Lawrence Berkeley National Laboratory

Title
ELEMENTAL SULFUR ANALYSIS USING X-RAY TECHNIQUES AND B -GAUGE MASS MEASUREMENTS

Permalink
https://escholarship.org/uc/item/25f6c74j

Author
Goulding, F.S.

Publication Date
1977-07-01

ELEMENTAL SULFUR ANALYSIS USING X-RAY TECHNIQUES
AND β-GAUGE MASS MEASUREMENTS

F. S. Goulding, J. M. Jaklevic, and B. W. Loo

July 1977

ELEMENTAL SULFUR ANALYSIS USING X-RAY TECHNIQUES

AND β-GAUGE MASS MEASUREMENTS

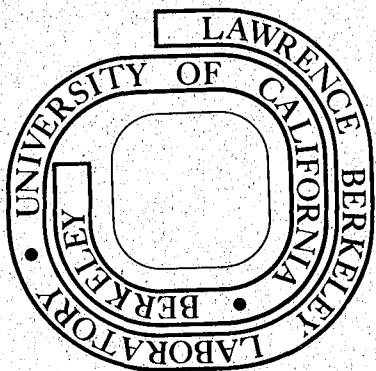F. S. Goulding, J. M. Jaklevic and B. W. Loo

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 U.S.A.

ELEMENTAL SULFUR ANALYSIS USING X-RAY TECHNIQUES
AND β-GAUGE MEASUREMENTS*

F. S. Goulding, J. M. Jaklevic and B. W. Loo

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 U.S.A.

SUMMARY

The activities funded under the present EPA/ERDA interagency agree-
ment have been concentrated mainly in two areas. An elemental sulfur moni-
tor for the measurement of fine particulates has been designed, construc-
ted, and is currently being tested at LBL. A prototype of the device will
be delivered in the near future. A second program has involved the de-
velopment of the β-attenuation technique for the large-scale measurement
of the masses of particulate deposits. The emphasis has been primarily
concerned with the fabrication of improved hardware to perform the meas-
urement conveniently and accurately.

Other activities included consultation with EPA on questions concern-
ing air sampling techniques and X-ray fluorescence analysis of aerosol
samples. An additional long-term interest has been the development of
X-ray techniques which are capable of determining the chemical form of
the sulfur atoms in an environmental sample. Since these latter activi-
ties are in a more speculative period of development, the present progress
report emphasizes the activities in the area of elemental sulfur monitoring
and β-gauge development. Subsequent reports will address themselves to
the other areas of interest.

Part A
SULFUR MONITOR

INTRODUCTION

The growing importance of sulfur as a component in air pollution
has placed emphasis on the development of methods to detect and accurately
measure the concentration of sulfur related compounds in atmospheric
aerosols. In the case of aerosol particulates, it has been demonstrated
that the X-ray fluorescence analysis of samples acquired on thin membrane
filters is a reliable and accurate method for the measurement of elemental
sulfur.[1,2] Studies have found that sulfur is present in fine particle
urban aerosol predominantly in the sulfate form.[3] The measurement of fine
particle elemental sulfur by X-ray fluorescence should then be a valid in-
dicator of sulfate concentrations for air pollution research and monitoring
purposes.

We have developed a combined air sampler/X-ray fluorescence analyzer
designed to automatically perform continuous measurement of particulate
sulfur concentrations.

DESCRIPTION OF INSTRUMENT

Figure 1 shows a schematic drawing the of LBL Particulate Sulfur
Monitor. It consists of a dichotomous virtual impactor, continuous
tape membrane filter supply X-ray fluorescence analyzer, and assorted
pumps and flow controllers. The instrument operates under the command
of a microprocessor oriented controller which sequences the filter tape
past the sampling head and X-ray fluorescence spectrometer. Under normal
operating conditions the samples are collected for a predetermined inter-
val (T_s), typically from 1 to 24 hours. The sulfur content is subsequently

measured at the spectrometer for a given analysis period (T_A) of 1000

to 10,000 seconds depending on the sensitivity and accuracy required.

(Obviously $T_A < T_s$) Calibration information is then applied to the acquired

data which is printed or otherwise communicated to a data monitoring system.

Virtual Impactor

The virtual impactor is adapted from an earlier version which has

been extensively field tested and validated over the past three years.[4]

The cross sectional view in Fig. 2 shows a total input flow of 16.7 1/min

which is split into two streams of 75% and 25% respectively. All of the

coarse particles above 2.4 µm aerodynamic diameter together with 25% of

the fine particles are contained in the smaller volume air stream and are

subsequently removed by the filter in the bottom of the sampler. The 12.5

1/min flow contains only these particles less than 2.4 µm. It is these

particles which are subsequently collected on the thin membrane filter

for analysis.

Since the coarse particles are not analyzed in the present mode of

operation, the collecting filter is designed to operate free of clogging

for long periods. This is done by designing the collector stage as a

large particle impactor which preferentially deposits the mass in the

center of the filter and allows a large area of flow around the periphery

of the filter. No significant change in impedance is expected until the

total area of the filter becomes heavily loaded with particulates. It is

assumed that periodic maintenance of the inlet device will include cleaning

of this filter. The virtual impactor has been designed to be easily acces-

sible and conveniently dismantled and reassembled.

The flow circuit for the dichotomous sampler is illustrated in Fig. 3.

There are shown two versions of the sampler utilizing two methods of flow

control. In Fig. 3a, a variable orifice is inserted in series with the collecting filter. A feedback loop maintains the combined impedance of the filter and orifice constant as the filter impedance is increased due to particle loading. The displacement of the variable orifice actuator can be used to indicate the degree of loading which the filter has experienced and appropriate measures taken when it becomes excessive. This design was used in the first prototype model.

In Fig. 3b, a constant differential flow controller is used on the output of the pump. The controller is a self-contained mechanical feedback device which maintains the pressure drop across the reference impedance constant by regulating the flow through the circuit. This device will be incorporated in future samples because of its simplicity and low cost.

In order to determine the degree of particle loading which the filter has experiences a separate pressure switch is used to monitor the pressure drop across the membrane filter itself.

