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X-RAY POWDER DIFFRACTION SYSTEM FOR CHEMICAL SPECIATION OF PARTICULATE AEROSOL SAMPLES

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June 1981

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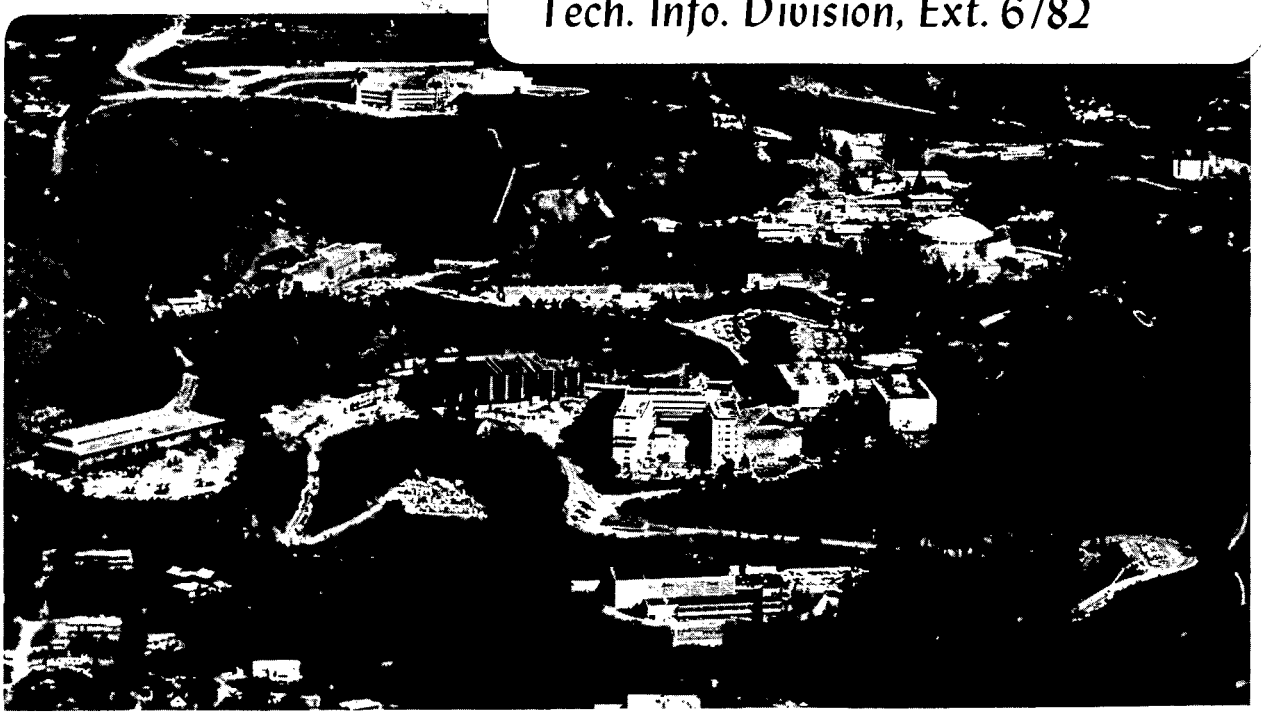

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Abstract

An x-ray powder diffraction system has been developed for the automated measurement and analysis of particulate aerosol samples. The system is optimized to process samples with particle loadings of about 100 $\mu g/cm^2$ which are acquired with dichotomous air samplers. A position-sensitive pressurized gas proportional chamber is used as the x-ray detector. This detector acquires information simultaneously over an angular range of up to seven degrees and increases the data acquisition rate by over twenty times compared to a conventional system. The use of a position-sensitive detector also reduces spectral artifacts resulting from preferred particle orientations since each spectral point is measured at many goniometer settings. The on-line data analysis procedure begins with a background subtraction of the radiation scattered from the sample substrate. A spectral analysis routine then automatically finds peaks and fits them with an analytic function to determine their position and

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intensity. A search-match procedure is then used to determine the major chemical species present on each sample. Results from this powder diffraction analysis are then combined with an x-ray fluorescence measurement of the elemental concentrations to give quantitative analysis of the major chemical compounds present on these environmental samples.

1. Introduction

Particulate aerosol samples collected with dichotomous air samplers are becoming widely used as convenient and accurate indicators of air quality. These samples are unique in that the particles are aerodynamically separated into two distinct particle size ranges before deposition on a filter subtrate. The urban aerosol has a bimodal size distribution with particles below 2 μm diameter generally considered as coming from combustion and industrial processes and being respirable while those greater than 2 μm are generated from mechanical processes and are not inhaled into the lung. Routine measurements are now made for sampling periods as short as several hours. Total mass loadings of up to 200 $\mu g/cm^2$ on the fine fraction filter are possible before the filter becomes clogged and the coarse fraction sample can have somewhat more mass deposited on it. Subsequent elemental compositions and total mass determinations provide useful information for the identification of pollutant sources and estimation of their relative contributions to air quality. Interpretation of these complex samples could, in many instances, be made more specific if an estimate could be made of the concentration of specific chemical compounds. X-ray powder diffraction has the potential for providing this information for that fraction of the sample which is present in crystalline form. Conventional powder diffraction procedures, although difficult, have

been applied with very encouraging results to samples from hi-vol and dichotomous samplers by Davis et al[1,2] and to those from dichotomous samplers by O'Connor et al[3].

In order to adapt the powder diffraction method to the study of these dilute yet complex samples, we have developed an automated system which incorporates two major improvements to the normal diffractometer design. The first is replacement of the single slit x-ray detector with a position-sensitive multiwire proportional chamber. Goebel[4] has previously described the use of these detectors for powder diffraction measurements of conventional samples. These detectors provide good spatial resolution over an extended distance together with a high counting rate capability. These factors combine to provide a data acquisition rate improvement of over twenty times relative to single slit diffractometers. The resultant spectra are less sensitive to x-ray tube intensity fluctuations and sample orientation effects since each spectral point represents the average of data collected over many slightly different goniometer positions.

