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Topical Review

Past, present and future—sample environments for materials research studies in scattering and spectroscopy; a UK perspective

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Abstract

Small angle x-ray scattering and x-ray absorption fine structure are two techniques that have been employed at synchrotron sources ever since their inception. Over the course of the development of the techniques, the introduction of sample environments for added value experiments has grown dramatically. This article reviews past successes, current developments and an exploration of future possibilities for these two x-ray techniques with an emphasis on the developments in the United Kingdom between 1980–2020.

Keywords: SAXS, XAFS, sample environment, soft matter, materials science

(Some figures may appear in colour only in the online journal)

1. Introduction

It is remarkable how x-ray based research on materials science has changed over the last 30 years. Where 30 years ago many diffraction experiments still used x-ray film as the

main detection method there is now a plethora of highly efficient electronic detectors available that can collect and store large data volumes in fractions of a second (Broennimann *et al* 2006). Some are even pushing the limit further (Dinapoli *et al* 2013, Mozzanica *et al* 2018, Martiel *et al* 2020). At the same time developments in x-ray generators, especially when synchrotron radiation (SR) storage rings are included, have allowed for ever more bright and brilliant x-ray bundles (Bilderback *et al* 2005, Weckert 2015). The improvement in x-ray optics has also been considerable: when the number of photons per unit cross section is measured, one can see that

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the achievable brilliance increases on SR beamlines even surpasses the well-known Moore's law which is so popular in the semi-conductor industry.

The increase in raw flux, in combination with improvements in detector technology, has allowed a paradigm shift from static structural determinations to time-resolved experiments where structural changes and reaction kinetics can be followed in real time. With this shift has come an increased interest in the development of sample environments and other instrumentation required to obtain relevant information. Increased control over the sample can raise an experiment to the level that it allows one to understand the physical and chemical events in, for instance, an industrial manufacturing process (Portale *et al* 2013) or the duty cycle of an artificial heart valve (Stasiak *et al* 2011).

X-ray spectroscopy and x-ray scattering are two classes of techniques that have greatly benefited from the technological developments and have consequently become workhorses for materials science research.

Although above we mention separate reasons for advances, in fact no single reason sparked these developments and the curiosity and inventiveness of groups of collaborating individual researchers and engineers, in combination with many hours of overtime, is certainly not the least important contributory factor. In the end it comes down to 'the ability to get things done' is a combination of two elements: the desire to do them and the capacity to triumph over the challenges associated with doing things that are difficult (James 1980).

We will briefly describe some of the historical developments and science that had been made in the first facility in the United Kingdom, specifically designed for the generation of SR, to become operational as a user facility and how this has progressed to the modern day.

2. Driving factors early days

The advent of dedicated storage ring beamlines (Dobson *et al* 1986, Kuroda 1989, Derbyshire *et al* 1989, Bark *et al* 1990, Bras *et al* 1993, Bilsborrow *et al* 1995, Latimer *et al* 2005), with high flux, in the 1980's and 1990's allowed the materials science community to start to think in terms of the real science problems they were engaged in. The opportunities to answer these scientific questions including 'how does a material behave in time when perturbed physically or chemically?' And 'what can we learn from that to improve the materials?' The development of a combination of simultaneous technique combinations and new sample environments led by, among others, people such as Greaves in Daresbury and Zachmann in Hamburg.

One of the most often used materials science characterization techniques is x-ray powder diffraction. Time- or temperature-resolved experiments were already implemented on laboratory x-ray generators but non static experiments with a reasonable time-resolution so that chemical and physical transformations could be followed, came completely of age on the first SR beamlines. Here the broad x-ray spectrum could be used to carry out energy dispersive x-ray diffraction experiments (Clark 1996). Apart from the time resolution that this

technique could bring, a second advantage was that only a small beam access opening in the sample environment had to be created. This in contrast with angle dispersive experiments where a large opening angle is required. This simplified the engineering issues and enabled high temperature and pressure experiments suitable for catalysis research. At the SRS (Martin 1988) (Synchrotron Radiation Source) in Daresbury this also led to the installation of a powerful multi anvil press suitable for large sample volumes (Clark 1996). In the early years this instrument was mainly used to gain insights in the transformations, and possible structural intermediates, in geological compounds (Yee *et al* 2006, Hunger and Benning 2007). In later years this technique was also used to observe the pressure induced formation of materials that could compete with diamond in hardness. On a modern synchrotron this technique has lost some of its appeal due to the very high fluxes to which the sample is exposed, and the use nowadays is mainly limited to experiments that are short and require a very high time-resolution (Bourgeois *et al* 2003). In the meantime, the angle dispersive techniques have become so advanced by the introduction of position sensitive or multiple point detectors that time resolved experiments have become routine as well (Tabatabaei *et al* 2009).

These sorts of questions were a paradigm shifts away from obtaining structural data for pure knowledge's sake but needed a whole new infrastructure to achieve them. The advent of detectors designed to cope with the flux levels in x-ray scattering experiments (Gabriel 1977, Bordas *et al* 1980) at these new facilities allowed this infrastructure to develop into the time-resolved experiments that are ubiquitous today. EXAFS studies of dilute systems were originally only possible at low count rates using photomultiplier tubes as detectors of the fluorescent x-rays (Hasnain *et al* 1984). The improvements in fluorescence detection of dilute components in a sample were the result of putting together a large number of elements on a single cryogenically cooled detector head (Cramer *et al* 1988), but the advent of multi-element, 30 and ultimately 100, solid state germanium detectors and improved processing electronics (Derbyshire *et al* 1992, Farrow *et al* 1998) allowed experimenters to make full use of available flux. A special development was the nine-element monolithic Ge detector developed by Canberra and using the Daresbury developed electronics. The monolithic design allowed a larger solid angle to be covered compared to single element type of detectors and a much more efficient use of the active area of the detector since no photons were lost in the space between individual elements (Derbyshire *et al* 1999). Not only were the detectors important, but to record time-dependent x-ray spectroscopic measurements, it was necessary to be able to record a spectrum in a time much faster than the typical ~ 1 h recording times of early facilities. New monochromators were developed which could record a complete spectrum in only a few seconds in a technique that became known as quick EXAFS, or QuEXAFS (Frahm 1989, Frahm 1991, Murphy *et al* 1995). The first low-profile monolithic Ge detector when combined with digital readout electronics such as XPRESS (Farrow *et al* 1995) allowed data to be collected rapidly from sub 1% dilutions (figure 1).

