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OPTIMIZATION OF EXPERIMENTAL PARAMETERS FOR
MEASUREMENTS OF EXTENDED X-RAY ABSORPTION FINE
STRUCTURE (EXAFS)

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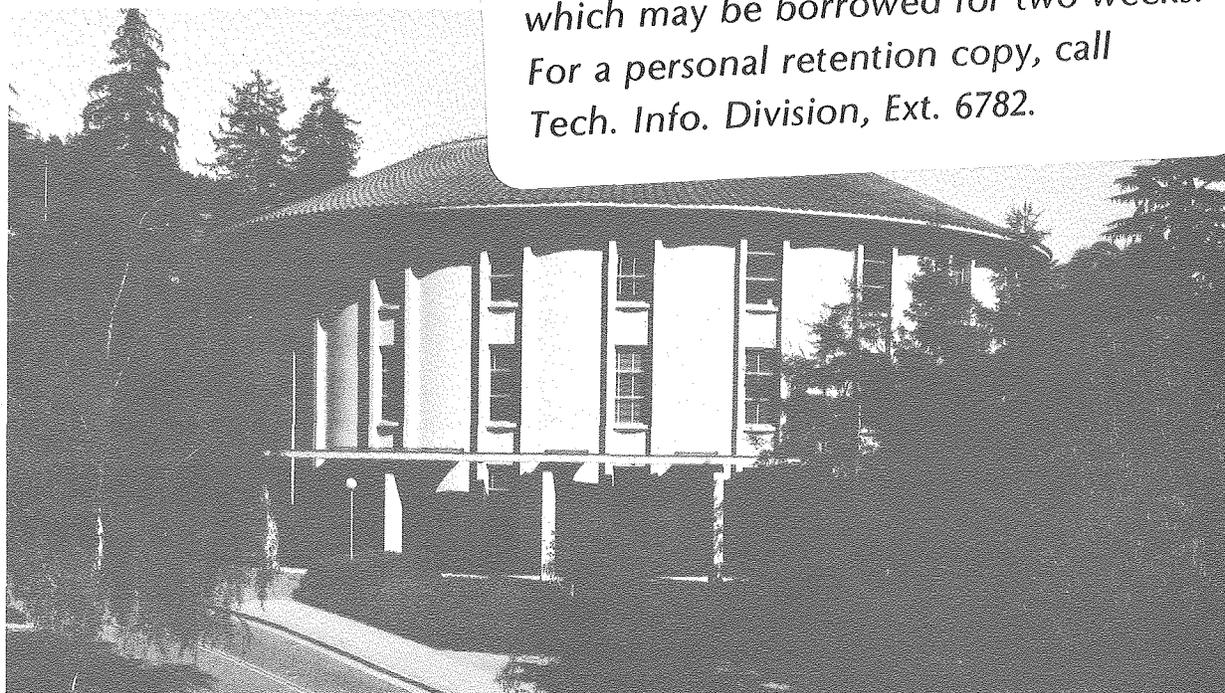
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Optimization of Experimental Parameters for Measurements of
Extended X-Ray Absorption Fine Structure (EXAFS).

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ABSTRACT

The factors which determine the signal-to-noise (S/N) ratio of measurements of x-ray absorbance with the ionization chamber system used at the Stanford Synchrotron Radiation Laboratory are analyzed. An operational definition of the S/N ratio for the detection of extended x-ray absorption fine structure (EXAFS) is proposed. The effect of sample composition on the S/N ratio is discussed. An equation which shows explicitly the dependence of the uncertainty in an absorbance measurement on sample thickness and ionization chamber absorbance is derived and its predictions are compared with experimental results. It is found that the uncertainties in absorbance measurements can be expected to be the same order of magnitude as those predicted by the model equation. The gain in S/N ratio obtainable through the optimum choice of ionization chamber absorbance and sample thickness is described.

INTRODUCTION

The advent of synchrotron radiation x-ray sources has led to a resurgence of interest in x-ray absorption spectroscopy. The intense x-ray beams available at facilities such as the Stanford Synchrotron Radiation Laboratory (SSRL) have, for the first time, made it possible to obtain useful x-ray absorption spectra of transition metals in metalloprotein samples where the absorber of interest contributes only a small fraction of the total absorbance. However, even with the very large photon fluxes provided by the synchrotron source, spectrum averaging is often required to increase the S/N ratio of spectra of biological materials in order to obtain sufficiently precise data. As a result, studies of the x-ray absorption spectra of biological materials can require large amounts of scarce beam time at synchrotron radiation facilities.

In this paper, the factors which determine the S/N ratio of measurements of x-ray absorption spectra are analyzed. The discussion will center on the direct measurement of x-ray absorption with the ionization chamber system described by Kincaid (1) and shown in Fig. 1. We will propose an operational definition of the S/N ratio for the measurement of extended x-ray absorption fine structure (EXAFS). The dependence of the S/N ratio on experimental variables such as the sample composition, sample thickness and ion chamber absorbances will be shown explicitly.

