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J. M. Jaklevic, B. W. Loo, and T. Y. Fujita

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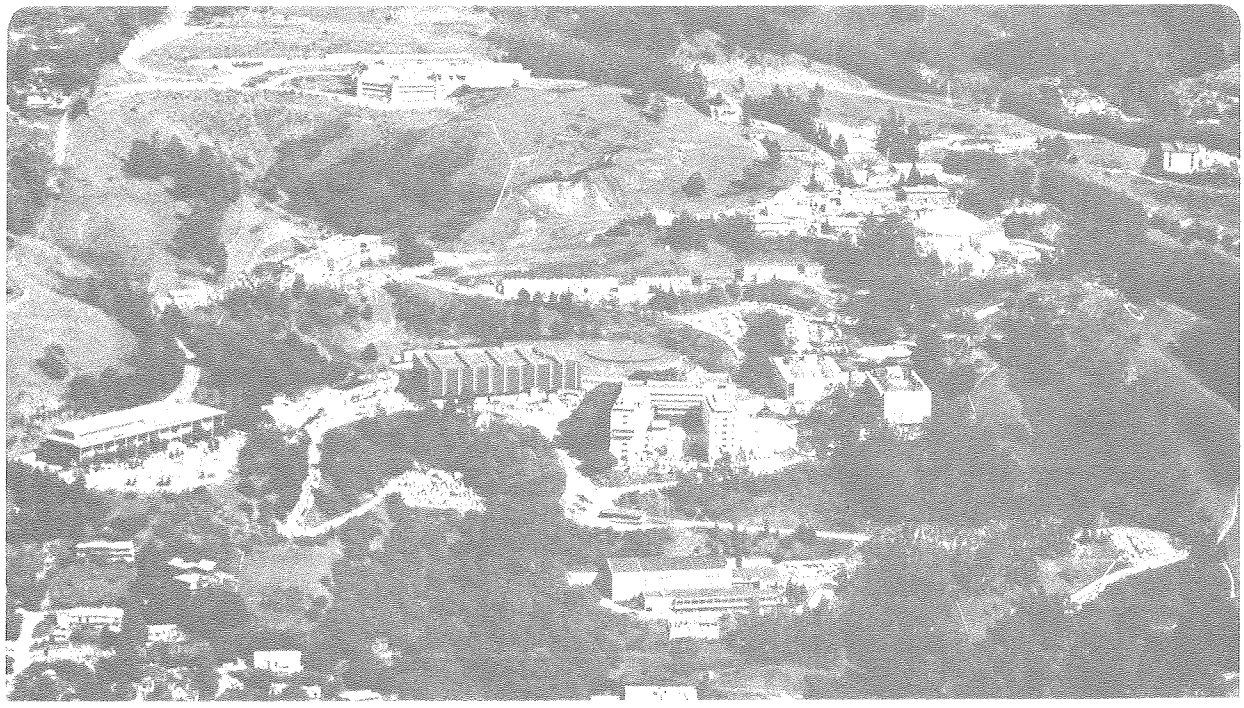

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ABSTRACT

An instrument is described which employs a dichotomous sampler to acquire fine particulate samples on a continuous tape filter. Analyses for elemental sulfur are performed immediately following acquisition using a sensitive X-ray fluorescence spectrometer. Sample sequencing, data acquisition, and calculation of concentrations are performed continuously using an on-line calculator. Precision and accuracy of the method are discussed and results obtained from ambient measurements are presented.

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INTRODUCTION

The increased emission of sulfur-containing compounds into the atmosphere has become a major consideration in the design of air pollution monitoring and control strategies. This has stimulated considerable interest in the development of monitoring equipment capable of analyzing the atmospheric aerosol for sulfur-containing compounds. We describe a rapid, sensitive and accurate X-ray fluorescence method for the analysis of elemental sulfur collected from ambient aerosol samples. The instrument includes a dichotomous sampler, air filter transport system and high-sensitivity wavelength dispersive X-ray fluorescence analyzer. An associated calculator/controller enables one to obtain real-time measurements of ambient particulate sulfur concentrations over short time intervals.

