# research papers

# Simultaneous XAFS measurements of multiple samples

**B. Ravel,[a]\* C. Scorzato,[b] D. P. Siddons,[c] S. D. Kelly[d] and S. R. Bare[e]**

[a]National Institute of Standards and Technology, Gaithersburg, MD 20899, USA, [b]Laboratório Nacional de Luz Síncrotron, Campinas, SP, Brazil, [c]Brookhaven National Laboratory, Upton, NY 11973, USA, [d]EXAFS Analysis, Bolingbrook, IL 60440, USA, and [e]UOP LLC, Honeywell Company, Des Plaines, IL 60017, USA. E-mail: bravel@bnl.gov

A four-channel ionization chamber has been designed, constructed and tested. This ionization chamber allows X-ray absorption spectra to be collected in transmission from up to four samples simultaneously. This results in spectra that are free of systematic uncertainty in relative energy alignment introduced by scan-to-scan stability of the monochromator or of numerical uncertainty associated with a post-processing alignment algorithm, allowing, in a single shot, an absolute measure of edge shift between four samples of different valence. As four samples can be measured in parallel, the time expended over the course of an experiment to cycle the measurement environment between its rest state and the measurement condition is substantially reduced. The ionization chamber is simple in design and could be implemented at virtually any XAFS beamline with a horizontal fan of radiation such as that provided by a bend magnet or wiggler.

## 1. Introduction

One measure of the productivity of an X-ray absorption fine-structure (XAFS) beamline is the rate at which samples can be measured with adequate statistical quality. There are several details of the XAFS experiment that set the time scale required to complete a single scan or a sequence of related scans. Some of these rate-limiting details are aspects of the beamline, *i.e.* photon flux, parameters of the scan (such as integration time or settling time) and detector efficiencies, while others are details of the sample, *i.e.* absorber concentration, size of an ensemble of related samples, and the overhead required to obtain and maintain environmental conditions for *in situ* measurements (*e.g.* cryostat, furnace, electrochemistry cell and so on). Many of these rate limitations have solutions. For example, the problem of photon flux can be addressed by performing the experiment at a beamline built on a source of higher flux, and the problem of scan overhead can be addressed by slewing the monochromator continuously throughout the scan (Frahm, 1988, 1989). Other issues are more difficult to address in a real experiment. As an example, the chemistry of a sample might be dependent upon concentration, thus requiring the measurement of a specimen of low concentration.

In this paper we present a four-channel ionization chamber for the parallel measurement of four transmission samples. The basic operation and design of ionization chambers has been discussed previously (Rossi & Staub, 1949; Sharpe, 1964; Knoll, 1979; Pettifer *et al.*, 1999). This ionization chamber can be used with an *in situ* measurement environment, provided that the four samples to be maintained in that environment meet the geometrical constraints imposed by the measurement apparatus. This offers the ability to measure the XAFS of four samples simultaneously, resulting in spectra that are free of systematic uncertainty in relative energy alignment introduced by scan-to-scan stability of the monochromator or of numerical uncertainty associated with a post-processing alignment algorithm. This allows, in a single shot, an absolute measure of edge shift between four samples of different valence. Furthermore, by allowing multiple parallel measurements of XAFS spectra, this four-channel ionization chamber addresses the time constraint imposed by obtaining and maintaining the conditions of the measurement environment. As four samples can be measured in parallel, the time expended over the course of an experiment to cycle the measurement environment between its rest state and the measurement condition is reduced by about a factor of four.

## 2. Experimental

The instrument consists of four copies of a parallel-plate ionization chamber fabricated using printed circuit board (PCB) technology. The aperture of each chamber is 4 mm × 8 mm, and the chambers are 50 mm long. The four collection electrodes are formed on a single PCB. The four bias electrodes are also formed on a single PCB, and then shorted together for supply by a single voltage source. The collector and bias plates are spaced apart by vertical PCBs, machined to

interlock mechanically with the bias and collector plates to form a rigid pre-aligned structure. The vertical plates are patterned with metal strips along the length of the chambers. The topmost strip is connected to the bias potential, and the bottom strip is grounded. Tiny surface-mounted discrete resistors are soldered to these strips to form a potential divider. The purpose of these strips is to restore the uniform field gradient which would otherwise be disturbed by the presence of the dielectric plate. (Fig. 1 shows an electrical schematic diagram of the ion chamber.) The presence of the plate is essential in order to prevent charge from diffusing laterally and to prevent low-energy fluorescence from causing cross-talk between adjacent channels. The collector plates are protected against surface leakage currents by guard electrodes surrounding each collector electrode. The guard electrodes are grounded so that any currents which would otherwise produce spurious signals are shunted harmlessly to ground.

