

# New fluorescence detection system for x-ray absorption spectroscopy

Stephen P. Cramer

*Exxon Research and Engineering Company, Linden, New Jersey 07036*

Robert A. Scott

*Department of Chemistry, Stanford University, Stanford, California 94305*

(Received 18 September 1980; accepted for publication 2 December 1980)

The design and performance of a 24-channel fluorescence detection system for use in x-ray absorption spectroscopy are discussed, and comparisons are drawn with other detection systems currently in use. Each channel of the current system consists of a NaI scintillation detector with a filter and collimator arrangement designed to reduce the scatter and filter fluorescence background. Given a sufficiently intense and stable x-ray source, this apparatus can record a useful EXAFS spectrum for an element ( $Z \geq 23$ ) at 100 ppm concentration in approximately 30 minutes. The new design permits the study of plate-like samples (such as molybdenum enzyme solutions) unsuitable for previously described slit assemblies. Breaking the detection system up into discrete elements also allows (1) optimization of filter thickness for each direction, (2) use of a weighting scheme to optimize the total S/N, and (3) operation at high total count rates, while retaining the advantages of pulse counting electronics. The relative merits of filters and crystal monochromators are discussed quantitatively, using the two criteria of efficiency and selectivity. It is shown that practical filters and barrel monochromators give similar performance over a 100-fold concentration range, for a given solid angle, and that the 20-fold solid angle advantage of the multielement approach makes it the design of choice for many cases. Finally, the construction of an array of solid-state detectors with the appropriate filters and collimating elements is proposed as a device capable of yielding unprecedented performance in x-ray absorption spectroscopy.

PACS numbers: 07.85. + n

## INTRODUCTION

Over the past decade, the exploitation of synchrotron radiation has resulted in a million-fold increase in the available intensity of broadband x rays,<sup>1</sup> and further increases in flux are occurring with the combined use of focussing mirrors and wiggler magnets, and (ultimately) undulator schemes.<sup>2</sup> These intensity improvements have naturally led to more rapid data collection and/or the use of more dilute samples in x-ray absorption spectroscopy. The use of fluorescence detection techniques has been critical for obtaining useful spectra on dilute samples. It is now well appreciated that measuring a fluorescence excitation spectrum is equivalent to and more efficient than the normal transmission experiment, at sufficiently dilute concentrations.<sup>3</sup> Several different fluorescence detection schemes have been described,<sup>3-7</sup> but the relative merits of these various approaches have not been well defined. The purpose of this paper is to describe a new design with exceptional versatility, and to make some quantitative comparisons between various existing systems.

## I. DESCRIPTION OF THE APPARATUS

### A. Mechanical aspects

The physical apparatus is designed to support a roughly spherical arrangement of detectors, collimators, and filters (Fig. 1). On the face of each 2 × 2 in. detector

is mounted an aluminum collimator, which tapers to a 1 in. square window over a distance of 4 in. Metal foil filters are supported on thin aluminum frames and held in place on the front of the collimators with spring clips. Each detector is mounted on an aluminum plate which is in turn secured to the positioning frame. Arc slots on the frame allow adjustment of the detector position and alignment. The main frame is a modified aluminum ring with an inner radius of 23 cm, an outer radius of 33 cm, and a slotted baseplate for centering. Extending out from a pivot point on the main frame are 4 semi-circular arms, each of which holds 3 detectors. The arrangement of these arms depends on the sample. For molybdenum enzyme solutions a symmetric configuration about the square sample is used [Fig. 1(b)], while for narrower samples such as iron and copper proteins the geometry of Fig. 1(c) is more appropriate. In some cases a final set of 4 detectors can be positioned in the horizontal plane with lab jacks. The face of each detector is about 6 in. from the center of the sample, for a total solid angle of about 20% of  $4\pi$  steradians.

