clean water and sanitation), 3 (good health and well-being) and 12 (responsible consumption and production).

To ensure safe disposal, perfect knowledge of radionuclide behavior in materials and environment is mandatory. Elements mobility and reactivity is mainly governed by their chemical form, i.e. their oxidation state and local environment. For example, in its U(IV) oxidation state, uranium is thousands of times less labile than in its U(VI) states. The same applies for many radionuclides and minor actinides for which immobilization/reactivity depends on their oxidation states. Common storage methods that are under constant development and significant implementation are immobilization in glass materials, notably for solid starting materials, and immobilization in concrete, notably for liquid waste forms. In both cases, the redox chemistry and local chemical environment of the metals and other multivalent elements is critical for understanding the long-term mobility of the stored radionuclide or otherwise hazardous species. This poses a significant analytical problem which has often been addressed with synchrotron radiation studies, but in many cases can now be studied with lab-based XAFS or XES.

Such work on glasses at the University of Sheffield (UK) and Pacific Northwest National Laboratories (USA) was conducted on commercial energy-stepping Rowland circle spectrometers (see section 3). Sulfur speciation of cements is proven by prior laboratory XES work [Holden 2018] and will soon be undertaken at the University of Washington. Studies of high-concentration actinide compounds, whether motivated by the desire for improved nuclear fuels or separations methods, have made use of lab-based XAFS at the University of Helsinki (FIN) [Bes2018] and at Los Alamos National Laboratories (USA) [Jahrman 2019]. Note that each of Pacific Northwest National Laboratory (PNNL, USA), Los Alamos National Laboratories (USA) and the University of Helsinki (FIN) either already have dedicated laboratory-based spectrometers dedicated to measurements of radioactive materials or else have efforts in progress. The need for improved access for XAFS is especially acute in the nuclear materials field due to the small number of synchrotron beamlines that accept radioactive materials and the need for rapid measurement before adventitious oxidation or natural nuclear decays affect material chemistry.

d. **Regulatory Compliance for Metal Speciation:** Several jurisdictions have strong regulations concerning allowable Cr levels in consumer products, a topic relevant for SDG 3 (good health and well-being) and, through eventual consequences of Cr deposition in landfills, SDG 6 (clean water and sanitation). For example, in the European Union this is addressed by RoHS/REACH which specifically address the Cr(VI) content in each component of consumer products, while in the United States the Food and Drug Administration (FDA) has authority over safety of, e.g., plastic food packaging, and requires a complete understanding of Cr(VI) in such applications. The difficulty arises because determination of the oxidation state of Cr in low-solubility matrices is a challenging analytical problem where species interconversion during liquid extraction is well-known. For example, XES studies have shown an effective failure due to species interconversion for the standard test method endorsed by the United States Environmental Protection Agency for liquid extraction to determine Cr(VI) fraction in paint sludges. Recent work with lab-based XES has shown the ability to speciate Cr in plastics [Jahrman2018] and other insoluble matrices [Jin 2019]. The consultants anticipate that there will be a broader range of such applications as the laboratory-based XES systems become more broadly distributed.

e. **The Life Cycle of Lithium Ion Batteries:** Metal oxide materials are central to several major industries with relevance to SDGs through their direct actions and their entire life cycle analysis from mineral extraction through to final product recycling or disposal. As one example, consider lithium ion batteries (LIBs) such as are central for vehicle electrification and at least local-grid storage such as complementing solar power production to regulate production fluctuations. The global efforts at mining of, e.g., cobalt, for use in LIB's has received high publicity for its social and environmental impact and more generally the production, use, and disposal or recycling of LIBs have relevance for SDGs 3 (good health and well-being), 6 (clean water and sanitation), 7 (affordable and clean energy), and 13 (climate action). There has been a plethora of XAFS studies of LIBs, with an emphasis on fundamental understanding of performance limitations. Recent work has shown that such work can sometimes be performed with the latest lab-based monochromators [Jahrman 2019]. More generally, lab-based XAFS or XES can also be applied to quantifying the content and chemistry of ores, quality control for slurries used in electrode preparation, and soil analysis at sites contaminated by relevant mineral extraction. There may also be applications relevant for LIB recycling. Such applications on very concentrated systems can likely be accomplished with any of the hard x-ray spectrometers described in section 3.