The pump employed in the present flow conditions can produce a pressure drop of 370 Torr the membrane filter at 1.5 cfm (42.5 1/m).

Continuous Filter Tape

The membrane filters are mounted on a continuous strip of 35 mm film backing. The active area of the filter is 1.6 cm^2 (1.43 cm diameter) and they are separated by 7.62 cm on the strip. The film is available with either thin polycarbonate or teflon membranes from a commercial supplier.[5] The pore size used in the present applicator is 2 µm. The film advance hardware uses standard 35 µm photographic film take-up reels. The film is optically located using additional 1 mm diameter holes which are punched in the strip at the same time as the membrane filters are being mounted.

The use of thin ($\sim$1 mg/cm^2) membrane filters is particularly important for accurate sulfur measurements. Earlier work has demonstrated that the most serious source of error in the X-ray fluorescence analysis of fine particle sulfur is due to the penetration of the particles into the membrane and the resulting attenuation of the sulfur X-rays as they leave the sample. For a 1 mg/cm^2 filter, the attenuation due to a uniform distribution of particles in this thickness of filter would be 18%. This would represent the extreme case of complete particle penetration which has previously been observed only in high ambient relative humidity with cellulose membrane filters. Since the teflon and polycarbonate membranes are hydrophobic, such occurrences are avoided.

A potentially serious drawback to the use of teflon filters is their susceptibility to increased impedance at moderate particle loading. For example, a 1.2 µm pore size Millipore filter can tolerate fine particle mass loadings of 200 µg/cm^2 before the impedance doubles. By contrast, the teflon show similar effect at less than 100 µg/cm^2 while polycarbonate membranes are intermediate between the two. Assuming an ambient fine particle concentration of 100 µg/m^3 of air, a 100 µg/cm^2 filter loading will occur in 127 minutes or 2 hours of sampling with the present design. The resultant doubling of filter impedance will cause the flow controller to exceed its maximum operating range. For this reason, the microprocessor controller is programmed to monitor the rate of loading of the filter and reduce the sampling interval if necessary.

X-ray Spectrometer

The X-ray analyzer consists of a single channel Bragg reflection (wavelength dispersive) spectrometer. It operates on the principle that

X-rays incident on a perfect crystalline array of atoms will be reflected

from the surface if the Bragg relationship is satisfied.

$$\lambda = 2d \sin\theta$$

where λ is the wavelength of the incident X-ray[*] (λ = 5.375Å for the

S K_α X-ray), d is the crystalline spacing of the atomic array.

(2d = 6.532Å for the Ge ⟨111⟩ atomic plane) and θ is the angle at which

the reflection occurs.   (θ = 55.4° for the present case as defined in

Fig. 4.) Of course other wavelengths which are incident on the crystal

can be reflected at other angles near to the main line of interest.   In

order to make the spectrometer selective for a given X-ray wavelength

(or energy) the range of incident angles must be restricted. The Söller

slits in Fig. 4 limit the angular divergence to 8×10^{-3} radians in the

plane of the reflection. From Eq. 1 we can derive a quantitative relation-

ship between angular divergence and energy resolution.

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

The excellent energy resolution of such spectrometer is achieved at

the cost of reduced intensity since the acceptance angle of the spectro-

meter is proportional to $\Delta\theta$. In the present design, an energy resolution

of 13eV at 2.307 keV was selected as a reasonable compromise between maxi-

mum intensity and sufficient resolution to avoid interference from the

Pb M_α X-rays at 2.342 keV.

Excitation of the fluorescence is provided by a Ag anode X-ray tube

operating at 15 kV and 6 mA. The output from the tube has intense char-

acteristic Ag L X-rays at 3 KeV which is slightly above the S K edge at

_____

[*]The wavelength and energy of X-rays are inversely related through the
  De Broglie relationship $\lambda(Å) = 12.4/E(keV)$.

2.47 keV and is nearly optimum for efficient excitation. The 90 watts of anode power are easily dissipated in an air-cooled heat exchanger.

As indicated in Fig. 4, the X-ray tube output is incident at the lower surface of the filter whereas the particulate deposit is on the upper surface facing the spectrometer. The particular geometry was designed to minimize the air path which the S K_α radiation must travel before reaching the detector. This distance is maintained at 2 mm corresponding to a 93% transmission in air. The Ag L excitation is transmitted 75% by a 2 cm path length. This slight reduction in excitation intensity is more than compensated by the convenience of analyzing the sample in ambient air as opposed to He or vacuum surroundings.

CONTROL AND AUTOMATION

Figure 5 illustrates the features of the calculator/controller which is used in automatic sulfur analysis. The instrument is first calibrated in terms of counts/second per $\mu g/cm^2$ using a thin sulfur standard. This number is corrected for the flow rate in the small particle branch of the sampler in order that the results can be expressed in $\mu g/m^3$ of air. It is then entered from the keyboard. A blank filter is run for a predetermined time and the results stored as counts/second (N_B).

The sampler is then ready for operation. The desired starting time, sampling interval, and analysis interval T_A are then entered via front panel switches. At the preselected starting time, a filter will be positioned and clamped and the flow will be maintained for the appropriate interval. At the end of that interval, the film is advanced and a new membrane filter is clamped in the sampling location as the previous filter advances to the analysis station. The sampling and analysis then proceed simultaneously.

At the end of the analysis period the results are calculated according
to Eq. 3 and the results printed.

$$C = \frac{(N_c - N_B T_A)}{T_A T_s} S \tag{3}$$

where N_c is the result of the present measurement, N_B is the background
counting rate, and S is the sensitivity factor. In the case of filter
overloads which result in a shortened T_A, the results are automatically
corrected for this reduced time.

RESULTS

The individual component including flow system, film transport, and
X-ray spectrometer have been tested and found to meet design specifications.
The first prototype is completed and awaits final debugging and field testing.
A second prototype is being designed and built in order to overcome certain
design problems which become obvious during the testing stage of the first
prototype. The newer design will incorporate an improved and consequently
more reliable mechanical transport system and a more efficient calculator/
controller design. The second prototype is due to be delivered to the
EPA in the fall of 1977.