THE MEASUREMENT OF ABSORBANCE

The linear absorption coefficient μ is defined by Lambert's law (2).

$$I_0/I = e^{-\mu x} \quad (1)$$

In eqn. 1, I_0 and I are the intensities of the incident and transmitted radiation, respectively, and x is the sample thickness. In practice, I_0 is estimated by absorbing part of the incident radiation in the front ionization chamber (Fig. 1). The transmitted intensity is measured by the rear ionization chamber which, under ideal circumstances, absorbs all of the transmitted radiation. For practical purposes, the x-ray absorption spectrum may be considered to be a plot of $\ln(I_0/I) = \mu x$ as function of x-ray energy.

OPERATIONAL DEFINITION OF THE S/N RATIO

The S/N ratio will be defined for a measurement of EXAFS, which is a small modulation of the photoabsorption cross section of the element of interest. To obtain the S/N ratio, we divide $0.01\mu_{pe}x$ (the magnitude of a 1.0% modulation of the photoabsorption coefficient of the element of interest in a sample of thickness x) by $\Delta(\mu x)$, the rms uncertainty in a measurement of μx . The S/N ratio is therefore

$$S/N = 0.01\mu_{pe}x/\Delta(\mu x) \quad (3)$$

In practice, the EXAFS modulation amplitude ranges from 50% to less than 0.10% of the photoabsorption coefficient in the energy range of interest. A one percent modulation is chosen as a convenient intermediate value.

For a fixed sample thickness, the magnitude of $0.01 \mu_{pe} x$ depends on sample composition. The EXAFS modulation will be small for samples where the concentration of the absorber of interest is low and will reach a maximum when the mole fraction of the absorber of interest is unity. On the other hand, $\Delta(\mu x)$ is independent of sample composition and depends only on the value of μx and the other experimental conditions. Therefore, in the paragraphs to follow we will consider separately the effects of sample composition, which determine the size of the "signal" ($0.01 \mu_{pe} x$) and the effects of other experimental variables which determine $\Delta(\mu x)$ on the S/N ratio. We will calculate $\Delta(\mu x)$, assuming that the precision of a measurement of μx is limited by photon counting statistics. Evidence will be presented showing that experimentally measured values of $\Delta(\mu x)$ approach the limit imposed by photon counting statistics. Finally, we will consider explicitly the dependence of the S/N ratio on experimental conditions.

EFFECT OF SAMPLE COMPOSITION ON THE S/N RATIO

The EXAFS modulation amplitude, when expressed as a fraction of the photoabsorption coefficient of the element of interest, is determined by the number, type and radial distribution of scatterers near the absorbing atom. In practice, one does not determine directly the photoabsorption coefficient for the element of interest, but rather the total x-ray absorbance, μx , which contains contributions from all of the elements in the sample compound as well as from solvent or matrix materials. The contributions of other elements and matrix materials to μx increase the total x-ray absorbance, making the EXAFS modulation a smaller fraction of the experimentally determined μx .

The fraction of the total absorption coefficient due to photoabsorption by the element of interest is given by

$$D = \frac{\mu_{pe}}{\mu} \quad (4)$$

The absorption coefficients in Eqn. 4 pertain to x-ray energies just above the absorption edge of interest. D is related to S, the "edge jump ratio", which is frequently used in the literature of x-ray analysis by

$$D = 1 - 1/S \quad (5)$$

Using tabulated data, one can easily calculate μ and μ_{pe} for a sample of any arbitrary composition (5). Assuming that the EXAFS modulation amplitude is 1% of the photoabsorption coefficient of the element of interest, the relative change in μ_x due to EXAFS will be 0.01D. For a sample with $D = 0.5$, for instance, the modulation of μ_x due to EXAFS would represent approximately a 0.5% change in the μ_x . It should be emphasized that 0.01D is used as an estimate of the relative magnitude of EXAFS only to place the dependence of the EXAFS "signal strength" on sample composition on a quantitative basis.

In Table 1, the D values for several neat (mole fraction = 1) metallic elements and for dilute aqueous solutions of the same elements are given. These numbers show that while the D values for the neat elements are of comparable magnitude, dilution of the metals in water causes a large decrease in D, with the decrease being most marked for elements of lower atomic number. This is a result of the absorption coefficient of water, which increases rapidly with decreasing x-ray

energy. For a given sample, the value of D increases with the concentration of the absorber of interest, reaching a maximum when the mole fraction of the absorber of interest reaches 1.0. For a fixed-precision measurement of μx , the S/N ratio for EXAFS varies directly with D . The smaller values of D for the aqueous solutions reflect the difficulty of detection of EXAFS in dilute systems by the absorption technique, especially for absorbers of lower atomic number.

