

Archive  
Closed  
LD  
175  
A40K  
Th  
737

A CHEMICAL ASSESSMENT OF AIRBORNE PARTICLE SOURCES  
" IN SPRUCE PINE, N. C.

A Thesis  
by  
STEVEN JAY BREINER

Submitted to the Graduate School  
Appalachian State University  
in partial fulfillment of the requirements for the degree of  
MASTER OF SCIENCE

August 1982

Major Department: Chemistry 147  
15

Appalachian Collection  
Appalachian State University Library  
Beene, North Carolina

A CHEMICAL ASSESSMENT OF AIRBORNE PARTICLE SOURCES  
IN SPRUCE PINE, N. C.

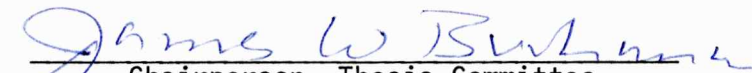
A Thesis

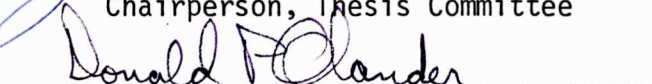
by

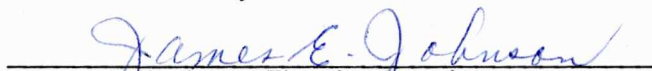
Steven Jay Breiner

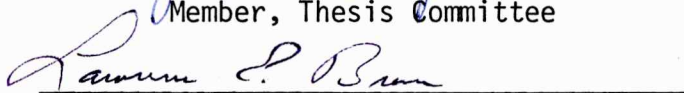
August 1982

APPROVED BY:

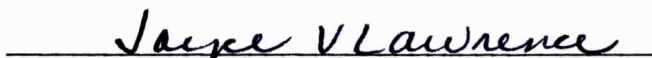
  
Chairperson, Thesis Committee

  
Member, Thesis Committee

  
Member, Thesis Committee

  
Chairperson, Department of

Chemistry

  
Dean of the Graduate School

## ABSTRACT

### A CHEMICAL ASSESSMENT OF AIRBORNE PARTICLE SOURCES IN SPRUCE PINE, N. C. (August 1982)

Steven Jay Breiner

B. S., Appalachian State University

M. S., Appalachian State University

Thesis Chairperson: James W. Buchanan

An investigation was conducted in the area around Spruce Pine, N. C. to identify major sources of particulate air pollution. Airborne particles were collected by high volume air samplers located in a four site network around the town. X-ray diffraction analysis of collected samples yielded qualitative and quantitative information about major crystalline components. A conspicuous absence of minerals normally associated with the local mining industry implies that major particle sources reside in such places as roadways, parking lots and cleared fields.

## Acknowledgements

I wish to express the utmost gratitude to my mentor, Dr. James Buchanan, without whose interminable patience and prodding this work would not have been possible. I also wish to express my appreciation to Dr. Donald Olander and to Dr. James Johnson who provided advice and technical expertise during the course of this study.

Lastly, I would like to thank Sherry Fonvielle, Dr. Briant Davis, Dr. John Callahan, Dr. Loren Raymond and Dr. Richard Abbott who provided unending assistance in various forms. Thank you all.



## Dedication

The following pages are dedicated to the spirits of those poor souls who waited until the last minute, and especially to my wife, Linda, who tolerated and supported me when she had reasons not to.

## TABLE OF CONTENTS

	<u>Page</u>
List of Tables .....	vii
List of Figures .....	viii
I. INTRODUCTION .....	1
A. Historical Background .....	1
B. Survey of Relevant Research .....	5
II. EXPERIMENTAL .....	8
A. Overview .....	8
B. Collection Apparatus .....	8
1. Samplers .....	8
2. Sampler Accessories .....	8
C. Siting .....	11
D. Sampling .....	13
1. Preparatory and Field Work .....	13
2. Quality Assurance .....	15
E. Analysis .....	16
III. RESULTS AND CALCULATIONS .....	23
A. Mass Analysis .....	23
B. X-Ray Diffraction Analysis .....	27
IV. DISCUSSION .....	40
V. SUMMARY AND CONCLUSIONS .....	44
References .....	46
APPENDIX A .....	49
APPENDIX B .....	63
VITA .....	68

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
I. Component Data for X-Ray Analysis .....	21
II. Sample Masses Collected .....	24
III. TSP Ambient Loading for Samples Collected during Northerly Winds .....	25
IV. TSP Ambient Loading for Samples Collected during Southerly Winds .....	26
V. Linear Regression Correlations for TSP Loading by Site and Wind Direction .....	28
VI. Transmission Ratios for Glass-Fiber Air Filters .....	31
VII. Mass Absorption Measurements for Glass-Fiber .....	32
VIII. Components Identified in Sample Filters .....	36
IX. Weight Percents of Eight Most Frequently Identified Components	
A. Samples Collected during Northerly Winds .....	36
B. Samples Collected during Southerly Winds .....	37
X. Relative Weight Percentages of Eight Components	
A. Samples Collected during Northerly Winds .....	38
B. Samples Collected during Southerly Winds .....	39

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Area map showing Spruce Pine nonattainment area and sampler sites .....	3
2.	GMW-2000 High Volume Air Sampler .....	9
3.	Diagram of wind activated switch assembly and cam .....	10
4.	Schematic of sampler and switch hookup .....	12
5.	Diffraction pattern from Filter 4D .....	19
6.	Computer printout for Filters 4J, 3K, and 4K .....	34

## CHAPTER I

### INTRODUCTION

#### A. Historical Background

Particulate matter in the atmosphere comprises probably the largest group of known air pollutants.<sup>1</sup> Compositions of particle dispersions are both dynamic and extremely diverse, principally due to the fact that any solid or semisolid material which can be finely divided by any means is a candidate for suspension in the atmosphere. Mineral dust, tire rubber, pollen, sawdust, combustion products and suspended paint droplets, to name only a few, illustrate the huge reservoir of potential particulate pollutants, and are routinely found to be components of airborne particulate suspensions. Total suspended particulate matter (TSP), refers to that portion of particulate matter small enough to be suspended in the atmosphere, even at great distances from its sources.