Table 1 is a summary of performance data obtained using the first
prototype. In general, the sampler/analyzer has realized the design goals
for sensitive and accurate sulfur measurements. Improvements in sensitivity
could be achieved by using thinner Be windows for the spectrometer and
proportional counter. In addition, an increase of 20% in counting rate
has been achieved by using a Ti anode instead of the Ag. However, the Ti
tube is not as reliable as the Ag due to the gas absorbing properties of
the Ti material. In view of the observed performance it is felt that
no additional refinements in the spectrometer parameters are necessary
at this time.

Part B
BETA-GAUGE MASS MEASUREMENTS

INTRODUCTION

As a consequence of an involvement in the analysis of large numbers

of samples in the St. Louis RAPS study we have developed a beta-gauge for

the automatic measurement of air particulate deposits. The beta-gauge

method is based on the attenuation which a continuous beta-spectrum under-

goes when traversing a thin layer of matter. The total number of trans-

mitted particles is given as

$$I = I_0 e^{-\mu x} \tag{4}$$

where I_0 is the incident flux, μ is the mass absorption coefficient in

cm^2/gm, and x is the thickness of the layer traversed expressed in gm/cm^2.

Although there are empirical expressions which relate the coefficient μ

to the energy of the beta spectrum, no complete theory for this particular

behavior has been developed. In practice the mass adsorption coefficient

is determined experimentally for a given set of conditions.

A typical measurement program consists of calibrating the instrument

using a series of uniform standards which span the mass range of interest

and which replicate the sample form. For the St. Louis RAPS study the

aerosol samples were deposited on cellulose membrane filter with a nominal

thickness of 4 mg/m^2. The parameters I_0 and μ are then determined from a

fit to the curve of I vs. x, where I is the number of counts measured in the

β-spectrum in a given time interval. For a stable, well-designed system

and accurately measured standards, the experimental data can be fit to a

pure experimental fraction to a root mean square accuracy of 3 $\mu g/cm^2$

for a 100 second measurement.

Subsequent measurements of unknown samples consist in counting for

a specified time interval and calculating the unknown mass from Eq. 4

assuming I_0 and μ as determined from the fit. The convenience of the

measurement causes it to be a candidate for use on large scale programs

where automation is necessary.

The subtleties of the β-gauge method as implemented in the St. Louis

RAPS study have been discussed in previous EPA reports.[6,7] The emphasis

of the present program has been to develop hardware which successfully

accomplishes this task. Second phase of this program will be described

following a brief general description of the basic instrument.

EXPERIMENTAL PROCEDURE

Figure 6 is a schematic of a simplified β-gauge consisting of source,

detector, and sample. The source to detector distance is maintained

constant by the rigid mounting yoke. The sample (or standard) is placed

between the source and the detector and the counting rate measure.

The overall stability of the source to detector geometry and the

associated counting electronics must be adequate to detect a 5 $\mu g/cm^2$

or less change in a nominal 4 mg/cm^2 mass. This also implies a statistical

accuracy in the counting measurement of 1 part in 10^3 which requires a

total number of counts exceeding 10^6. For a spectrometer capable of 10^5 cps,

this implies a measurement time of 10 or greater. In the analysis of the

St. Louis samples analysis times of 30 seconds for the unknown sample

and 100 seconds for standards were routinely employed.

Additional constraints placed upon amplifier gain and geometric sta-

bility were in the range of 1 part in 10^4 over a period of several hours.

They were achieved only through careful design of the hardware and constant control over the ambient operating conditions.

Fortunately one of the less critical parameters is the reproducibility of placement of the samples in the measurement region. This allows the use of automatic sample handling devices which greatly facilitates a large scale study. In the current analysis program, a computer based control and data acquisition system is used for the large scale mass measurement. β-gauge mass determinations are performed on membrane filters before and after the collection of air particulates and are written on magnetic tape output. A computer program performs the necessary calibration fits and converts the scaler counts to mg/cm^2. The result of mass determination before and after exposure are then compared and the mass of the particulate deposit determined.

β-GAUGE WITH LIQUID NITROGEN COOLED DETECTOR

The first version of the β-gauge employed a 25 mm diameter, 6 mm thick Si(Li) detector which was maintained at liquid nitrogen temperature (-196°C) in a vacuum cryostat. The low temperature operation was presumed necessary in order to reduce the electronic noise to an acceptable level. This device operates at approximately 7 keV energy resolution with a 2 μsec shaping time at counting rates of the order of 10^5 counts per second. The β-source was a Pm^{147} 300 μC source purchased commercially. The specifications called for a 1 cm diameter deposit uniform to ±10% over that area. The source was covered with a thin layer of polyamide varnish in order to insure physical integrity while handling. The source is mounted in a separate vacuum chamber with a 0.025 μm Al window.

Since the construction of this system almost three years ago, it has operated continually in the St. Louis RAPS program. More than 45,000 individual mass measurements have been made to date with 25,000 yet to go. These data are accurate to ± 10 $\mu g/cm^2$ and have been validated in intercomparison studies.

THERMODUCTICALLY COOLED β-GAUGE SYSTEM

The principle drawback of the liquid nitrogen cooled detector is the required replenishment of the nitrogen supply in the cryostat and the bulk of the associated dewar. Operating experience gained with this early system showed that an increase in energy resolution could be tolerated without a significant effect on the β-gauge measurement.

The second β-gauge consisted of a similar Si(Li) detector cooled to approximately -70°C by means of a thermoelectric cooling device. In place of the LN cryostat, this device requires only a small vacuum chamber to prevent the detector from collecting condensable vapors and a power supply to drive the thermoelectric cooler. However in order to maintain the 1 part in 10^4 stability it was found necessary to stabilize the temperature of the detector by means of a feedback loop which controls the power level of the cooler. This, together with the pumping equipment required to maintain the vacuum chamber, we increased the complexity of this device beyond the original sample concept.

A prototype of this system together with an automatic sample charger was built and evaluated at this laboratory. In November 1976 it was shipped to the EPA laboratories at Research Triangle Park for their evaluation.