One of the earliest examples of a kinetic study in small angle x-ray scattering (SAXS) was where temperature was used to explore the behaviour of polymeric material by Koch *et al* (Koch *et al* 1979). They followed the crystallisation process of pre-stretched polyisobutylene fibres, finding that the half-time for the crystallisation was approximately 50 seconds. Zachmann and co-workers (Elsner *et al* 1981) studied the evolution of SAXS from amorphous poly(ethylene terephthalate), (PET), during isothermal crystallization using SR. Data was recorded in 1 sec intervals while the samples were heated to temperatures between 117 °C and 145 °C to explore the kinetics of the process.

A crucial driving force was the concept that, to understand evolving samples, required one to obtain information over several decades in length scales, which consequently called for the combination of several experimental techniques in a single experiment. This led to parallel developments of combined SAXS/WAXS beamlines in Hamburg and Daresbury (Bark *et al* 1992, Bras *et al* 1993), indicating that both the time and technology were ready for such developments. Preceding structure formation, in for instance zeolite formation, chemical reactions are taking place which can be elucidated by x-ray spectroscopy (Gottler *et al* 1989, Clausen *et al* 1993). The subsequent crystallization process requires a combination of small and wide-angle x-ray scattering, where initial signatures from phase separation come from larger length scales accessible by SAXS and the ultimate crystallisation kinetics require time resolved WAXS (Beelen *et al* 1993, Dokter *et al* 1995). Early attempts to record fast WAXS results were limited by the technology: the only system capable of recording a complete WAXS spectrum without moving the detectors was the INEL streamer discharge detector (Evain *et al* 1993), but its maximum count rate was only a few kHz: building on technology developed for high energy physics experiment, gas microstrip (Zhukov *et al* 1997, Bateman *et al* 2002) detectors were used which were up to 500 times faster. The WAXS data was also collected using the RAPID multiwire proportional counter (Lewis *et al* 1997a) which was capable of recording at a global rate of 200 MHz (figure 2).

An area where combining SAXS with WAXS was crucial was in the crystallisation of cordierite glass ceramics (Bras *et al* 2005, Bras *et al* 2009). This material, because of its low average thermal expansion coefficient, high thermal shock resistance, excellent chemical stability, low dielectric constant and optical transparency was of significant interest to the automotive industry as the honeycomb support for exhaust catalysts but also for substrates in electronic packaging and in the development of tuneable lasers and solar concentrators. Independent studies could not give the whole picture, whereas the newly arrived combined SAXS/WAXS capability on 8.2, instigated by Greaves *et al*, unambiguously showed the crystallization pathway. Studies to explore crystallisation in homopolymers (Ryan *et al* 1994) and phase behaviour in block copolymers (Forster *et al* 1994, Khandpur *et al* 1995) soon followed. This seminal work on block copolymers is still being cited today. Combined SAXS/WAXS beamlines are now

the norm for materials science studies which makes it impossible to give a comprehensive list (Riekkel *et al* 1996, Kellermann *et al* 1997, Bras *et al* 2003, Cernik *et al* 2004, Krywka *et al* 2007, Hexemer *et al* 2010, Weigand and Keane 2011, Buffet *et al* 2012, Kirby *et al* 2013, Smith *et al* 2021).

The development of time-resolved methods also required an increased control over, for instance temperature, which was most often the parameter driving the reaction or crystallisation kinetics. Subsequently many novel homemade devices (Fan *et al* 2007, Sankar 2007, Sankar *et al* 2007) as well as more commercially driven solutions such as the Linkam hot-stages (Oversluizen *et al* 1995, Bras *et al* 2005) and DSC cells (Russell and Koberstein 1985, Kellens *et al* 1991, Bras *et al* 1995a) were introduced to further improve temperature control; the latter providing additional chemical information in the form of glass transition temperature, melting and crystallisation points. As with many scientific advances they rarely stay unique to the field that developed them. Temperature control was soon exploited to explore the structure of the lipid channels in human skin (Bouwstra *et al* 1996) relevant for transdermal drug delivery and later also for understanding of skin diseases like eczema and psoriasis (Janssens *et al* 2012). Soon many fields were exploiting the techniques developed including food science where the development of starch structure during cooking was explored (Jenkins *et al* 1994).

For even more accurate temperature control Peltier devices were deemed necessary for some investigations. An exploration of undercooled water (Dings *et al* 1992) required 4 Peltier units surrounding the sample but gave the investigators 0.05 °C gradients to work with.