The second innovation is the use of a small computer system to automatically load the sample in the goniometer, optimize the position of scattering slits as the goniometer is scanned, control the data transfer from the wire chamber detector into the memory and to provide rapid complete analysis of the spectrum. Development of this system has enabled the automated and rapid analysis of environmental samples for the chemical speciation of the crystalline component in a non-destructive and convenient manner.

2. Description of Instrument

A Bragg-Bretano diffraction geometry was used in this instrument. The general configuration of the system is shown in Fig. 1. In the ideal Bragg-Bretano geometry, the x-ray tube focus and the detector are both on the

focusing circle and the sample is curved on a radius given by R/2 sinθ where R is the goniometer radius (175 mm in this case) and θ is the Bragg angle. This instrument, however, uses a flat sample geometry and a position-sensitive detector. The sample media which is used in dichotomous samplers is a 51 mm x 51 mm square frame which has a 37 mm diameter hole in which the sample substrate is mounted. We have designed our instrument to process these samples with no remounting of the sample. The particulate material is collected on the sample substrate in a 34 mm diameter area. The substrate material is usually a thin teflon filter (1 μm pore size and 1 mg/cm^2 areal density) or a cellulose ester (1.2 μm pore size and 4 mg/cm^2). Although the instrument was optimized to process samples from dichotomous samplers, hi-vol samples can be studied by cutting out a 37 mm diameter area from a hi-vol sample and mounting it in a standard frame with a retainer ring.

The x-ray source is a standard 800 W Norelco* Cu anode x-ray tube with a focal spot of 0.1 mm x 10 mm and is operated at 40 kV and 20 mA. A 7 μm Ni filter is placed between the x-ray tube and the sample in order to reduce the K_β component of the radiation source by a factor of six while reducing the K_α by only 25%.

A slit arrangement is designed to irradiate a large fraction of the collection area and to minimize defocusing and scattering from the air and the sample frame.

Both vertical and horizontal slits are used to collimate and control the x-ray beam onto the sample and to limit the field of view of the x-ray detector to the part of the sample which is irradiated by the x-ray beam. The spectrum defocusing due to vertical divergence is limited by Soller slits (8 cm long and 3 mm foil spacing) which are placed in both arms of the spectrometer. The horizontal defocusing due to the vertical divergence is 0.01° at 20°(2θ) with

this geometry. The horizontal slits are controlled by the instrument's computer using stepper motors. One slit is placed in the incident arm of the spectrometer and is used to maintain constant coverage of the sample area by the x-ray beam as the goniometer angle is varied. Since the computer controls the horizontal coverage, this value is an input parameter of the running conditions and can be chosen by the experimenter. The other computer controlled slit is in the detector arm and is used to limit the field of view of the detector to the irradiated area of the sample. Since the samples are flat and should be curved, the diffraction peaks are broadened. The aberration associated with a sample coverage of 15 mm horizontally (and 10 mm vertically) produces a spectrum broadening of 0.03° at 20°(2θ). As the Bragg angle is increased this broadening also increases.

The effect on the final results is minimized in the spectral analysis procedure by using an analytic function with a variable width as the fitting function and then using the intensity of a peak in the search-match procedure rather than its peak height.

There are slight variations in the placement of the sample in the analysis position which can arise from the tolerances in the sample holders and the filter mounting procedures. Displacement of the sample plane from the goniometer axis produces a shift in the peak positions given by:

$$\Delta_{2\theta} = \frac{2\Delta R}{R} \cos\theta$$

A displacement of less than 0.05 mm is maintained by the sample holder geometry. This gives a peak position error of less than 0.03° which is quite adequate in the search-match operation. This systematic error is also routinely monitored using the strong diffraction lines from readily identifiable phases such as $(NH_4)_2SO_4$ and SiO_2 which are generally present.

The x-ray detector in this instrument is a position-sensitive multiwire proportional chamber. This type of detector has a high-resolution, one-dimensional position readout and can be used at the high counting rates available in this system. The geometry of the detector is shown in Fig. 2. Since the detector itself is the equivalent of the final slit in a conventional system, it is important to keep the thickness of the detector small to avoid defocusing of the spectra. The active detector volume is only 3 mm thick and is pressurized to five atmospheres with Ar-CH_4 (93% - 7%) gas in order to increase detection efficiency. Under these conditions, the efficiency is 30 for 8 keV photons. The entrance window is 0.64 mm beryllium and has a diameter of 25 mm. Since the system is a sealed one, it is possible to use more expensive gases such as Xenon for further increases in efficiency.

The encoding of the position is based on the time difference of the two pulses at the ends of the delay-line which is linearly related to the position of the photon in the chamber. The anode plane is made of 20 μm gold-covered tungsten wire spaced 2 mm apart. The cathode plane behind the anode wires is used to generate the high resolution position information. This is accomplished by measuring the delay between the arrival of the charge pulses between the two ends of the delay-line cathode. This readout method has the advantages that the linearity of the detector is excellent and the electronic readout is relatively simple and easily calibrated. The delay-line cathode is an etched conduction pattern on a teflon backing material which gives an impedance of 100 ohms and a delay of 0.8 ns for each mm in the readout direction. The position resolution of the detector was measured using a pinhole x-ray source to be 80 μm FWHM which corresponds to an angular resolution of 0.027°. Because the detector is 3 mm thick and the angular range collected at one goniometer position is up to 7°, there is some defocusing of the spectra at each side of the angular range. However, this defocusing of the spectrum is averaged over

all angles since the scan is done in small stepping increments of 0.04°. The electronic readout system is shown in Fig. 3. The time difference between the two cathode ends (16 ns/cm or 5.1 ns/deg) is measured by first amplifying the cathode signals with a fast amplifier and then creating logic pulses using constant-fraction discriminators. One cathode signal is used as the start input to a TAC (time-to-amplitude converter) and the other is delayed by 25 ns and used as the stop input to the TAC. The output of the TAC is digitized with a fast ADC which is interfaced to the microcomputer memory. The gain of the TAC is adjusted to give a digital gain of 25 channels for each degree in 2θ of the goniometer.