ANALYSIS METHOD

The technique of X-ray fluorescence analysis has been previously demonstrated to be a sensitive and accurate method for the analysis of elemental sulfur in air particulate samples collected on thin-membrane substrates.[1,2] Although much of this work has involved multiple element analysis using energy dispersive X-ray spectrometers, the use of single-channel wavelength dispersive analyzers is preferred when only one particular element is to be analyzed.[3] The wavelength dispersive method has the advantages of simplicity and compactness when used for transportable X-ray analyzers. Figure 1 is a simplified schematic of a wavelength dispersive X-ray spectrometer optimized for the detection of sulfur Kα characteristic X-rays. The spectrometer depends upon the coherent reflection of X-rays from selected

lattice planes of a critically-oriented germanium crystal. X-rays incident on the crystal will be reflected only if the wavelength (λ) satisfies the Bragg condition:

$$\lambda = 2d \sin \theta \tag{1}$$

where d is the lattice spacing of the crystal planes (in this case Ge <111>, $2d = 6.532$ Å) and θ is the angle between the incident X-ray and the lattice plane. If the range of angles incident on the crystal is restricted by means of narrow slits, then only a limited range of wavelengths (or energies) are reflected into the proportional counter. The resolution of the spectrometer is determined by the angular divergence of the slits $d\theta$ as follows:

$$\frac{dE}{E} = \frac{d\lambda}{\lambda} = \frac{d\theta}{\tan \theta} \tag{2}$$

In the present design, 2.31 keV sulfur Kα X-rays are detected at $\theta = 55.4^{\circ}$ with a resolution of 13 eV. In the application of the sulfur spectrometer to ambient aerosol analysis, it is important that the energy resolution is sufficient to eliminate interfering X-rays resulting from excitation of the lead M_{α} lines at 2.34 keV. It is characteristic of wavelength dispersive spectrometers that the very good energy resolution is achieved at the expense of reduced geometrical efficiency.

An improvement over the planar geometry can be achieved by using a curved crystal for the reflecting element. By appropriately bending and grinding the surface of the Ge crystal it is possible to achieve a reflection geometry whereby all X-rays of a given wavelength which originate in a narrow slit can be refocused in a slit image at a complementary location. Different wavelengths focus at different locations in the same manner as before except that the focusing properties increase the geometrical efficiency considerably.

We have constructed such a spectrometer using a commercially obtained Ge <111> crystal that had been bent to a 15 cm diameter focusing circle. Figure 2 is a schematic of the spectrometer. The narrow range of wavelengths over which the spectrometer is sensitive is determined by the orientation of the crystal with respect to the defining slit in front of the proportional counter. The Bragg condition is then satisfied for all 2.31 keV X-rays which originate from the sample and with directions within the angular spread indicated by the virtual source. The sensitivity of this spectrometer has been measured to be approximately 10 times the simple geometry shown in Figure 1.

There are several other features of the spectrometer design which are important to consider. The chamber enclosing the major portion of the path between sample and counter is hermetically sealed in order to permit operation in a helium gas environment. The use of a helium environment in preference to a vacuum chamber was dictated by the presence of 50 μm Be windows on both the proportional counter and spectrometer entrance. The transmission of the helium path for 2.31 keV X-rays is 98% compared with less than 1% for an equivalent air path. Absorption of the sulfur X-rays is further reduced by exposing the top surface of the membrane filter samples to the aerosol deposit and placing the sample within 2 mm of the Be entrance window. The transmissions of the air path and 50 μm Be window are 94% and 92% respectively.

Irradiation of the sample is provided by a 40-watt, Ag anode air-cooled X-ray tube illuminating the sample from below. The 3 keV Ag X-rays are transmitted 86% by the approximately 1 mg/cm^2 filter substrate. Although the close-coupled geometry produces more scattering than normally desired, the increased efficiency for detection more than compensates.

SAMPLING METHOD

The sulfur compounds of interest in normal ambient monitoring result principally from the large-scale combustion of fossil fuels. It is well known that the sulfur containing particulates are concentrated in the fine particle fraction.[4] The sulfur monitor design includes a 16.7 ℓ/m single-stage virtual impactor with a 2.5 μm cutpoint to separate the coarse and fine particle fractions before they are deposited on the filter.[5] This increases the sensitivity for sulfur analysis by removing potentially interfering material from the sample and eliminates many X-ray analysis problems associated with the larger particles sizes.

Figure 3 shows a cross section of the modified impactor design. The small particles are directed onto a 1.6 cm^2 circular teflon membrane filter area which is incorporated into a continuous 35 mm wide paper tape. The filters and associated optical locating holes are spaced at 3.81 cm intervals along the strip.

The coarse particles are collected on a 37 mm diameter cellulose filter. The filter was chosen to minimize the impedance in the coarse particle flow circuit. Since the coarse particles are not included in the analysis, the associated filter is changed infrequently. Our operating experience has indicated that once per month is adequate under normal operating conditions. If coarse particle loading becomes significant, it is possible to modify the flow pattern to impact the particles preferentially in the center of the filter thereby decreasing the effects of filter clogging.

The fine particle filters are changed frequently depending upon the experimental protocol. A pneumatic flow controller, flow rate meters and a diaphragm vacuum pump are incorporated into the monitor hardware. The flow

controller compensates for the variation in fine particle filter impedance as the loading increases; a vacuum actuated switch is used to detect overload conditions and initiate filter changes where appropriate.