CALCULATION OF THE UNCERTAINTIES IN ABSORPTION MEASUREMENTS

We will now present a method for the calculation of the uncertainties in a measurement of μx by the direct absorption technique. Our approach will be similar to that of Kincaid (1), who assumed that uncertainties in the measurement of I_0 and I were dominated by the statistical fluctuations in the number of photons detected in the front and rear ionization chambers. Kincaid (1) calculated optimum values for μx and for the absorbance of the front chamber for the ideal case of 100% absorbance by the rear chamber. Beyond stating that under nearly optimum conditions the S/N ratio was not strongly sensitive to the choice of either μx or the front chamber absorbance, Kincaid presented no quantitative dependence of the S/N ratio on the experimental conditions.

We have derived a formula which shows explicitly the dependence of the uncertainty in the absorbance on the total absorbance of the sample and the absorbances of the ionization chambers. This derivation is a special case of the calculation of the uncertainty in a measurement of absorbance using an instrument whose response is linear in percent transmittance (6). We assume that the uncertainties in the ionization chamber currents are dominated by the random fluctuations in the photon

count rate (1). Accordingly, the average numbers of photons absorbed in the front and rear ion chambers, M_F and M_R , respectively, during a measurement of the absorbance have standard deviations given by

$$\Delta M_R = (M_R)^{\frac{1}{2}} \quad \text{and} \quad \Delta M_F = (M_F)^{\frac{1}{2}} \quad (6)$$

We define the absorption of the front and rear chambers, F and R , respectively such that

$$F = \mu_F x_F \quad \text{and} \quad R = \mu_R x_R \quad (7)$$

where μ is the absorption coefficient and x is the thickness of the appropriate ionization chamber. M_F and M_R can be expressed as functions of F , R , μx and N , the total number of photons incident on the front ionization chamber during the measurement

$$M_F = N(1 - e^{-F}) \quad (8)$$

$$M_R = N e^{-F} e^{-\mu x} (1 - e^{-R}) \quad (9)$$

To calculate μx we need to know the flux incident on, and transmitted by, the sample. These are called I_0 and I , respectively.

$$I_0 = M_F e^{-F} (1 - e^{-F})^{-1} \quad \text{and} \quad I = M_R (1 - e^{-R})^{-1} \quad (10)$$

the standard deviations of I_0 and I are given by

$$\Delta I_0 = e^{-F}(1 - e^{-F})^{-1}\Delta M_F \quad (11)$$

and

$$\Delta I = (1 - e^{-R})^{-1}\Delta M_R \quad (12)$$

To calculate the uncertainty in μ_X , the uncertainties in M_R and M_F are propagated by a power series technique (7).

$$\mu_X = \ln(I_0/I) \quad (13)$$

$$\Delta(\mu_X) = \left[\left(\frac{\partial \ln(I_0/I)}{\partial I_0} \right)^2 (\Delta I_0)^2 + \left(\frac{\partial \ln(I_0/I)}{\partial I} \right)^2 (\Delta I)^2 \right]^{1/2} \quad (14)$$

$$\Delta(\mu_X) = \left[\frac{1}{N(1-e^{-F})} + \frac{e^F e^{\mu_X}}{N(1-e^{-R})} \right]^{1/2} \quad (15)$$

We define E, the relative uncertainty in μ_X by

$$E = \frac{\Delta(\mu_X)}{\mu_X} = \frac{1}{\mu_X \sqrt{N}} \left[\frac{1}{(1-e^{-F})} + \frac{e^F e^{\mu_X}}{(1-e^{-R})} \right]^{1/2} \quad (16)$$

Eqn. 16 shows that E decreases as $(N)^{1/2}$, a result expected from the original assumption (eqn. 6) of Poisson photon counting statistics. If any one of the variables F, R or μ_X is zero, the relative uncertainty becomes very large. The same is true of very large values of F or μ_X . As R increases, F decreases to a constant value. These results are consistent with the intuitive feeling that a reasonable measurement of μ_X cannot be made if no radiation is absorbed in the sample or in either one of the two detectors.

EXPERIMENTAL DEPENDENCE OF E ON μx

In order to test the assumption that E is dominated by photon counting statistics, the absorbance μx , and the standard deviation in the absorbance of a 0.2 M FeCl_3 solution were measured for 19 different values of μx ranging from 0.8 to 6.5. Using a variable thickness solution cell, the absorbance was measured above and below the iron K edge at 7.11 KeV for 10 sample thicknesses. The SSRL EXAFS II monochromator, ion chambers and amplifier system were used. Nitrogen was used as the ion chamber gas in both the front and rear ion chambers, giving F and R values of 0.14 and 0.43, respectively.