The computer system used in this instrument consists of a pair of microcomputers. The system configuration is shown in Fig. 4. A Texas Instrument 9900* microprocessor is used for direct control of the x-ray power supply, sample changer, goniometer, two movable slits, the sampling period timer and the ADC interface. It is programmed in TI Power Basic and the program is stored in a permanent read only memory. Using this software allows the computer to conveniently and rapidly perform calculations of the optimum slit positions and the appropriate ADC digital offset as the goniometer is scanned. The other computer in the system is a Digital Equipment LSI 11/2* processor which is equipped with a color graphics terminal as the operator console, a printer for output of results, a 5 Mbyte disk for program and data storage and a floppy disk for permanent storage. The two processors are linked together by a 16-bit digital interface. The LSI 11 system is used for setup and storage of the running parameters for each spectrum and then for analysis of a previous spectra while the TI 9900 system acquires the current spectrum simultaneously.

The interface between the ADC and microcomputer is designed to operate at high rates (5 μsec per event) and to have a computer controlled acceptance

window and digital offset. The acceptance window determines the angular acceptance of the detector by setting upper and lower bounds on the accepted events. The angular acceptance is entered as a running parameter for each sample and can be varied to give an angular range of from 0.04° (1 channel) to 7° (175 channels). If an event is within the preset range, the digitized ADC value is then used to increment a channel in the computer's memory using a direct memory access (DMA) interface. The location incremented must include an offset which is related to the current position of the goniometer. The microcomputer calculates the appropriate offset for each goniometer position and loads it into the offset register before starting the data acquisition at each scan position.

3. Data Acquisition Procedure

The first step in the data acquisition procedure is to enter the running parameters for each sample into the LSI 11 computer. The parameters include the sample position in the input tray, the starting and ending 2θ values, the x-ray beam coverage of the sample, the angular acceptance range of the detector, the sampling time at each data point and sample identification information. These data are stored in a file for each sample and are transferred from the LSI 11 to the TI 9900 system.

After the TI 9900 system receives the parameters from the LSI 11, it inserts the designated sample, turns on the x-ray tube and moves to the starting positions of the goniometer and the slits. It also loads the upper and lower bounds on the ADC channels and sets the initial value of the ADC offset. The timer is preset for the sampling period and then started. When the timer period ends, the data acquisition is halted and the microcomputer then moves the goniometer and slits to new positions, adjusts the ADC offset and restarts

the timer. The slit positions for constant sample coverage and minimum background are calculated for the next data point while the data acquisition is in progress. The microcomputer requires about 0.25 seconds at each position to move the motors and restart the acquisition.

Scanning parameters for a typical environmental sample are an angular range from 14° to 60° and a sample coverage of 15 mm horizontally by 10 mm vertically. The angular acceptance of the detector is usually set at 4° and the sampling period is set at ten seconds. With these conditions, the rate in the detector is about 25 kHz at low angles and less than 5 kHz at 60°. For some samples a second scan is done from 5.5° to 14° with a sample coverage of 5 mm and an angular acceptance of 1° to verify the presence of some compounds.

The use of the TI 9900 computer as a combined multichannel analyzer and hardware controller provides a great deal of flexibility in implementing the data acquisition. The ability of the LSI 11 to perform data analysis during the running cycle is also an important advantage for on-line analysis of samples.

4. Data Analysis Procedure

The goal of the data analysis procedure is to extract from the spectra estimates of the identity and concentration of the chemical species present in the sample. The first step is to subtract a background spectrum of x-rays scattered from the substrate material. The remaining peaks in the spectrum are then fitted to an analytic function which estimates their position and intensity. The final step in the procedure is the application of a search-match technique to identify possible compounds and estimate their concentration. The elemental concentrations obtained from the x-ray fluorescence measurement can then be used to verify the identities and concentrations of the chemical species present.

The background subtraction procedure enhances the signal-to-background ratio by removing contributions from scattered x-rays not originating in the sample deposit. The background shape is based on a high statistics run of a blank teflon or cellulose ester filter blank. The background shapes for these two commonly used substrate materials are very different as can be seen in Fig. 5. The teflon substrate has a lower overall background (≈25% of cellulose) but the spectra has several intense peaks. The normalization of the teflon background to the unknown spectrum is based on the intensity of the broad peak at 18°. Figure 6 shows a 230 $\mu g/cm^2$ gypsum rock sample on a teflon substrate before and after background subtraction. In the processed spectrum the teflon peaks have been removed, the background has been linearized and the peak-to-background ratio is significantly improved. For samples with a cellulose ester substrate, a region 0.5° wide in the spectrum near 20° is used for determining the normalization factor. Figure 7 illustrates the dramatic improvement in the spectrum which is made by background subtraction from a heavily loaded aerosol particulate sample.

The second step in the analysis is to find and measure the parameters of the peaks in the spectrum. The peaks are found using a routine from the Digital Equipment Corporation's Laboratory Subroutine Package (PEAK)*. This program applies a digital filter and then looks for significant changes in the first derivative of the data to locate peaks. Once the peak positions and heights have been estimated, these values are used as starting values for an analytic fitting routine. This routine uses a function given by the ratio of two fourth degree polynomials:

$$N(C) = N_{0p}(C-C_0)$$

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

where C_0 is the centroid, N_0 the amplitude, and the fitting function, p(C), is defined as:

$$p(C) = \sum_{k=0}^{4} A_k C^k \Big/ \sum_{k=0}^{4} B_k C^k \qquad \text{for C in peak base width}$$

$$p(C) = 0 \qquad \text{for C outside peak width}$$

to fit the spectra over a range of 10 channels on each side of the peak. The parameters in this function can be related to familar parameters of peak position, height, width, background intercept and background slope. A detailed description of this routine has been given by McKee[7]. The parameters in the function are determined by sequentially varying each parameter and finding the minimum in the chi-squared value of the function to the spectrum. Since all the parameters in the function are linear, the routine is fast and finds reliable parameters in less than 30 seconds per peak. Regions with overlapping peaks are also fitted by this routine using several peak positions and heights but with the same width and background parameters. The intensity of the peaks is determined by subtracting the fitted background and summing the data remaining. The position of the various peaks is converted from an angle value to a d-space value using the relation d= 0.7709/sinθ which is obtained from the Bragg law using the wavelength of Cu K_α x-rays. The search-match procedure uses these d-space-normalized intensity pairs to estimate the possible compounds in the sample. In general, three or four peaks are found for each compound so the identification of the chemical species can be specific. In cases where the quality of the data is not sufficient to eliminate ambiguous interpretations, other factors can be included. In particular, the elemental analysis of the sample by x-ray fluorescence analysis serves to substantially reduce the number of possible interpretations. In cases where there is

still some ambiguity, a reasonable interpretation is usually possible based on compounds generally present in the atmospheric environment.