SAMPLER OPERATION

The filter tapes are obtained in continuous rolls in lengths of 30-meters corresponding to a supply of 800 filters per roll.[6] A takeup reel is used to advance the strip past the sampling and analysis locations. Normal operating protocol calls for a sample to be acquired for the appropriate interval followed by an advance of the tape to the next sampling location. The previously exposed sample is now in the analysis position in the spectrometer sample position. Analysis results for the preceeding sample are generated simultaneously with the acquisition of the subsequent filter sample. Normal operation requires that the analysis interval be equal to or less than the sample interval. However, for very short sample intervals, it is possible to operate in a mode where sample analysis is deferred for batch processing at a later time.

The sequencing of samples, timing of sampling and analysis intervals and monitoring of experimental parameters are performed with an on-line calculator interfaced to the appropriate hardware as illustrated in Figure 4. The calculator is also used to store calibration data, perform concentration calculations, and output data to either printer or magnetic tape cassette.

The only calibration data contained in the calculator are a blank concentration obtained from an average over several unexposed filters and a

sensitivity factor obtained from a carefully prepared particulate sulfur standard. The calculator automatically adjusts the result for changes in sampling and analysis intervals. Additional control features include the ability to automatically change filters if, during an air pollution episode, the maximum filter loading is reached before the end of the regular sampling period.

CALIBRATION AND RESULTS

The results of the X-ray analyses are calculated from the following formula:

$$C(\mu g/m^3) = K \frac{(N_S - N_B)}{S\, T_S} \qquad (1)$$

where N_B is the background counting rate obtained as an average over several blank filters, N_S is the counting rate obtained for the sulfur peak in the exposed sample, T_S is the sampling interval, and S is the sensitivity of the spectrometer as obtained from a standard. A typical value for S is 4.2 cts/sec per $\mu g/cm^2$ for an X-ray tube power of 30 watts using the curved crystal spectrometer. N_B is 0.7 cts/sec under these conditions. The factor K is a constant which includes the equivalent flow rate per unit area on the fine particle filter. The sensitivity factor S is obtained by measuring the counting rate obtained from a known concentration of fine particle sulfur. Standards for this measurement are prepared by generating fine 0.3 μm particle $CuSO_4$ aerosols and collecting them on a membrane filter. The concentration per unit area is measured by a carefully calibrated energy dispersive X-ray spectrometer. A cross check on the sulfur results is obtained from a measurement of the copper concentration assuming 1:1 stoichiometry.

Agreement between these measurements verifies that particle size or filter matrix effects associated with the low-energy sulfur X-rays have been minimized. Several standards spanning the concentration range from 1 to 30 $\mu g/cm^2$ have been prepared and measured to ensure linearity of calibration equation (1). Although the sulfur X-rays are attenuated in their passage through the spectrometer system, the fact that the standards and unknowns experience identical conditions cancels the discrepancy.

Assuming that the automatic flow controller, X-ray current stabilizer, helium pressure and other easily regulated parameters are maintained within $\pm$ 1%, the most serious sources of measurement error are variability in background counting rate, changes in sensitivity and measurement artifacts associated with X-ray matrix and particle size effects.

The variation in background from one blank filter to the next is probably due to small-scale non-uniformities in the filter structure which result in unpredictable changes in scattering probability or filter transmission characteristics. A series of 10 blank filters have been measured and the root mean square variation determined. The error associated with these variations is equivalent to $\sigma \approx 0.030$ $\mu g/cm^2$. Variations in sensitivity have been observed to be limited by the precision of the X-ray tube voltage and current control to a few per cent. Periodic checks can be made using the $CuSO_4$ standard to ensure that major systematic shifts have not occurred. Such shifts can be the result of defective He atmosphere in the spectrometer or changes in the proportional counter gain.

Problems associated with X-ray particle size and matrix effects are greatly reduced by the use of dichotomous size separation and thin membrane filters. Assuming a mean particle diameter of 0.3 μm for the sulfur aerosol particles, the correction due to particle size effect is < 1%. The larger

correction for thick deposits can be estimated to be 3% for 100 $\mu g/cm^2$ up to 13% for 500 $\mu g/cm^2$. The nominal overload condition for the flow controller will trigger at 150--200 $\mu g/cm^2$. Since the particle deposit is on the filter surface facing the spectrometer, no correction for filter attenuation effect is required. Results obtained with the current X-ray fluorescence analyzer have been cross checked with other X-ray measurements with excellent agreement.