The outputs of the I_0 and I voltage-to-frequency converters ($10.0V = 1 \times 10^6$ Hz) were counted 6 times for 7 seconds per count at each value of the absorbance. Dark current readings were taken and subtracted from the gross count rates to give net count rates. For each measurement of μx , the net count rates were converted to voltages and subsequently to ionization chamber currents. The number of photons absorbed in each detector was calculated from the number of ions collected, assuming a yield of one ion pair per 34 eV of x-ray energy absorbed in the counting gas (8). The numbers of photons absorbed in the front and rear ionization chambers were converted to flux incident on and flux transmitted by the sample as per eqn. 10.

The absorbance μx , was calculated for each measurement of the incident and transmitted intensities as per eqn. 13. The mean value of μx and the standard deviation of the mean value were calculated for each set of seven measurements at a given energy and sample thickness. In Fig. 2, the experimentally determined values of E are plotted as a function of μx . In the same figure, the predicted dependence of E on μx is shown for

$R = 0.43$, $F = 0.14$ and $N = 2.7 \times 10^8$, which was the average total photon flux per seven second counting period. The ratio of the experimentally determined relative uncertainty to the predicted relative uncertainty had a median value of 2.2 with an extreme value of 15.

Any experimental estimate of the relative uncertainty in u_x can only approach as a lower limit the values predicted by photon counting statistics. However, the limited data set presented in Fig. 2 does show that the standard deviation of an experimentally measured value of u_x can be expected to be of the same order of magnitude as the error predicted on the basis of photon counting statistics.

OPTIMIZATION OF EXPERIMENTAL CONDITIONS

In eqn. 3, an operational definition of the S/N ratio was proposed. Subsequently, the functional dependence of the relative uncertainty on μx , F and R was derived. By combining eqns. 3, 4 and 16, it can be seen that

$$S/N = \frac{0.01D}{E} \quad (17)$$

A calculation of the S/N ratio for a given sample composition (which determines D) and experimental conditions (which determines E) provides an estimate of the difficulty of detecting EXAFS. For instance, if $D = 0.005$ and $E = 0.001$, which are not atypical values for studies of biological materials, the S/N ratio would be 0.05. Assuming that this value is unacceptable, we now consider that steps which can be taken to improve it.

The brute force approach would be to increase N, either by performing the experiment when the storage ring provides a higher flux, or by taking data for a longer period of time. Another strategy is to decrease E by optimizing the values of μx , F or R. Kincaid (1) has calculated optimum values for μx and F of 2.58 and 0.245, respectively, for the case of complete absorption of the transmitted radiation in the rear ion chamber.

In Fig. 3, the dependence of the S/N ratio on μx for $N = 10^8$ is shown. The shapes of the curves are not dependent on N, but their ordinate values are scaled by $N^{1/2}$. A family of curves is presented for $F = 0.11$ with R values as indicated. The maximum value of the S/N ratio increases 700% as R changes from 0.01 to 2.31. It should be noted that

the maxima in the S/N functions get broader as R increases, making the S/N ratio less dependent on the choice of sample thickness. In Fig. 4, R has been set to 2.3 and the S/N function has been plotted for several values of F. This figure shows that the S/N ratio is not as sensitive to the choice of the front ionization chamber absorbance (F) as it is to the choice of the rear ionization chamber absorbance. In Table II, the results of an optimization of μx and F for several fixed values of R are presented. Within the resolution of the calculation ($\pm 1\%$ transmittance) the optimum values of F and μx for large R approach those given by Kincaid (1).

An experimenter may maximize the S/N ratio for a given sample composition and photon flux by proper selection of ion chamber thickness. In many cases, however, experimenters at SSRL do not construct ion chambers of special lengths for their experiments. The standard SSRL ion chambers are operated in a continuously flushed mode and as a result, the custom mixing of counting gases is often prohibitively expensive.

The results presented above serve as a guide as to how much can be gained by striving for optimum experimental conditions. As an example, suppose that for a high D sample such as a metal foil or a neat, low molecular weight compound, data of acceptable quality can be obtained in 30 minutes under ideal experimental conditions ($R = 2.3$, $F = 0.25$ and $\mu x = 2.5$). Consider the effect of changing R to 0.36. The present calculations indicate that the S/N ratio would decrease to 62% of its original value. In practice, to obtain data of the same quality as that collected in 30 minutes of ideal condition operation, the data collection time would have to be increased to about 75 minutes. For high D samples,

an increase in data collection time of this magnitude could probably be tolerated and the merits of spending a lot of money or effort to increase R to 2.3 would be questionable. Now consider the effect of a similar change in R on a measurement of the absorption spectrum of a low D metalloprotein solution that requires 4 hours of beam time per spectrum. It should be clear that in this case, significant amounts of time could be saved by the optimization of experimental conditions. An experimenter contemplating a study of low D samples would do well to expend some effort to see that the experimental conditions are optimized. This is especially true for studies requiring large amounts of scarce high energy beam time.