### B. Filters

The use of metal foil filters to remove  $K_{\beta}$  lines and white radiation is common in x-ray diffraction,<sup>8</sup> and their use for fluorescence EXAFS measurements has been described.<sup>5,7</sup> The basis for the filtering process is illustrated in Fig. 2. For a filter of thickness  $t$ , with absorp-

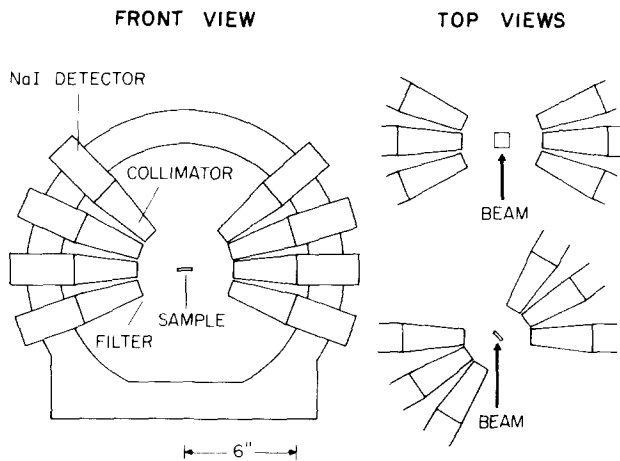


FIG. 1. Schematic of the fluorescence detection apparatus: (a) side view of the mainframe; (b) top view of geometry for square samples such as Mo protein solutions; (c) top view of geometry for thin line samples such as Fe or Cu protein solutions.

tion coefficient  $\mu_f$  at the energy of the sample fluorescence, and  $\mu_s$  at the elastic scattering energy, the ratio of transmitted fluorescence to transmitted scatter can be enhanced by a factor of  $\exp[(\mu_s - \mu_f)t]$ . Were it not for filter fluorescence, the optimum filter thickness would then be given by

$$t = \ln[K(\mu_s - 2\mu_f)/\mu_f]/(\mu_s - \mu_f). \quad (1)$$

Unfortunately, the efficiency of filters for background rejection is compromised, because absorption of scattered photons by the filter gives rise to filter fluorescence with quantum yield  $\phi$ . This filter fluorescence degrades the signal to noise (S/N) enhancement. As one means of reducing the acceptance of filter fluorescence, Stern and Heald used a slit assembly applicable to samples which are roughly line sources.<sup>5</sup> Such a design is not appropriate for the platelike samples used in molybdenum

enzyme studies. At the Mo *K* edge the optimum path length for a dilute aqueous sample is about 2 cm, which is also a typical horizontal beam dimension. This is one reason for our alternative geometry. In either case the goals are to minimize the product of the solid angle of scatter from the sample incident on the filter and the solid angle of filter fluorescence accepted by the detector, and to maximize the solid angle of sample fluorescence reaching the detector. These contradictory goals result in a compromise geometry which depends on the application at hand.

### C. Detectors and electronics

The present setup utilizes Harshaw NaI(Tl) scintillation detectors, with  $2 \times 2$  in. faces coupled with a light pipe to a 2 in. diameter photomultiplier tube. The square geometry of these detectors yields a 27% increase in solid angle over circular detectors at a given distance from the sample, and it is more appropriate for the square or rectangular samples we typically use.

The detection system electronics components are all commercially available. Particular attention was paid to linearity at high count rates, and for this reason, a number of amplifiers were tested. We found that with several amplifiers count rates in excess of 200 kHz could be measured with negligible nonlinearity (Fig. 3), although this was not the case with the Canberra 1718 previously used.<sup>9-11</sup>

## II. RESULTS

### A. Experimental performance

As a test of the typical performance of this system, data were obtained on a 2 mM (130 ppm) sample of aqueous Cu(II) nitrate. With an unfiltered detector in the