f. **Clean and Energy Efficient Catalysis:** Efficient, clean catalysis is a central goal of modern chemistry research having high relevance to human health (SDG 3, good health and well-being) through pharmaceutical development, total energy consumption, (SDG 13, climate action), and wastes (SDG 15, life on land), in the processing of fossil fuels whether for eventual fuel use or for fabrication of plastics, and obviously also for global industrial infrastructure (SDG 9, industry, innovation and infrastructure). Catalysis research relies heavily on synchrotron-based XAFS, and the ongoing growth of lab-based alternatives is seeing strong early adoption by the

catalysis research community. For example, from 2019 on, UniSysCat excellence cluster in Berlin-Brandenburg region of Germany that is dedicated to understanding structure-function relations in various catalytic systems, will have a laboratory-based EXAFS spectrometer (see section 3.2a) for daily analysis of bulk samples and for training of research fellows. From a more analytical perspective and the question of environmental impact on an industrial scale, there are important questions about, again, life-cycle analysis for the catalytic materials industry where the capabilities of the new instruments could have high impact. These are like those for LIB, immediately above, and encompass: mineral extraction, associated mine tailings and their impact on the environment and human health, quality control of metal-containing catalyst fabrication, monitoring of catalytic processes at the industrial scale, investigation and monitoring of the disposal or recycling of catalytic materials at the industrial scale.

g. **Materials Exposed to High Radiation Levels:** Materials in fission and fusion reactors, as well as space applications such as satellites and spacecraft, are exposed to extreme environments including high irradiation flux and high temperature gradient. Maintaining their properties during their lifetime requires a strong knowledge of the correlations between atomic structure, composition, irradiation history and material properties. Our understanding of interaction between atoms and defects is then a key knowledge to assess such correlation, and subsequently to design, control or improve a given material property whatever its environmental conditions, *de facto* complying with SDGs 9 (industry, innovation and infrastructure) and 12 (responsible consumption and production). As a first example, the structural materials of a fusion reactor are under high neutron flux, leading to the formation of a high density of defects and a subsequent embrittlement of the metallic alloys. To avoid that issue, one solution is the regular replacement of structural pieces before their potential failure, but this leads to increased costs and larger waste quantities to manage. As a second example, the interaction between vacancy defects created under irradiation and gaseous fission products such as Kr and Xe leads to the formation of gaseous bubbles in fission reactor fuels. These bubbles reduce the thermal conductivity of the nuclear fuel and can increase its local temperature up to the melting point. The fuel lifetime in a reactor is then strongly limited to a few years to ensure safety margin, but this induces a larger amount of required resources and of nuclear waste to manage. By developing new materials with finely tuned properties, one can improve the material capabilities, especially its radiation resistance. One key detail is the link between the local environment and oxidation states of elements in the presence of defects produced by irradiation. One famous example is the case of oxide dispersion strengthened alloys (ODS), for which the yttria nano-cluster local structure and speciation play a strong role in their peculiar irradiation resistance properties. This understanding was out of reach of standard X-ray Diffraction (XRD) techniques due to its well-known long-range order sensitivity, but perfectly in line with the short-range order sensitivity of XAS. Until recently, only XRD was possible at both laboratory and synchrotron radiation facilities, but, now, XAS is also a solution that can be performed at laboratory, allowing quick and routine characterization of newly synthesized and freshly irradiated steels and alloys directly at the chemistry or accelerator laboratories. Note that the University of

Helsinki is in the process of coupling their ion beam facility to a laboratory-scale XAS spectrometer for irradiation in-situ characterizations.

h. **Equitable Innovation and XAFS/XES Access:** Finally, SDG 9 (industry, innovation and infrastructure) addresses sustainable, equitable innovation. In this regard, it is useful to return to the relationship between synchrotron XAFS and lab-based XAFS. Scientists from developing countries have greatly constrained access to the synchrotron facilities -- this occurs as a consequence of distance, cost, and also preparation. Given the importance of synchrotron facilities for innovation in many topics listed above (LIBs, catalysis, environmental studies, etc.) and many topics not yet elaborated (drug discovery, chemical kinetics, photovoltaic research), this disparity in synchrotron access has a substantial impact on innovation in many countries that do not have synchrotron facilities.

In this way, lab-based XAFS and XES can serve two important roles. First, for a significant range of samples and frequency of access to the facility, they can provide a simple alternative to synchrotron use. Second, they can serve as prototyping systems whose results greatly strengthen the likelihood of success when applying for synchrotron beamtime. Some of these issues are discussed in [Ditter 2019].

1.2. Background on X-ray Absorption Fine Structure and X-ray Emission Spectroscopy

When X-rays were discovered at the end of the 19th century, different methods evolved from this new light, e.g. widely used and known techniques as X-ray diffraction and X-ray fluorescence. Even when first X-ray absorption spectra were measured in 1913 and their oscillations, the x-ray absorption fine structure (XAFS) have been observed in 1920 it took until the 1970s to come up with a theory describing these oscillations..