ACKNOWLEDGEMENTS

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Table I
D Values for Neat Metals and Aqueous Solutions

| Element (Z) | Edge Energy ¹ | D Value | |
|-------------|--------------------------|-------------------------|---|
| | | Neat Metal | Aqueous Sol'n. (6.25 x 10 ⁻⁴ M) |
| Ca(20) | 4.038 | 8.88 x 10 ⁻¹ | 2.96 x 10 ⁻⁴ |
| Mn(25) | 6.540 | 8.80 x 10 ⁻¹ | 7.68 x 10 ⁻⁴ |
| Fe(26) | 7.112 | 8.74 x 10 ⁻¹ | 8.84 x 10 ⁻⁴ |
| Cu(29) | 8.979 | 8.69 x 10 ⁻¹ | 1.42 x 10 ⁻³ |
| Zn(30) | 9.659 | 8.63 x 10 ⁻¹ | 1.66 x 10 ⁻³ |
| Mo(42) | 19.999 | 8.45 x 10 ⁻¹ | 5.27 x 10 ⁻³ |

¹ Edge energies and cross section data were taken from reference

5.

Table II
Optimization¹ of F and μ_x for Fixed Values of R and $N = 10^8$

| $R(\%T)^2$ | Optimum F(%T) | Optimum $\mu_x(\%T)$ | S/N ³ |
|------------|------------------|-------------------------|------------------|
| 4.61(1) | 0.261(77) | 2.55(8) | 44.5 |
| 2.30(10) | 0.248(78) | 2.52(8) | 42.7 |
| 1.61(20) | 0.221(80) | 2.52(8) | 40.7 |
| 1.20(30) | 0.211(81) | 2.49(8) | 39.6 |
| 0.92(40) | 0.198(82) | 2.46(9) | 36.4 |
| 0.69(50) | 0.186(83) | 2.46(9) | 33.6 |
| 0.36(70) | 0.186(83) | 2.30(10) | 27.3 |
| 0.22(80) | 0.128(88) | 2.29(10) | 22.8 |
| 0.11(90) | 0.094(91) | 2.23(11) | 17.1 |
| 0.05(95) | 0.073(93) | 2.15(12) | 12.1 |
| 0.01(99) | 0.030(97) | 2.08(12) | 5.6 |

¹ Equation 18 was used as a model for the optimization of F and μ_x . For each value of R the values of F and μ_x were found that gave the maximum S/N.

² %T means the percent of radiation transmitted through the sample or ionization chamber.

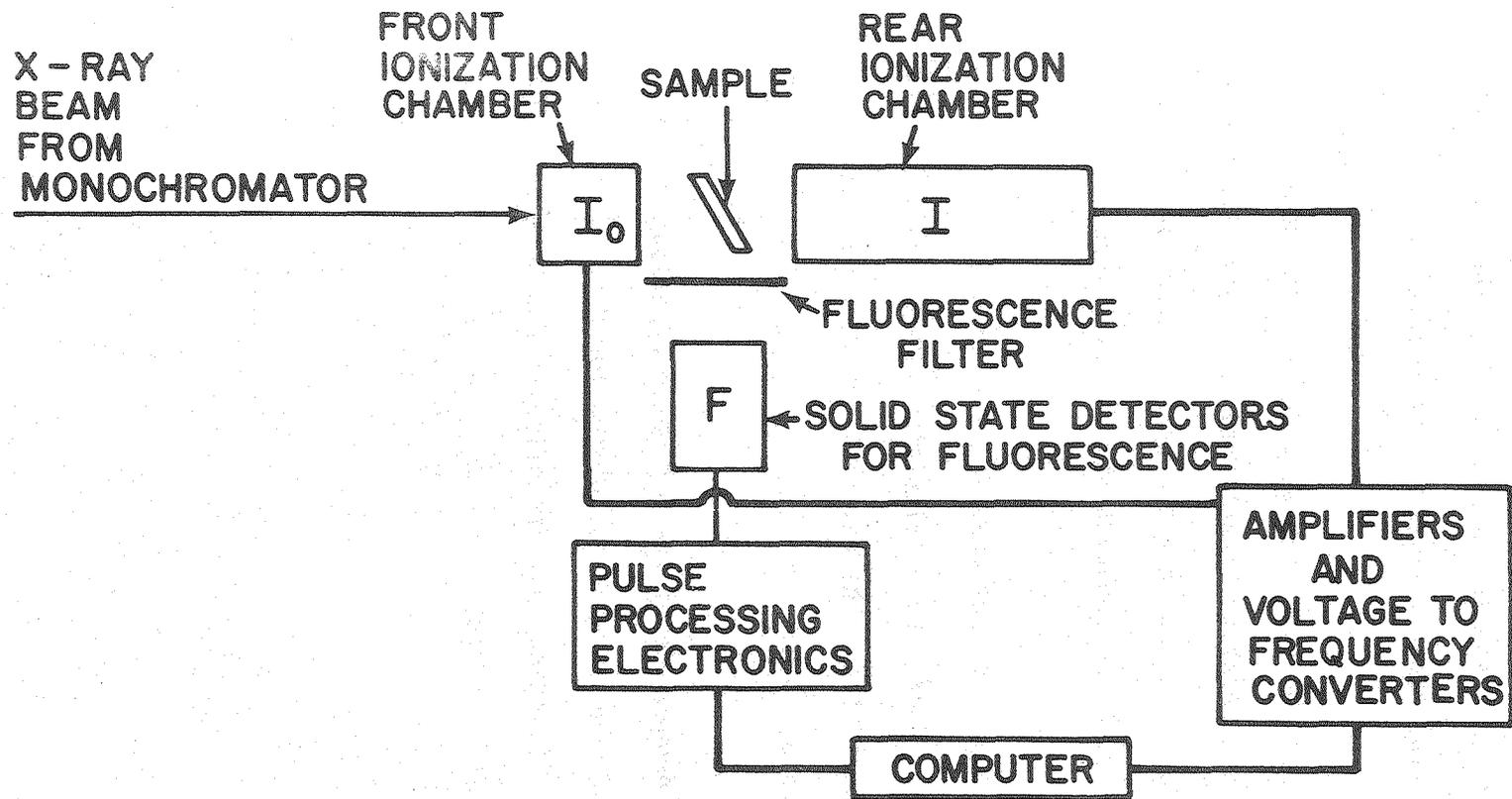
³ The S/N ratios were computed for a sample with $D = 0.80$.