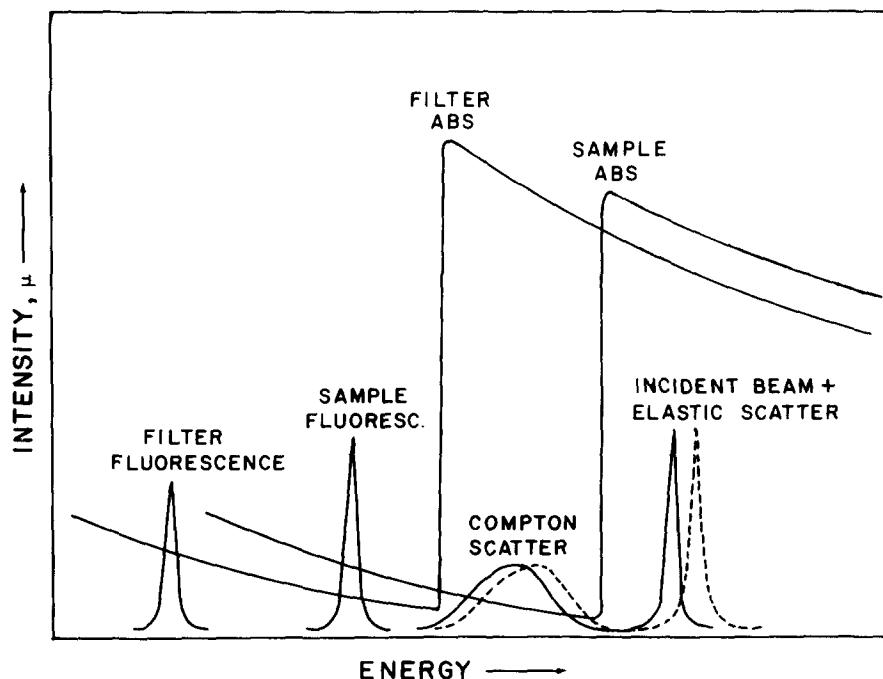


FIG. 2. The physical basis for using filters with fluorescence EXAFS measurements. The filter is highly absorbing for the elastic and Compton scatter from the incident beam, while it is relatively transparent to the sample fluorescence.

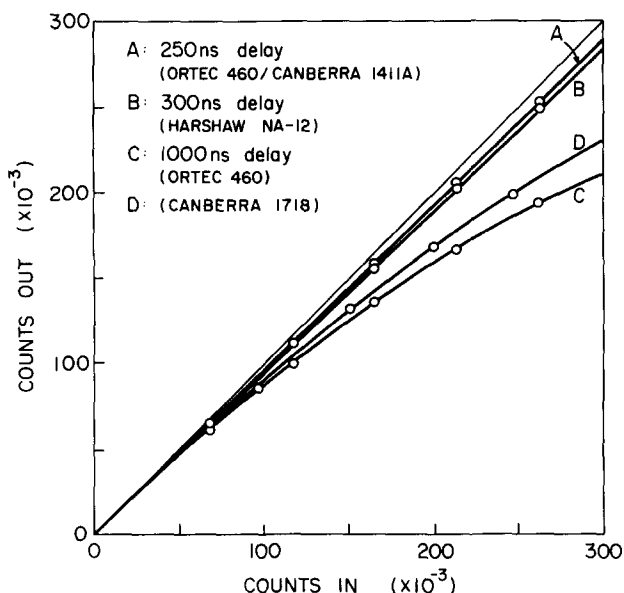


FIG. 3. Count rate performances of some commercially available amplifiers. All measurements used a Canberra 1407R noise pulser (guaranteed accurate to 5%) and an Ortec 550 SCA with 200 nm pulse pair resolution (except for the Canberra 1718, which has a self-contained SCA).

ideal position (perpendicular to and in the horizontal plane of the incident beam), we measured ca. 20% fluorescence and 80% scatter just above the copper  $K$  edge. However, at more oblique angles, the scattering intensity was larger and the fractional contribution of Cu fluorescence diminished to ca. 2%. The introduction of 10 or 20  $\mu$  Ni filters raised the Cu fraction to between 25% and 49% on all detectors, while roughly half of the Cu signal was lost (on an absolute scale). The consequent improvement in S/N ranged from a factor of 1.5–3. Even greater improvements appear feasible with sharper collimation and careful optimization of filter thickness for each detector.