A major concern of those involved with studies of pollution is the determination of pollutant origins, or source apportionment. Routine problems encountered by analysts are small sample sizes, identification of multicomponent samples, post collection reactions, and variable meteorological conditions. The determination of anthropogenic versus natural origin is often, at best, a well educated guess, since many components of TSP have both sources.

This study was an attempt to source apportion certain areas around Spruce Pine, N. C. with respect to TSP.

Original interest in this project arose during conversations with Dr. R. W. Van Tilburg and Mr. Paul Wilms, officials in the North Carolina Department of Natural Resources and Community Development. Their interest concerned the fact that in February 1978 an area around Spruce Pine, N. C. had been classified by the U. S. Environmental Protection Agency as a "nonattainment area" with regard to federal TSP maximum allowable limits (See Figure 1). Nonattainment status denotes that the air in an area exceeded a maximum TSP level of 150 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) more than once during four consecutive quarters. A nonattainment classification results in a virtual blacklisting of the area by industries wishing to avoid federal scrutiny.<sup>2,a</sup>

Support of the N. C. Department of Natural Resources and Community Development aided in the obtainment of a \$20,000 grant from the North Carolina Board of Science and Technology for the purpose of studying air quality in northwestern North Carolina. A portion of the grant was used to fund the Spruce Pine TSP study.

Work on the Spruce Pine project began in meetings with the Mitchell County Economic Development Commission Advisory Committee, a group of representatives from the mining interests around Spruce Pine. The advisory board was convinced that the study would provide

<sup>a</sup>The nonattainment status was lifted in late 1981.



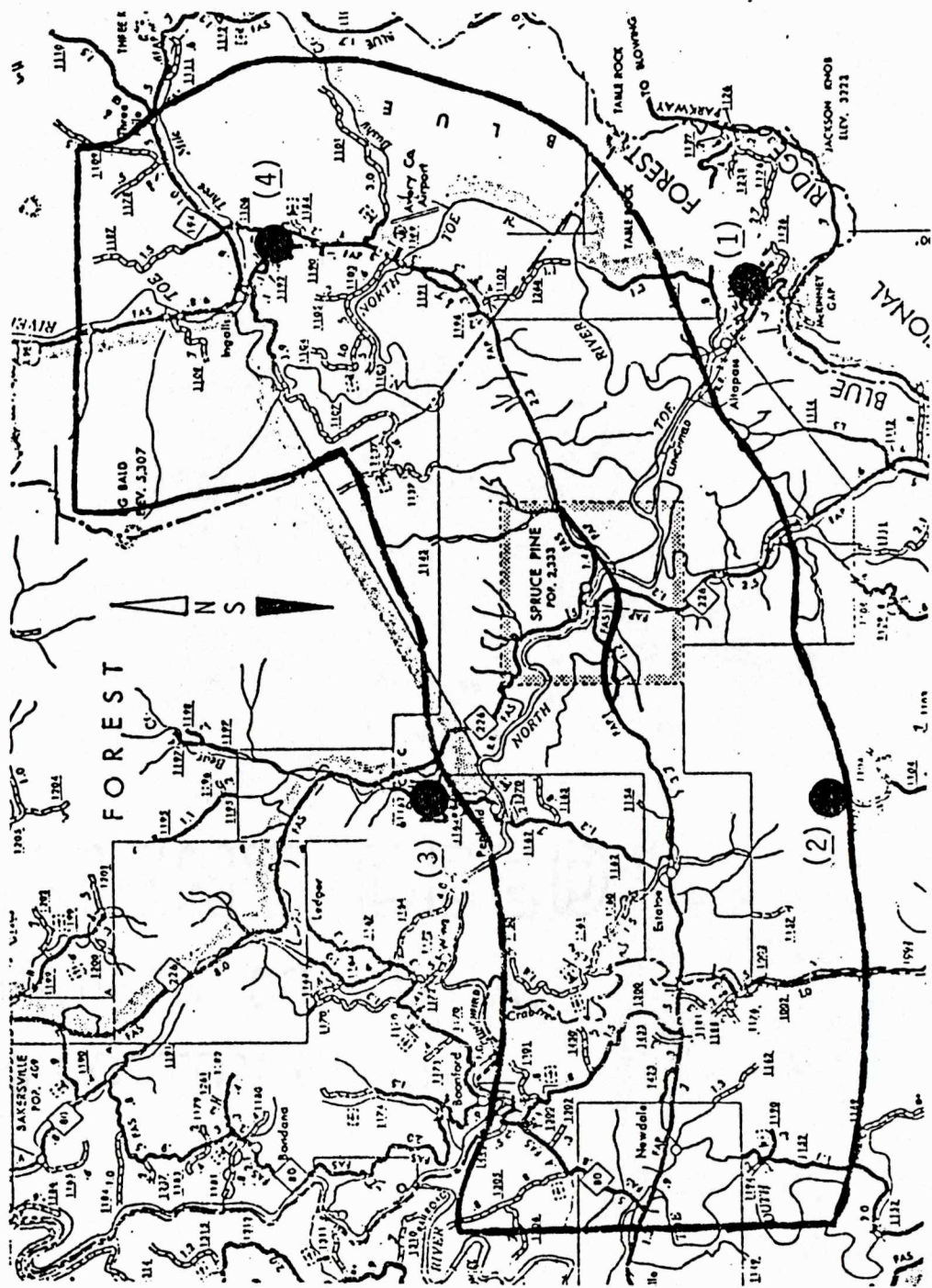


Figure 1. Area map showing Spruce Pine nonattainment area and sampler sites

objective information to all concerned parties, not evidence to promote further sanctions.