Starting with the development and opening of synchrotron x-ray light sources, XAFS has been developed to be a tool that is widely used in various fields of applications, e.g. physics, chemistry, material sciences, medicine, environmental studies and catalysis research. This wide applicability of XAFS is due to its flexibility and versatility concerning the **element-specific** information that can be obtained: electronic structure, local geometry, coordination and binding distances to neighboring atoms – all without need for long-range order. XAFS spectra are usually divided in several parts depending on the interpretation and also theoretical description. There is the pre edge region right before the edge itself with transitions in unoccupied orbitals, the X-ray Absorption Near Edge Structure (XANES) region in an interval around the edge itself with information **on the local geometry and oxidation state**, and last the Extended X-ray Absorption Fine structure (EXAFS) regime up to 1 keV above the edge that contains information on **coordination number and bonding distances to neighboring atoms** (see XAS spectra depicted in Figure 1.1 a).

While XAFS was performed in the laboratory until the development of the synchrotron x-ray light sources in the 1970's and 1980's, the poor performance of that earlier generation of laboratory-

based instruments led to the almost entire abandonment of lab-based XAFS. The restriction of XAFS to the synchrotron radiation facilities led to a great increase in the scientific quality of such studies, but also to an extreme limit to its access. However, with the advance in laboratory-based sources, optics and detectors in recent years, there has been a rebirth in both research and commercialization of laboratory based XAFS. This is enabling a steady stream of new analytical and research applications for XAFS that either fall outside the synchrotron access model or else are somehow notably problematic.

X-ray Emission Spectroscopy (XES) is a closely related method. It is well-described as very high resolution x-ray fluorescence spectroscopy (XRF). However, while XRF seeks to quantify the elements that are present, XES instead seeks to understand the *oxidation states and other local electronic and even magnetic properties of the selected element of interest* (see example in Figure 1.1 b). While XES is less commonly applied at synchrotron x-ray light sources and is, in many ways, less technically versatile, it has unique advantages when performed in the laboratory environment.

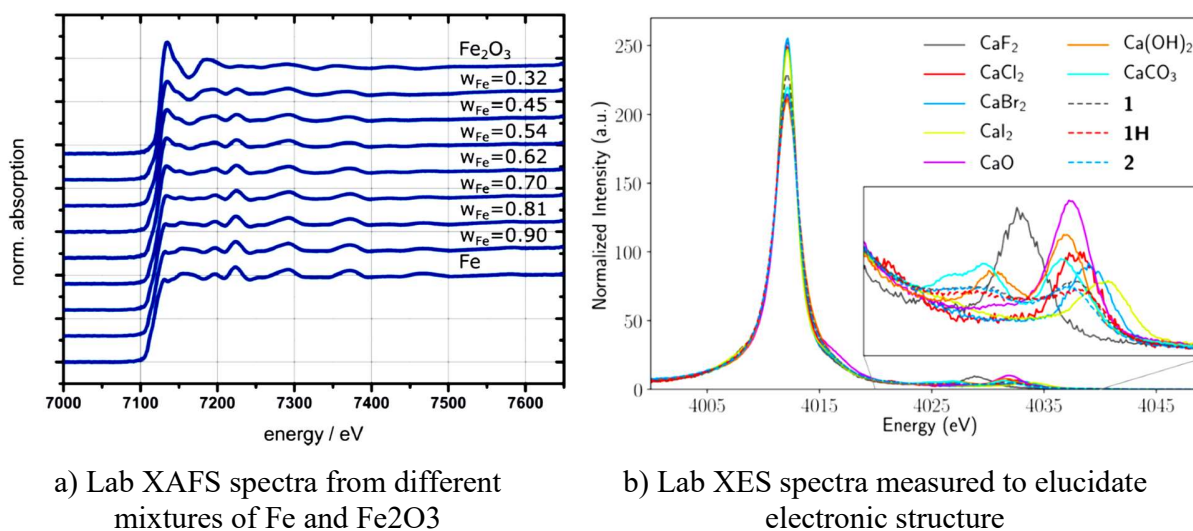


Figure 1.1 Illustration of information available from XAFS (conducted at BLiX, courtesy C. Schlesiger) and XES spectra (conducted at MPI CEC, [Mathe 2019])

For lab XAFS, there is a need to select a ~ 1 -eV band from the bremsstrahlung spectrum of the x-ray tube, rejecting most of source photons. On the other hand, for XES all photons whose energy range from the binding energy of the desired shell to roughly twice that energy can usefully stimulate fluorescence for the resulting spectroscopy (shown in Fig. 1.2). Higher energy photons are less effective because of two reasons: the decrease of photo-electric cross sections with energy and the fact that higher energy x-rays penetrate so deeply into the sample that the produced x-ray fluorescence often cannot escape. The very high core-hole generation rates for lab-based XES compare favorably to those at synchrotron beamlines [Seidler 2014], and consequently laboratory

XES is much closer to synchrotron-level capability, especially for dilute systems, [Jahrman 2018, Holden 2018], than is the case for laboratory XAFS.

