
BY R. P. PHIZACKERLEY, Z. U. REK* AND G. B. STEPHENSON†

Stanford Synchrotron Radiation Laboratory, SLAC, PO Box 4349, Bin 69, Stanford University, Stanford, CA 94305, USA

S. D. CONRADSON AND K. O. HODGSON

Department of Chemistry, Stanford University, Stanford, CA 94305, USA

T. MATSUSHITA

Photon Factory, National Laboratory For High-Energy Physics, Oho-machi, Tsukuba-gun, Ibaraki 305, Japan

AND H. OYANAGI

Electrotechnical Laboratory, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

(Received 7 September 1982; accepted 21 October 1982)

Abstract

The design and evaluation of an energy-dispersive spectrometer to measure X-ray absorption spectra rapidly using a synchrotron-radiation source is presented. The method employs a cylindrically bent triangular crystal to focus and disperse a quasi-parallel polychromatic X-ray beam onto the sample. The beam passing through the sample then diverges towards an X-ray detector where beam position can be correlated to energy. Both concentrated and dilute samples were measured on X-ray film and with an electronic linear photodiode array detector and the data analysed to determine the resolution obtained and the data quality. This method is shown to provide an efficient way to obtain high-quality EXAFS and absorption-edge data and should permit kinetic studies to be performed on small samples with good counting statistics. The method should find application in the fields of biophysics, chemistry and materials science.

Introduction

The utility of X-ray absorption spectroscopy (XAS) for investigating electronic and structural details of absorbing metal atoms has markedly increased during the past decade. This is in part due to improved theory (Sayers, Stern & Lytle, 1971) and to the availability of synchrotron-radiation sources. The high X-ray flux available from electron storage rings allows absorption spectra to be collected in a few minutes with excellent signal-to-noise ratio compared with the many hours typical for even the most intense conventional X-ray sources.

The applications of XAS to solve structural problems in biophysics, materials science and chemistry have been extensively reviewed (Shulman, Eisenberger & Kincaid, 1978; Cramer & Hodgson, 1979; Teo, 1981). Analysis of features on and just above the elemental absorption edge can provide information about site symmetry and electronic structure. The fine structure extending above the absorption edge (EXAFS) provides metrical details (distances and numbers of atoms) for coordination shells surrounding the absorbing atom.

Most XAS studies reported to date have utilized spectra recorded using monochromatized radiation in a point-by-point mode. To study transient or short-lived species, it would be useful to record the whole spectrum simultaneously. This is possible using an X-ray dispersive geometry and a position-sensitive detector. Several different dispersive methods have previously been used on laboratory X-ray sources (Taniguchi, Oka, Yamaki & Ikeda, 1980; Kaminaga, Matsushita & Kohra, 1981) and on a laser plasma source (Mallozzi, Schwerzel, Epstein & Campbell, 1979). These spectrometers have all utilized a flat dispersing crystal and cannot practically be applied to a synchrotron-radiation source since a very large crystal and detector would be required owing to the long source-to-spectrometer distance necessary at storage-ring facilities. Another type of dispersive
Method

A description of the optics of this method has been discussed in detail before (Matsushita & Phizackerley, 1981). In the present paper, we will review some of the most important features which are relevant to the interpretation of our results. The experimental geometry is shown schematically in Fig. 1. A cylindrically bent triangular Si(111) crystal, placed 17.54 m from the synchrotron-radiation-source point, is used in the reflection geometry to disperse and focus the quasi-parallel polychromatic beam of X-rays. This energy-dispersed beam converges to a focus at the sample position; the beam transmitted through the sample then diverges towards an X-ray detector. The position of the beam, incident on the X-ray detector, can be correlated to the X-ray energy. The beam position was found to be almost linearly related to energy. If the spatial intensity distribution across the dispersed beam is measured, in the presence and absence of the sample, an X-ray absorption spectrum can subsequently be obtained. As the angular range within the dispersed beam is very small (typically only a few degrees) the variation in path length through the sample is negligible. Since the source is located at a distance and outside the Rowland circle, the focal point is located within the Rowland circle and in practice has a horizontal dimension of about 0.6 mm. This is the optimum position for the sample since it minimizes both the effects of nonuniformities in the sample and the volume of sample required for the experiment. In each of the experiments presented in this paper, the full horizontal width of the focal point was used and the sample size was larger than the dimensions of the focus.

When the surface of the dispersing crystal is parallel to the diffracting planes, the crystal-to-focus distance $q$ can be derived from

$$1/q + 1/p = 2/(R \sin \theta_B),$$

where $p$ is the source-to-crystal distance, $R$ is the radius of curvature of the crystal and $\theta_B$ is the Bragg angle for the central X-ray beam.

The total energy range $\Delta E$ obtained in this geometry, for a fixed crystal position, depends on its radius of curvature $R$ and is given by the formula

$$\Delta E = 2 \pi R \sin \theta_B.$$
\[ \Delta E = E_0 L (1/R - \sin \theta_B/p) \cot \theta_B \]

where \( E_0 \) is the energy of the central beam and \( L \) is the length of the crystal which is irradiated. In the experiments presented here, the energy range varies between 500 and 1000 eV, although an even larger range is possible.

The energy resolution of the method is primarily dependent on (1) the horizontal width of the X-ray source, (2) the spatial resolution of the detector and (3) the intrinsic angular width of diffraction by the dispersing crystal.

When a bent and ground crystal (Johansson-type geometry) is considered, the energy spread, \( \delta E_1 \), owing to the horizontal width (\( \Delta S \)) of the X-ray source, can be derived from

\[ \delta E_1 = E_0 k \left( \frac{1}{R \sin \theta_B} - \frac{1}{p - k} \right) \frac{\Delta S}{\cot \theta_B} \]

by using graphical representations that are discussed by Matsushita & Kaminaga (1980), where \( k \) is given by

\[ k = \left( \frac{2}{R \sin \theta_B} - \frac{1}{q + d} \right)^{-1} \]

and where \( d \) is the focus-to-detector distance.