The precision of the measurement for short-term samples or light filter loadings is limited primarily by statistical variations in the counting rate averaged over the analysis interval. Table 1 is a summary of operating performance under a variety of sampling situations. The 3δ minimum detectible limits are quoted for both types of spectrometer for different sample intervals and assuming a constant analysis time of 600 sec. The improved sensitivity of the curved crystal design is apparent.

Figure 5 is a plot of continuous sulfur measurements made on an hourly average during an eight-day interval in St. Louis. These results were a part of an intercomparison study involving several sulfur analysis methods. Results of the comparison will be published separately.[7] The plot is shown here to illustrate the continuous monitoring capability of the present instrument. The results shown were available to the experimenters automatically on a continuous basis during the course of the study. Discontinuities in the data are the result of operator intervention in the experiment and do not reflect upon the reliability of the continuous sampler. The sensitivity of the combined sampler/analyzer system is such that sampling time of 20 minutes or less could be employed. It is important to note that these results are for elemental sulfur only; equivalent sulfate concentrations would be three times greater. A comparison of these measurements with the minimal detectable limits

given in Table 1 illustrates the sensitivity of the instrument for ambient aerosol measurements. For example, using the curved crystal spectrometer, it would be possible to perform sampling and analysis with five-minute time resolution during the peak sulfur concentration episodes.

CONCLUSIONS

Results obtained from the intercomparison of these results with other analytical methods support the validity of the present technique. The inherent advantages of the X-ray method include stability of calibration, relative immunity from chemical interferences, and the non-destructive processing of samples. Operating experience has demonstrated the ease of calibration and set-up procedures. The availability of the samples following X-ray fluorescence analysis permit the use of the sampler for the collection of particulates for use with multiple analytical methods. The present instrument is approximately 1 meter high and 0.5 meters on a side and weighs less than 35 kgms and is thus easily transportable to field locations.

ACKNOWLEDGEMENTS

The authors acknowledge the participation of W. Searles and S. Wollenburg in much of the mechanical and electronic design phases. F. S. Goulding, D. Landis, N. Madden and other members of the Lawrence Berkeley Laboratory Department of Instrument Techniques contributed significantly to the success of the project. We appreciate the assistance of R. Gatti and R. Giauque in the preparation of standards and validation of the results.

References to a company or product name does not imply approval or recommendation of the product by the University of California or the United States Department of Energy to the exclusion of others that may be suitable.

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6. Filter tape supplied by Ghia Corporation, 7071 Commerce Circle, Pleasanton, CA. 94566.

7. Results of a conversation with Dr. D. C. Camp. Information to be published as an Environmental Protection Agency report, 1980.

TABLE I. Minimum Detectible Limits (3 σ) for Elemental Sulfur

SAMPLE INTERVAL (16.7 ℓ/m)	ANALYSIS WITH FLAT CRYSTAL (600 sec)[a]	ANALYSIS WITH CURVED CRYSTAL (600 sec)[b]
1 min.	31.8 $\mu g/m^3$	5.7 $\mu g/m^3$
5 min.	6.36	1.14
1 hr.	0.53	0.10
6 hrs.	0.089	0.016
12 hrs.	0.044	0.008
24 hrs.	0.022	0.004