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FIGURE CAPTIONS

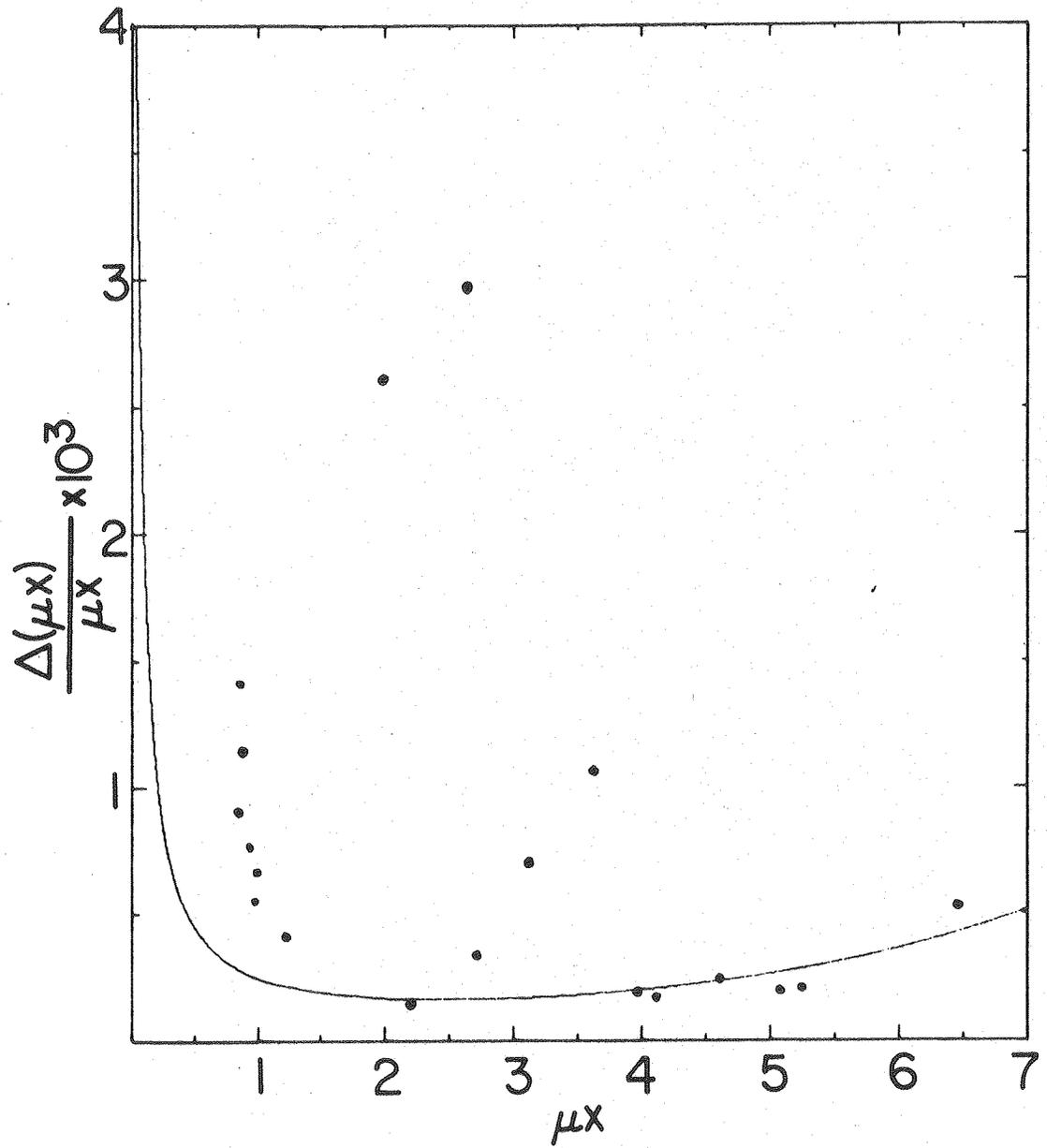
- Fig. 1. Schematic diagram of apparatus for the measurement of x-ray absorbance showing the position of the ionization chambers, fluorescence detector and sample.
- Fig. 2. Comparison of the experimentally determined (dots) values of the relative uncertainty in μx with the values predicted by assuming that the uncertainties are dominated by photon counting statistics (curve).
- Fig. 3. Predicted dependence of the S/N ratio on sample absorbance. Curves were calculated for $N = 10^8$, $R = 2.3$ and F as indicated. The calculations were done for a sample with $D = 0.8$.
- Fig. 4. Predicted dependence of the S/N ratio on sample absorbance. Curves were calculated for $N = 10^8$, $F = 0.11$ and R as indicated. The calculations were done for a sample with $D = 0.8$.