It has operated successfully there although it has not been used as
extensively as the liquid nitrogen cooled device which we have at LBL.

ROOM TEMPERATURE β-GAUGE

The next step in reducing the complexity of the system is to eliminate
the detector cooling altogether. We are currently testing such a spectro-
meter which employs a 400 μm depletion depth surface barrier detector with
21 mm diameter active area. The resolution of the system is approximately
20 keV. Tests of electronic stability are currently being performed. In
addition, a series of experiments are proposed which will take advantage
of the flexible detector geometry available without the cooling apparatus.
By optimizing source, sample, and detector configuration, it is hoped that
certain artifacts observed in the earlier β-gauge measurements could be
reduced.

This device will likewise be incorporated in an automatic β-gauge.
A smaller calculator/computer (Hewlett Packard 9815) will be used to con-
trol the sample sequencing and storage of the data. In addition, the cal-
culator will be capable of performing on-line least squares fits to the
calibration data together with the calculation of individual sample
masses.

REFERENCES

1. Loo, B. W., R. C. Gatti, B. Y. U. Liu, C. S. Kim and T. G. Dzubay,

    "Absorption Corrections for Submicron Sulfur Collected in Filters",

    In X-ray Fluorescence Analysis of Environmental Samples, T. B. Dzubay,

    Ed., Ann Arbor Science, 1977, pp. 187-202.

2. Loo, B. W., W. R. French, R. C. Gatti, F. S. Goulding, J. M. Jaklevic,

    J. Llacer and A. C. Thompson, "Large Scale Measurement of Airborne

    Particulate Sulfur", proceedings of the International Symposium on

    Sulfur in the Atmosphere, Sept. 7-14, 1977, Dubrovnik, Yugoslavia.

    To be published in Atmospheric Environment, V. 12, No. 1, 1978.

3. Steven, R. K., T. G. Dzubay, G. Russwurm and D. Rickle, "Sampling

    and Analysis of Atmospheric Sulfate and Related Species", proceedings

    of the International Symposium on Sulfur in the Atmosphere, Sept. 7-14,

    1977, Dubrovnik, Yugoslavia. To be published in Atmospheric Environ-

    ment, V. 12, No. 1, 1978.

4. Loo, B. W., J. M. Jaklevic and F. S. Goulding, "Dichotomous Virtual

    Impactors for Large-Scale Monitoring of Airborne Particulate Matter",

    in Fine Particles: Aerosol Generation, Measurement, Sampling and

    Analysis, B. Y. H. Liu, Ed., Academic Press, 1976, New York,

    pp. 311-350.

5. Available from the Ghia Corporation, Pleasanton, California.

6. Goulding, F. S., J. M. Jaklevic and B. W. Loo, "Fabrication of
    Aerosol Monitoring System for Determining Mass and Composition as
    a Function of Time", Environmental Protection Agency Report
    No. EPA-650/2-75-048, EPA Research Triangle Park, North Carolina,
    1975.

7. Goulding, F. S., J. M. Jaklevic and B. W. Loo, "Development of
    Air Particulate Monitoring Systems" Progress Report to the
    Environmental Protection Agency, Lawrence Berkeley Laboratory
    Report No. LBL-6497, 1977.

Table 1. Measure Detectabilities for Sulfur Analysis[a]

Sample Interval T_s (hrs)	Analysis Interval T_A (sec)	Detectable Limit[b] $\mu gm/m^3$
1	1000	0.32
1	2000	0.23
2	1000	0.16
2	4000	0.10
12	1000	0.026
12	10000	0.008

[a]Assumes 100 watts at anode power.

[b]Expressed as 3σ where σ is the standard deviation in the background obtained with a blank filter.