[a] 3 σ = 0.21 $\mu g/cm^2$

[b] 3 σ = 0.037 $\mu g/cm^2$

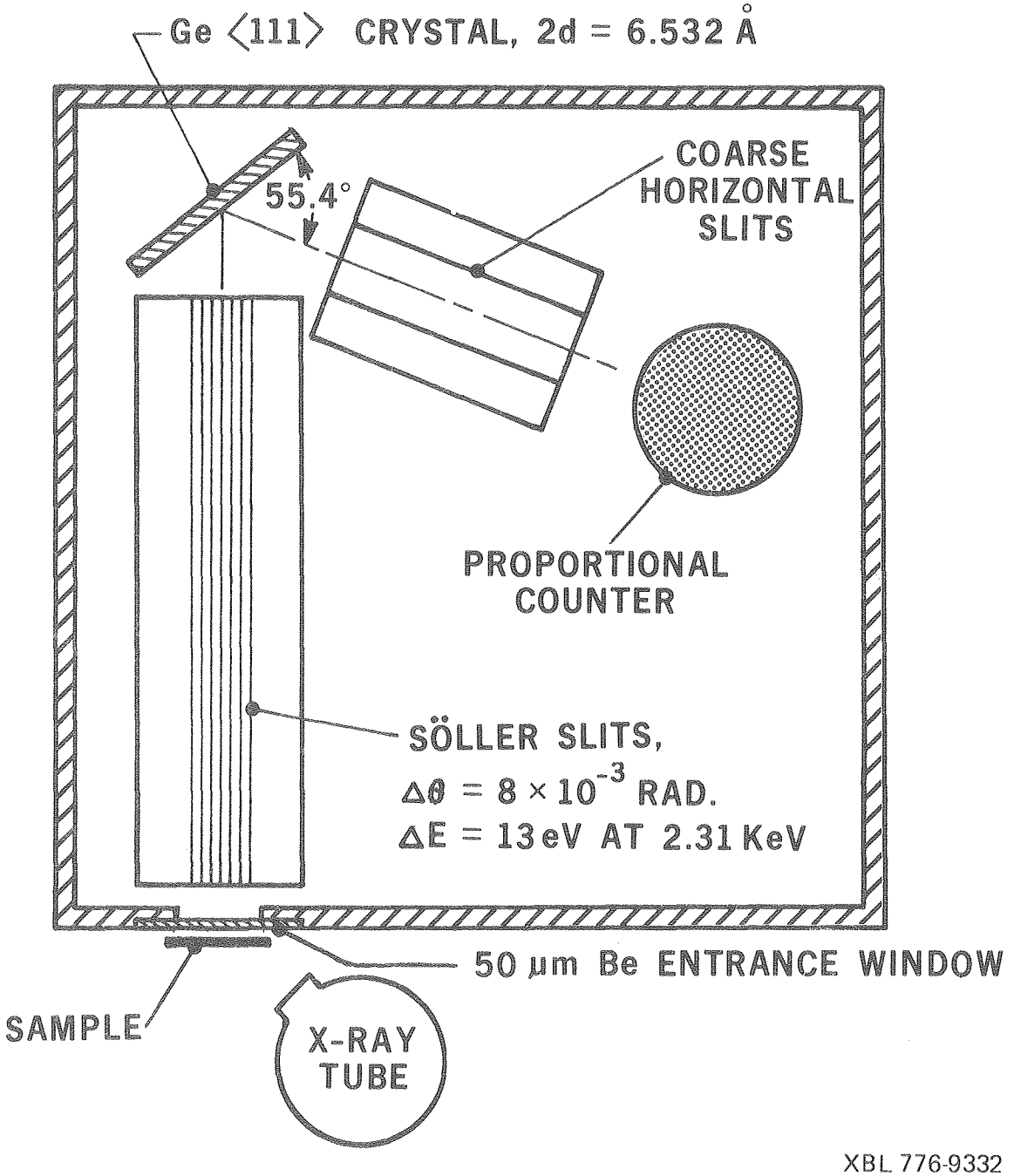

Figure 1. Schematic drawing of wavelength dispersive spectrometer. Ge <111> crystal is tuned to the sulfur Kα emission energy.