This four-channel ionization chamber is assembled much like any ionization chamber. It is placed in a metal box, which acts as a Faraday shield. Windows covered with polyimide film allow transmission of the X-ray beam. Electrical feedthroughs provide the high voltage and the four signal channels. The signal from each channel is routed to an independent signal chain of a sort typically found at an XAFS beamline, consisting of a variable gain electrometer and a voltage-to-frequency converter. A gas feedthrough is used to connect the ion chamber to a gas manifold that supplies a gas mixture appropriate to the length of the ionization chamber and the energy of the particular XAFS experiment. Argon was used for all data shown in this paper.

The experiments shown herein were performed at the National Institute of Standards and Technology XAS beamline X23A2 at the National Synchrotron Light Source, which uses a bend magnet source. The beam size is first defined by a slit assembly upstream of the monochromator of dimensions 25 mm × 1 mm. (This and all following dimensions are width by height.) After passing through a double-crystal monochromator [containing two Si(311) crystals], the beam passes through in-hutch slits of dimension 20 mm × 0.8 mm, and over a flat Rh-coated harmonic rejection mirror. A secondary slit assembly is then used to define four separate beam profiles for passage through the four-sample ionization chambers.
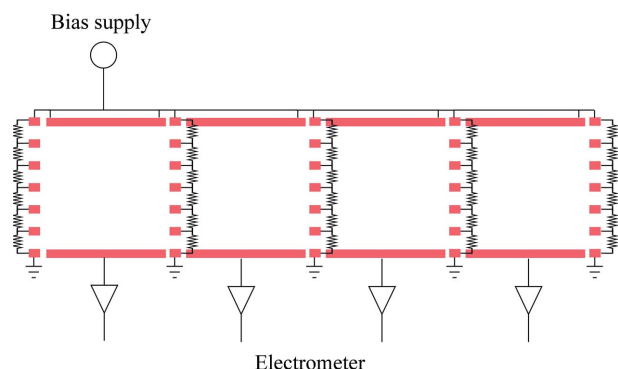


**Figure 1**
Electrical diagram of the ion chamber.

This secondary assembly consists of four 3.5 mm × 5 mm holes machined into a tantalum plate and centered in the beam defined by the hutch slits. The horizontal extent of the secondary slits thus defines the horizontal extent of each beam. The vertical extent of each beam is defined by the hutch slits.

Two such four-channel ion chamber constructions are required for the transmission XAFS experiment, one providing the four independent measurements of the incident intensity and the second providing the four independent measurements of the transmitted intensity. Both ion chambers are placed in alignment with the Ta slit assembly. Care is necessary to adjust both the lateral positions of the ion chambers and their yaw, to ensure that the sampling volume of each ion chamber is parallel with its corresponding beam. The excess vertical height of the secondary slits and of the chambers themselves makes alignment in that direction very easy.

The experiment for which these detectors were developed involves *in situ* reduction of catalytic materials in $H_2$ flow during a ramp in temperature. The samples are heated in a tube furnace of clam-shell design and are contained in a metal cylinder sample holder which fits snugly in a quartz tube resting at the center of the furnace. The sample holder is bored with four holes for sample containment. These holes are spaced commensurately with the spacing of the ionization chamber with each hole slightly wider than the holes in the Ta slit assembly. In this way the sample is larger than the beam, thus a homogeneously packed sample will be measured properly by the incident beam. This sample holder proved to be a useful sample holder even at room temperature, thus much of the data presented in this manuscript were measured using it.

The natural log of the ratio of the incident and transmission channels is computed on a point-by-point basis for each of the four measurement channels. The raw data files thus contain at least nine columns: the incident energy, four columns of incident intensity and four columns of transmitted intensity. A small program was written to convert each data file into the native project format of the *Athena* data analysis program (Ravel & Newville, 2005), which was used for all subsequent data processing.