The quantitative estimates of the concentration of each chemical species are much more difficult than qualitative identification since the intensity of the diffraction peaks is not related to the concentration in a general way, but must be determined for each compound. The calibration factors are established by taking several mg of the compound to be determined and grinding it up in a ball mill to generate small particles. This material is then dispersed above a dichotomous air sampler and the collected fine and coarse samples are analyzed by both x-ray fluorescence and powder diffraction. The XRF measurement is used to determine the sample concentration in ng/cm^2 and the powder diffraction system measures the major diffraction peak intensities which then establish the calibration factor for a given incident x-ray intensity. Different sample loadings are analyzed for each compound to verify the linearity of the calibration. This calibration is currently in progress for most of the major compounds observed in environmental samples.

To test the sensitivity of particular diffraction line intensities to the sample collection site, we have measured a variety of calcite samples which were obtained from a number of widely scattered sites. These calcite rock samples were powdered and collected onto teflon filters using the same procedure as for the standard samples. The coarse fraction samples were then analyzed by both powder diffraction and XRF and the intensity of the prominent diffraction lines per ng of calcium calculated. The results of this study, which are given in Table 1, indicate that these samples from five widely dispersed sites and sample morphologies give similar sensitivities for the five diffraction lines measured. Some of the variation of the calibration of the samples may be due to the presence of some non-crystalline calcium

compounds being present in some of the samples. Any non-crystalline calcium is measured by the x-ray fluorescence system but is not identified as calcite by the powder diffraction system and therefore the sensitivity is changed.

5. Conclusions

An x-ray powder diffraction instrument has been developed for routine chemical speciation of size-segregated environmental samples. The system is optimized to process samples acquired with a dichotomous air sampler. With total mass loadings of 10 to 300 $\mu g/cm^2$ the instrument provides a measurement in several hours of the major crystalline species present in the sample. The system uses a pair of microcomputers to give automated data acquisition and rapid on-line analysis. Use of this system in combination with an elemental analysis using x-ray fluorescence provides a non-destructive sensitive analysis of a sample in a convenient and rapid manner. Such systems may be very useful in understanding the chemistry and the related health effects of the complex urban aerosol.

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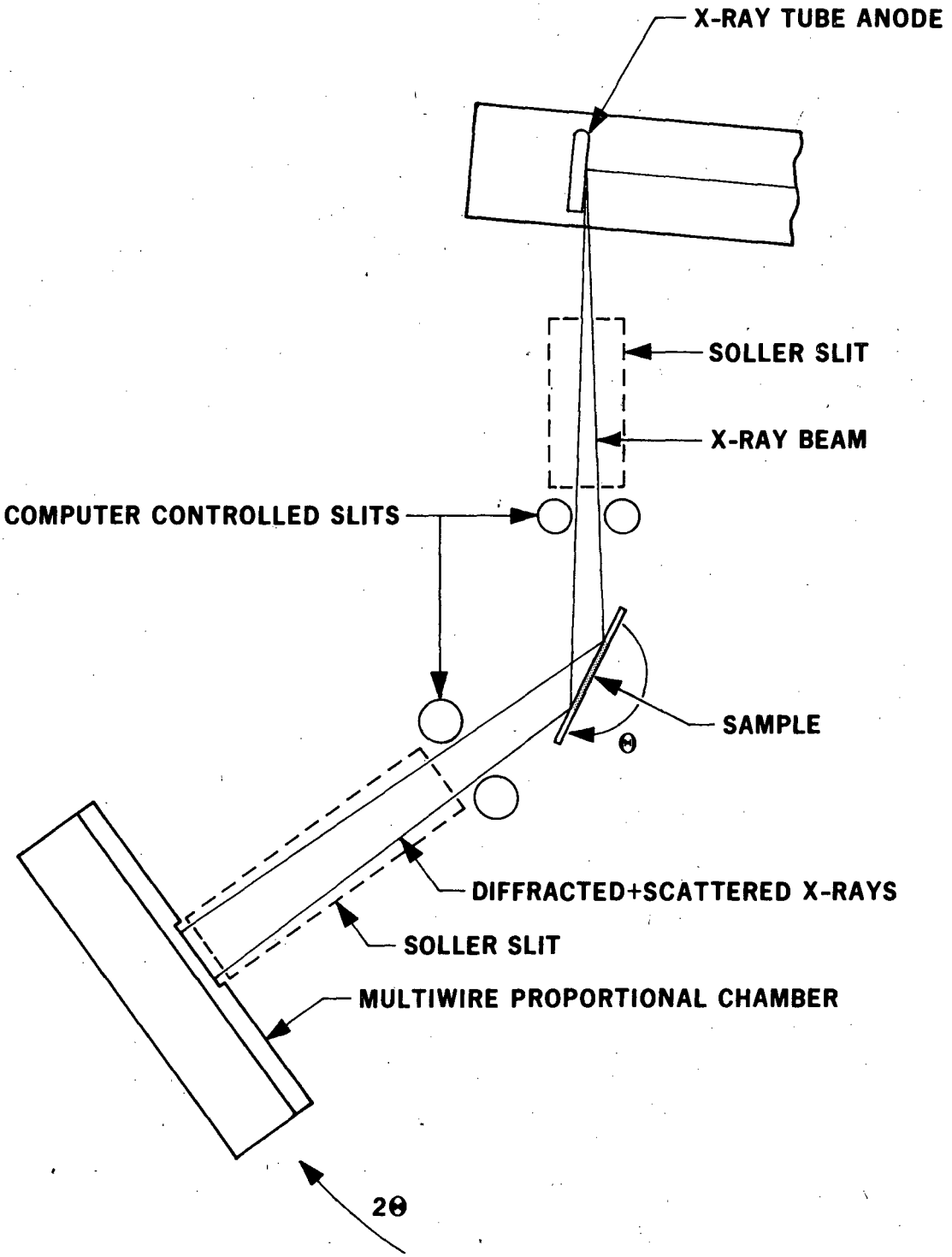

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Fig. 1. General layout of powder diffraction system.