The energy spread, \( \delta E_2 \), owing to the spatial resolution (\( \Delta r \)) of the detector, is given by

\[ \delta E_2 = E_0 \frac{\Delta r}{d} \left( \frac{1/R - \sin \theta_B/p}{2/R - \sin \theta_B/p} \right) \cot \theta_B. \]

Ray-tracing methods confirmed that the above equations for \( \delta E_1 \) and \( \delta E_2 \) also apply well to the cylindrically bent crystal used in this spectrometer.

The energy spread, \( \delta E_3 \), owing to the intrinsic angular width (\( \omega \)) of diffraction by the dispersing crystal, is given by

\[ \delta E_3 = E_0 \omega \cot \theta_B. \]

Using the above equations, values for \( \delta E_1 \), \( \delta E_2 \) and \( \delta E_3 \) were estimated to be 0.78, 1.31 and 1.08 eV, respectively, for a single bent silicon crystal with the face parallel to the (111) reflecting planes and using the following parameters: \( R = 295 \text{ cm}, \ p = 17.54 \text{ m}, \ d = 375 \text{ mm}, \ \Delta S = 4.4 \text{ mm}, \ \Delta r = 0.025 \text{ mm}, \ \omega = 2.7 \times 10^{-5} \text{ rad} \) and \( E_0 = 9 \text{ keV} \).

The overall energy resolution, \( \delta E \), can be estimated from

\[ \delta E = (\delta E_1^2 + \delta E_2^2 + \delta E_3^2)^{1/2}. \]

Using the parameters derived above, the overall energy resolution has been estimated to be 1.87 eV, which compares well with our experimental estimates.

**Description of the spectrometer**

The energy-dispersive X-ray absorption spectrometer is shown in Fig. 2. It employs a cylindrically bent triangular silicon crystal, similar to that described by Lemonnier, Fourme, Rousseaux & Kahn (1978), as an energy-dispersing element. This triangular crystal measures 108.5 mm from base to apex, and has a base of length 28 mm and a thickness of 0.6 mm. The reflecting surface was measured to be parallel to the Si(111) planes to within a small fraction of one degree, and both the reflecting surface and the back surface have been polished and etched. The crystal is supported by a holder that was designed to accommodate a range of crystal lengths from 62 to 114 mm. Different crystal cuts, symmetric and asymmetric, can also be
accommodated. The crystal is clamped at the base of the triangle, shown in more detail in Fig. 3. The apex of the triangular crystal is displaced by a spring-loaded ball race which is translated by means of a micrometer adjustment. The ball race ensures a repeatable and almost frictionless contact to the crystal. This assembly is mounted on a Klinger TR80 rotation stage which allows the crystal to be rotated about a horizontal axis perpendicular to the crystal plane. This adjustment, which is under micrometer control, has been provided so that most, or all, intensity 'glitches' in the dispersed beam resulting from multiple-diffraction effects can be shifted away from the energy range of interest. This rotation stage is mounted on a Klinger MR80.25 translation stage which is used to position the surface of the crystal at the center of the incident beam of white radiation. The whole assembly is then mounted on a Huber 410 goniometer to permit the crystal to be accurately inclined to the incident beam. The goniometer is driven by a stepping motor through a 20:1 gear box, with one motor step providing a rotation of 0.00025°.

The dimensions of the white X-ray beam, incident on the dispersing crystal, are defined by a set of Huber tantalum X-Y slits. These slits are adjustable from 0 to 26 mm in both the horizontal and vertical directions. The direct beam can be rapidly switched on and off by means of a high-speed lead shutter attached to a pneumatic piston. Since the X-ray beam is dispersed in the horizontal, resulting in a horizontal energy-dispersed spectrum, the lead shutter is translated in the vertical direction. This ensures that all energies are recorded for the same time interval. The shutter is controlled by an electronic timer which provides exposure times from approximately 0.1 to 1000 s. The shutter and the incident-beam pipe are enclosed in lead shielding to eliminate background scattering.

The other spectrometer components are mounted on a Klinger GCM80 optical bench which extends 798 mm from the center of the dispersing crystal. This bench is mounted in turn on a Klinger TR120 rotation stage, which is coaxial with the crystal goniometer and permits the optical bench to be rotated through an angle of up to 57° from the direct beam. This angle is set to accept the central energy ray of the absorption spectrum. The maximum 2θ angle of 57° corresponds to an X-ray energy of 4.144 keV when a Si(111) energy-dispersing crystal is used. Owing to the horizontal polarization of synchrotron radiation, the X-ray flux is reduced by approximately 46% at this angle. However, although this reduction is significant, it is clearly not a serious problem. At the Fe K edge, with an X-ray energy of 7.1112 keV, the reduction in intensity is only 16%.

Since the optical bench and components are relatively heavy, a stainless-steel wheel assembly has been placed beneath the optical bench for additional support. This wheel makes contact with a large flat aluminium base plate which is aligned in the horizontal plane. The base plate is kinematically located to three positioning pads which can be fitted to the base of the radiation protection hutch at the experimental station. Three adjustment screws, two of which are positioned beneath the direct-beam path and the third positioned half-way between and to one side of the other two, make the alignment of the complete spectrometer to the direct beam straightforward and simple operation.