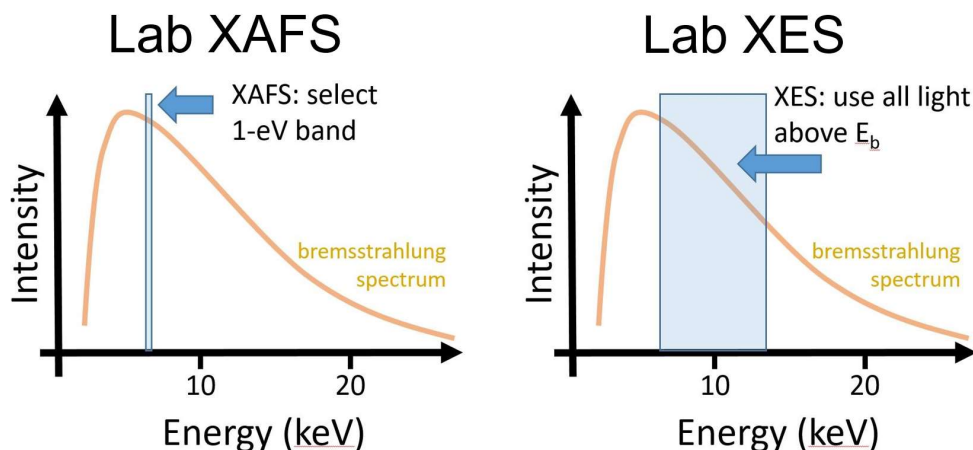


Figure 1.2: An illustration of the use of the bremsstrahlung spectrum of conventional x-ray tubes for XAFS (left) or XES (right). The more efficient use of the spectrum for XES often leads to count rates that are comparable to those achievable at synchrotron beamlines (courtesy G. Seidler).

2. Instrument Options

There are several ongoing efforts at Universities and in commercial entities to advance the technology for laboratory-based XAFS and XES. These efforts are often motivated by the representative applications in section 1.1, above. The first type, Energy-stepping Rowland spectrometers, can be viewed as modernized versions of the older, 1970's-era laboratory-based XAFS systems. Further, the von Hamos geometry was possible due to the availability of microfocus x-ray sources and the important innovation of high-quality graphite x-ray optics. The dispersive Rowland refocusing (DRR) approach to XES, as developed by University of Washington is also presented, which has proven especially adept at speciation of somewhat lighter elements, such as S and P. Finally, this section provides a look to the future, and the potential use of transition edge sensor arrays in this field.

2.1. Energy-Stepping Rowland spectrometers

The earlier, 1970's era laboratory XAFS systems used an energy-stepping Rowland circle geometry, especially the so-called 'linear spectrometer' approach. These instruments made use of cylindrically-bent crystal analyzers for dispersion and typically used gas ionization chambers for final detection. When synchrotron x-ray beamlines became available in the 1970's, it became immediately apparent that the quality and reliability of the laboratory based systems was inferior, and often notably inferior. This was primarily due to both intrinsic (optical effects) and extrinsic (poor optic quality) properties from the cylindrical analyzers that were used, and due to the

inability of the gas ionization detectors to reject the detection of higher order diffraction harmonic contributions. Efforts began in the early 2010's to modernize this approach by using in laboratory set-ups better quality optics and solid-state detectors capable of easily discriminating and rejecting harmonic contamination and other backgrounds, as used in synchrotron applications. [Seidler 2014]. Those instruments immediately showed synchrotron quality XAFS spectra and also very good performance for XES, the latter even at low concentrations.

In the energy-stepping Rowland spectrometers, XAFS is most often measured in transmission mode, where the sample can be placed anywhere in the path from the source to the optic to the detector, each of which is appropriately positioned on the Rowland circle for a monochromatic configuration (excluding harmonics). In some cases, measurements can also be performed in fluorescence mode, where the sample is illuminated by the monochromatized beam and the absorption coefficient is then inferred from the strength of the fluorescence from the sample. For XES configuration, on the other hand, the sample replaces the X-ray source on the Rowland circle. It is then illuminated using the X-ray tube and the spectrometer is now energy dispersing the fluorescence lines emitted by the sample itself. These configurations are illustrated in Fig. 2.1. A large number of publications have shown the capabilities of this class of instrument.