SINGLE ORIFICE
SINGLE STAGE
VIRTUAL IMPACTOR

INLET 16.7 l/min

12.5 l/min FINE
PARTICLE FRACTION

WAVELENGTH
SPECTROMETER

14 mm DIAMETER
MEMBRANE FILTERS
ON 35 mm FILM STRIP

Ag ANODE X-RAY TUBE

0   10   20 cm

TO PUMP AND FLOW CONTROLLER
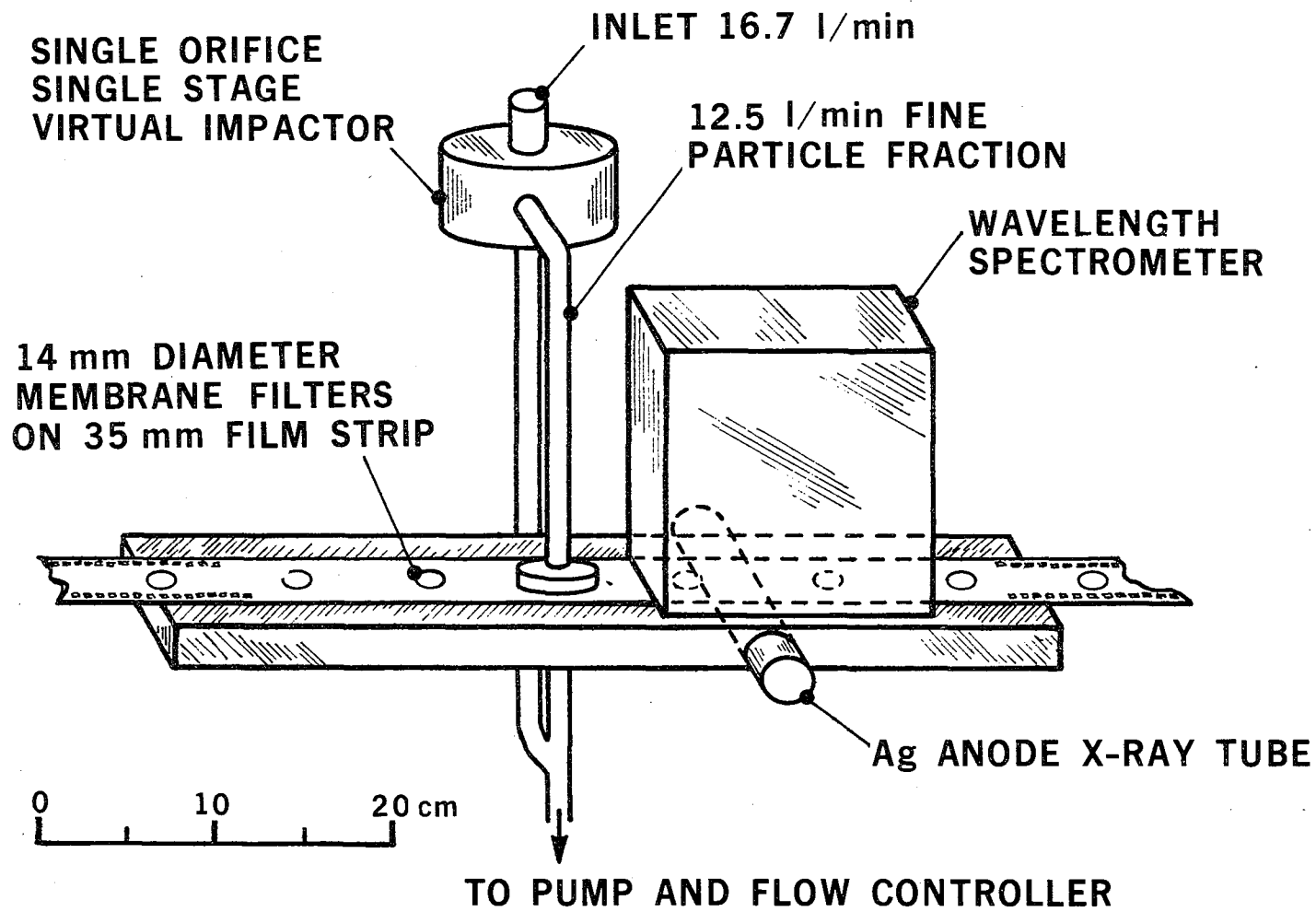
Fig. 1.   Schematic Drawing of Sulfur Monitor.

XBL 776-9331

16.7 l/m

COARSE
PARTICLE
FILTER

LIMITING
ORIFICE

4.2 l/m

**12.5 l/m
TO FINE
PARTICLE
FILTER**

0 1 2 3 4 5 cm
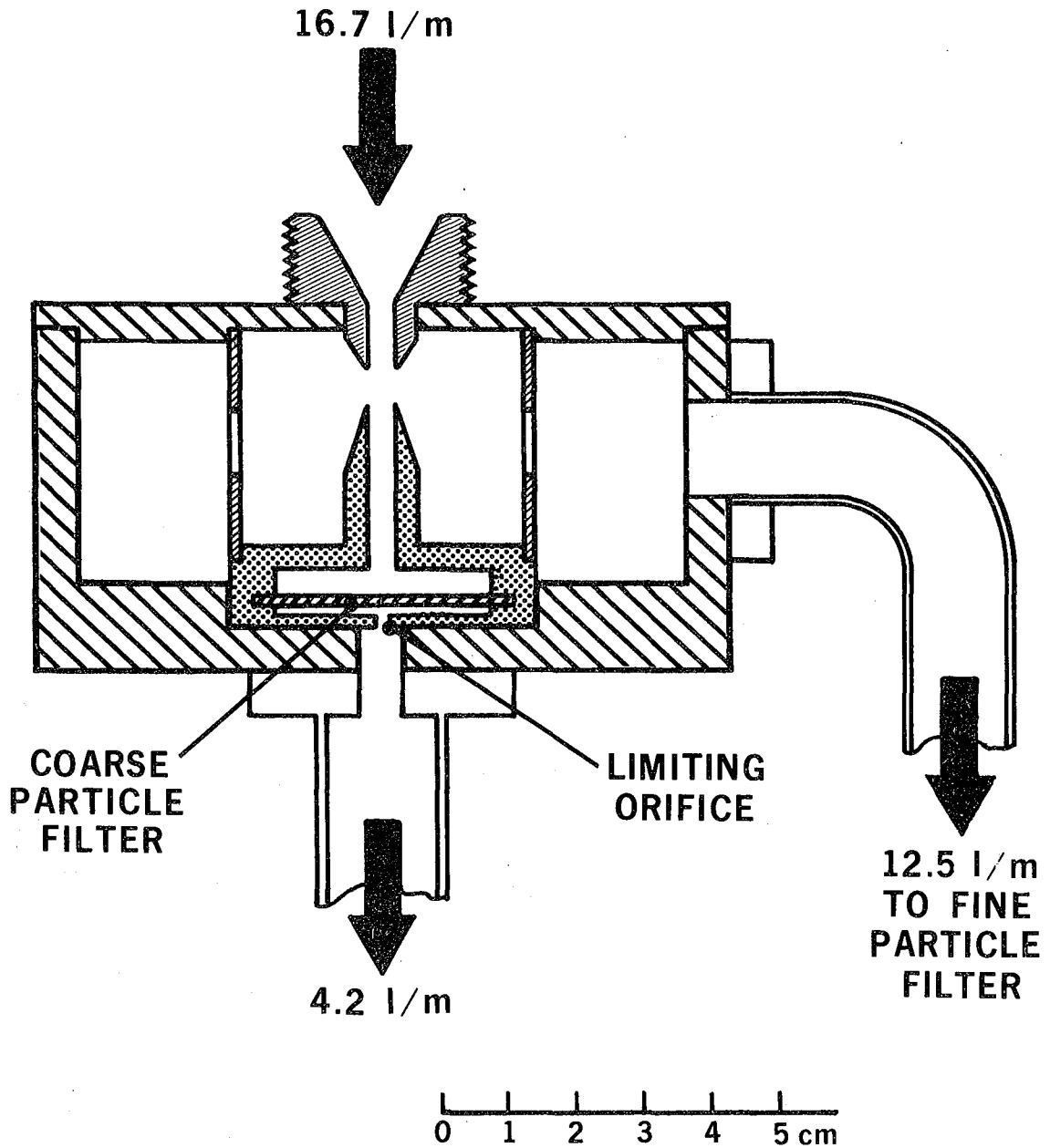
XBL 776-9333

Fig. 2. Cross-Section of Virtual Impactor.