The desire to be able to perform time-resolved and combinations of techniques was also felt in the x-ray spectroscopy community. Greaves in Daresbury became one of the most ardent advocates of these developments. Initially experiments were performed by the energy dispersive EXAFS (EDE) community, where the first dedicated diode array detector system for collecting data was developed at Daresbury by Allinson *et al* (Allinson *et al* 1988). In the early days, Hamburg was also developing the technique and the first combined EDE/XRD experiments (Clausen *et al* 1993) were carried out there by measuring the diffraction from an individual peak. The first combined experiments at Daresbury on beamline 7.4 followed the structural and chemical changes that occur within the layered mineral aurichalcite ($\text{Cu}_{5-x}\text{Zn}_x(\text{OH})_6(\text{CO}_3)_2$) when heated in dry air to approximately 450 °C. This experiment showed the value of combining the techniques and including temperature control (Couves *et al* 1991).

Quick EXAFS (QuEXAFS), by using scanning monochromators instead of energy dispersive methods, soon followed and gave the opportunity for improved data quality the required time resolution (Frahm *et al* 1995, Murphy *et al* 1995). Once available the technique showed its value in a range of scientific areas including zeolites (Sankar *et al* 1993, Thomas *et al* 1994) and the field for which Greaves is most remembered, random network glass (Houde-Walter *et al* 1993). Dedicated sample environments soon followed (Dent *et al* 1995) again, influenced by the need to study inorganic materials in operating conditions (Thomas *et al* 1995). For a further

improvement in the possible time resolution, one had to wait until the advent of the third generation of synchrotron sources (Grunwaldt *et al* 2001, Lützenkirchen-Hecht *et al* 2001).

If the combination of other x-ray based techniques is an obvious development, the addition of non-x-ray based techniques broaden the possibilities to increase the information content of an experiment but often at the expense of a more complicated protocol, where for instance access by two different type of probe beams has to be enabled. This was already clear in the development of on-line DSC, where the normal thermal isolation of the sample has to be breached in order to allow access with the x-ray beam. It is even more so when optical access to the sample has to be allowed. An example where birefringence was combined with x-ray scattering shows the ingenuity which was required to achieve this (Gleeson *et al* 1995), but also the benefits of having the possibility to correlate the macroscopic behaviour with events at the molecular level for liquid crystals subjected to changing electric field.

For spectroscopy at different wavelength ranges one can encounter issues with discrepancies in penetration depth and sample environment windows transparency, but the promise of a more complete insight in the processes under consideration drove many researchers to team up with beamline scientists in attempts to overcome these issues. Sometimes the data quality was maybe not optimal, but acceptable and of sufficient quality to be analysed, instead of remaining stuck at the proof of principle level.

2.1. SAXS/WAXS/chemical spectroscopy

Combining SAXS/WAXS/Raman spectroscopy allowed chemical reaction kinetics to be established alongside any structural changes. Bryant *et al* used this to good effect in the polymerisation reaction of styrene into polystyrene (Bryant *et al* 1998). Raman spectroscopy can be realised through the application of fibre optics and is therefore highly versatile and has been successfully combined with XRD/EXAFS (Kongmark *et al* 2009) and SAXS/WAXS/EXAFS (Beale *et al* 2011) and is now utilised widely, including for determining the ratio of bundled to isolated carbon nanotubes. Without the Raman spectroscopy data this would be an ill-posed problem, whereas its inclusion allows one to apply the appropriate constraints in the modelling of the SAXS data (Haas *et al* 2014). Davies *et al* incorporated microRaman spectroscopy (Davies *et al* 2009) with microdiffraction onto ID13 (Engström *et al* 1995) at the ESRF. The combined technique was used to study the sol-gel synthesis of silica in an ionic liquid (Nayeri *et al* 2015). Even more recently Raman spectroscopy has been combined with SAXS to explore the ozonolysis of oleic acid-sodium oleate cooking aerosol proxies (Milsom *et al* 2020, Milsom *et al* 2021). Similar developments were attempted with infra-red spectroscopy but despite the promise of this approach it never developed a widespread following (Bogg *et al* 1995, Bras *et al* 1995b).

2.2. Exploitation for polymer processing

During materials processing, mechanical performance as well as determining lifetime of components it is relevant to

understand what the reaction of the materials is when exposed to mechanical forces. This can be in the liquid state where an inevitable step in the processing of polymers is to be exposed to shear forces or the ultimate breaking strength of fibres intended to be used in composite materials.

Although high on the list of polymer scientists, the use of shear devices or rheometers in the early years was not widespread (Pople *et al* 1998, Mitchell *et al* 1998, Hamley *et al* 1998). One of the reasons was that these devices would benefit from a somewhat higher penetration power. This was not available on the fixed energy beamlines which were mainly tuned to the traditionally available Cu K α wavelength. Some interesting work was carried out using a multipass rheometer that followed the evolution of crystallisation, as molten polyethylene flows into a slit geometry (Mackley *et al* 2000). However, home built or modified commercial stretching devices were introduced to the beamlines for the study of polymers (Blundell *et al* 1994, Butler *et al* 1995, Stribeck *et al* 1997). Even biaxial deformation has become possible (Gurun *et al* 2009). It should be mentioned that for these studies the data analysis was still primitive due to a lack of computational power. Elaborate attempts to remedy this were undertaken (Stribeck *et al* 1997) but to access all the available information that was embedded in these experiments had to wait until computing power caught up with the data volume.

These developments led to new questions which required higher brightness to solve. Experiments by Ryan *et al* (Terrill *et al* 1998), using an on-line polymer extruder on 16.1 at Daresbury (Bliss *et al* 1995) and elsewhere (Miyata *et al* 1997), reignited the debate about the onset of polymer crystallization (Schultz *et al* 2000). The common wisdom at that time was that this was a nucleation and growth process but combined SAXS/WAXS data showed the existence of a mesophase before the onset of crystallization (Olmsted *et al* 1998). This caused some heated debates in the polymer crystallization community (Heeley *et al* 2003). The accepted outcome of this debate is that indeed a mesophase appears before crystallization starts.