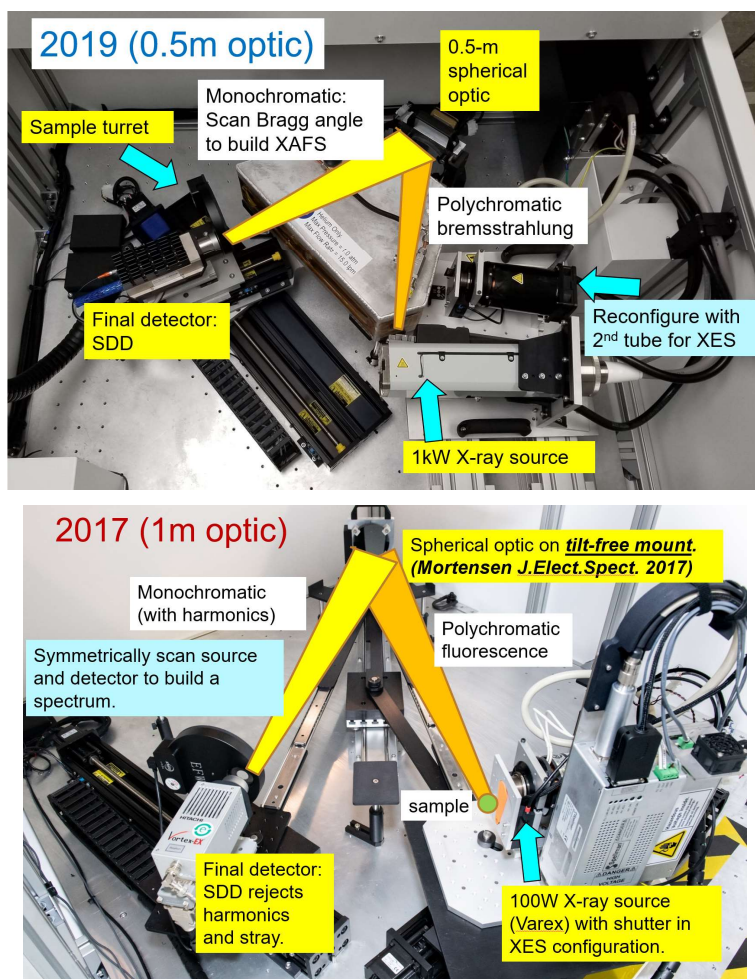


Figure 2.1: Energy stepping Rowland circle instruments (Courtesy of G. Seidler and easyXAFS). (Top): A high-powered lab XAFS system. (Bottom) a laboratory XES system.

Instruments of this type have been built at the University of Washington, including for a mail-in XANES facility [Ditter2019] and for placement in a radioactive materials laboratory at Los Alamos National Lab (USA) [Jahrman 2019b]. At the University of Helsinki one instrument has been built for general use [Honkanen2018] and has shown good performance for heavy element study. A second spectrometer is currently being built in the Radiochemistry unit at the University of Helsinki to allow radioactive material studies such as actinide's chemistry. A third is already planned and will be dedicated to material study under irradiation at their accelerator laboratory, so that at least one additional system is being built.

This general approach has been commercialized by easyXAFS [easyXAFS1], who have placed about 12 instruments in labs in North America and Europe, where they are being used for research in catalysis, electrical energy storage, and nuclear materials.

2.2. *von Hamos spectrometers*

The dispersive von Hamos scheme was already developed in 1934. In this configuration, the dispersive element is cylindrically bent, thus producing dispersion in one direction while refocusing in the other. Using a divergent and polychromatic source as well as a spatial resolving detector, one can acquire a certain bandwidth without moving any parts of the spectrometer. Therefore, this approach can be useful both for X-ray absorption (XAFS) and emission (XES) spectroscopy. In the first case, the source might be the X-ray source itself, e.g. a microfocus X-ray tube, which is simply attenuated by the sample, or even refocused by x-ray optics onto the sample for performing micro analysis. For XES, the sample is irradiated by a focused X-ray source and the subsequent sample's emitted fluorescence is then captured by the large solid angle optic and refocused or otherwise dispersed into the detector. Figure 2.2 depicts XAFS and XES configurations, as implemented in TU Berlin. Due to the dispersive approach, it is only possible to acquire XAS spectra in transmission mode (TM). To overcome the usually low integrated reflectivity of ideal crystals, one can choose to use mosaic crystals as the optic elements for higher flux at a cost of spectral resolving power. The versatility of this approach and the high quality of optics now available has led to considerable recent interest and efforts. There are presently ~10 laboratory-based instruments in existence using these approaches.