A)

FIXED
IMPEDANCE

FILTER →

PRESSURE
SWITCH

VARIABLE
IMPEDANCE

PUMP

B)

FIXED
IMPEDANCE

FILTER →

PUMP

DIFFERENTIAL
FLOW CONTROLLER

REFERENCE
IMPEDANCE

XBL 776-9358

Fig. 3.   Flow diagrams for two versions of the single state dichotomous sampler.

Ge $\langle 111 \rangle$ CRYSTAL, 2d = 6.532 Å

55.4°

COARSE
HORIZONTAL
SLITS

PROPORTIONAL
COUNTER

SÖLLER SLITS,
$\Delta\theta = 8 \times 10^{-3}$ RAD.
$\Delta E = 13\,eV$ AT 2.31 KeV

50 μm Be ENTRANCE WINDOW

SAMPLE

X-RAY
TUBE
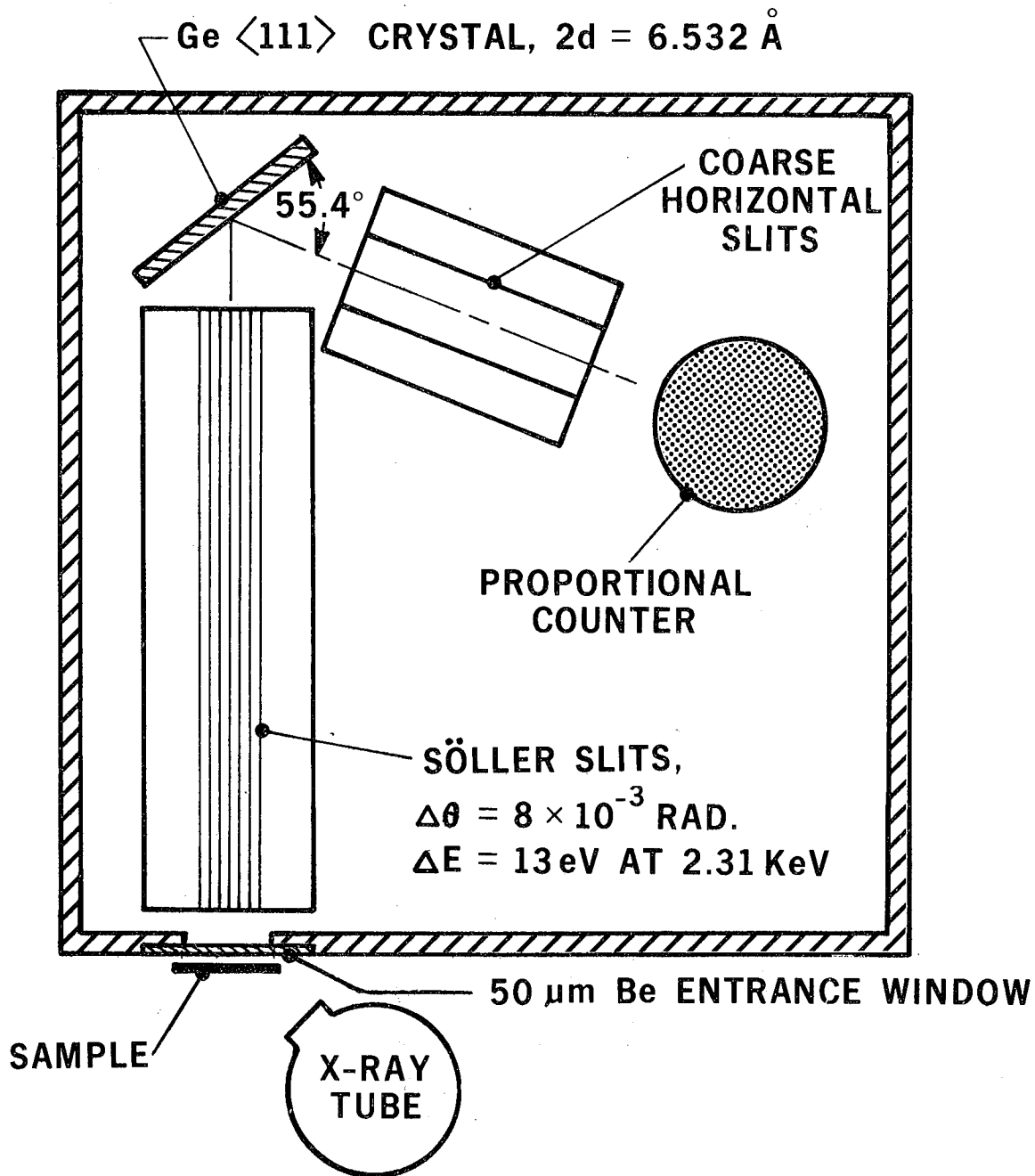
XBL 776-9332

Fig. 4.   Schematic drawing of the wavelength spectrometer.

```
        ┌─────────────────┐              ┌─────────────────────┐
        │    PROGRAM      │              │      STORED         │
        │   SEQUENCING    │              │  BACKGROUND AND     │
        │                 │              │   SENSITIVITY       │
        └────────┬────────┘              └──────────┬──────────┘
                 │                                  │  ↑