## 3. Results

### 3.1. Detector performance

As an initial test of the ionization chambers, a single platinum foil, wide enough to cover all four measurement channels, was placed between the incident and transmission detectors. Each channel represents an individual transmission XAFS scan. Fig. 2 shows the results of four parallel simultaneous XAFS measurements of the Pt foil. The signal from each of the four channels is highly reproducible, even well above the absorption edge, indicating that the detector works well.

The potential for cross-talk between the four channels was investigated by translating one vertical blade of the hutch slits
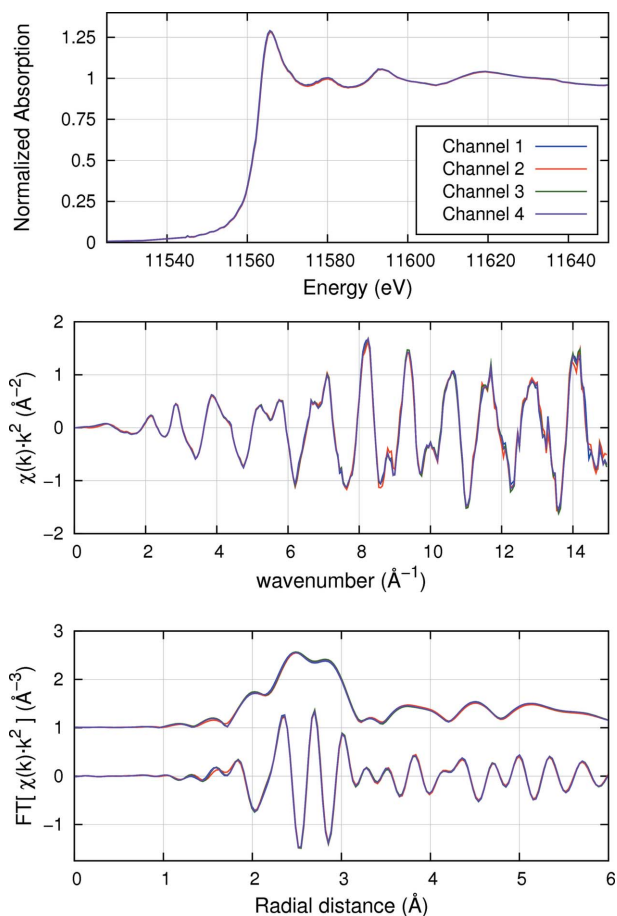
# research papers



**Figure 2**
Pt $L_3$-edge XAFS data measured on a platinum foil in all four channels. The XANES (top), extracted EXAFS signal (middle) and the magnitude and real part of the Fourier transform (bottom) are shown.
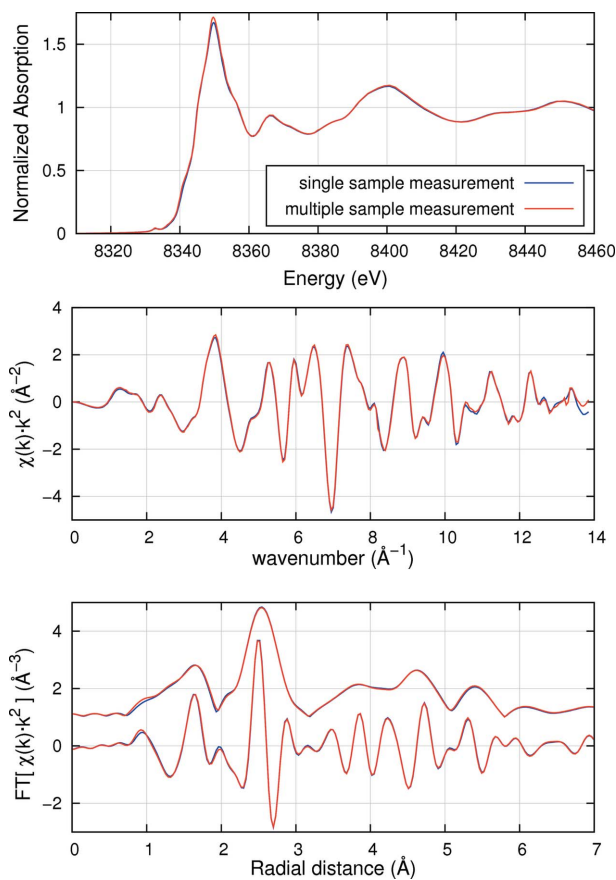