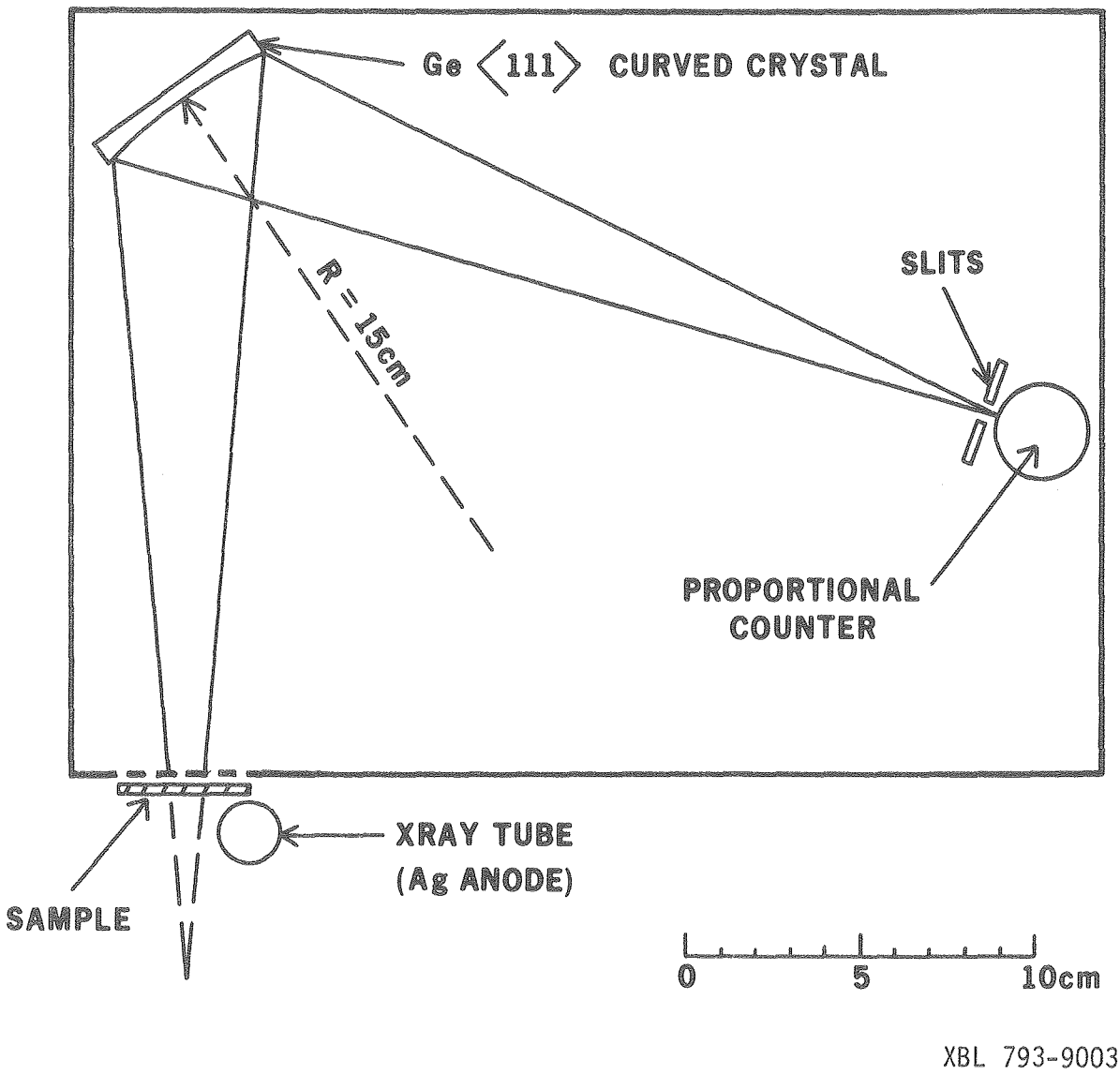

Figure 2. Wavelength spectrometer incorporating curved crystal X-ray optics.