                 ↓                                  ↓  │
┌──────────────────┐   ┌─────────────────────┐   ┌─────────────────┐
│  INTERFACE TO    │ ← │                     │ → │                 │
│  MECHANICAL      │   │  MICROPROCESSOR/    │   │   CALCULATOR    │
│  HARDWARE AND    │ → │                     │ ← │                 │
│    X-RAY         │   │    CONTROLLER       │   │                 │
│  SPECTROMETER    │   │                     │   │                 │
└──────────────────┘   └──────────┬──────────┘   └─────────────────┘
                                 ↑ ↓
                        ┌─────────────────────┐
                        │   INPUT/OUTPUT      │
                        │     PRINTER         │
                        │     DISPLAY         │
                        │     KEYBOARD        │
                        │ FRONT PANEL CONTROLS│
                        └─────────────────────┘
```
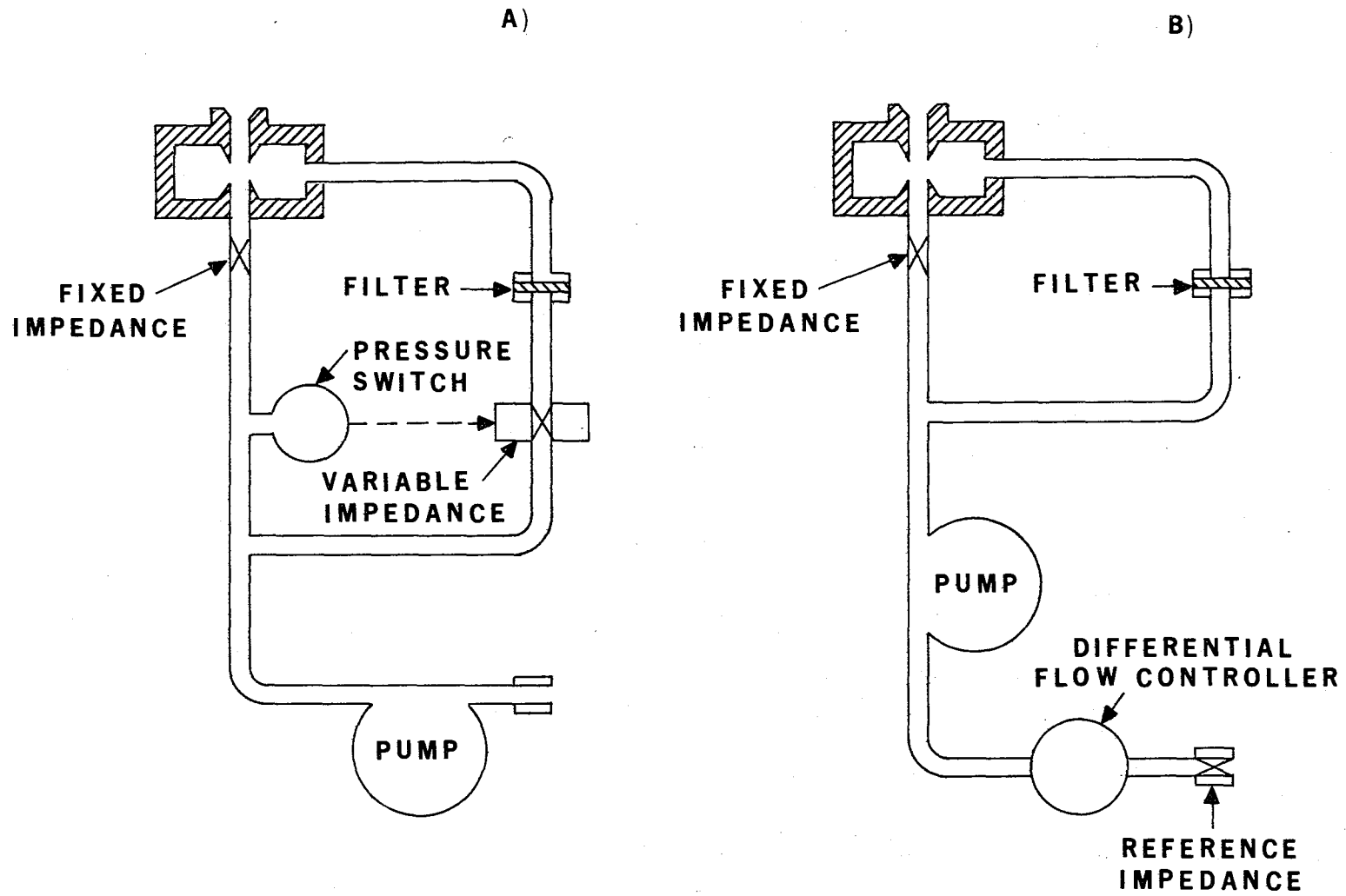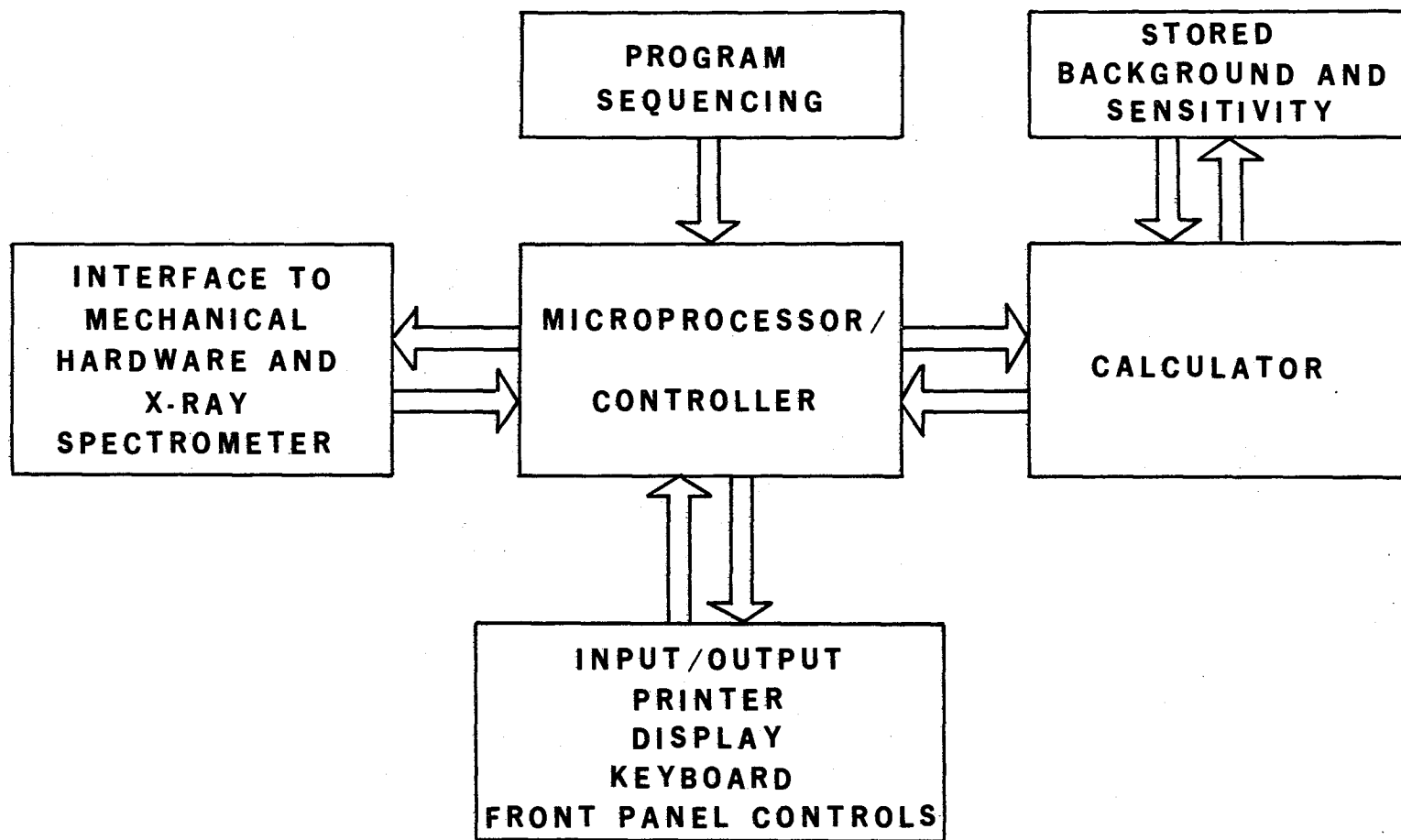
XBL 776-9446