3. Modern beamlines and combined exploitation

3.1. SAXS

The sample environment types described above are still the workhorses for much of the productivity of SAXS beamlines globally today. For example, the Linkam DSC is still used for continuing work on studying hybrid glasses from metal organic framework liquids (Bennett *et al* 2015).

The use of pressure in soft materials research has more recently become well established. A number of cells have been designed which match the requirements of soft matter (Duesing *et al* 1996, Kato and Fujisawa 1998, Steinhart *et al* 1999, Woencckhaus *et al* 2000, Ando *et al* 2008, Krywka *et al* 2008). These allow the experimenter to vary the pressure and measure morphological properties of the material of interest. More recently kinetics has started to be considered, pressure may well be a cleaner medium to understand phase transitions than temperature. A P-jump cell developed by Brooks *et al*

(Brooks *et al* 2010) has been extensively used in soft matter studies (Brooks *et al* 2011, Tang *et al* 2012, Tyrsted *et al* 2012, Barriga *et al* 2015, Schroer *et al* 2016, Schroer *et al* 2018, Le Vay *et al* 2020) on I22 at diamond.

The study of reaction kinetics is also fairly common, even under environmental science conditions (Stawski *et al* 2020), as is the use of bespoke reaction cells for monitoring reaction progress (Brotherton *et al* 2019, Alauhdin *et al* 2019). Flow cells and the associated stop flow technique (Grillo 2009) has also been used extensively in soft matter research. As long as the research team has enough material this can be a good way of accessing very fast timescales indeed (Graceffa *et al* 2013). Microwave annealing (Toolan *et al* 2017) has also been utilised as an alternative to thermal annealing for optimising block copolymer self-assembly by targeted annealing of specific regions of a multi-component system, opening routes for the development of ‘smart’ manufacturing methodologies. On-line chemistry, following the structure formed by chemical reactions, also have become feasible even when using high pressure equipment like super critical CO₂ chemistry cells (Hermida-Merino *et al* 2014). On-line chemical installations to drive structural deformations in block co-polymers, mimicking the behaviour of muscle, have also been reported (Howse *et al* 2006).

Evermore complex sample environments mimicking real world processing conditions have been exploited, even in grazing incidence mode (Proller *et al* 2017), an excellent review of those used in polymer science has recently been written (Portale *et al* 2016).

To obtain very high temperatures, well beyond those developed for early thermal studies, alternative solutions have been explored. These include aerodynamic levitation laser heating (Hennet *et al* 2011) for which study of molten glass (Hennet *et al* 2007, Greaves *et al* 2008, Greaves *et al* 2009) was of particular note. The beauty of this method is that the sample is suspended without need for sample holder simplifying any background subtraction and allows for the integration of additional techniques. An excellent recent review discussing these sample levitation developments in several international x-ray and neutron sources is published by Benmore and Weber (Benmore and Weber 2017).

With the reduced beam sizes and lower divergencies associated with modern SAXS beamlines, microfocus studies have expanded dramatically. While many are associated with mapping (Hermes *et al* 2006, Seidel *et al* 2008) microfluidic devices which have been developed in most of the soft matter fields (Barrett *et al* 2006, Kadirak *et al* 2017, Hashemi *et al* 2019, O’Connell *et al* 2019) are already being exploited to study flow (Martin *et al* 2016, Lutz-Bueno *et al* 2016, Levenstein *et al* 2019) and rheological properties of soft matter (Komorowski *et al* 2020, Dinic *et al* 2017).

Improvements in beam quality allowed grazing incidence SAXS/WAXS to become mainstream, indeed it is the mainstay of the science programme on MINAXS (Buffet *et al* 2012) at Petra III. Early experiments at the ESRF on ID13 (Engström *et al* 1995) showed that position-sensitive sample surface information of multiple-scaled polymer films (Müller-Buschbaum *et al* 2003) was possible with micro-focused

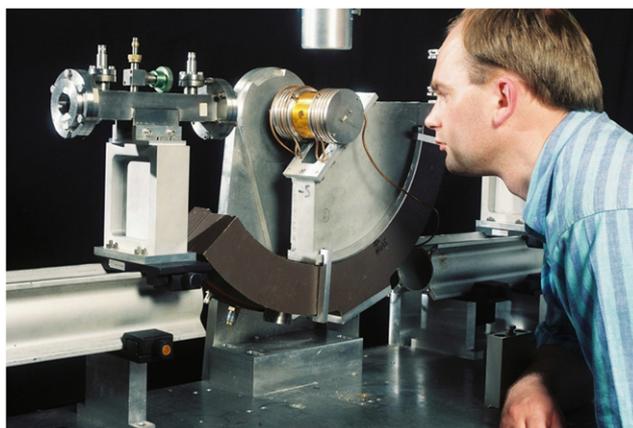


Figure 1. A combination of QuEXAFS and powder diffraction installed on beamline 9.3 of the SRS in Daresbury. This was a prime example of technique combinations used in time-resolved experiments. The high temperature furnace was developed in the Royal Institution. Above the furnace the measuring head of the 13-element monolithic Ge fluorescence detector can be seen. The curved INEL detector was used to collect powder diffraction data at the same time. Photo credit: STFC.