Referring to Fig. 2, the components shown mounted on the optical bench from right to left are as follows: (1) Tantalum adjustable X–Y slits to define the dispersed beam before the sample and to reduce the X-ray scattering from the crystal support and the surrounding air. (All the components which are near to the X-ray beam have been constructed, where possible, of aluminium to reduce fluorescence.) (2) Sample holder which can accommodate a variety of standard and non-standard sample holders and cells. (3) One of a set of helium tubes, of different lengths, to reduce air absorption and scattering. (4) A flat platinum-coated fused quartz X-ray quality mirror which is 20 cm long, 6 cm wide and 2 cm thick. A platinum coating was chosen since it offers a high reflectivity, a relatively large critical angle for the X-ray wavelengths used in these experiments and has been found to be stable over long periods in a high-flux X-ray beam, providing the mirror is coated under ultra high vacuum and the surface is electrically grounded when used in the X-ray beam. This mirror, which can be translated vertically by means of a Klinger MV80 vertical motion adjustment and inclined to the horizontal X-ray beam with a Klinger TG80 inclination stage, is used to eliminate the transmission of the higher-energy harmonic components of the dispersed X-ray beam. This is achieved by setting the mirror to just below the critical angle for the fundamental energy range of interest. Without a mirror, the harmonics due to the 333, 444, 555, ... reflections are also reflected, when a silicon crystal cut parallel to the (111) planes is used as the dispersing element. The 222 reflection is systematically absent in the diamond-type structure of the silicon crystal. At the normal SSRL storage-ring beam energy of 3 GeV, the intensity of these harmonic components would severely reduce the signal-to-background ratio of the recorded X-ray absorption spectra. The mirror is mounted inside a helium enclosure, which has kapton windows, to reduce absorption in the beam path. (5) A set of tantalum adjustable X–Y slits, with a lead screen attached, to reduce scattering from the air path and mirror and fluorescent scattering from the sample before the dispersed X-ray absorption spectrum is passed to the X-ray detector. (6) The X-ray detector shown in Fig. 2 is X-ray film. Interchangeable Enraf–Nonius film cassettes are mounted on a speci-
an energy-dispersive X-ray spectrometer. This holder incorporates a vertical translation, with a spring-loaded ratchet, to permit 11 separate X-ray absorption spectra to be recorded on a single piece of X-ray film. Alternatively a computer-controlled photodiode array detector is used, which is described in detail below.

Each of the components described above is mounted on the optical bench by means of a Klinger CM80 adjustable carriage. These carriages allow each component to be optimally positioned for any given energy range. A computer program has been written to calculate the angular and translational positions of all adjustable spectrometer components for a given energy range, crystal type, etc. In the near future, many of the adjustments will be motorized and under computer control.

**Film**

The X-ray film should have a high quantum-detection efficiency at the X-ray wavelengths used in these experiments. It should also have a grain size which is small compared with the size of the X-ray absorption features to be recorded to provide sufficient resolution and ensure a statistically accurate measurement of optical density. Since the film speed is dependent on the grain size, clearly a compromise has to be made. We used Kodak Industrex SR-5 single-coated X-ray film in these experiments. This film has a very small grain size and is the slowest Kodak X-ray film available. Using 7 keV radiation, we estimated the film speed to be between 80 and 100 times slower than the Kodak no-screen NS-2T film (the fastest Kodak X-ray film available) used in our earlier experiments. It should be noted that an increase in absorption in the sample results in a decrease in optical density recorded on the film. The relation between the incident X-ray flux and the resulting optical density of X-ray film is approximately linear up to about 1-2 optical density units (Morimoto & Uyeda, 1963). The useful optical density range can be extended to approximately 2-5 OD by using a parabolic correction, although no correction was made in the data presented here. During film scanning, care was taken to select a microdensitometer aperture which is small enough so that the OD range within the measuring aperture is not too large, otherwise the measured optical density will be lower than the average optical density within the aperture (Wooster, 1964). However, the aperture should not be too small or the film granularity will reduce the accuracy of the measurement.

The **linear position-sensitive detector**

Clearly the success of the energy-dispersive method ultimately depends on the availability of a detector system which has a high quantum-detection efficiency for X-ray photons in the energy range 5 to 20 keV, is capable of handling high count rates and can resolve the energy-dispersed absorption spectrum to high resolution. Furthermore, since the angular spread of X-rays from the dispersing crystal is quite small, the detector should have fairly small dimensions.

The linear position-sensitive detector system used in these trial experiments has been designed around a light- (and soft-X-ray-) sensitive monolithic self-scanning silicon photodiode linear array manufactured by EG&G Reticon (model RL1024SF) (EG&G Reticon, undated; Koppel, 1976; Gamble, Baldeschwieler & Griffin, 1979; Borso & Danyluk, 1980; McGinnis, 1980). The advantages of photodiode arrays over position-sensitive proportional counters include much higher count-rate capability, which is due to the integration of the signal on the detector, higher spatial resolution and solid-state mechanical stability. The major disadvantage is their higher absolute background noise, which is due to the extremely small signals to be measured.

The photodiode array used in these experiments has 1024 sensing elements, each 2.5 mm high and spaced 25 μm apart giving an overall active area of 2.5 × 25.6 mm. Each pixel, therefore, has a rectangular geometry with a 100:1 aspect ratio which provides an adequate resolution with a wide dynamic range. Although X-rays can be detected directly by the photodiode array, irreversible radiation damage occurs unless the sensitive areas on the device are carefully shielded. To avoid this problem, the detector used in these experiments incorporates an X-ray phosphor which is optically coupled to the array by means of a 3.2 mm thick coherent fibre-optics face plate. This face-plate thickness permits the detection of X-ray photons up to an energy of 100 keV with no radiation damage. We have coated the fibre-optics face plate with an approximately 25 μm thick layer of YVO₄:Eu phosphor, which has a high intrinsic quantum efficiency and provides a red fluorescence. This phosphor layer was made by suspending powdered YVO₄:Eu in a solution of 10% rubber cement and 90% hexane. This suspension was poured onto a 6 μm thick kapton film and after the phosphor had settled, excess liquid was removed and the layer allowed to dry. The phosphor was then adhered to the fibre optics with glycerol.