## B. Theoretical comparisons

For relatively concentrated samples (on the order of 1000 ppm), the fluorescence signal is more intense than the scatter background, and the optimum detection system simply collects a large solid angle at a high count rate. In this regard a 9-element array of scintillation detectors was used successfully for the study of rubredoxin<sup>9</sup> and hemoglobin.<sup>10</sup> However, at concentrations an order of magnitude lower, removing the scatter background becomes essential, and the design of a total detection scheme requires a choice of the appropriate scatter rejection method. Both our design and that of Stern and Heald<sup>5</sup> rely on filters for scatter rejection, while the Hastings barrel monochromator uses Bragg reflection,<sup>4,6</sup> and the early work of Jaklevic *et al.*<sup>3</sup> relied on electronic discrimination.

In a fluorescence-detected x-ray absorption experiment, involving measuring the ratio  $I_f/I_o$ , the ultimate signal to noise ratio is determined by photon statistics applied to the  $I_f$  measurement, i.e., the signal is propor-

tional to  $I_f$ , whereas the noise is proportional to the square root of the total intensity reaching the detector ( $I_f + I_s$ ):

$$S/N = I_f/(I_f + I_s)^{1/2} = [I_f/(1 + K)]^{1/2}. \quad (2)$$

This allows straightforward comparison of the efficiency of various scatter rejection methods. If one defines the efficiency parameter  $\epsilon$  as the fraction of fluorescent photons transmitted, and the selectivity parameter  $\sigma$  as the factor by which the fluorescence-to-scatter ratio is improved, then the S/N resulting from a particular background rejection scheme is

$$(S/N)' = [\epsilon I_f/(1 + K/\sigma)]^{1/2}. \quad (3)$$

The improvement in the S/N ratio is then given by  $Q$ , where

$$Q = \frac{(S/N)'}{(S/N)} = \left[ \epsilon \left( \frac{1 + K}{1 + K/\sigma} \right) \right]^{1/2}. \quad (4)$$

Thus, for any improvement in S/N (i.e., for  $Q > 1$ ), this leads to the requirement that

$$K > \frac{1 - \epsilon}{\epsilon - 1/\sigma}. \quad (5)$$

For a barrel monochromator,  $\epsilon$  and  $\sigma$  were reported as 0.35 and 100, respectively,<sup>4</sup> from which it follows that  $K$  must be greater than ca. 1.9 for this scheme to improve the S/N.

Calculating the performance of a filter system is more complex, since the selectivity and efficiency are both functions of filter thickness.

$$\epsilon = \exp(-\mu_f t), \quad [6(a)]$$

$$\sigma = \exp[(\mu_s - \mu_f)t]. \quad [6(b)]$$

For an ideal nickel filter for copper fluorescence ( $\mu_f = 0.216$ ;  $\mu_s = 1.178$ ), the optimum thickness (in microns) from Eq. (1) is

$$t = 1.04 \ln(3.45 K).$$

It follows that even an ideal filter gives no improvement in S/N for  $K < 0.29$ . At optimum thickness the efficiency and selectivity of an ideal nickel filter are given by

$$\epsilon(\text{Ni}) = (3.45 K)^{-0.225} \quad [7(a)]$$

$$\sigma(\text{Ni}) = 3.45 K. \quad [7(b)]$$

The S/N improvement for this ideal nickel filter can then be calculated from Eqs. (4), (6), and (7).

$$Q = 0.766 K^{-0.112} (1 + K)^{1/2}. \quad (8)$$

Calculation of the optimum thickness of a practical filter requires consideration of the amount of filter fluorescence incident upon the detector. A substantial amount of filter fluorescence is actually reabsorbed by the filter, and this has prevented our determination of an analytical solution for the correct thickness. Instead, we have calculated the S/N improvement ( $Q$ ) as a function of thickness, using the formula:

$$Q = \left[ \frac{(1 + K) \exp(-\mu_r t)}{1 + K \left[ \exp(-\mu_s t) + \phi \Omega \left( \frac{\mu_s}{\mu_s - \mu_r} \right) (\exp(-\mu_r t) - \exp(-\mu_s t)) \right] \exp(\mu_r t)} \right]^{1/2}, \quad (9)$$

where  $\mu_r$  is the absorption coefficient of the filter for its own fluorescence,  $\phi$  is the filter quantum yield, and  $\Omega$  is the effective solid angle of filter fluorescence seen by the detector.  $\Omega$  can be adjusted to account for the fact that in the geometry employed a significant amount of filter fluorescence is generated by scattered photons not travelling in the direction of the detector. The appropriate thickness is then chosen as the value of  $t$  which gives the greatest value of  $Q$ . In practice, this is done by a computer program which calculates  $Q$  for a range of thicknesses and then chooses an optimum value.