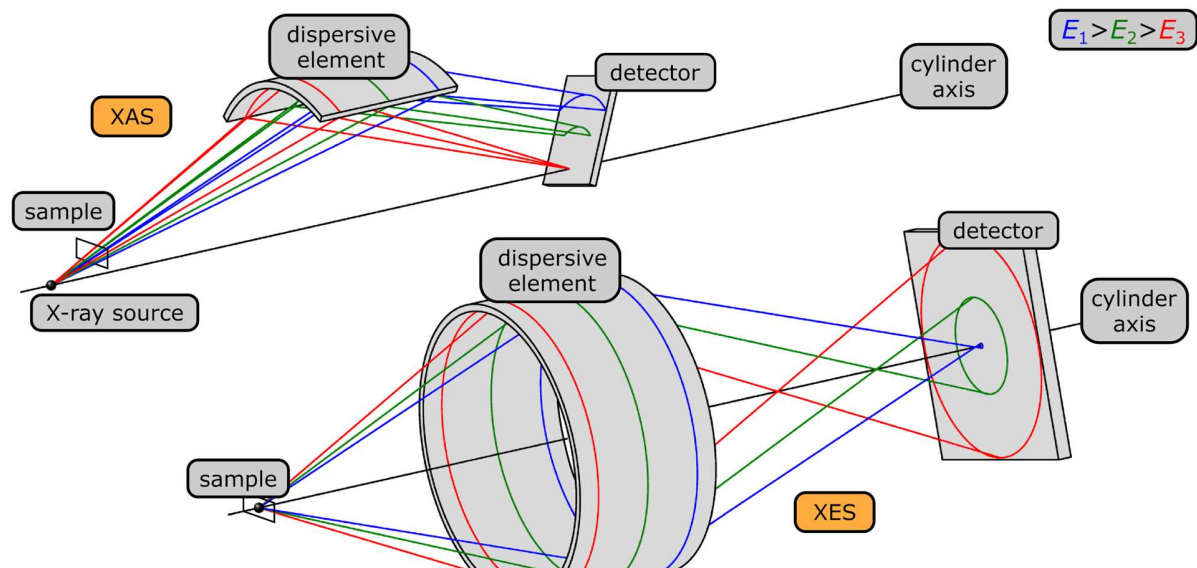


Figure 2.2:(adapted) von Hamos schemes for XAS (top) and XES (bottom), as used by TU Berlin/BLiX. (Courtesy of Christopher Schlesiger, TU Berlin).

The XAS spectrometer of TU Berlin is using a standard low power microfocus X-ray tube, Highly Annealed Pyrolytic Graphite (HAPG) and a standard pixelated detector [Schlesiger 2015]. This approach can be either optimized for XANES (even with compared to ideal crystal spectrometer lower spectral resolving power) or EXAFS at high bandwidth and lower spectral resolving power. The combination of high integrated reflectivity and von Hamos schemes ensures a high photon flux. The paths can be evacuated if needed but in principle the measurements are conducted in air environment. Based on this scheme, two spectrometers are being developed to start operation in 2019, one for the Max-Planck-Institut for chemical energy conversion (MPI CEC) and one for the UniSysCat excellence cluster in Berlin-Brandenburg region. Both spectrometers will be dedicated to EXAFS studies.

A spectrometer dedicated to XES was developed in cooperation between the MPI CEC and the TU Berlin/BLiX, and transferred to the MPI CEC [Malzer 2018]. This spectrometer followed the experience gained in developing a first prototype at TU Berlin/BLiX [Anklamm 2014]. For investigation of the weak valence to core transitions, a high efficiency is especially of interest and therefore the above described scheme was adapted to the full cylinder geometry as well as using a high brilliance metal jet x-ray source and a direct detection CCD. The whole setup as well as the sample itself are allocated in high vacuum and additional cooling of the sample is possible.

An alternative von Hamos style spectrometer (developed at the Hungarian Academy of Science) uses diced, ideal crystals, e.g. Si (111), to measure XES (however not optimal for that purpose) and XAS (TM) [Németh 2016]. The purpose of this spectrometer development is also but not limited to long time studies of samples over days. There is also a recent report of a similar spectrometer based on the use of ideal crystals in von Hamos geometry in a double spectrometer

for simultaneous acquisition of XES and XAS spectra [Błachucki 2019]. In contrast to the approach mentioned before, here cylindrically bent and not diced ideal crystals are used as well as a standard X-ray tube with integrated focusing optics and two direct detecting CCDs. One spectrometer using this approach that will be dedicated to XANES experiments is currently also under development in the frame of the above-mentioned cooperation between TU Berlin/BLiX and MPI CEC.

Finally, in the context of von Hamos systems, the EXAFS mode in the commercially available Sigray QuantumLeap XAS [Sigray1] relies on a deep depletion CCD camera and HAPG or Highly Oriented Pyrolytic Graphite (HOPG) together with a proprietary microfocus X-ray tube. Complete details for performance, energy range, etc. are presently unclear, due to the absence of refereed publications and limited publicly available information.

2.3. Dispersive Rowland spectrometers

The Rowland circle geometry can also be used in a dispersive geometry. This can be done when using a point source in a ‘usual’ dispersive approach or can be done with an extended source in the so-called ‘dispersive Rowland refocusing’ (DRR) geometry (Figure 2.3).