Cooperation by the members of the advisory committee was crucial to the success of the project, since the sampling devices needed were those owned by the mining companies whose representatives composed the committee. Tentative approval for the loan of the samplers was granted, pending the committee's acceptance of a plan for sampling which would render the samples collected invalid for environmental enforcement.

The plan involved the following steps:

1. Wind directional switches, operated by a wind vane and cam arrangement, would be designed, built, and installed on the air samplers borrowed from the mining companies. These switches would allow actual sampling only when the wind direction was from a predetermined sector.
2. The samplers would be sited at carefully chosen locations around the Spruce Pine corridor. The sites chosen would be sufficiently distant from obvious industrial sources that ambient air would be sampled (See Figure 1).
3. Samples would be collected from the sampler network for a period of several months, including February, as February was historically a month having high TSP levels.
4. An attempt, based on compositional and mass analysis of the samples, would be made to identify general areas of origin for the TSP collected.
5. Reports on progress would be written and distributed to members



of the Mitchell County advisory committee whenever substantial progress was realized.

After the general procedure was approved by the advisory committee, cooperation and assistance by the mining industry was invaluable and extensive. The mining interests facilitated obtainment of site access, electrical power, and materials during the initial and sampling phases of the experiment. Particularly important was the access to processed mining products and personnel provided by the Feldspar Corporation.

#### B. Survey of Relevant Research

Airborne suspended particulate matter has become the focus of many investigations within the past 12 years. In addition to direct effects of particulate pollution, much interest has been generated because surfaces of particles provide sites for reactions among gaseous pollutants as well as sites for adsorption which concentrates other pollutants.<sup>1</sup>

Recent interest has generated much work in all phases of TSP collection and analysis. A comparison of collection efficiencies of the two most common sampling systems, high volume air samplers and dichotomous particle samplers, was recently published by Kolak and Visalli.<sup>3</sup> The comparison included assessment of common filter media used with various samplers and listed advantages and disadvantages for each material. Less well known methods for collection, such as aerodynamic particle size separators and some prototype collectors, have been examined by several authorities who participated in a symposium on the subject.<sup>4</sup>

Analytical methods commonly used for TSP identification and quantitation have been reviewed, along with several promising new methods, by Fox and Jeffries.<sup>5</sup> The analyses mentioned in the review are predominantly elemental or ionic in nature, and therefore unable to yield direct information about compounds present. Methods not restricted to elemental determinations have been reported by Davis and Cho, using X-ray diffractometry,<sup>6</sup> and by W. Davis, using continuous mass spectrometry.<sup>7</sup>

The analytical method used in this study was based on work done by Chung pertaining to quantitative analyses of crystalline mixtures by X-ray diffraction, using an added internal standard.<sup>8,9</sup> The original Chung method was modified for use on thin film samples by Davis and Cho.<sup>6</sup> A later modification by Davis eliminated the requirement of an added internal standard, relying instead on previously determined data, thus greatly improving the utility of the method.<sup>10,11</sup>

An assessment of the usefulness of various filter media for X-ray diffraction analysis of TSP showed glass fiber filters similar to the ones used for this study to be suitable for use when heavily loaded with sample.<sup>12</sup> A study of errors involved in X-ray diffraction analysis of high volume air filters shows that the most important variable in the assessment of analytical uncertainty is the reference intensity constant, which must be determined for the analytical peaks of each component being analyzed. The reference intensity constant for a given peak of a component is the relative intensity of the peak with respect to the major

peak of a standard. The constant for each peak is determined by making an X-ray diffraction pattern of the material mixed 1:1 with the standard. Davis has found that, in the determination of the mean intensity constant for a particular mineral peak, the use of samples having different geological backgrounds can introduce a standard deviation as high as 50% of the mean value. Weight percentages calculated using the intensity constants so determined may then deviate up to 50% from the true values. Better accuracy can be achieved using intensity constants taken from standard materials having origins similar to the sample components.<sup>13</sup>

Davis and co-workers have applied the Davis method to an analysis of the ash emitted by St. Helens volcano, and found good agreement with determinations based on X-ray fluorescence spectrometry.<sup>14</sup>

## CHAPTER II

### EXPERIMENTAL

#### A. Overview

This project involved three major phases. The first phase involved the construction of wind directional switches and installation of the switches on the samplers borrowed from the mining companies. The second phase involved the collection of samples from sites around the Spruce Pine, N. C. area. The final phase involved analyses of the collected samples.

#### B. Collection Apparatus

##### 1. Samplers

High volume air samplers were used for the collection of TSP during this study. The samplers consist of a motor unit connected to a filter support and the assembly housed in an aluminum enclosure (See Figure 2). The samplers used were GMW-2000 samplers manufactured by General Metal Works Inc., of Cleves, Ohio.