Figure 2. The first purpose built combined SAXS/WAXS set-up on beamline 8.2 of the SR source, Daresbury, UK. Ca 1991. Third from the left is Greaves who inspired the development of combined experimental techniques in Daresbury Laboratory. Photo credit: STFC.

beams from 3rd generation facilities. An excellent review of what is currently possible can be found in the review article by Hexemer *et al* (Hexemer and Müller-Buschbaum 2015). Sample environments have developed in this field too from fairly rudimentary heated cells (Carmichael *et al* 2001) to very elaborate systems that can sputter new layers of gold *in situ* (Roth *et al* 2006, Al-Hussein *et al* 2013, Schwartzkopf *et al* 2013), even showing that such complicated systems are ‘portable’ (Dohrmann *et al* 2013, Roth *et al* 2015) in

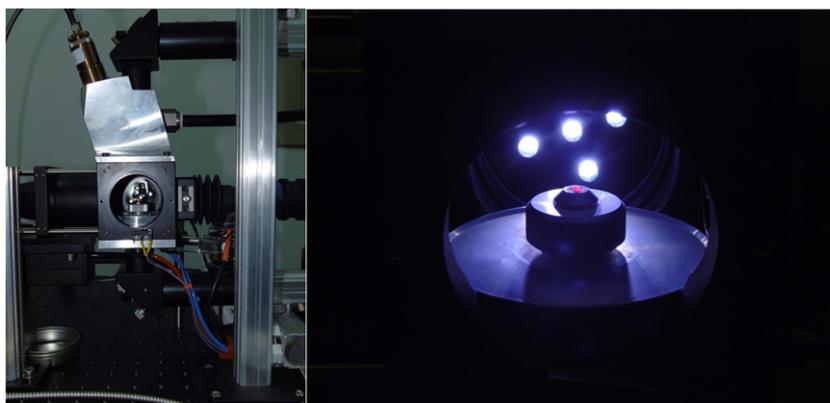


Figure 3. The aerodynamic levitation furnace installed at Wuhan University of Technology. Left shows the sample cell with heating lasers supplied top and bottom and shadow casting laser supplied from the left. Photo on the right shows nozzle jet with sample illuminated by low power alignment lasers. Photo credit D Langstaff (c) 2015.

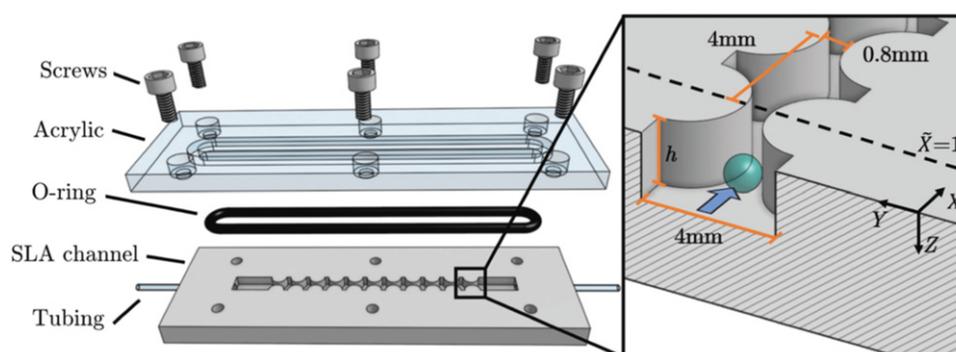


Figure 4. Schematic of a millifluidic porous medium used to study deformable particle transport. Reproduced from M G O'Connell *et al* 2019 with permission of The Royal Society of Chemistry.

some instances, or even follow the evolution of structure via laser/surface modification (Rebollar *et al* 2015). Others have used the slot-die printing (Proller *et al* 2016) or doctor blade formation (Pineda De La O *et al* 2021) of thin films *in situ* to gain a fuller understanding of the evolution in structure in photovoltaic devices. Understanding the preparation of poly(3-hexylthiophene) (P3HT), used in in some of these organic photovoltaic devices, has been studied by x-ray absorption fine structure (XAFS). It was widely thought that FeCl_3 acted as an oxidant. A study by Hirai *et al*, however, showed that the generated Fe(II) reoxidized to Fe(III) suggesting that FeCl_3 behaves as a catalyst rather than an oxidant (Hirai *et al* 2015) (figures 3–6).

3.2. XAFS

The early developments of combining auxiliary techniques with x-ray spectroscopy to gain insights in structure formation during the synthesis of catalytic materials and observing the functioning of catalysts in realistic environments have been expanded in recent years. Catalysis research has been the driving force, but many other research fields have benefitted from these developments as well.

Following the pioneering work of the early synchrotrons the third-generation facilities have implemented sample

environments from the start including appropriate control software to enable experiments to be performed seamlessly. A very good example of this is the spectroscopy village at diamond (Diaz-Moreno *et al* 2018). In summary, four beamlines are in operation which cover hard x-ray microfocus applications (I18, (Mosselmans *et al* 2009)), a quick-scanning multipurpose beamline with a wide energy range (2–34 keV to cover most absorption edges) and a large volume where a variety of sample environments can be placed including a solid-state position sensitive detector for XRD, B18 (Dent *et al* 2009). The wiggler beamline I20 (Diaz-Moreno *et al* 2009) has 2 branches. The first branch, I20-scanning, is a high flux line for dilute fluorescence spectroscopy and includes an emission spectrometer for high energy resolution fluorescence detected (HERFD) as well as non-resonant and resonant x-ray emission spectroscopies. The second branch I20-EDE is an energy dispersive EXAFS beamline (EDE) capable of measuring full spectra down to microseconds.