**Figure 3**
Measurement of cross-talk between adjacent channels of the four-channel ionization chamber. The blue line (left-hand axis) is the signal measured from one of the channels, and the red line (right-hand axis) is the signal from the adjacent blocked channel.

to successively cover channels of the ionization chambers. By repeatedly measuring Pt XAFS scans with one or more channels blocked by the vertical blade, it was possible to quantify cross-talk between the channels. Fig. 3 shows the



**Figure 4**
Ni $K$-edge XAFS data measured on NiO using one channel of the four-channel apparatus compared with the same sample measured using the normal XAFS beamline instrumentation. The XANES (top), extracted EXAFS signal (middle) and the magnitude and real part of the Fourier transform (bottom) are shown.
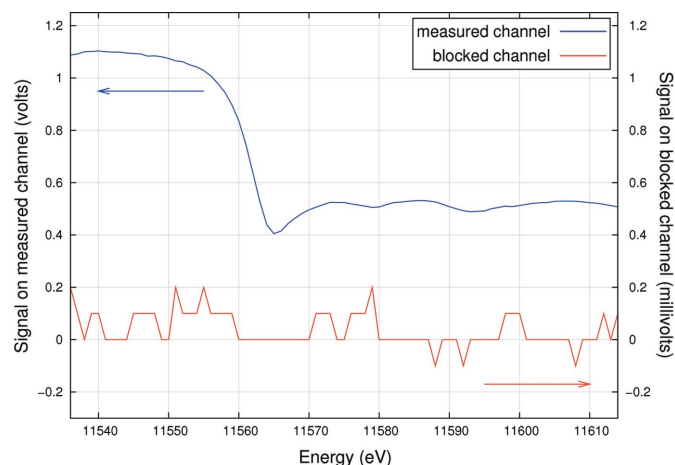
results of one such experiment. In this example, the middle inboard channel was blocked while the middle outboard channel was measuring normally. In the outboard channel, the voltage measured on the transmission detector drops substantially above the edge, as expected. The adjacent channel shows no response crossing the edge. It can thus be concluded that the guard electrodes and patterned vertical plates perform well, protecting the signal quality on each channel. Given the large number of signal channels, care must also be taken to avoid coupling elsewhere in the signal chains.

It is instructional to compare the quality of the XAFS data obtained using this four-channel ionization chamber with that obtained using the standard experimental configuration of the beamline, *i.e.* using one full-size standard ion chamber to measure the incident intensity and one to measure the transmitted intensity. Fig. 4 shows the results of such a comparison where the Ni $K$-edge XAFS data of NiO from the two experiments are shown. Note that the comparison is between a spectrum measured using a single channel of the four-channel detector and one measured using the standard configuration. There is excellent agreement between the two spectra, even well above the absorption edge. This provides confidence that the signal quality from a single channel measured using this

detector is comparable with that measured using a more traditional ion chamber.

## 3.2. Applications

To demonstrate some of the potential applications of this four-channel ionization chamber we show two examples: (i) the use of the detector to minimize systematic scan-to-scan uncertainties in the determination of the position of an absorption edge, and thus to determine the edge shift as a function of formal oxidation state, and (ii) the ability to quickly compare the *in situ* chemistry of four catalyst samples.

First, the determination of the absorption-edge energy for four samples simultaneously. In this experiment, samples of appropriate absorption thickness were prepared from rhenium metal, rhenium (IV) oxide (ReO$_2$), rhenium (VI) oxide (ReO$_3$) and the Re(VII) compound ammonium perrhenate (NH$_4$ReO$_4$). Each sample was mounted so that its absorption spectrum was measured by one of the channels in the four-channel ionization chamber. In this manner the XAFS of all four samples was collected simultaneously, with a single energy scan of the monochromator. The resulting Re $L_3$-edge XANES data from a single scan are plotted in Fig. 5.