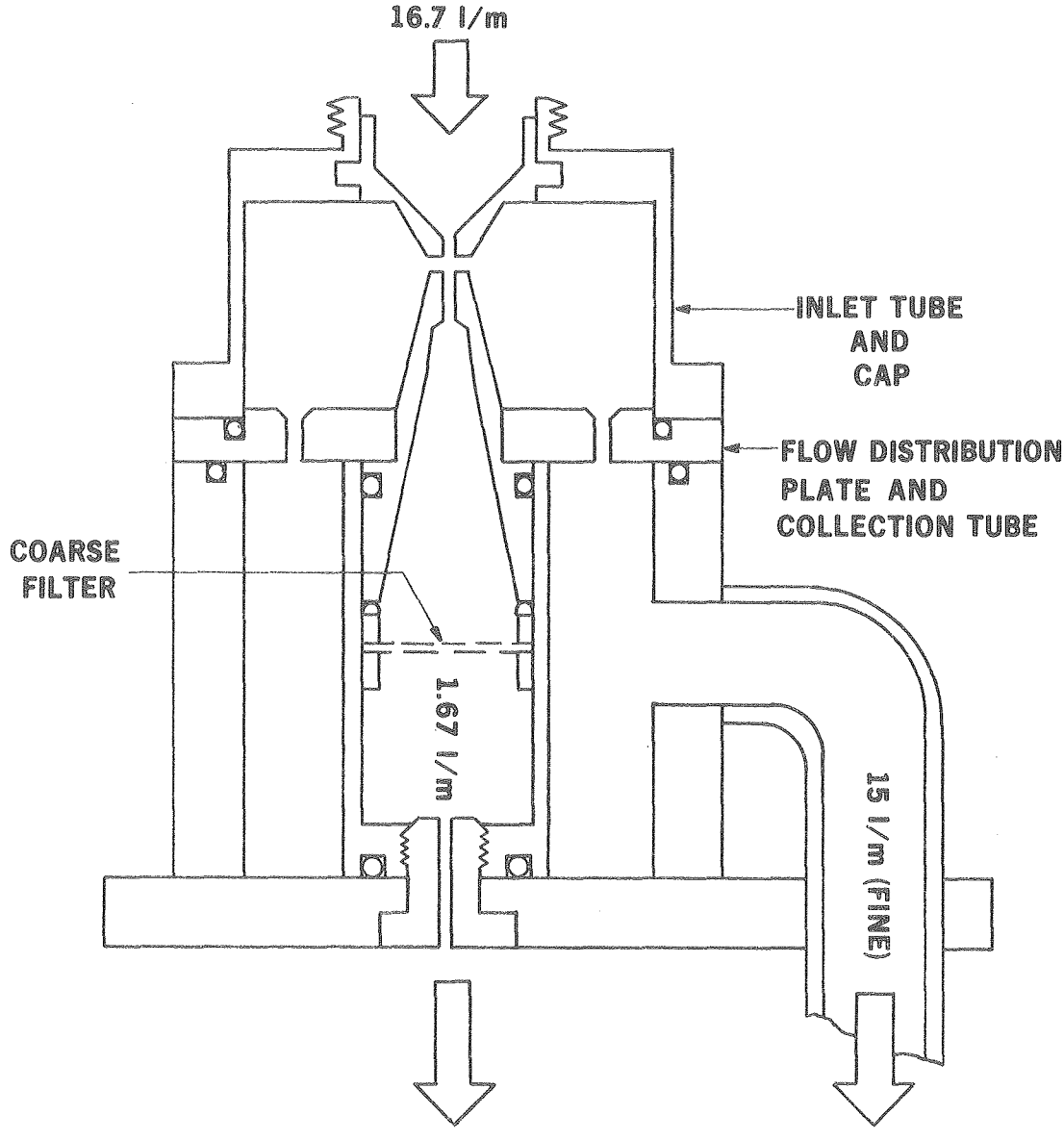

Figure 3. Diagram of modified dichotomous sampler. Coarse particles are collected within sampler, fine particles are extracted for deposition on continuous filter strip.

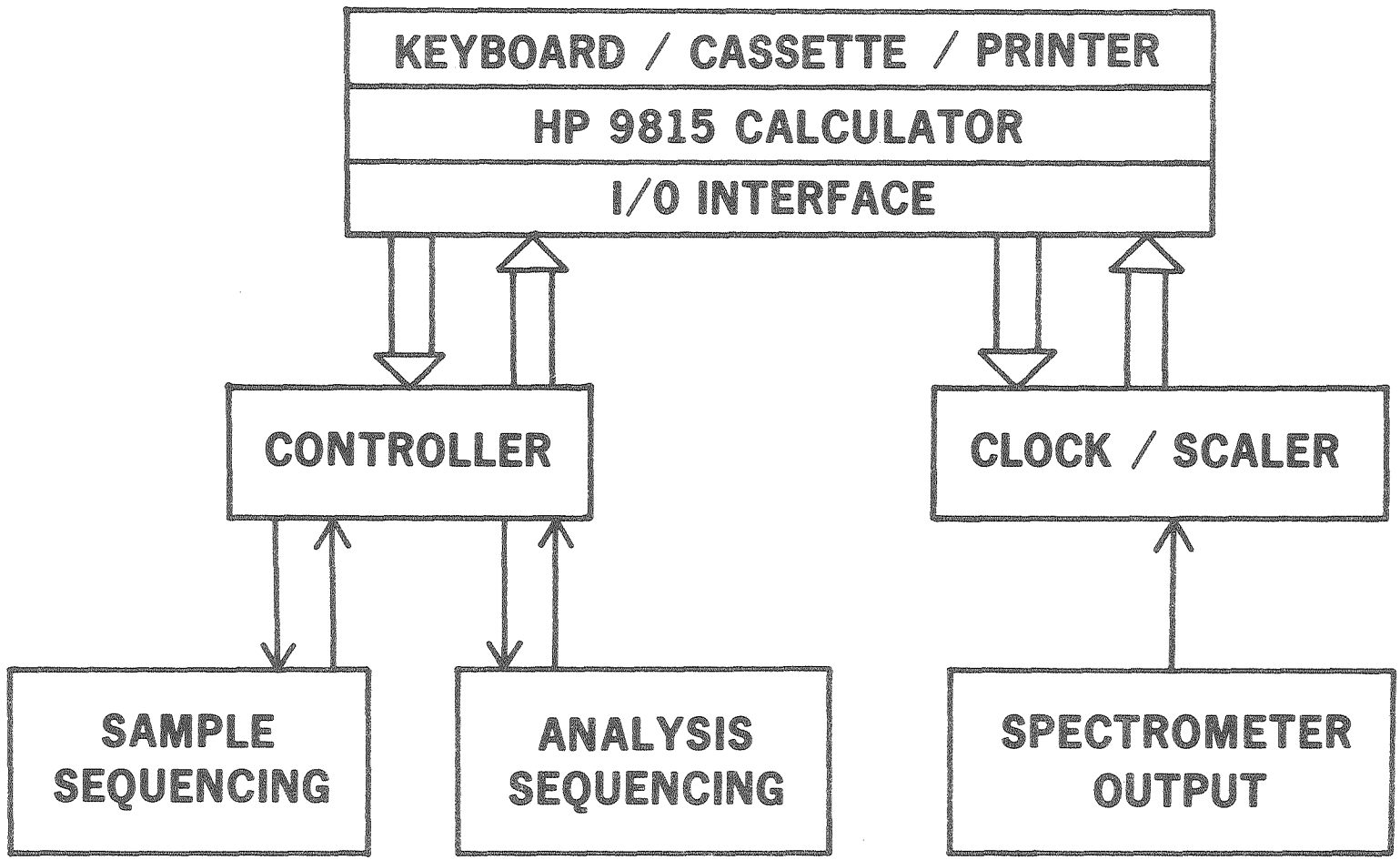

Figure 4. Block diagram of data acquisition and analysis electronics.