The detector array is attached to a cooled copper block which is mounted inside an evacuated enclosure to eliminate condensation. The array is operated at 223 K to reduce both the magnitude and the fluctuations in the thermal dark current of the photodiodes to a negligible level. X-rays enter the enclosure through a 7 μm thick Kapton entrance window.

The design of the electronic system, which controls the array and processes the output, is very similar to that described by Vogt, Tull & Kelton (1978). During operation, each photodiode is reverse biased to 5 V and left to float with a charge due to its intrinsic
capacitance. Incident X-ray photons are converted to light by the phosphor, some of which are conducted by the coherent fibre-optics face plate to the diodes beneath. Photoelectrons produced in each silicon diode reduce the charge by an amount proportional to the time-integrated light intensity incident on that diode. After a preset integration period, the diodes are connected in sequence to one of two output lines (one for odd numbered pixels and the other for even numbered pixels) and the amount of charge which flows to recharge each diode provides the output signal. This integration period is under computer control and is variable from 0.125 to over 1600 s.

Commercial DC coupled charge-sensitive preamplifiers (Canberra 2001), mounted in close proximity to the array, amplify these charge pulses into voltage steps. A multiplexer sequences all the pulses onto a single line. This signal is fed to a differentiating amplifier and then to an integrator, each with an appropriate time constant for low- and high-frequency-noise immunity, respectively. The signal is subsequently digitized by a CAMAC 12-bit A/D converter and fed to a CAMAC-based 8085 microprocessor which stores the image on flexible diskettes for further processing.

This detector system had been optimized for the low signal levels obtained in a dynamic small-angle scattering study (Stephenson, 1982) and the readout electronics saturates at approximately $1.4 \times 10^4$ 8.9 keV photons element$^{-1}$ (0.7% of the saturation value for the sensing element itself). At the shortest available integration time, this corresponds to a maximum flux of approximately $10^5$ counts s$^{-1}$ element$^{-1}$. Owing to the high intensity of transmission X-ray absorption experiments, it is necessary to attenuate the incident beam to avoid saturation in the electronics. If, however, the detector read-out electronics are optimized for these high intensities by a reduction in overall gain, an order of magnitude improvement in the shot-noise-limited statistics could be obtained. Alternatively, the speed of the read-out could be increased by a factor of 100 for rapid kinetic studies (approximately 1 ms per read-out) with the same incident flux.

For each pixel, the r.m.s. fluctuation in the measured signal due to the intrinsic noise sources in the detector is equivalent to approximately 48 incident 8.9 keV photons, resulting in a dynamic range of approximately 300. (The dynamic range is the ratio of the saturation signal to the noise level.) This noise level corresponds to a charge of approximately 2200 electrons at the detector, which is slightly higher than the theoretical noise level due to the capacitance of the photodiode $[(kT/C)^{1/2}]$. Noise sources and methods of their elimination have been discussed in the literature (Vogt, Tull & Kelton, 1978; Simpson, 1979).

The detector response as a function of energy has not been measured. The response is estimated by the amount of energy absorbed in the approximately 25 μm layer of YVO$_4$:Eu phosphor. Owing to light spread within the phosphor, the thickness of this layer limits the resolution of the detector to approximately 2 pixels as estimated from the image projected by a copper mask. We are pursuing the development of a thinner and more homogeneous fast phosphor at this time.

Data analysis

When X-ray film was used as a detector, multiple exposures were taken of each sample and background (with no sample in place), over a range of exposure times. The size of the recorded X-ray absorption pattern was typically 1 to 1.7 mm in the vertical and between 25 and 30 mm in the horizontal. Not only the edge, but also the EXAFS features are clearly visible on the X-ray film (see Fig. 4). These multiple exposures of the same sample were visually inspected to estimate which exposure time would provide the greatest signal intensity without being overexposed. Film scanning was then performed on a Perkin Elmer model 1010A microdensitometer with a 10-bit A/D converter. The scanning-slit size was set to 10 μm in the horizontal and 400 μm in the vertical. Films were scanned by making between two and four horizontal passes over the exposure, the number determined by the height of the exposure. A sufficient margin was left between the edges of the measuring slit and the exposed area to avoid edge effects. Passes on the same exposure were not averaged at this point in the data analysis.

The Reticon linear photodiode array detector system provided 1024 pixels of digital data each time it was scanned. Care was taken to avoid saturation of the detector by choosing a sufficiently short time interval between scans (typically 125 ms) and by inserting aluminium foils, if necessary. In order to achieve adequate counting statistics, it was necessary...
to sum the data from many consecutive scans. Since the detector dark current varied between individual pixels and also slowly changed with time, a dark-current scan was recorded immediately before data collection so that a correction to the data could be made. Data were collected, with and without the sample in place, for a preselected number of scans, typically 100, and with a preselected time between each scan.

If the data were not ratioed with a background, to convert to absorbance, they were 'inverted' by subtracting each value from the highest A/D converter number (1024 for the scanner and 4096 for the Reticon detector) so that the numerical values increased across the absorption edge. The dark current for each pixel of the Reticon detector was processed in an identical manner, and was then directly subtracted from the signal data.