For the four samples measured at a time, this measure of absorption edge shift is free of systematic uncertainty introduced by scan-to-scan stability of the monochromator (which should be excellent for a monochromator equipped with an axial encoder) or of numerical uncertainty associated with a post-processing alignment algorithm. However, if the monochromator crystals are not carefully aligned parallel to the incoming beam, the four beams will differ slightly in horizontal angles resulting in small energy shifts. Thus this detector provides, in a single shot, an excellent measure of edge shift between four mounted samples of different valence.
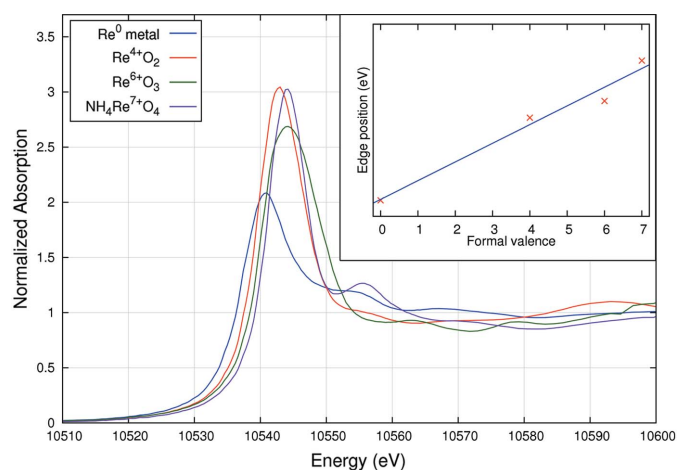


**Figure 5**
Re standards of four different formal valence states measured in parallel using the four-channel ionization chamber. As these are simultaneous measurements, the energy shifts in edge position are measured without certain systematic or numerical uncertainties associated with sequential measurements. Inset: plot of the Re $L_3$ absorption edge position *versus* formal oxidation state of the rhenium in a series of oxidic rhenium compounds. The line is a linear fit to the data.

The resulting absorption edge shift (edge position is defined as the maximum of the first derivative of the XANES spectrum) as a function of formal oxidation state of the four rhenium compounds is plotted in the inset of Fig. 5. There is a linear correlation of the absorption-edge energy position as a function of oxidation state, as is commonly found for many metal oxides (Wong *et al.*, 1984; Ressler *et al.*, 2002; Bare & Ressler, 2009).

The more far-reaching example is the application to *in situ* XAFS studies of catalysts. As discussed in the *Introduction*, a benefit of this apparatus is to allow the parallel measurement of samples under a particular *in situ* condition. A catalyst often needs to be activated prior to characterization and analysis. This activation might involve calcination or reduction, or some combination of these. Indeed it may also be useful to study these calcination and reduction steps themselves as each of these provides information on the catalyst that could be linked to catalytic activity. For example, changes in the XANES spectra during a linear temperature ramp indicate the rate of reduction of the materials under H$_2$ flow thus providing information on the dispersion of a metal or of the degree of interaction with other components in the system. These thermal cycling sequences can often last for several hours: ramp rates of a few degrees per minute, maximum temperatures of a few hundred degrees Celsius, and an extended dwell at the maximum temperature. Thus, if such processes are to be studied *in situ*, this poses a severe limitation for sample throughput at an XAFS beamline. This is particularly true for the study of catalysts of industrial importance where often many similar samples are compared. While a brighter source (an insertion device or a high-field bend) would certainly allow for faster collection of individual spectra from a single sample, the lengthy (few hours) temperature ramp and dwell would still dominate the time budget. Although a brighter source would allow more rapid sequential measurement of multiple samples during and after the ramp, the method described here presents a significant advantage in that the four samples are guaranteed to be measured under identical conditions using the four-channel ionization chamber.