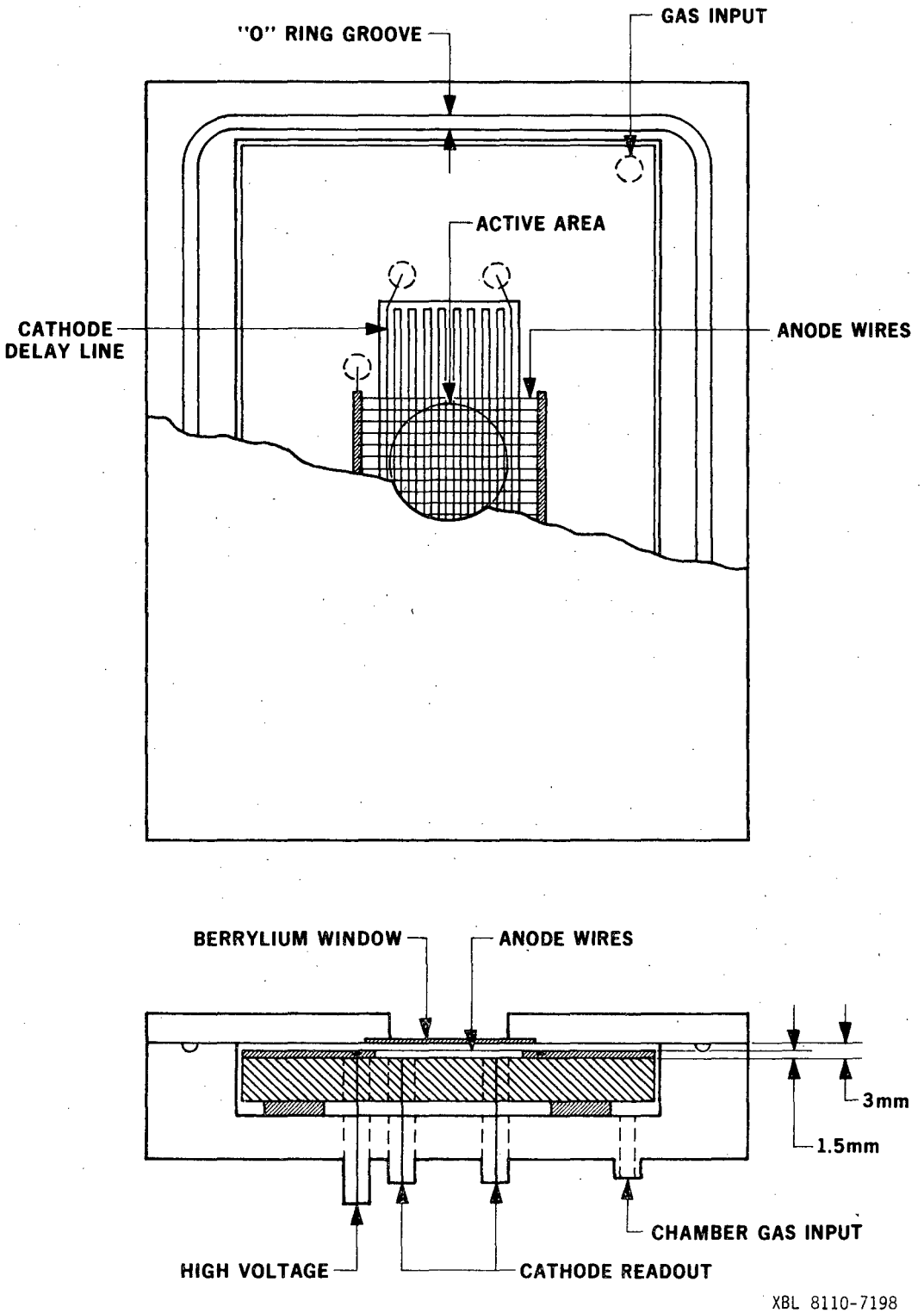

Fig. 2. Multiwire proportional chamber layout.