##### 2. Sampler Accessories

Switches were designed and built to allow air sampling when the wind was from a predetermined  $90^\circ$  sector. A cam and wind vane mechanism activated a 5 ampere roller microswitch, completing an electrical connection to the sampler motor (See Figure 3). The cam was machined from 3 inch round aluminum stock with a  $90^\circ$  depression milled  $1/8$  inch into the edge. The switches were

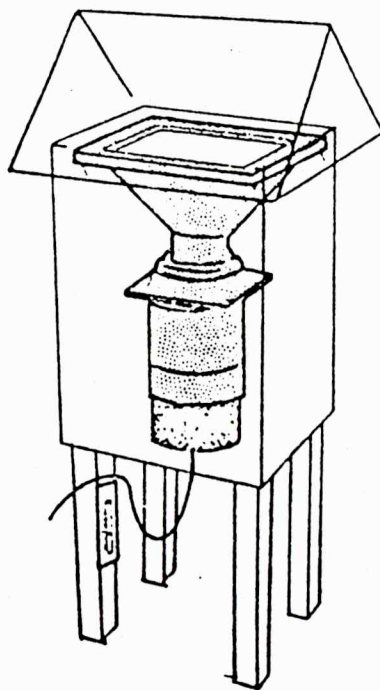
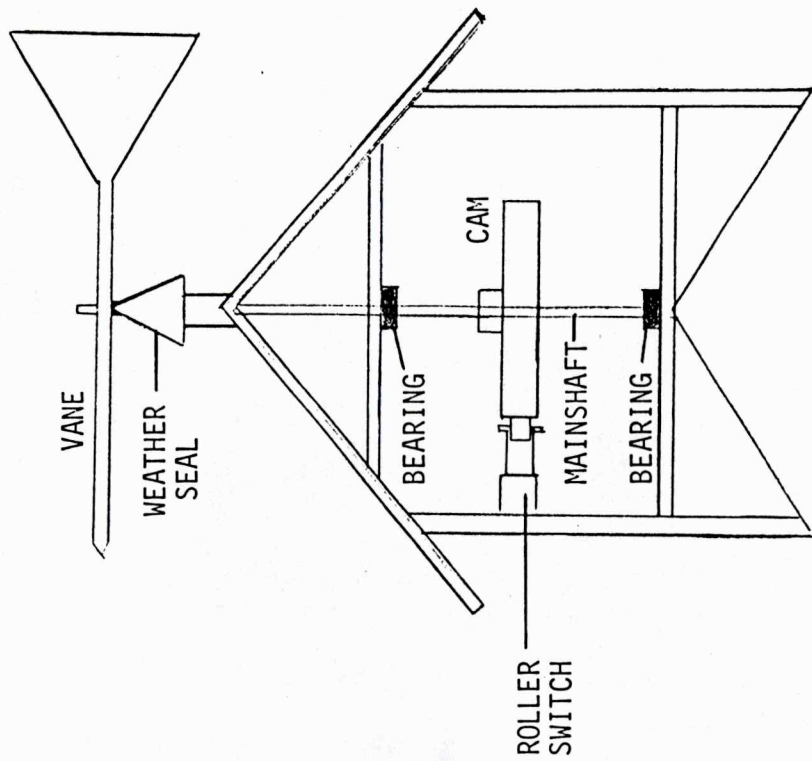


Figure 2. GMW-2000 High Volume Air Sampler





TOP VIEW OF CAM AND SWITCH

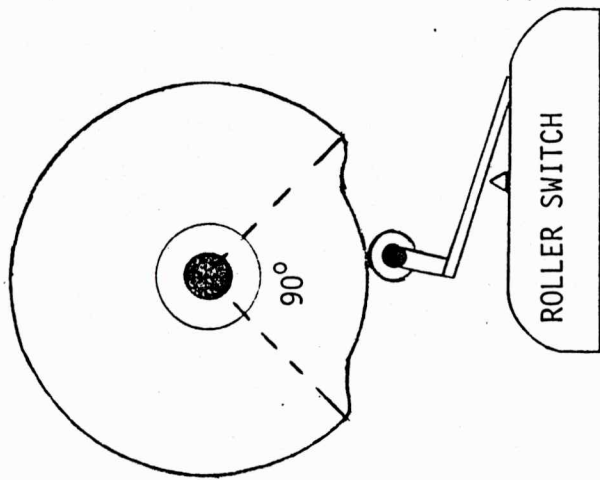


Figure 3. Diagram of wind activated switch assembly and cam

connected in series with the motors and timers of the high volume samplers. Choice of sampling direction was set using a compass to determine direction and turning the cam to achieve the desired cut-on point.

Timers on the samplers recorded actual on-time of the samplers, while timer-switches, also on the samplers, were set to allow a sampling window of between two and one hundred sixty-six hours (166), during which time sampler operation depended on wind direction (See Figure 4). The bearings, cam and electrical portions of the switches were enclosed in housings made from pressure treated lumber sealed with roofing cement.

#### C. Siting

Samplers were sited at four positions strategically located around Spruce Pine, N. C. At each site the samplers were mounted on pressure treated foot pads and stabilized by means of annealed steel guy wires. After each sampler was secured, a wind directional switch was mounted on its roof, secured with guy wires and connected to the electrical circuit of the sampler. The sites chosen are shown in figure 1.

Site 1: One sampler was positioned on the roof of the Veterans of Foreign Wars post on Altapass Road approximately 2 miles southeast of Spruce Pine.

Site 2: A second sampler was sited on the roof of a television transmitter shed located adjacent to the Spruce Pine fire tower on Woody's Knob approximately 2 miles southwest of Spruce Pine.