Following these operations, each data set was inspected to check signal quality and to identify and remove 'glitches' caused by multiple diffraction by the dispersing crystal, inhomogeneities in the sample and imperfections in the surfaces of the crystal and mirror. Excessively noisy or overexposed channels were not used in further processing. Some glitches were beam-height dependent in that they occurred in the same horizontal scanning pass of each exposure of the same sample but not in the data from every pass on a single exposure. This was confirmed by visual inspection of the film, and was caused by sample defects or was a characteristic of the optical system. The acceptable scans were subsequently directly averaged.

After averaging and de-glitching, the data were interpolated into a different series of data points representing a pre-edge region with widely separated points, an edge region which retained the maximum resolution obtained from the measurement, and one or more EXAFS regions with increasing intervals between points as the energy increased. This accomplished two purposes. (1) It made the data compatible with our previously developed XAS analysis programs, which run on a DEC PDP 11/55 computer and were programmed to handle fewer than the number of points typically collected by the dispersive method, and (2) it enhanced the signal-to-noise ratio at the expense of resolution in the EXAFS region, where this is advantageous. This changes the appearance of the data from the equally spaced points of the dispersive method to that of data taken by the conventional point-by-point method.

The data were then energy calibrated and ratioed. Calibration was accomplished by matching features with those of known energy based on spectra taken of the same sample by the conventional method. This was done from the edge to as far above the edge as these features could be detected with certainty, which was normally between 200 and 400 eV. An alternative method, giving a larger calibration energy range, was to measure the position of two elemental edges recorded simultaneously prior to measuring the sample [e.g. Cu and Zn edges are 681 eV apart (see Fig. 5) and Ni and Cu edges are 649 eV apart]. These points were fitted by a polynomial and the extrapolated energy values calculated. Optimum results were obtained with a linear interpolation, weighting the inflection point of the absorption edge by a factor of between five and ten. Results were improved by selecting points approximately the same distance apart from each other in eV. The alternative, using all identifiable points, had a density of values inversely proportional to the energy above the edge, and was not as successful a calibration. The CuCl_2 solution data were calibrated using points from a 12.5 μm Cu foil, recorded immediately before the solution data.

Ratioing with the unattenuated beam intensity converted the intensity measurement into transmission and subsequently into absorbance values by:

\[
\text{Absorbance} = \ln \left( \frac{\text{intensity without sample}}{\text{intensity with sample}} \right).
\]

It should be noted that different sample and background exposure times merely add a constant to the absorbance. This is subsequently eliminated when the baseline is adjusted and the absorbance is normalized. Ratioing should also minimize the effects of glitches, to the degree that these are proportional with and without the sample in place and that the detectors'
response is linear. However, comparison of the sample and background data showed that many of the glitches appeared only with the sample present and that a change in the sample position between different data-collection exposures resulted in a change in the glitch locations. Therefore, all large glitches were removed prior to ratioing. Ratioing was usually carried out with a polynomial-based extrapolation of the background rather than the background itself. This method also permitted ratioing a data set where the background was cut off before the end of the sample measurement, by extrapolating the background over the entire range of the sample. Non-ratioed data simply used the inverted intensities as explained previously.

The baseline of the absorbance was adjusted by setting the extrapolated value of the pre-edge at an arbitrary but consistent E0 to 0, and was normalized by setting the average value of the absorbance within 5 eV on either side of E0 to 1. The EXAFS was determined by approximating the smooth portion of the absorbance fall off above the edge with a polynomial spline, and normalized by linearly approximating the fall off in absorption coefficient such that the absorbance 1000 eV above E0 was 0.65 of the value at E0 for Fe and 0.75 for Cu. Fourier transforms were taken with a slow transform algorithm using a k3 weighted basis. For comparisons, data from identical samples were collected by the conventional point-by-point method and analyzed in the conventional manner so that the treatment was identical to that of the dispersive data after ratioing.

**Energy resolution**

Resolution is an important factor in utilizing edge features to understand and monitor changes in the electronic structure of the absorber. The resolution obtained experimentally by the dispersive approach is illustrated in Fig. 6 which shows the Cr K absorption edge of K2CrO4 in solution. The FWHM of the pre-edge transition peak at 5974 eV is 1.4 eV as measured by the normal point-by-point method. This pre-edge absorption feature results from the transition from the Cr ls atomic orbital to a molecular orbital comprised of Cr 3d and oxygen p character (Kutzler, Natoli, Miser, Doniach & Hodgson, 1980). The FWHM in the dispersive spectrum is 1.9 eV. This clearly demonstrates the ability of the spectrometer to determine accurately the shape of narrow features with minimal broadening resulting from poor resolution. Furthermore, two features approximately 5 eV apart obtained from the K absorption edge of Cu foil could easily be resolved, indicating an absolute resolution consistent with the chromate results.

**Accuracy of energy calibration**

The accuracy of the energy scale in the dispersive method is illustrated in Fig. 7 which shows the K edge of Fe foil. The energy calibration range was almost 300 eV and was performed using a linear interpolation, so that no attempt was made to maximize the energy accuracy at the edge. Nevertheless, it is apparent that in the shape, size, and location of edge features, the dispersive method accurately coincides with the spectrum recorded by the point-by-point method. The maximum error is approximately 2 eV which is small enough so that no significant distortion of the edge-shape occurs. This error could be further

**Results and discussion**

The ability of the dispersive method to record X-ray absorption spectra has been demonstrated in a previous paper (Matsushita & Phizackerley, 1981). The important questions to be addressed in this paper concern the quality of data that can be obtained by the dispersive approach and the time required to record data of sufficient quality for a number of specific types of problem. The question of data quality is addressed below by considering factors such as the energy resolution, the energy range available in the dispersive mode, the accuracy in both edge and EXAFS features in energy and magnitude, and the sensitivity of the method. This comparison is made where possible by utilizing data recorded from the same sample by both the dispersive and the point-by-point methods. A discussion of the advantages and disadvantages involved in two approaches is then presented.