The early developments of combining auxiliary techniques with x-ray spectroscopy to gain insights in structure evolution during the synthesis of catalytic materials and observing the functioning of catalysts in realistic environments have been expanded in recent years. Catalysis research has benefited particularly from the application of spectroscopic methods primarily because the elements of interest are present in

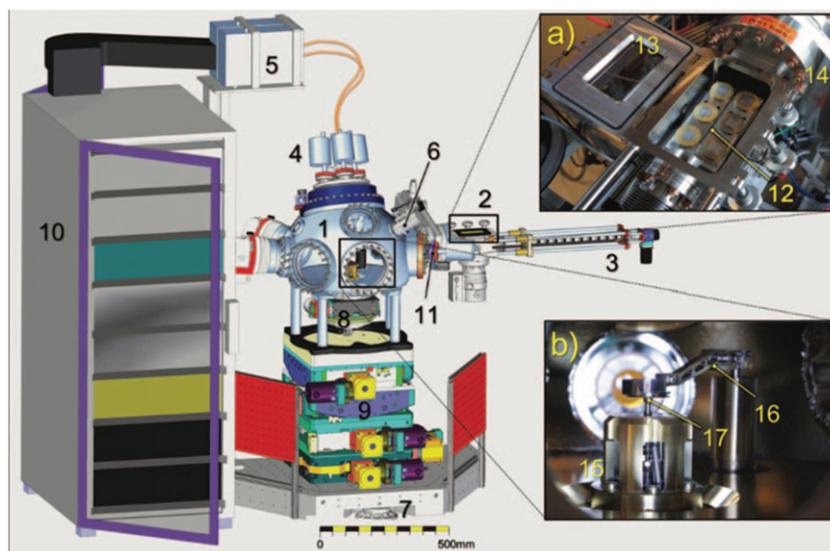


Figure 5. Overview of the highly automated sputter equipment. Reprinted from R Dohrmann *et al* 2013 with the permission of AIP Publishing.

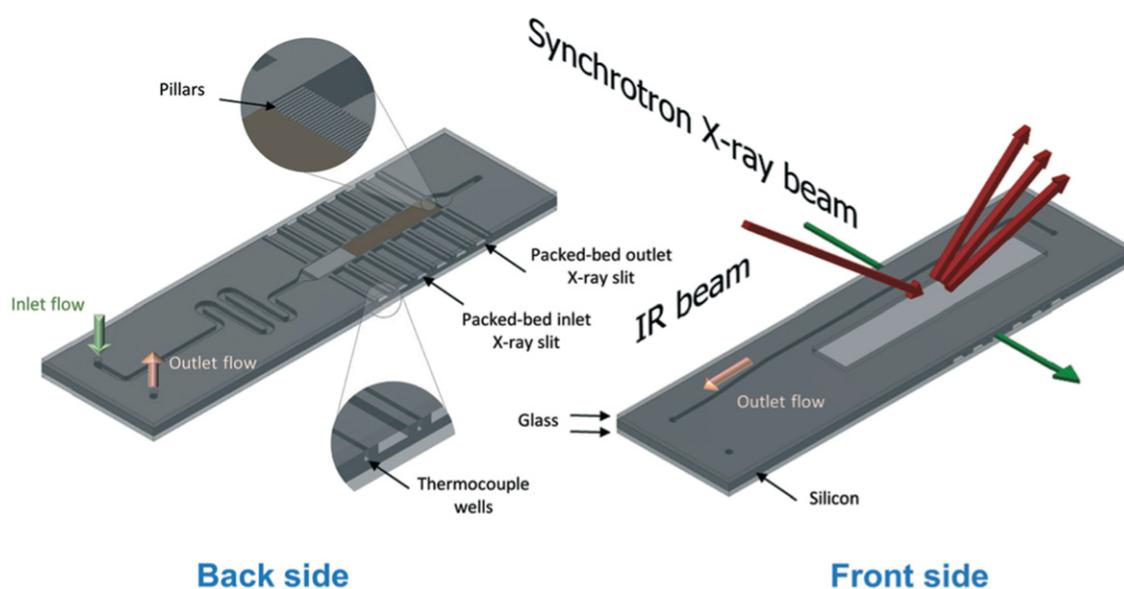


Figure 6. Schematic representation of the back and front side of the microreactor for operando XAS/MS and DRIFTS/MS studies. A packed-bed catalyst (brown) and glass beads (light grey) upstream of the catalyst bed are depicted on the back side image. Insets show detailed view of the pillars used for retaining the catalyst particles and the thermocouple wells. Reproduced from B Venezia *et al* 2020. CC BY 3.0.

too low concentrations ($\sim\%$) to be amenable to interrogation using scattering techniques. By providing a significant driving force for this purpose, many other research fields have benefitted from these developments. An excellent review of early developments for liquids has already been published (Filipponi 2001).

The capillary cell is a regular fixture on beamlines where catalysis is performed although it is very versatile having been used for the study of liquids and gels including crystallisation and reaction studies (Couves *et al* 1991, Clausen *et al* 1993, Newton and van Beek 2010, Beale *et al* 2011, Rabeah *et al* 2020) The last two references illustrate the modularity of modern-day synchrotron beamlines allowing multiple

techniques (i.e. multiple x-ray measurements or in combination with optical techniques) to be combined together to study sample evolution simultaneously (Beale *et al* 2011, Rabeah *et al* 2020). When these types of experiment were first performed over 15 years ago the setup alone would take many days (Nikitenko *et al* 2008). Miniaturisation and facile integration of the multiple techniques into the x-ray data acquisition process renders these setups tractable nowadays in a matter of hours. A greater amount of space for the sample environment means that it is now possible to integrate large magnetic resonance instruments such as an electron paramagnetic resonance or nuclear magnetic resonance into central facilities (Rabeah *et al* 2020, Leutzsch *et al* 2018). One notes

that the same part of the sample is not interrogated in all cases, but this is less of an issue for soft matter samples.