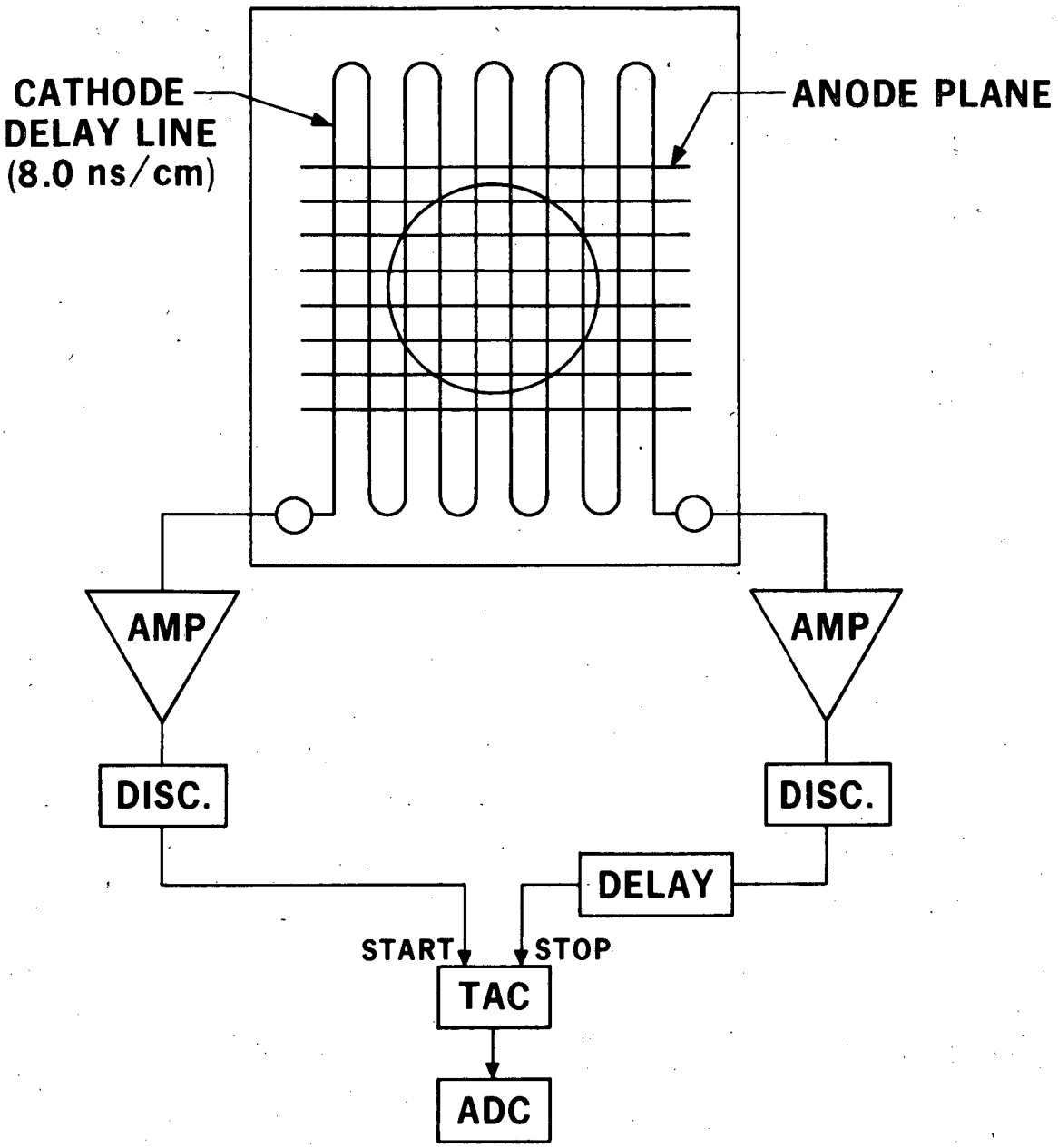

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Fig. 3. Electronics associated with multiwire proportional chamber.

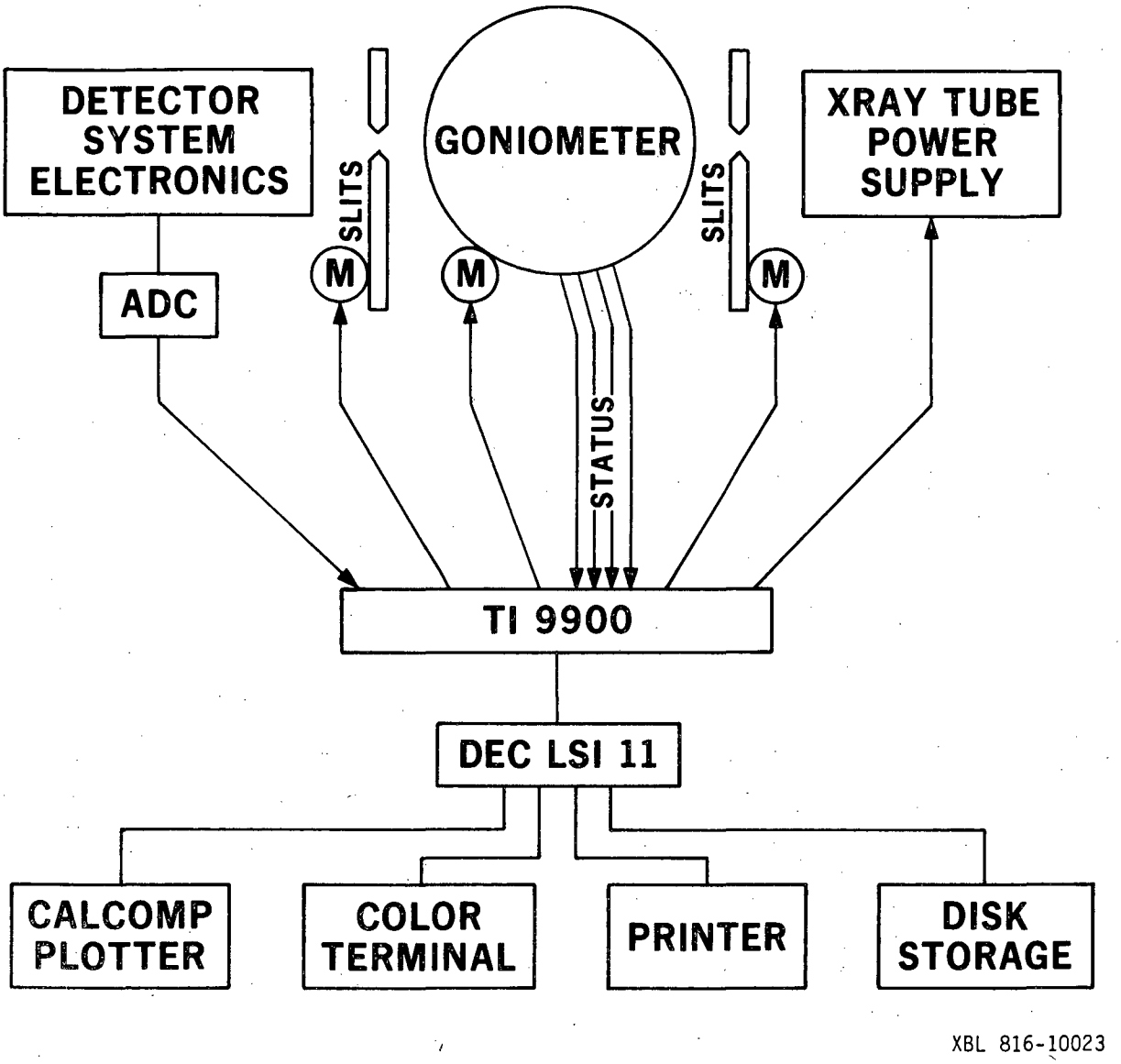

Fig. 4. Computer system used for data acquisition and analysis.