**Energy resolution**

Resolution is an important factor in utilizing edge features to understand and monitor changes in the electronic structure of the absorber. The resolution obtained experimentally by the dispersive approach is illustrated in Fig. 6 which shows the Cr K absorption edge of K2CrO4 in solution. The FWHM of the pre-edge transition peak at 5974 eV is 1.4 eV as measured by the normal point-by-point method. This pre-edge absorption feature results from the transition from the Cr ls atomic orbital to a molecular orbital comprised of Cr 3d and oxygen p character (Kutzler, Natoli, Miser, Doniach & Hodgson, 1980). The FWHM in the dispersive spectrum is 1.9 eV. This clearly demonstrates the ability of the spectrometer to determine accurately the shape of narrow features with minimal broadening resulting from poor resolution. Furthermore, two features approximately 5 eV apart obtained from the K absorption edge of Cu foil could easily be resolved, indicating an absolute resolution consistent with the chromate results.

**Accuracy of energy calibration**

The accuracy of the energy scale in the dispersive method is illustrated in Fig. 7 which shows the K edge of Fe foil. The energy calibration range was almost 300 eV and was performed using a linear interpolation, so that no attempt was made to maximize the energy accuracy at the edge. Nevertheless, it is apparent that in the shape, size, and location of edge features, the dispersive method accurately coincides with the spectrum recorded by the point-by-point method. The maximum error is approximately 2 eV which is small enough so that no significant distortion of the edge-shape occurs. This error could be further

Fig. 6. The experimental spectra of the chromate (K2CrO4) edge region obtained with (a) the conventional point-by-point method and (b) the dispersive method. The halfwidth of the peak at 5974 eV is 1.4 eV in (a) and 1.9 eV in (b). The exposure time in the dispersive method, for this approximately 400 μm thick and 40 mmol dm⁻³ solution, was 2 s using Kodak Industrrex SR-5 film. SPEAR was operated at 3 GeV and 52 mA.
Fig. 7. The absorption spectrum obtained from a 20 μm thick Fe foil. The exposure time on Kodak Industrex SR-5 film was 4 s. SPEAR was operating at 3 GeV and 60 mA. Curve (a) was obtained by the conventional point-by-point method and curve (b) was obtained by the energy-dispersive method. Only the edge (K edge) and a short region of EXAFS above the edge is shown. The pre-edge peak at 7111 eV is from the 1s to 3d transition.

Fig. 8. The EXAFS spectra for the 20 μm Fe foil derived from the absorption curve shown in Fig. 7, but including data beyond 7170 eV. Curve (a) was obtained by the conventional point-by-point method and curve (b) was obtained by the energy-dispersive method.

Fig. 9. The Fourier transforms, over a k range of 4 to 12 Å⁻¹, for the EXAFS spectra shown in Fig. 8. Curve (a) was obtained by the conventional point-by-point method and curve (b) was obtained by the energy-dispersive method. The largest peak represents the first shell of Fe atoms and the second-largest peak represents the third shell. The peak positions shown are shifted by an average of about 0.35 Å below the true distance because of the linear phase-shift term α(k) (Cramer & Hodgson, 1979).

EXAFS amplitudes and phases

The actual EXAFS (x k²) of an Fe foil taken by both the dispersive and conventional methods is shown in Fig. 8. The Fourier transforms of these spectra are compared in Fig. 9. The similarity between the two, especially in the phases in the EXAFS and corresponding location and shape of the Fourier transform peaks is quite striking. The dispersive spectrum obtained has a sufficiently high resolution, accuracy of energy and EXAFS amplitude so that all scattering shells out to an R of around 6 Å are accurately produced in both location and relative amplitude in the Fourier transform. The absolute amplitude (but not the relative amplitudes) is increased for the dispersive spectrum, probably a result of non-linearity in the X-ray film and by collecting the sample and background data sets at different times under slightly different conditions. Fast alternation of background and absorbance data collection would overcome this problem, and increase the accuracy of amplitude/scatterer-number determinations. The accuracy of distances and relative Debye-Waller factor determination using the Fe-foil data is already as good as the data taken by the conventional method.

EXAFS amplitudes and phases

The actual EXAFS (x k²) of an Fe foil taken by both the dispersive and conventional methods is shown in Fig. 8. The Fourier transforms of these spectra are compared in Fig. 9. The similarity between the two, especially in the phases in the EXAFS and corresponding location and shape of the Fourier transform peaks is quite striking. The dispersive spectrum obtained has a sufficiently high resolution, accuracy of energy and EXAFS amplitude so that all scattering shells out to an R of around 6 Å are accurately produced in both location and relative amplitude in the Fourier transform. The absolute amplitude (but not the relative amplitudes) is increased for the dispersive spectrum, probably a result of non-linearity in the X-ray film and by collecting the sample and background data sets at different times under slightly different conditions. Fast alternation of background and absorbance data collection would overcome this problem, and increase the accuracy of amplitude/scatterer-number determinations. The accuracy of distances and relative Debye-Waller factor determination using the Fe-foil data is already as good as the data taken by the conventional method.
Energy range of EXAFS determination

The accuracy and resolution of radial distribution functions determined by EXAFS analysis is also directly dependent on the energy range over which the analysis is done. Fig. 5 shows data from a sample consisting of overlayed Cu and Zn foils. The amplitudes are distorted because these data have not been ratioed with a background. What is important is that the useable energy range is greater than 1000 eV at the Cu edge and, even allowing for a sufficient region of pre-edge measurement, an upper limit on the total energy range would correspond to a $k$ of about 14–15 Å$^{-1}$. Almost all EXAFS analyses use data over this range or less. The dispersive method is thus capable of duplicating the accuracy of results obtainable from the conventional method as they are limited by the analysis range available in $k$ space.