The stop-flow ‘freeze-cell’ continues to be a go to setup for elucidating the evolving structure of homogeneous systems and can be used in combination with techniques such as UV–Vis (Venderbosch *et al* 2020). These have been largely superseded by the development of flow cells in order to mitigate the influence of the x-ray beam on sample stability (Mesu *et al* 2006, Bartlett *et al* 2019, Levenstein *et al* 2020). To date there appears to be very few actual XAFS studies using such setups largely because of the volume of sample needed for continuous operation.

Continued improvements in source brightness and detector sensitivity over the years has allowed for the collection of more data in shorter timescales. This has been exploited for example for obtaining (a) better time resolution, (b) better spatial resolution and or (c) better sensitivity particularly for photon hungry ‘photon-in/photon-out’ techniques. In the case of (a) perhaps the highest time resolution achieved to date was that of 60 ms resolution when Kong *et al* studied the decomposition of $(\text{NH}_4)_2[\text{PtCl}_6]$, identifying the *cis*-stereoisomer as an intermediate in the process (Kong *et al* 2012). Despite the insight this study gleaned it has to our knowledge, not been repeated. This is largely due to the belief that mechanistic insight into soft and hard matter reaction processes at the nano-macro scale occurs more slowly than this (s–min.) rendering high time-resolutions redundant. Fundamental bond breaking and making processes in contrast are simply too quick occurring in femtoseconds. Notwithstanding the insight obtained there is an additional challenge when carrying out experiments that require a stimulus (e.g. heat/change in composition) to elicit a sample response in the same time-scale. This is difficult to achieve in catalysis experiments using gas switching as the stimulus as the time resolution is limited by the switching valves to a few ms. However, rapid heating of both liquids and solids can be achieved with lasers and this has been well demonstrated on levitating samples using gas or ultrasound (Egry and Holland-Moritz 2011, Hennet *et al* 2011, Nguyen *et al* 2017). It should be noted that when high time resolution has not been needed/exploited, it has been possible to measure multiple samples either in series or else simultaneously (Ravel *et al* 2010). For these studies it has also been possible to obtain data under well controlled and industrially relevant operation conditions (Martis *et al* 2014); the infrastructure required to allow this to happen will bring additional challenges to acquiring data with a higher time resolution. Pressure has also been a useful tool in EXAFS as it has been in SAXS. After early high-pressure experiment using EXAFS on a FeS_2 solid sample using a Bridgman-anvil method (Ingalls *et al* 1978) the technique has been used widely in the field (Filipponi 2001). Recent developments of a diamond anvil cell with internal heating shows the continuing development of the field for *in situ* studies (Mijiti *et al* 2020).

Imaging (including 2D mapping and 3D tomography) studies are becoming more prevalent nowadays as they allow heterogeneity in the composition or response of a material to be studied and correlated for a more complete understanding of

materials performance (Meirer and Weckhuysen 2018). Full-field XAFS and mapping studies under *in situ* or *operando* conditions are now considered commonplace. In some instances, XAFS has been combined other x-ray imaging modalities i.e. XRF/XRD or combination with optical techniques like IR (Price *et al* 2017, Dann *et al* 2019). Although the basic capillary design first demonstrated by Clausen *et al* is still in effect, the modern setup has been engineered to minimise thermal variance in sample heating thereby minimising the effect of temperature on evolving material response. The most recent incarnations have been reported to operate with no dead volume and negligible mass and heat transfer resistances (Venezia *et al* 2020).

The spectroscopic techniques derived from the combination of x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy, such as resonant inelastic x-ray scattering and HERFD XAS have been exploited now for a number of years to yield new insights into the local structure (identity of coordinating ligands) and electronic state, complementary to what can be gleaned from XAFS, particularly since the same types of reaction cell can also be used on these beamlines (Tromp 2015).

Especially in combination with XAFS the technique is particularly powerful in studying calcium oxide formation from hydroxyl gels (Aletru *et al* 1999). One area that has always been a strong science driver for the spectroscopy field is catalysis. More recently detailed studies have been possible under well controlled and industrially relevant operation conditions (Martis *et al* 2014).

A convergence between x-ray scattering and x-ray spectroscopy has become feasible on modern bending magnet beamlines. By carefully deciding upon the design parameters with respect to flux and energy tuneability it has shown to be feasible to build a combined SAXS/WAXS/XAFS experiment (Nikitenko *et al* 2008) which also enabled the implementation of several non-x-ray based experimental techniques (Beale *et al* 2006). With further improvement in monochromator and detector technology this also has the promise for the future to be able to incorporate time-resolved anomalous scattering experiments. Such a set-up would render a whole gamut of chemical and physical information which certainly in the catalysis field will be very beneficial.

4. Future

With beams getting ever smaller and flux continuing to rise, careful thought must be given to what experiments can truly exploit the new facilities being established/considered. The more so since lab-based instruments are becoming more powerful due to a combination of an increase in the flux that modern technology allows to generate as well as by more efficient detector technology. Lab-based SAXS instruments can now perform time-resolved experiments on the level of 10 seconds/frame using metal jet technology (Adibhatla *et al* 2018) and x-ray spectroscopy (Seidler *et al* 2014, Zimmermann *et al* 2020) systems are becoming so capable that standard material characterisations are becoming feasible. Truly fast experiments, such as those proposed for biomolecules on

XFELs (Levantino *et al* 2015) will require detector developments beyond what is currently possible even for the XFELs themselves (Sztuk-Dambietz *et al* 2013, Mozzanica *et al* 2018).