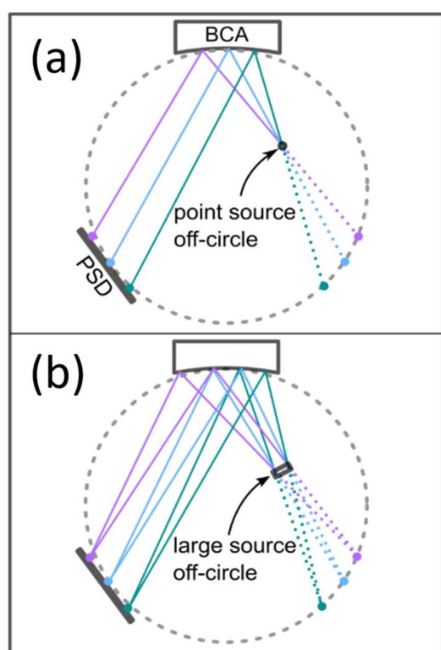


Figure 2.3: Dispersive Rowland schemes

(a) Point-focusing dispersive operation of on the Rowland circle. The ‘Bent Crystal Analyzer’ (BCA) is a Bragg optic, typically a semiconductor material (Si, Ge) but sometimes other materials, such as quartz or mica.

(b) Using a large source, high spectral resolution is still possible due to the spectral refocusing forced by the Rowland circle geometry. [Holden 2017]

(Courtesy of G. Seidler)

The DRR geometry is used with a conventional non-focusing x-ray tube in the work from the Seidler group at the University of Washington for nonresonant XES [Holden 2017], and is available commercially from easyXAFS, both for applications in the 2-6 keV energy range [easyXAFS1]. The University of Washington instrument shows count rates that are fully comparable to those at 3rd generation synchrotron facilities for XES of S or P, and has seen several

published studies. [Stein 2018, Holden 2018]. There are presently three of these instruments at the University of Washington or at Los Alamos National Laboratories.

The point-source dispersive geometry is used in the commercial instrument from Sigray corporation [Sigray1] for XANES studies with microfocus capability.

2.4. Transition Edge Sensor Arrays

All the above described approaches make use of diffractive optics. Such instruments are highly developed, going back to the earliest days of hard x-ray spectroscopy. However, in a fundamental way, their efficiency is quite limited: Bragg's law selects a single wavelength (ignoring harmonics) to be reflected with all other wavelengths absorbed. This is of course why wavelength-dispersive XRF is so much less efficient than energy-dispersive XRF, for example.

Traditional energy-dispersive detectors, such as silicon drift detectors, have energy resolution of $\sim 150\text{eV}$ in the hard x-ray range, and therefore cannot be used to directly perform high-resolution x-ray spectroscopy needed for XAFS or XES. However, ongoing work on a new generation of energy-dispersive detectors suggests a path forward. A transition edge sensor (TES) x-ray detector makes use of a bolometer approach. [Morgan2018] Specifically, when a sufficiently small mass at low temperature ($\sim 100\text{mK}$) absorbs an x-ray photon it will have a small change in temperature that can be detected by a superconducting thermometer held in the middle of its superconducting transition.

The TES is therefore a new type of energy dispersive detector, with an energy resolution that can be as good as 2-4 eV in the energy range of 2-10 keV. A multipixel array of TES could be used for some XAFS in the lab, albeit with some reduced energy resolution, and has proven useful for time-resolved XAFS in the lab setting [Miaja-Avila2016]. TES arrays can also be used for XES in the laboratory setting, although count-rate limitations can be problematic and the energy resolution is not yet sufficient for some applications.

3. Relevant University Groups and Commercialization

The development of laboratory based XAFS and XES spectrometers in recent years has been undertaken by a handful of research teams. Contact information for these teams is provided below

- Group of Prof. Gerald Seidler, X-ray Spectroscopy
University of Washington, Department of Physics, 3910 15th Ave. NE, Seattle, WA 98195, USA
Website: <http://faculty.washington.edu/seidler/>
Associated instrument options: Energy-Stepping Rowland, XAFS and XES,
Dispersive Rowland Refocusing

- Group of Prof. Simo Huotari
Department of Physics, University of Helsinki, P.O. Box 64, FI-00014 Helsinki, Finland
Website: <http://www.xraylab.fi/index.php/research/9-research/15-helxas>
Associated instrument options: Energy-Stepping Rowland, XAFS, XES
- Group of Prof. Birgit Kanngießner, Analytical X-ray Spectroscopy
Technical University Berlin, Institute of Optics and Atomic Physics, Hardenbergstr. 36, 10623 Berlin, Germany
Website: https://www.axp.tu-berlin.de/ag_kanngiesser/
Associated instrument options: von Hamos, XAFS, XES
- Group of Prof. Jakub Szlachetko
Institute of Nuclear Physics, Polish Academy of Sciences, 152 Radzikowskiego Street, 31-342 Kraków, Poland
Website: https://www.ifj.edu.pl/www-old/phone/ed_person.php?id=918&active=1&lang=en
Associated instrument options: von Hamos, XAFS and XES
- Group of György Vankó, Femtosecond Spectroscopy and X-ray Spectroscopy
Wigner Research Centre for Physics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary
Website: <http://mffo.rmki.kfki.hu/vanko>
Associated instrument options: von Hamos, XAFS
- easyXAFS (commercially available)
Website: <http://easyxafs.com/>
Associated instrument options: Energy-Stepping Rowland, XAFS and XES
- Sigray (commercially available)
Website: <http://www.sigray.com/>
Associated instrument options: von Hamos, XAFS; Dispersive Rowland Refocusing