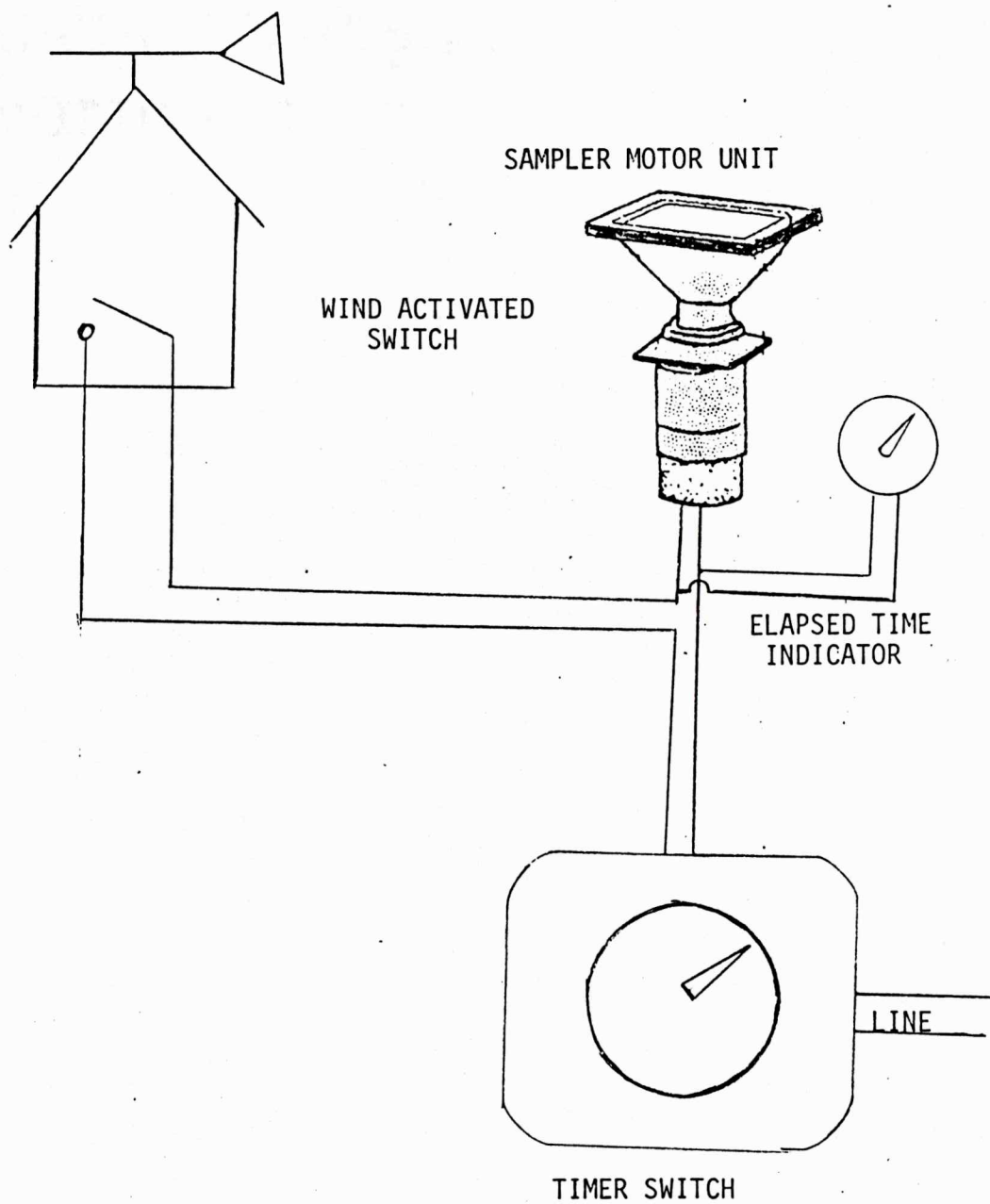


Figure 3. Schematic of sampler and switch hookup



Site 3: A third sampler was located on the roof of the Appalachian School building on Penland School Road, approximately 2 miles northwest of Spruce Pine.

Site 4: A fourth sampler was placed on the roof at Joe Howell's Store located on highway 19E approximately 3 miles northeast of Spruce Pine.

#### D. Sampling

##### 1. Preparatory and Field Work

The sampling phase of the project took place between October 10, 1981 and February 27, 1982. During this interval thirteen (13) sets of 4 samples each were initiated. Spacing of sampling periods was irregular due to equipment malfunctions and severe weather. The sampler at site 2 developed chronic problems with a ground fault circuit interrupter. Power to the sampler was interrupted on several occasions during sampling, rendering those samples invalid. At site 3 the sampler was vandalized during a number of sampling periods. The tampering ceased when students of a nearby boarding school left the area for the winter.

Several preparatory steps were required prior to installation of collection filters in the samplers. Filter elements were first dessicated in a converted oven at  $21 \pm 5^{\circ}\text{C}$  for a minimum of 48 hours prior to taring. Tare masses were then determined to the nearest .1 mg on a Mettler B analytical balance.

On site, each filter was installed in the sampler per instructions in the sampler operations manual.<sup>15</sup> The arc of wind direction which would allow sampling was set by holding the cam in the

position which just tripped the microswitch, then rotating the loosened wind vane until it was aligned with the edge of a predetermined sector. The adjustment was maintained by a lock-screw on the vane. Next the timer switches were set to provide power to the samplers during a period which varied from 24 hours to 144 hours, each period beginning and ending on midnight of the chosen days. Initial flow rates through the filter were then determined using a floating ball rotameter.

Collection of samples at the end of a sampling period also followed rigid protocol. Prior to removing a filter, a final flow rate through the filter was determined using the rotameter. The integrity of switch operation and direction setting was then rechecked and the filter was removed from its holder. Each filter was folded lengthwise, exposed portion inward, and transported to the laboratory in a manilla folder. After the collection of an exposed filter a new filter was placed in the sampler and a new sampling cycle begun.