### III. DISCUSSION

In Fig. 4 we compare the performance of a practical barrel monochromator with perfect and less than perfect filtering schemes. Our calculations indicate that for a scatter/fluorescence ratio ( $K$ ) less than 10, the S/N improvement is not extremely sensitive to the quality of the background rejection scheme. In this regime, practical filter schemes are actually better than barrel monochromators with the previously reported performance. On the other hand, for  $K > 10$  the performance of the filtering schemes depends critically on the amount of filter fluorescence accepted by the detector. In principal, a well-devised filter system can still exceed the monochromator design in performance, but collimation procedures to reduce the acceptance of filter fluorescence become much more important in this regime.

The solid-angle advantages conferred by our multi-detector scheme are considerable. With 24 detectors we achieve a solid angle of about 20%, and we could gain roughly a factor of 3.5 in S/N over the barrel scheme because of this 14-fold increase in fluorescence count rate. In practice, the detectors which operate at large angles from perpendicular have a lower S/N because of the larger scatter background, but a 2-fold S/N improvement is a reasonable figure to expect. The data of Fig. 4 indicate that with this factor of 2, even a relatively inefficient filter scheme will exceed the barrel design performance beyond scatter/fluorescence ratios of 100. For aqueous copper solutions, this is equivalent to concentrations less than a few hundred micromolar.

Dividing the detection system into small individual components yields several benefits over slit systems which put all the flux into a single detector.<sup>5</sup> First of all, it permits the use of the optimum filter thickness for each particular direction. Since the Compton and elastic intensity vary dramatically with scattering angle, the ratio of scatter/fluorescence is different for each detector. Experimentally, we have found the correct filter thickness to vary by a factor of 3 from one position to another. A second beneficial aspect to multichannel data collection is the capability to perform the appropriate weighting for signals from different directions. If one

considers each detector channel to involve a measurement of  $\mu_r$  with a different scale factor, then the best S/N is obtained by weighting inversely by fluorescence signal and directly by  $(S/N)^2$ , which yields a weighting factor of  $1/(1 + K)$ . Finally, multichannel pulse counting gives our system a wide dynamic range, from a few hundred counts per second to several million. Such a system should be useful for fluorescence EXAFS with in-house systems using conventional x-ray generators as well as the most powerful synchrotron radiation sources.

It should be clear at this point that the ideal detection system for EXAFS measurements depends upon the nature of the sample being studied. Jaklevic *et al.*<sup>3</sup> have shown that for aqueous Fe solutions, fluorescence becomes superior to transmission in the region of 33 mM (assuming 20% solid angle acceptance), and using their procedure we calculate a breakeven point of 30 mM for aqueous copper. From the curves of Fig. 4 one can see that filters or other scatter rejection schemes become of significant value at a scatter/fluorescence ratio of ca. 3, corresponding to a copper concentration of about 10 mM. Our calculations have shown that this filtered multi-element system is the configuration of choice down to concentrations of a few hundred micromolar or less. The ultimate tradeoff point between filter and monochromator schemes will depend on the degree to which filter fluorescence can be rejected and on possible improvements in monochromator solid angle and reflectivity.