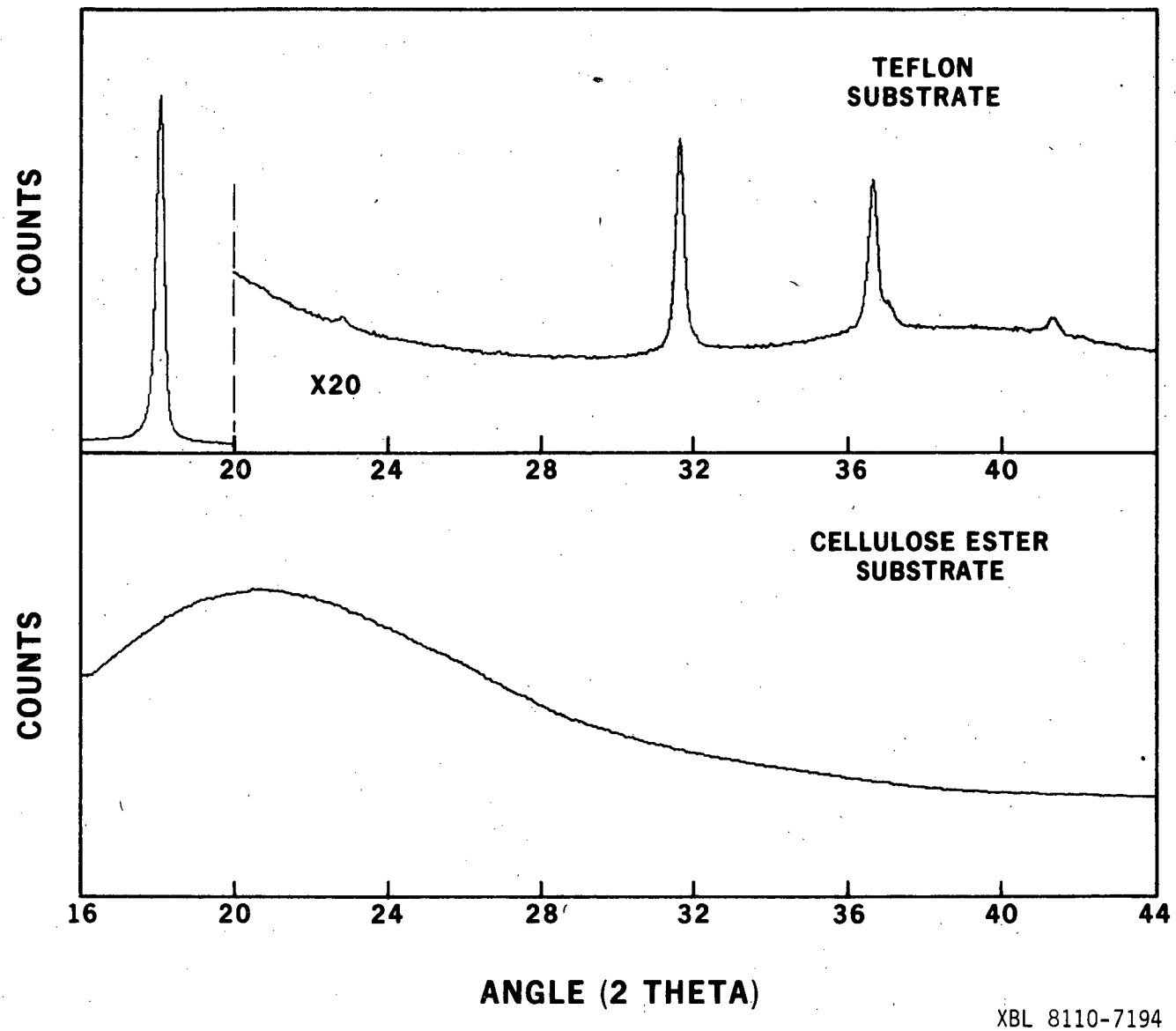

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Fig. 5. Spectra measured from blank teflon and cellulose ester substrates.