The wind directional switches functioned adequately during the first half of the sampling stage of the project. It was noted that when ambient temperature fluctuated more than 20°C during a sampling period expansion and contraction of the directional switch components adversely affected switch operation. A decision was made to disconnect the wind directional switches and complete the project using climatological data collected by the U. S. Climatic Control Center in Asheville, N. C.<sup>16</sup>

In the laboratory exposed filters were dessicated for at least 48 hours then massed to determine the quantities of sample collected. Massing of filters, both before and after sample collection, was restricted to relatively nonhumid days to minimize effects of filter or sample hygroscopicity.

## 2. Quality Assurance

Quality assurance for this project involved procedures pertaining to filter handling and sampler operation. One filter acted as a control for each tare and final massing of filters. The first filter in a series was massed and then set aside during the massing of the other filters. After all filters were massed, the mass of the first filter was redetermined and compared to the original value. At no time did the two masses vary significantly.

Sampler operation quality assurance involved three calibrations with respect to air flow for each sampler. Calibration curves were constructed for determination of true air volume flow rate (corrected to 0°C and 760 torr), based on the average of the rotameter readings taken at the beginning and end of each sampling period. Calibration data was obtained using a metered calibration orifice, which was itself calibrated by the N. C. Department of Natural Resources and Community Development Air Planning Division laboratory in Raleigh, N. C.

Calibration of the metered orifice was performed once prior to and once during the sampling phase of the project. Details of calibration procedures for both the metered orifice and samplers

are available in the Federal Register.<sup>17</sup> Quality assurance data and calibration curves may be found in Appendix A.

#### E. Analysis

Preliminary analysis of collected samples involved a simple determination of ambient air particulate loading. Sampler air volume flow rates and net sample masses were used to determine the TSP concentration of sampled air in micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ).

Chemical analysis of the samples involved assessment of the type and relative concentrations (weight percentages) of major crystalline components present. This was accomplished using an X-ray diffraction method for identification and quantitation of crystalline species. The method was chosen because it requires minimal sample preparation and is nondestructive. The instrument used for obtaining diffraction patterns was a General Electric XRD-5 X-ray diffractometer equipped with an SPG-2 spectrogoniometer, an SPG-4 preamplifier and an 8-SPG counter tube. The goniometer unit was of the Brentano parafofocussing geometry.<sup>18</sup>

All diffraction scans were made using  $\text{Cu K}\alpha$  radiation from an X-ray tube held at 35.0 kV target potential and 15 mA current. Detector potential was maintained at 1.34 kV. Medium resolution Soller slits having a  $1^\circ$  aperture focussed the X-ray beam onto the samples. Diffracted radiation was passed through medium resolution Soller slits, a  $0.1^\circ$  scatter slit and a nickel foil  $\text{K}\beta$  filter before entering the detector.



Prior to sample analysis, beam transmission ratios were determined for 4 blank filter samples for use in subsequent calculations. Small strips were cut from each of 4 massed filters and mounted in a clamp which held the strip in or out of the X-ray beam path as desired. The spectrogoniometer was adjusted to position the detector to measure the most intensely diffracted peak,  $2\theta = 26.41^\circ$ , of a standard quartz-ceramic block ( $2\theta$  is twice the angle between the X-ray beam and sample plane). A blank filter strip was then positioned between the standard block and detector and a ten second counting of detector pulses was made; the filter strip was removed from the beam path and another ten second counting taken. This pair of measurements was made four or more times for each filter strip. The ratio of intensities for each pair of measurements was calculated and used to obtain blank filter mass absorption coefficients (mass absorption coefficient is a measure of a substance's ability to absorb radiation). These measurements will be discussed in the following chapter.

Sample filters were prepared for scanning by cutting a 2 cm by 5 cm strip from the center portion of the filter. Optimum scanning characteristics were determined by systematically scanning a heavily loaded filter with various scanning speeds and instrument operating parameters. The results of these trials showed that the slowest scanning speed ( $0.2^\circ$  per minute), which is the rate of change of the angle between the X-ray source, sample, and detector, provided the best scan reproducibility. Recorder range, the maximum number of detector pulses which could register

on the recorder, showed the best peak readability when a 100 cycle per second (cps) full scale deflection was chosen. The time constant setting, which is the amount of time over which the instrument averages counter pulses, was set according to the manufacturer's recommendations. Detailed operating procedures may be found in the operations manual for the XRD-5.<sup>18-20</sup>

Diffraction patterns of all samples scanned were made using the optimum settings as previously described. If a peak height exceeded recorder capacity, full scale range was increased to a value which allowed the entire peak to be recorded. Background scattering patterns were recorded using a blank filter. The background patterns were recorded with instrument settings identical to those used during sample measurements.

X-ray diffraction patterns were made of each valid TSP sample collected. Samples considered invalid were those during whose collection sampler failure or tampering had occurred. Scans were recorded over a  $2\theta$  range of  $5^\circ$  to  $47^\circ$  for each filter. A reproduction of a representative scan is shown in figure 5.