Fig. 5. Control electronics for automatic sulfur sampling and analysis.
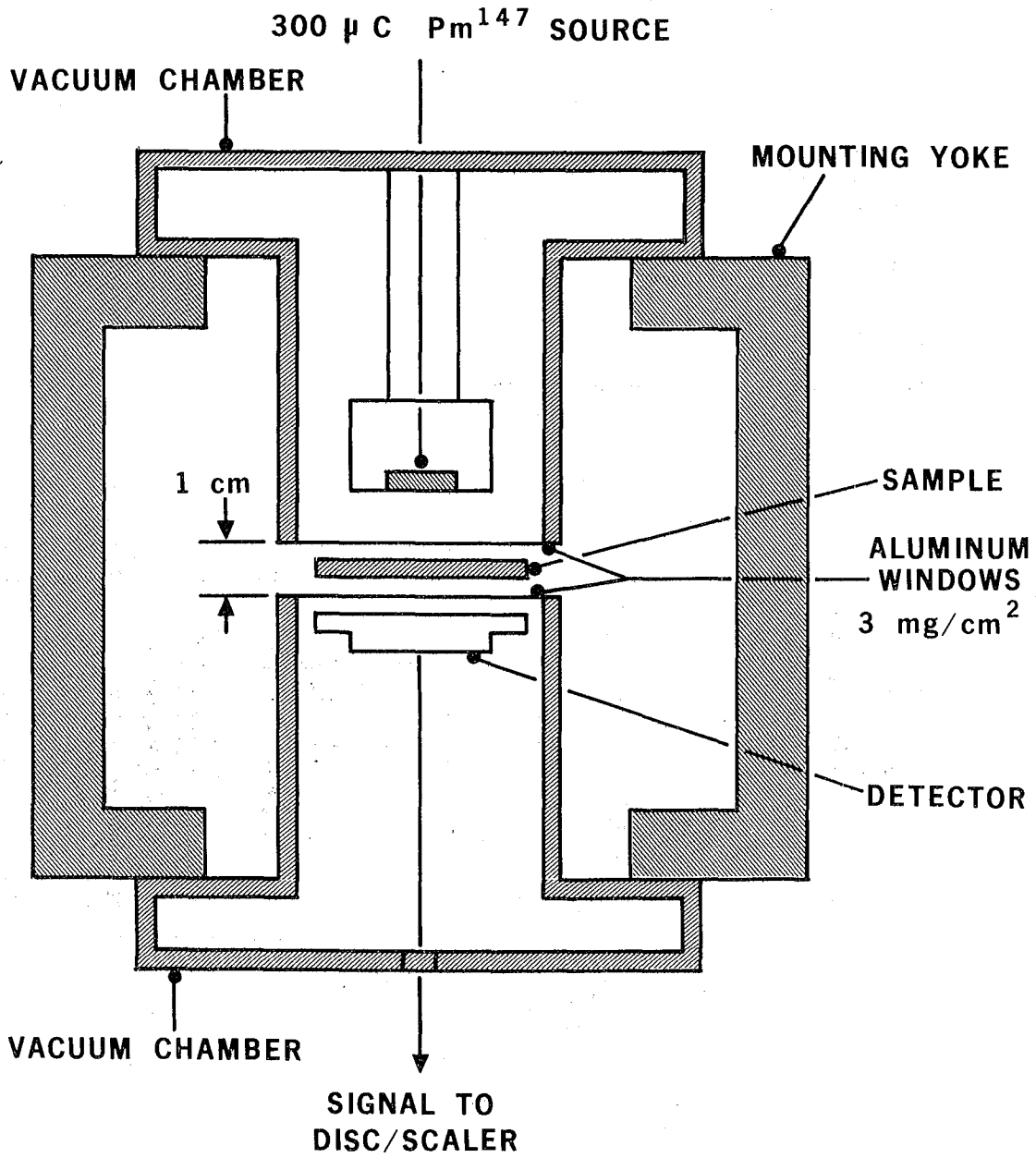
300 μ C Pm^{147} SOURCE

VACUUM CHAMBER

MOUNTING YOKE

1 cm

SAMPLE

ALUMINUM
WINDOWS
3 mg/cm^2

DETECTOR

VACUUM CHAMBER

SIGNAL TO
DISC/SCALER

XBL 752-327 A

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720