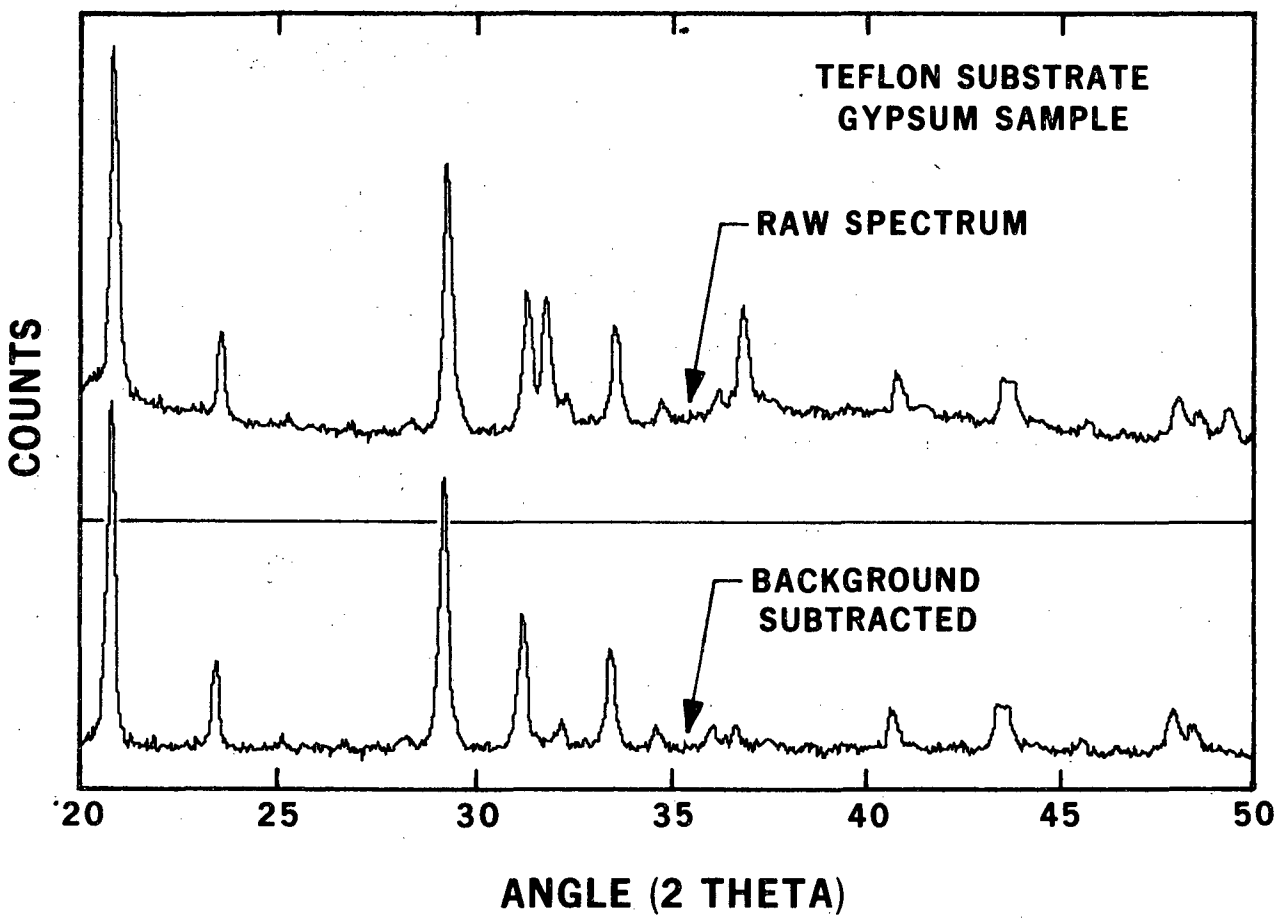

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Fig. 6. Spectrum from a 230 $\mu g/cm^2$ gypsum rock sample before and after subtraction of the teflon substrate background.

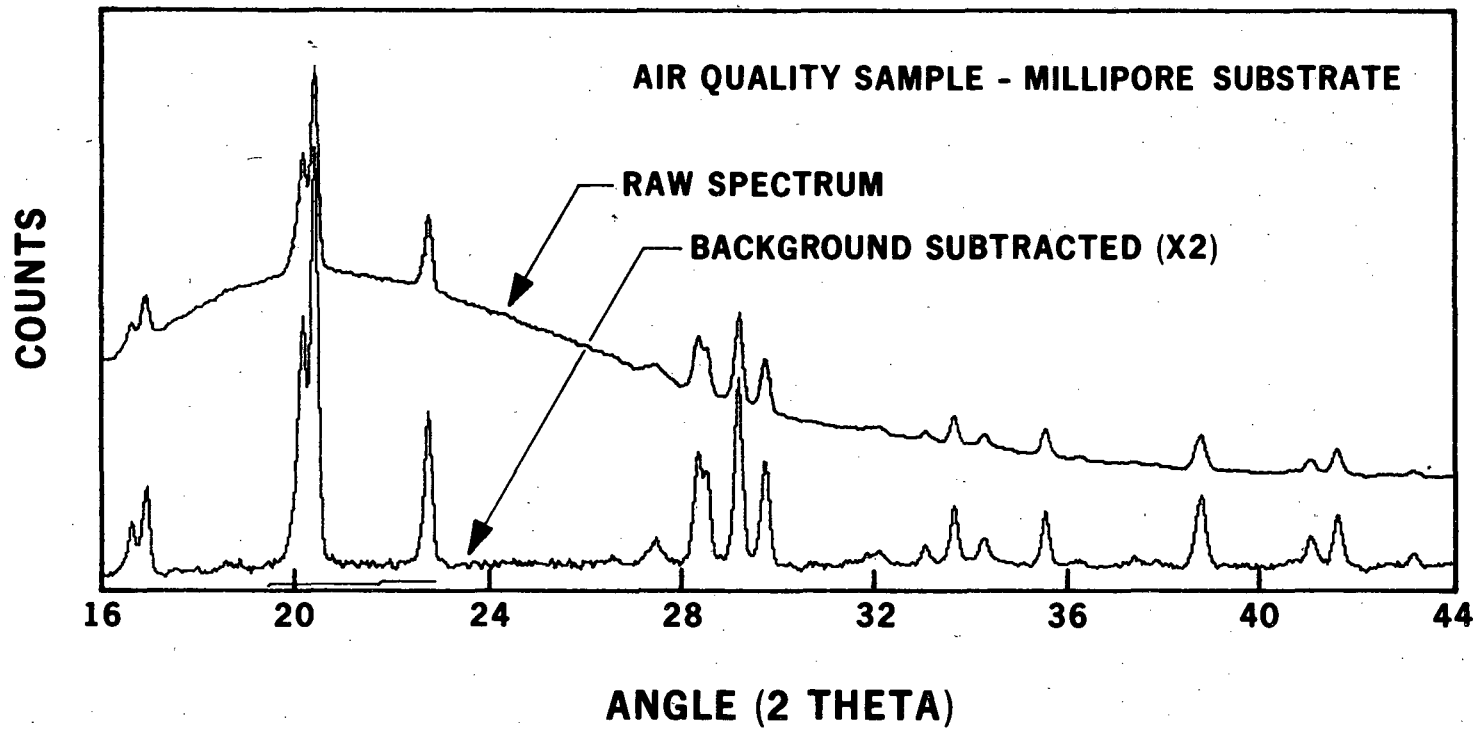

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Fig. 7. Spectrum from an air quality sample before and after subtraction of the cellulose ester background.

MEASURED SENSITIVITIES FOR CALCITE (cts/sec/μg/cm^2)

SOURCE	Ca CONCENTRATION (μg/cm^2)	d-SPACING (Å) / REFLECTION INDICES				
		3.030 <104>	2.279 <113>	2.093 <202>	1.908 <018>	1.871 <116>
West Germany	159	125	29.5	17.5	19.0	21.1
Calaveras County, CA	51.3	182	22.1	17.1	24.2	24.3
India	41.2	142	17.3	19.8	15.2	15.7
Crestmore, CA	14.4	206	16.2	19.1	20.5	22.6
Mexico	11.7	203	23.1	17.3	20.2	20.4
	Mean Values	172	21.6	18.2	19.8	20.8
	RMS Deviations	36	5.3	1.2	3.2	3.2
	% Deviation	21%	25%	7%	16%	15%

Table 1. Sensitivities of calcite diffraction peaks from various calcite sample locations.

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