Samples of mineral products produced in the Spruce Pine, N. C. area were obtained and their diffraction patterns recorded. The products so treated were feldspar flour, mica, kaolin clay, and silica sand. All were ground in an agate mortar, passed through a 200 mesh sieve and pressed into a bakelite sample well for analysis. As these diffraction patterns were used only for peak position comparisons, the very slow scanning speed needed for sensitivity in the sample analysis was unnecessary. Scanning

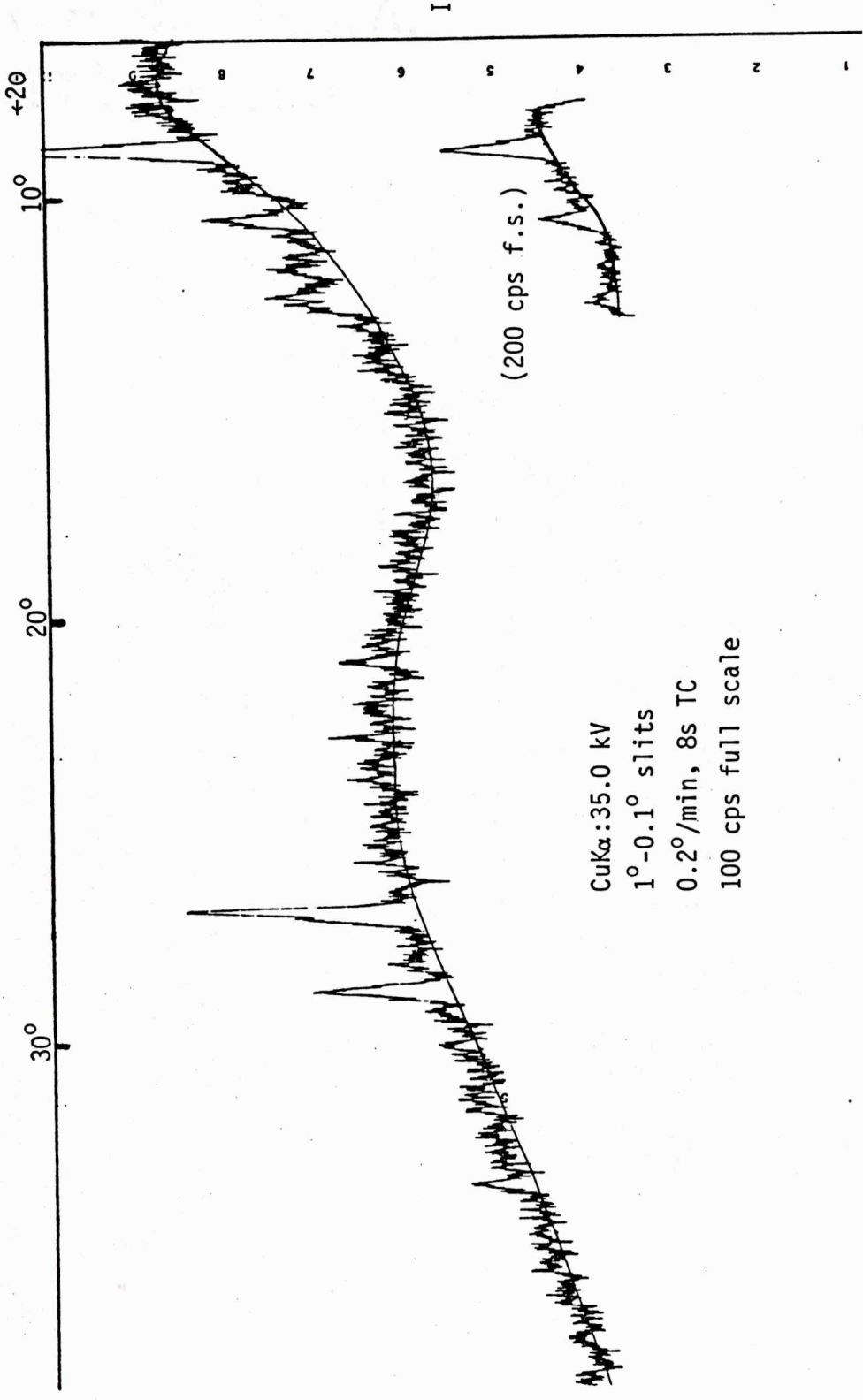


Figure 5. Diffraction pattern from Filter 4D

speed was therefore increased to  $2^\circ$  ( $2\theta$ ) per minute and the recorder range increased to 5000 cps to accommodate the peak signals produced.

The final stage in the analytical procedure involved the determination, based on diffraction patterns, of the qualitative and quantitative composition of the crystalline portion of the collected samples. Tentative identification of sample components involved the comparison of  $2\theta$  values of prominent peaks to  $2\theta$  values listed in a table of analytical peaks for various common minerals.<sup>21</sup> This table contained, in addition to peak positions ( $2\theta$  values), crystal plane coordinates, mass absorption coefficients, and other information pertaining to the minerals. A portion of the table listing those values used in this experiment is reproduced in table I. Information supplied by the table was supplemented with additional mineral diffraction data.<sup>22,23</sup>

Tentative mineral identifications were discussed with several geologists from Appalachian State University in Boone, N. C. These discussions concerned the regional abundances, or absences, of the minerals tentatively identified. Particularly helpful were suggestions that the appearances of certain minerals were very unlikely.

Final identification of a sample peak was primarily based on the  $2\theta$  value for the peak when substantiated by one or more additional peaks. When no other peaks for a given mineral were