In the example shown here, four different 4.6 wt% Ni/$\gamma$-Al$_2$O$_3$ catalysts were loaded into the *in situ* reactor that was specifically designed to be compatible with the four-channel ionization chamber. The full details of this study are reported elsewhere (Bare *et al.*, 2009). Briefly, the catalysts were prepared by incipient wetness impregnation of $\gamma$-Al$_2$O$_3$ with nickel nitrate solution followed by calcination for varying lengths of time at different temperatures either in nitrogen or in 5% steam in air. Appropriate amounts of each catalyst were pressed into a custom sample holder which was placed inside the *in situ* XAFS reactor. The reactor was a modification of the design used previously (Bare *et al.*, 2006). The Ni $K$-edge XANES data were recorded as the samples were heated to 923 K at a ramp rate of 5 K per minute in a flow of 100% hydrogen. These spectra are plotted in Fig. 6. Each panel shows the evolution of the XANES spectra as a function of temperature for each of the four samples. From these data it can be seen that the reducibility of the Ni is a strong function
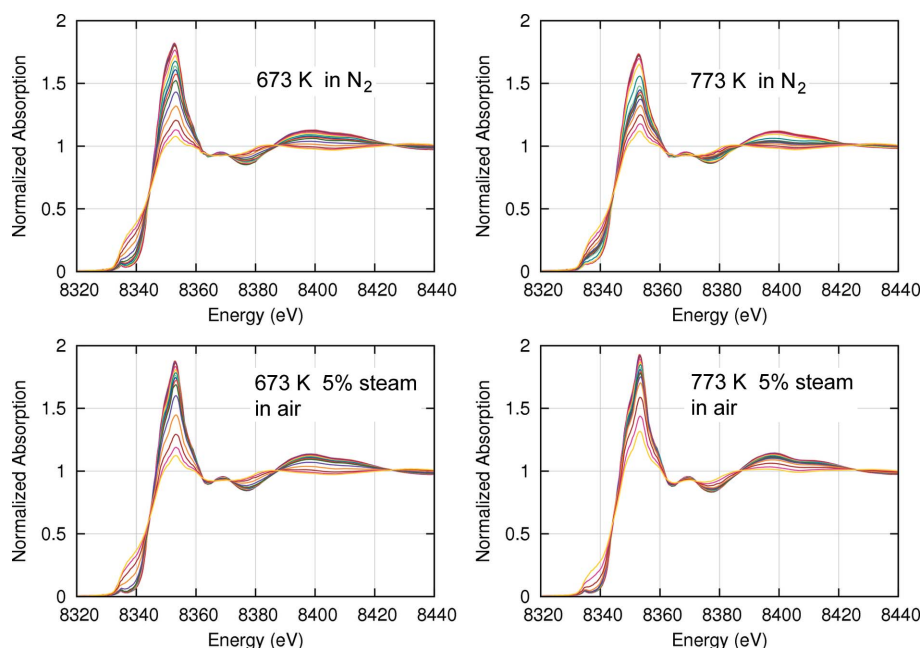
# research papers



**Figure 6**
Temperature programmed XANES at the Ni *K*-edge during the *in situ* reduction of four different preparations of Ni/$\gamma$-Al$_2$O$_3$. The calcination conditions were 673 K for 8 h in nitrogen, 773 K for 8 h in nitrogen, 673 K for 8 h in 5% steam in air, and 773 K for 8 h in 5% steam in air. The ramp rate was 5 K min$^{-1}$ from room temperature (highest intensity of the white line at 8353.0 eV) to 923 K (lowest intensity of the white line).

of the initial calcination temperature and also whether steam was present during the calcination. Full analysis of these data is discussed in a separate paper (Bare *et al.*, 2009). In this way, the ensemble of sample preparations that we were able to characterize was substantially larger than what we could characterize by other means. At the same time, this characterization benefits by having groups of four samples measured under identical conditions of temperature and H$_2$ flow.

## 4. Future prospects

We believe that this four-channel ionization chamber can be used to drastically improve the productivity of many XAFS beamlines throughout the world as beam time is always a precious commodity. The technology described here could be implemented at virtually any XAFS beamline with a horizontal fan of radiation (typically a bend magnet or a wiggler). The detectors could be patterned and assembled by any electronics shop. Automation of the lateral and yaw positioning of the detectors and the sample holder would tremendously simplify the tedious chore of aligning all the components required for the experiment. Also, this methodology requires a large number of signal chains. While many different signal chain solutions are in use at synchrotrons around the world, one common solution involves commercial single-channel electrometers housed in rather large boxes. The large number of measurement channels requires that substantial space be allocated in close proximity to the ionization chambers to house all these electrometers. Consequently, a compact combined electrometer and voltage-to-

frequency conversion solution would be a huge benefit. Additionally, for experiments requiring specialized *in situ* measurements, custom sample holders and ancillary equipment are required which are commensurate with the detectors.