4. Conclusion

The consultants highlighted the potential impact of laboratory based XAFS and XES instruments for the mission of IAEA and NSIL by providing eight categories of likely applications where the suitability of existing instruments is either already demonstrated or else can be reasonably expected due to known capabilities. These applications span: Bioaccumulation of toxic elements; Industrial Mineral Extraction and Processing; Nuclear Wastes and Fuels; Regulatory Compliance for Metal

Speciation; the Life Cycle of Lithium Ion Batteries: Clean and Energy Efficient Catalysis; Materials Exposed to High Radiation Levels; and Equitable Innovation and XAFS/XES Access.

Laboratory based XAFS and XES are advantageous for adaptive research projects contributing to solve problems of high interest to IAEA Member States. These capabilities do not compete with synchrotron capability, such as is now supported by IAEA, but serve as the basis for routine daily application across the range of applications listed above without the limitations for access inherent to synchrotron-based studies.

Based on these conclusions, the consultants recommend the IAEA to consider:

- To foster the introduction of laboratory based XAFS and XES techniques in the list of nuclear analytic techniques suggested to the Member States for solving a variety of research/technological problems.
- To organize a Technical Meeting (2021) focusing on further developments in implementation and applications of these techniques.
- To consider organizing a Coordinated Research Project (2022-23) aiming at both, current developments in the field of innovation and to facilitate the access of research teams to existing facilities.
- To explore the possibility of incorporating institutions with laboratory based XAFS-XES techniques to the IAEA collaborating Centers.
- To publicize the advantages of the techniques through presentations, leaflets and promotional materials targeting the Technical Cooperation Program.

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Annex 1: Cost Estimates

The below values are estimates based on personal experience or publicly available information.

Name	mode	best energy range	typical applications	cost (introductory, self-built)	cost (high-performance, commercial or special contract)
von Hamos (HAPG)	XAFS, unfocused, dispersive	hard x-ray	bulk XANES (red. resolving power) or EXAFS	~70 k€	
vonHamos (Si or Ge)	XAFS, unfocused, dispersive	hard x-ray	bulk XANES or EXAFS	~85 k€	
vonHamos (Si or Ge)	XAFS, focused, dispersive	hard x-ray	microfocus XANES or EXAFS		Sigray: >1000k€
Rowland monochromator	XAFS, XES, energy stepping	hard x-ray	bulk XANES, EXAFS, XES	30k€	easyXAFS: 150k€ - 270k€
Rowland dispersive, focusing	XANES	tender and hard x-ray	microfocus XANES		Sigray: >1000k
Rowland dispersive, nonfocusing	XES	tender and hard x-ray, depending on detector	bulk XES	30k€	easyXAFS: 100k€
Transition edge sensor array	XAFS, XES	tender and hard x-ray	time-resolved XAFS and XES	N/A	US NIST: ~1000k€
von Hamos (HAPG)	XES	hard X-ray	bulk XES	> 200 k€	

Annex 2: Meeting Agenda

	Tuesday, November 12 Room A2311	Wednesday, November 13 Room M0E61	Thursday, November 14 Room M0E61
9:00–10:30	Official Opening, Danas Ridikas, Head Physics Section Objectives of the meeting, Roman Padilla, IAEA NSIL Brief Introduction of participants Selection of the Chairperson	Discussion Needs vs capabilities of laboratory based XAS and XES	Writing meeting report
10:30-10:45	Coffee Break		
10:45-11:30	Introduction to Physics Section and NSIL activities, R. Padilla <i>Session 1: Experiences of each participating laboratory</i>	Discussion Needs vs capabilities of laboratory based XAS and XES	Writing meeting report
11:30-12:15	Prof. Gerald Seidler, University of Washington, USA		
12:15-13:30	Lunch Break		
13:30-14:14	Dr. Christopher Schlesiger Faculty of Mathematics and Natural Sciences Institute for Optics and Atomic Physics	Discussion Needs vs capabilities of laboratory based XAS and XES	Review of meeting report draft
14:15-15:00	Dr Rene Bes Department of Physics, Helsinki Accelerator Laboratory Helsinki Institute of Physics	Discussion on Instrument design options and costs	Review of meeting report draft
15:00-15:15	Coffee Break		
15:15-16:45	Round Table: Sustainable Development Goals and Needs of IAEA MSs	Discussion on Instrument design options and costs	Final remarks and meeting closure