Another aspect that has to be taken into account is the limit to the x-ray exposure that materials can handle. The increase in brilliance can lead to the destruction of the sample or, as is becoming more recognised, modify the electronic state or phase of the materials. This is unfortunately not limited to the soft matter and biological samples anymore but increasingly recognised in the hard matter and catalysis community as well (Bras and Stanley 2016). Obviously, a prolonged exposure to x-rays, as is required in a time-resolved experiment, is an extra factor in this.

For synchrotron radiation-based experiments to stay relevant in materials science it is clear that the brute force method, by increasing the flux, will not work in future. Hence future developments probably have to be sought in increased experimental sophistication where either the new technical possibilities of the latest multi-bend achromat storage rings, for example, increased coherence or the use of nanosized beams, can be exploited. Alternatively, more elaborate approaches where a combination of sample environments, technique combinations and a new approach to analysing combined data sets might bring the required return in scientific investment.

One new feature of all of the 4th generation facilities proposed or in build is significantly enhanced coherence (Magnuson 2006). While on 3rd generation facilities the coherent fraction of the beam might account for 1%–2% of the total at most, on sources such as Max IV this value can increase to as much as 10⁺% making XPCS possible for SAXS which opens up possibilities for studying chain dynamics in (bio)polymers (Moller *et al* 2019), microrheology (Papa-georgopoulos *et al* 2005) and even the anomalous dynamics of magnetic anisotropic particles (Pal *et al* 2018). Coupled to new sub-microsecond detection technologies opens up real opportunities for this technique (Zhang *et al* 2018).

The intrinsically small beams, <10 μm being delivered at the ESRF after its recent upgrade (Raimondi and Einfeld 2018) and expected on DLS-II, will allow all of the experiment types hitherto exploited to be miniaturised or any heterogeneity to be measured. While currently the preserve of biomaterials such as bone (Liebi *et al* 2015) and teeth (Schaff *et al* 2015), it is certain that SAXS tensor tomography will also play a growing role in the future developments in soft condensed matter, for example, the study of foams and orientational heterogeneity in manufactured materials as can be seen now in hard material studies using tomography in other fields (Maire and Withers 2014). Indeed, early examples can already be found in literature looking at microfibrillar-reinforced composite precursors from PEBA and PET (Stribeck *et al* 2008).

While detectors are rarely developed for SAXS, the early wire chambers (Gabriel *et al* 1978) and RAPID being one of a limited number (Lewis *et al* 1997b), the soft matter community are very quick to adapt new detector technologies. Developments in single pixel photon counting technologies including energy discrimination (Martiel *et al* 2020), integrating detectors will allow new areas to develop. Anomalous SAXS as

applied to soft matter has a few devotees (Goerigk *et al* 2004, Haas *et al* 2010, Sztucki *et al* 2012, Ingham *et al* 2018) but is not currently mainstream. Advances in energy discrimination, especially in ‘windowed’ mode would open up new areas for pink-beam SAXS instruments where spectroscopy could be combined with scattering.

An area where major gains are still to be had in scattering experiments is the field of data analysis. While data reduction (Hammersley 2016, Filik *et al* 2017) and some preliminary analysis (Wu *et al* 2020, Doucet *et al* 2020, Manalastas-Cantos *et al* 2021), even GiSAXS (Lazzari 2002, Benecke *et al* 2014, Liu and Yager 2018), is available at some beamlines, with the increases in computing power it should become possible to implement multidimensional correlation spectroscopy to data sets obtained via different experimental techniques (Haas *et al* 2014) or even reverse Monte Carlo analysis on-line. For mechanical deformations one can envisage a larger role for a combination of SAXS/WAXS with computational methods like digital image correlation Thomas (Engqvist *et al* 2014). The increased use of artificial intelligence methods might also open up new possibilities (Timoshenko and Frenkel 2019). Just as a thought experiment, one could envisage a polymer extrusion experiment where the data is analysed on-line with AI techniques and the information is fed back to the extruder controls to change the processing parameters. In this way a faster convergence to processing conditions-structure-property relations might be achieved than has hitherto been possible for bulk polymers (30–40 years) and we might deliver expertise levels necessary for processing newly developed polymers which will be required for a sustainable level of materials use.

Many of the things already mentioned above also apply in x-ray spectroscopy. In some cases new undulator insertion devices may replace wigglers on spectroscopy beamlines. The availability of higher energies capable of accessing 2nd row absorption edges, while keeping the beam footprint very small, will allow the ability to analyse smaller samples with lower (i.e. environmentally relevant) concentrations of higher activity materials, including transuranic radionuclides. The same higher energy, and therefore, more penetrating characteristics of the beams will also open up new areas in development of more realistic sample environments. Some examples of areas of science that will open up with new spectroscopy beamlines are metal-based chemotherapy drugs (Anthony *et al* 2020) which hold much promise for development of selective activity to specific cancer cell types, although the precise cellular targets for many of these compounds remains unclear. Organometallic complexes of ruthenium, iridium and osmium promise this selective activity with low levels of toxicity (Zaki *et al* 2019, Simpson *et al* 2019, Renfrew *et al* 2019). Micro x-ray techniques (x-ray fluorescence imaging and XAS) will offer important insights into the action of these complexes by probing the chemistry and interactions between the introduced agents and their biological targets in a truly spatial manner. This is essential so that investigations of the drug and their interactions are at therapeutically relevant concentrations. This is currently challenging as the signal from the metal compounds is extremely weak. The enhanced flux levels delivered

using new undulator technologies on 4th generation storage rings will make these measurements possible and expand the usefulness of x-ray spectroscopy.

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Data availability statement

No new data were created or analysed in this study.

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