The methodology presented in this manuscript specifically addresses simultaneous measurements of XAFS in the transmission geometry. It is also useful to consider the potential application of this methodology to fluorescence XAFS. The fluorescence geometry would require reconfiguration of the sample and replacement of the transmission chamber with an array of fluorescence detectors. Perhaps the simplest approach would be to stagger the samples in the direction of the beam path so that each of the four beams strikes its sample at a different distance from the incidence detector. Each sample would then use its own fluorescence detector, which could be either an ionization chamber or an energy-discriminating detector. In this configuration, shielding between the samples would be essential to avoid cross-contamination of the fluorescence signals. A second approach would involve projecting the four fluorescence signals onto a strip detector and either collimating or geometrically deconvoluting the signals. This would work best with the strip detector close to the sample, which may be incompatible with *in situ* measurements. A third approach would be to use collector optics from a confocal detection system with one such optic pointed at each position where a beam strikes the sample holder. None of these approaches offers a clear advantage, although the appeal of simultaneous fluorescence detection is as obvious as for transmission.

Although this apparatus is of substantial immediate benefit to our scientific objectives and to operations at beamline X23A2, its real impact would be at a wiggler beamline with the experimental station situated far from the source. With high flux and broad horizontal fan, a larger number of parallel channels could be used. Consider the damping wiggler proposed (NSLS-II, 2007) for NSLS-II, which is expected to be operational in 2015. With an experimental hutch placed 40 m from the source and with no focusing of the divergent wiggler beam, the beam profile available to the experiment would be in excess of 50 mm at the sample position. Maintaining the same channel dimensions as the current apparatus, an expanded design could incorporate ten channels. Each 3.5 mm slice of beam from the unfocused wiggler would be brighter than the entire X23A2 NSLS bend magnet beam. This detection apparatus could be combined with a slew scanning monochromator to increase beamline productivity enormously. With a modest slew scanning speed and with the

exceptional brightness of the wiggler source, a statistically significant EXAFS scan out to a photoelectron wavenumber of 15 Å$^{-1}$ or higher could be obtained in under 60 s. It would thus be possible to screen around 600 samples per hour by exploiting both slew scanning and parallel measurement.

## References

Bare, S., Kelly, S. & Ravel, B. (2009). Unpublished.

Bare, S. R., Mickelson, G. E., Modica, F. S., Ringwelski, A. Z. & Yang, N. (2006). *Rev. Sci. Instrum.* **77**, 023105.

Bare, S. R. & Ressler, T. (2009). *Advances in Catalysis*, Vol. 52, pp. 339–465. New York: Academic Press.

Frahm, R. (1988). *Nucl. Instrum. Methods Phys. Res. A*, **270**, 578–581.

Frahm, R. (1989). *Rev. Sci. Instrum.* **60**, 2515–2518.

Knoll, G. (1979). *Radiation Detection and Measurement*. New York: Wiley.

NSLS-II (2007). *Summary of NSLS-II Source Properties*. BNL Technical Report. Brookhaven National Laboratory, New York, USA.

Pettifer, R. F., Borowski, M. & Loeffen, P. W. (1999). *J. Synchrotron Rad.* **6**, 217–219.

Ravel, B. & Newville, M. (2005). *J. Synchrotron Rad.* **12**, 537–541.

Ressler, T., Wienold, J., Jentoft, R. E. & Neisius, T. (2002). *J. Catal.* **210**, 67–83.

Rossi, B. & Staub, H. (1949). *Ionization Chambers and Counters*. New York: McGraw-Hill.

Sharpe, J. (1964). *Nuclear Radiation Detectors*. London: Metheun.

Wong, J., Lytle, F. W., Messmer, R. P. & Maylotte, D. H. (1984). *Phys. Rev. B*, **30**, 5596–5610.