APPARATUS FOR EXAFS MEASUREMENT

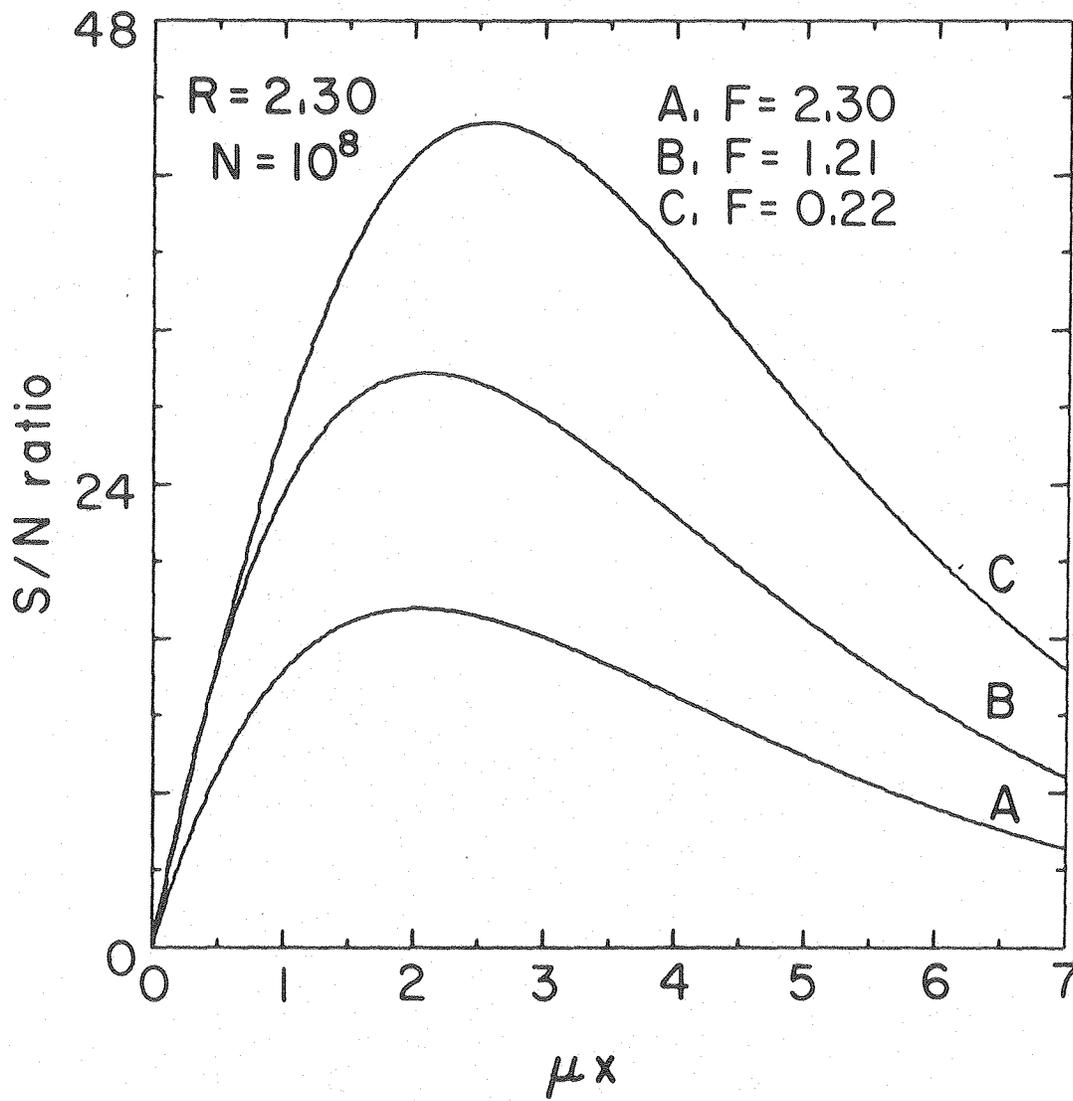
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Fig. 1, Smith, Kirby,
Thompson & Klein