A possible improvement to our current system would

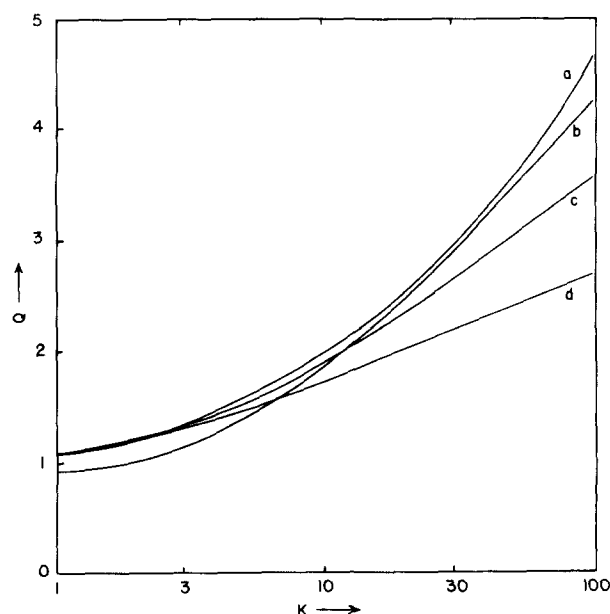


FIG. 4. Calculated S/N improvement ( $Q$ ) vs scatter/fluorescence ratio ( $K$ ) for several scatter rejection schemes: (a) ideal filter; (b) practical monochromator; (c), (d) two practical filters (see text).

be the use of semiconductor detectors instead of the current NaI detectors, which would permit electronic rejection of residual transmitted scatter and filter fluorescence. A filtered multielement solid-state detection system would perform as well as or better than the perfect filter system of Fig. 4, and would permit x-ray absorption studies at parts per million concentration levels. In fact, the original work of Jaklevic *et al.*,<sup>3</sup> involved a Ge-Li detector, and it was only because of the higher speed of NaI detectors that the latter were preferred in subsequent fluorescence studies. It has been our experience in many cases that filters reduce the total count rate to levels (10–50 kHz) which can be handled by solid-state detectors, so that a transition back to silicon or germanium detectors might be in order.

#### ACKNOWLEDGMENTS

We would like to thank the staff of the Stanford Synchrotron Radiation Laboratory for their assistance with this work, especially Robert Filippi for help with the

original design. R.A.S. is an NIH postdoctoral fellow. Experiments at SSRL are supported by National Science Foundation Grant DMR-77-27489 in cooperation with SLAC and the Department of Energy.

- <sup>1</sup> H. Winick and A. Bienenstock, *Annu. Rev. Nucl. Part. Sci.* **28**, 33 (1978).
- <sup>2</sup> H. Winick and J. E. Spencer, *Nucl. Instrum. Methods* **172**, 45 (1980).
- <sup>3</sup> J. Jaklevic, J. A. Kirby, M. P. Klein, A. S. Roberston, G. S. Brown, and P. Eisenberger, *Solid State Commun.* **23**, 679 (1977).
- <sup>4</sup> J. Brown, Ph.D. Thesis, Princeton University (1978).
- <sup>5</sup> E. A. Stern and S. M. Heald, *Rev. Sci. Instrum.* **50**, 1579 (1979).
- <sup>6</sup> J. B. Hastings, P. Eisenberger, B. Lengeler, and M. L. Perlman, *Phys. Rev. Lett.* **43**, 1807 (1979).
- <sup>7</sup> F. S. Goulding, J. M. Jaklevic, and A. C. Thompson, in "Workshop on X-Ray Instrumentation for Synchrotron Radiation Research," SSRL Report 78/04, edited by H. Winick and G. Brown (1978).
- <sup>8</sup> *International Tables for X-Ray Crystallography*, Vol. III (Kynoch Press, Birmingham, England, 1974).
- <sup>9</sup> R. G. Shulman, P. Eisenberger, B. K. Teo, B. M. Kincaid, and G. S. Brown, *J. Mol. Biol.* **124**, 305 (1978).
- <sup>10</sup> P. Eisenberger, R. G. Shulman, B. M. Kincaid, G. S. Brown, and S. Ogawa, *Nature* **247**, 30 (1978).
- <sup>11</sup> B. K. Teo, R. G. Shulman, G. S. Brown, and A. E. Meixner, *J. Am. Chem. Soc.* **101**, 5624 (1979).