Sensitivity and results on dilute samples

Although it is apparent that high-quality data can be obtained from metal foils, it is unlikely that systems of interest will generally be as high in concentration or stability. Acquiring data of the quality shown in Figs. 6 and 7, by recording on X-ray film, was an elaborate process involving wide variations of exposure time and low-energy (Al foil) filter thickness. As observed in the $K_2CrO_4$ spectrum, dilute samples produced much higher noise levels because of the necessity of limiting data collection times to prevent overexposure of the film. It is therefore apparent that real applications of the dispersive method mandate the use of an integrating detector system. High fluxes prevent the use of a proportional counter, unless equipped with expensive multiple read-out electronics, but present optimum conditions for the Reticon photodiode-array detector. Use of this detector avoids the problems inherent to film. The balance of noise levels versus time resolution is experimentally determined by selecting the optimum counting time for different beam conditions and absorber concentrations. The sensitivity of the dispersive method is thus increased by using higher integration times.

The X-ray absorption spectrum of a 100 mmol dm$^{-3}$ aqueous Cu$^{2+}$ solution (made from CuCl$_2$) in a 2 mm path-length cell, collected using the Reticon detector system, is shown in Fig. 10. It is clear that even at this concentration, absorption edges are very much larger than the noise levels to the extent that even the first EXAFS oscillations are readily observed. Work is now in progress to increase the speed, signal-to-noise ratio and the resolution of the Reticon detector system. We also intend to devise a method to alternate rapidly between sample, background and calibration scans to further increase the quality of the data.

At present, the Reticon detector requires the use of aluminium foils to attenuate the primary beam. Hence, the measured flux is much smaller than the actual flux resulting in a greater statistical error. Using the dimensionless variable $x = \mu d$, where $d$ is the thickness of the sample) to define the signal-to-noise ratio, we get the formula for statistical fluctuations

$$\Delta x = 1/(N_m)^{1/2} + 1/(N)^{1/2},$$

where $N_m$ is the measured number of primary photons after attenuation and $N$ is the measured number of photons (per pixel) transmitted through the sample. Just above the edge we get

$$N_m = 4.10 \times 10^5 \text{ photons in 12.5 s}$$

$$N = 4.48 \times 10^5 \text{ photons in 12.5 s}.$$

This leads to a $\Delta x$ value of 0.003, which agrees with the experimentally estimated fluctuations. Owing to the averaging of odd and even detector channels, the statistical fluctuations in Fig. 10 are actually closer to 0.001. Using the jump across the edge in the variable $x$, we obtain an edge jump to statistical fluctuation ratio of approximately 800, which is quite adequate.

![Fig. 10](image-url)
considering such short exposure times and low concentrations.

Comparison of measurement time for the standard and dispersive methods

This comparison is complicated because of the large number of experimental parameters involved. The requirement that the final EXAFS curve be identical in both methods means that the energy resolution and the signal-to-noise ratio should be the same. In the normal point-to-point method using a two-crystal monochromator, vertical slits are used to provide a resolution of around 2 eV (which also reduces the incident X-ray flux). However, in the dispersive method the beam height does not influence the resolution. For the sake of this comparison, assume that the number of points in the standard point-by-point method \( n_s \) is the same as the number of detector pixels \( n_d \) in the dispersive method. In order to provide the same signal-to-noise ratio, the total number of photons per point in the standard method should be equal to the number of photons per pixel in the dispersive method and is denoted as \( N_0 \) below. The total measurement time for the standard \( (T_s) \) and dispersive \( (T_d) \) methods is given by:

\[
T_s = n_s \left( t + N_0 / \phi_s \right)
\]

\[
T_d = n_d N_0 / \phi_d
\]

where \( t \) denotes the time taken to step and to stabilize the crystal monochromator before data acquisition can again be initiated. The SSRL monochromator design requires a delay of 0.3 s. Clearly this could be reduced if a considerable effort is invested in further development of the monochromator mechanism. The variables \( \phi_s \) and \( \phi_d \) represent the total X-ray fluxes impinging on the sample in the standard and dispersive methods, respectively.

It should be noted that the number of points \( n_s \) need not coincide with the number of pixels \( n_d \) since these parameters depend on the experiment (the energy range and resolution required) but can be presumed to be of the same order of magnitude. For most experimental situations, the ratio of total fluxes \( \phi_d / \phi_s \) can be estimated to be somewhere between 1 and 5. This value is controlled by the geometrical arrangement, the beam polarization, the aperture dimensions of the slits, the crystal type, the length and type of mirror, etc.