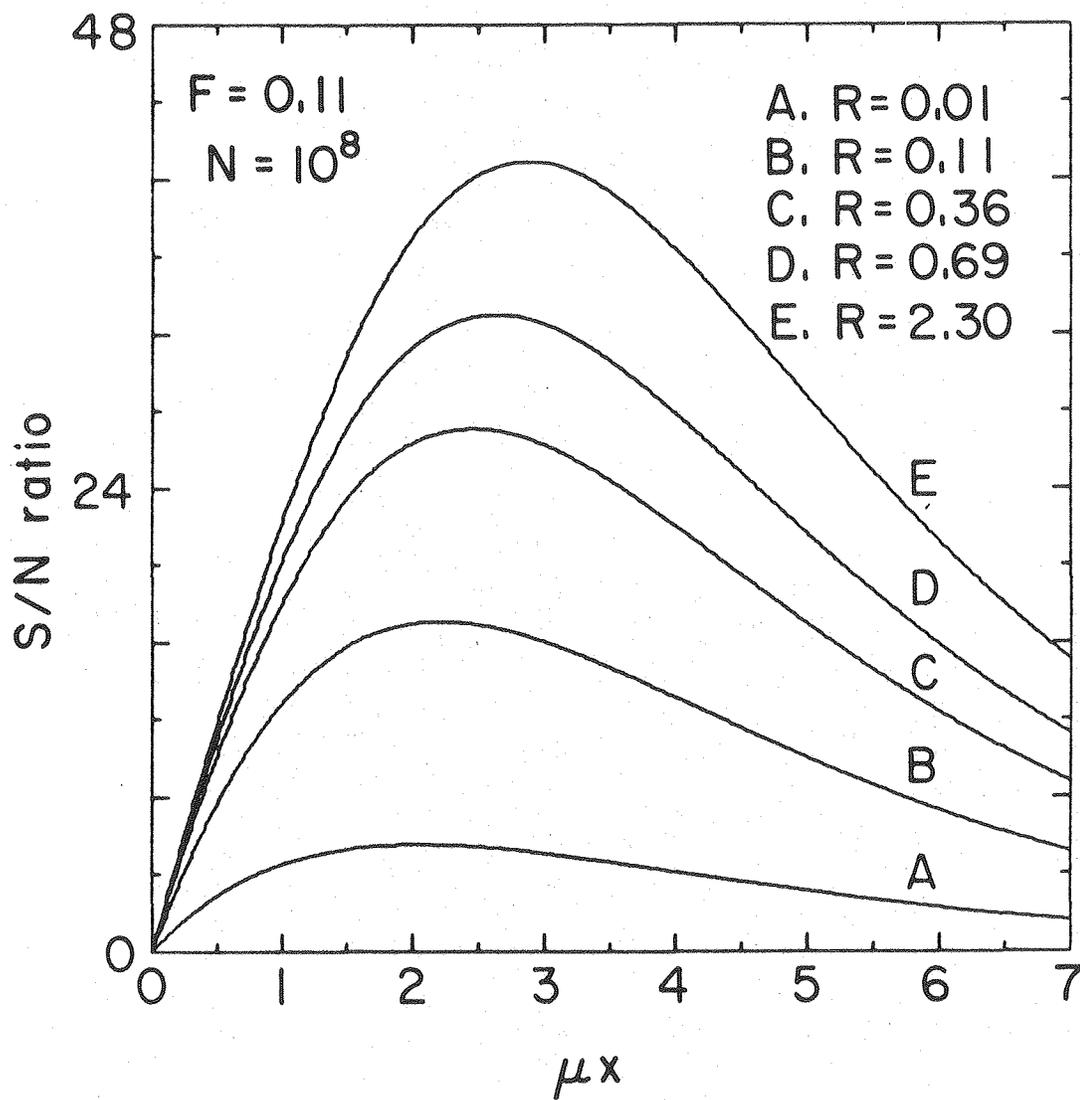
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Fig. 2, Smith, Kirby, Thompson and Klein.



XBL 797-4946

Fig. 3, Smith, Kirby, Thompson and Klein



XBL 797-4947

Fig. 4, Smith, Kirby, Thompson and Klein.