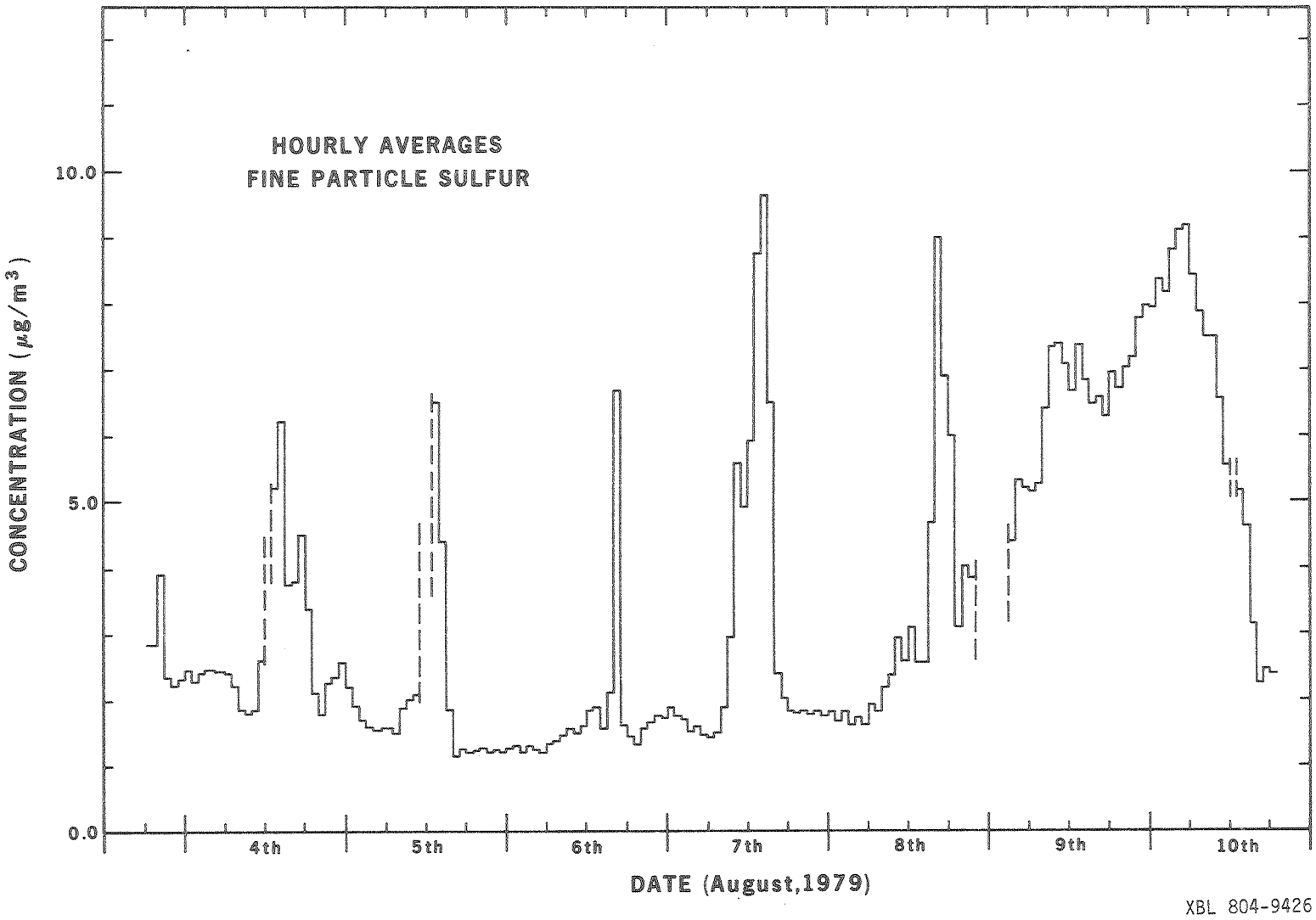

Figure 5. Plot of continuous particulate sulfur measurements obtained over a seven-day period. The sampling interval was one hour.

FIGURES

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