Using the general Compton–Allison formalism (Compton & Allison, 1935) one can show (Rek, 1983) that the curvature of the crystal has little influence on the total flux, within the range of curvature applicable to this experiment (Taupin, 1964). The monochromator stepping and stabilization time, \( t \), in the standard method has by far the greatest influence on the efficiency of the method when high X-ray fluxes are available or when concentrated samples are measured. The major advantage of the dispersive method is in its ability to acquire a complete absorption spectrum simultaneously with a static experimental arrangement. This would become very significant for fast measurements of concentrated samples where the monochromator stepping and settling time is of the same order or greater than the integration time. To illustrate the decrease in measurement time for a highly concentrated sample using the energy-dispersive method, we take as an example an EXAFS curve measured from an 8 \( \mu \)m Cu foil (optimum thickness at this energy) with a signal-to-noise ratio of 100 within the EXAFS region \( (N_0 = 3.9 \times 10^6 \text{ photons s}^{-1}) \), assuming the beam to be 90% polarized in the horizontal plane and with an intensity of \( 10^{12} \) photons eV \(^{-1} \) s \(^{-1} \) mrad \(^{-2} \), a Si(111) crystal and a 2 eV energy resolution and assuming a time \( t \) of 0.3 s. The EXAFS curve would be obtained approximately \( 10^4 \) times faster using the dispersive method. This shows the usefulness of the dispersive method for concentrated samples. However, it should be noted that this assumes a higher count rate than is available at present with the linear detector used in these experiments, although this could be achieved with a modification to the read-out circuitry. This figure of \( 10^4 \) also assumes that the full vertical beam aperture is used. In our current design, however, the length of the mirror is limited by the space available in the radiation protection hutch at the experimental station and can only intercept approximately \( 1/3 \) of the vertical aperture at these X-ray wavelengths. If a longer X-ray mirror can be used in the future, we will focus the spectra in the vertical direction by bending the mirror. This would permit the entire vertical aperture to be used with the 2.5 mm high Reticon detector.

Conclusions and summary

The results presented in this paper unequivocally demonstrate the feasibility of recording X-ray absorption edges and EXAFS by the dispersive method using polychromatic synchrotron radiation. Compared with the conventional point-by-point approach, recording X-ray absorption spectra in a dispersive mode takes advantage of several features which make the method ideal for a number of diverse applications.

Perhaps most significant is that the entire spectrum can be recorded simultaneously with an energy resolution and a statistical accuracy sufficient to allow analysis using methods developed for data obtained by the more conventional point-by-point approach. The dispersive system is static during data acquisition and therefore does not require any monochromator motion. Thus the instabilities and time delays associated with changing the energy do not exist. The sample required is very small since the dispersed beam passes through a focus at the sample position. If larger
samples are available, however, the effects due to inhomogeneities in the sample thickness could be minimized by oscillating the sample during data acquisition. Since each point in the spectrum is recorded simultaneously, the method is less sensitive to beam fluctuations and instabilities. The dispersive spectra therefore contain fewer glitches and discontinuities. If the storage ring becomes unstable or beam loss occurs, the integration can be interrupted and restarted after a stable beam becomes available.

Dispersive edge and EXAFS spectra can be recorded in a relatively short time period. Exposures obtained in a few seconds are routine on concentrated samples, permitting a larger number of samples to be scanned for a given amount of beam time. With improvements to the electronic linear detector system, time frames on the millisecond time scale will be within reach, especially with the development of wiggler magnets to further increase the flux available from synchrotron-radiation sources (Winick & Spencer, 1980). Certainly, exposures in this time domain will be possible with a sufficiently high signal-to-noise ratio to permit the recording of edge spectra on mmol dm$^{-3}$ concentrations and EXAFS spectra might also be obtainable. Typically the metalloproteins range in size from 10 000 to 150 000 daltons and the concentration of the absorbing metal is of the order of 0.5 to 10 mmol dm$^{-3}$, requiring data acquisition times of up to 15 h using the normal point-by-point method. Unfortunately, one cannot take advantage of the fluorescence method of recording data in order to improve the sensitivity by reducing the background which is due to the absorbers in the sample other than the one of interest. This will ultimately limit the dilution of the sample that can be studied using the dispersive method.

It is useful to recall that the X-ray absorption spectrum divides logically into two regions – the edge and the EXAFS. The dispersive method provides the ideal approach to record simultaneously both regions in a rapid time domain. Absorption-edge features are sensitive to oxidation state, absorber site symmetry and the nature of the liganding atoms. EXAFS spectra can be analyzed in terms of the distances to, numbers of and types of ligands surrounding the absorber. Changes in all these parameters as a function of time can in principle be measured with the dispersive method by time-slicing the spectra using the electronic detector and a fast programmable memory. Computer-controlled systems of this type are currently under development at both the Stanford Synchrotron Radiation Laboratory and the Photon Factory. The time-slicing memory will be synchronized to the stimulating signal and the data integrated for each time period over many cycles to obtain good counting statistics. The method is also well suited for use with traditional kinetics approaches such as stop-flow. Examples of applications are the study of phase transitions in materials, structural studies of transiently stable intermediates in biochemical and chemical systems and study of geometry changes in excited states. We anticipate that the dispersive approach will evolve into an important new methodology for studying the structural and electronic properties of absorbers in systems where time is an important variable.

The authors would like to thank H. Waschkowski of the SLAC machine shop for his help in machining many of the components used in the spectrometer and N. Unwin and J. Murray of the Department of Structural Biology at Stanford for their advice and assistance with the microdensitometer used for film scanning. We thank G. Brown and S. Doniach for helpful scientific discussions. The design of the electronic detector system has benefitted greatly from useful discussions with R. Hettel and J. Yang of SSRL and R. Hopwood and J. McGinnis of E.G. and G. Reticon Corp. We would also like to thank J. Faust for the photographs of the spectrometer. One of us (GBS) is supported by a Fannie and John Hertz Foundation Fellowship.

Synchrotron-radiation beam time and most of the equipment and resources used in this study were provided by the Stanford Synchrotron Radiation Laboratory with the financial support of the National Science Foundation (under Contract DMR 77-27489) in cooperation with the Department of Energy, and by the National Institutes of Health SSRL Biotechnology Resource (RR01209). In addition, this work was supported by grants from the National Science Foundation [PCM 79-04915 (KOH) and DMR 79-08554-A1] and by Japanese-American Cooperative Research Program grants from the National Science Foundation (INT 80-17322) and the Japanese Society for the Promotion of Science.

References

EG&G RETICON (undated). Data sheet for S-type arrays and application note 101. 345 Potrero Ave, Sunnyvale, CA 94086, USA.