Table I. Component Data for X-Ray Analysis<sup>a</sup>

Component (abbr.)	2 $\theta$	$\mu^*$	$\sigma_\mu$	$k_i$	$\sigma_k$
Biotite (b)	8.73	96.5	12.8	2.43	.94
Muscovite (M)	8.89 26.86	45.36 45.36	5.46 5.46	0.27 0.27	0.03 0.03
Chlorite (C)	6.3 12.43	65.3 65.3	23.3 23.3	0.28 0.46	0.05 0.08
Quartz (Q)	20.85 26.66	34.9 34.9	2.2 2.2	0.51 2.84	0.07 0.33
Halite (Ha)	27.37 31.72	74.7 74.7	1.50 1.50	0.35 2.70	0.08 0.59
Selenite (S)	11.70	65.7	6.6	1.52	0.15
Bytownite (By)	27.8	49.15	1.39	1.71	0.17
Hornblende (H)	10.51	87.9	10.7	0.67	0.21
Natrojarasite (N)	17.59	131.4	13.1	1.143	0.11
Goethite (G)	21.20	206.1	20.6	2.00	0.20
Fluorite (F)	28.28	96.8	9.7	3.57	0.36
Calcite (Ca)	29.47	81.21	5.77	2.01	1.15
Siderite (Si)	32.18	148.7	13.3	2.16	0.22
Kaolinite (K)	12.36	36.0	2.1	0.59	0.19
Hematite (He)	33.20	229.29	3.5	2.05	0.21
Phlogopite (P)	10.84	50.3	5.0	2.35	2.4

<sup>a</sup>Reprinted with permission of the author from reference (21)

Note: 2  $\theta$  is twice the Bragg diffracting angle;  $\mu^*$  is the mass absorption coefficient of the component in  $\text{cm}^2/\text{g}$ ;  $k_i$  is the reference intensity constant for the component at the 2  $\theta$  angle stated referenced to the  $\text{CaF}_2$  III peak;  $\sigma$  is the standard deviation for the quantity subscripted.

found a determination of identity was based on information received from the geologists.

Quantitation of components involved the integration of diffracted peak intensities. A Dietzgen polar planimeter, model D-1804-AM, was used to determine peak areas and the areas converted to intensities with a detector pulse to area ratio. The results of integration were then mathematically corrected for error due to the small mass to area ratios of the samples. Detailed discussions of the calculation may be found in Chapter III.

CHAPTER III  
RESULTS AND CALCULATIONS

A. Mass Analysis

During the sampling phase of this project, 36 high volume air filter samples out of 52 samples initiated were collected and found to be useable for mass analysis. The filters not used were declared invalid for reasons mentioned earlier in this report.

The initial step in the analysis was the determination of the mass of TSP collected on each filter (See Table II). Masses collected ranged from 51.9 milligrams (mg) to 653.9 mg. These masses were then used to calculate average TSP loading of sampled air in  $\mu\text{g}/\text{m}^3$  using the formula

$$\text{TSP loading} = \frac{\text{mass of TSP}}{\text{sampler flow rate} \times \text{sampler on time}} .$$

These calculations and dates of collection are compiled in Tables III and IV.

TSP loading data were then subjected to linear regression analysis to determine if correlations existed between loadings at various sites. For example, in an analysis of the correlation between any two sites, X and Y, a point (x, y) is generated where x and y represent the TSP loading at sites X and Y respectively. Such points are generated for each sampling period of interest. The correlation coefficient is a measure of how closely these

Table II  
Sample Masses Collected (mg)

Site	Filter Series											
	A <sup>a</sup>	B <sup>a</sup>	C <sup>a</sup>	D <sup>a</sup>	E <sup>a</sup>	F	G	I <sup>b</sup>	J	K	L	M
1	-	56.4	505.6	67.4	653.9	324.7	135.7	130.1	186.9	122.0	143.2	100.6
2	101.8	-	132.0	137.7	-	-	-	166.4	101.0	51.9	86.5	56.1
3	-	-	126.9	52.7	120.8	98.2	92.6	149.0	209.2	166.4	115.0	93.7
4	52.3	183.1	456.6	504.7	292.1	206.4	-	330.5	300.1	264.9	243.0	142.7

<sup>a</sup>Wind directional switches used during these collections

<sup>b</sup>Series H voided

Table III. TSP Ambient Loading for Samples Collected  
during Northerly Winds

Series	Collection Dates	TSP loading of ambient air ( $\mu\text{g}/\text{m}^3$ )			
		Site 1	Site 2	Site 3	Site 4
A	10/16 - 10/18	-	9.1	-	39.5
E	12/8 - 12/13	54.6	-	31.2	54.7
F	12/18 - 12/20	55.2	-	17.7	35.9
I	2/8 - 2/10	22.7	28.3	25.5	58.3
J	2/11 - 2/13	31.7	17.4	34.7	50.7
L	2/21 - 2/23	23.0	15.9	19.8	40.9
Average		37.4	17.7	25.8	47.8

Table IV. TSP Ambient Loading for Samples Collected  
during Southerly Winds

Series	Collection Dates	TSP loading of ambient air ( $\mu\text{g}/\text{m}^3$ )			
		Site 1	Site 2	Site 3	Site 4
B	10/19 - 10/22	127.5	-	-	23.6
C	11/9 - 11/15	107.4	24.4	47.6	47.9
D	11/30 - 12/6	14.5	29.9	19.1	32.7
G	12/25 - 12/27	22.6	-	16.5	-
K	2/14 - 2/16	21.3	9.2	28.0	44.8
M	2/25 - 2/27	17.3	10.0	16.0	24.3
Average		51.8	18.4	25.4	34.5



points approximate a straight line. A value close to  $\pm 1$  represents a high degree of linearity, a value closer to 0 represents a very poor correlation. Correlations of TSP loading for all possible pairs of sites are shown in Table V.

#### B. X-Ray Diffraction Analysis

The filter samples collected during this work were analyzed using a technique which allows the calculation of weight percentages of identifiable crystalline components in a mixed sample. The analytical scheme is based on the Chung equation,<sup>9</sup>

$$W_i = \left( \frac{k_i}{I_i} \sum_{j=1}^n \frac{I_j}{k_j} \right)^{-1}, \quad (1)$$

where  $W_i$  is the weight fraction of component  $i$  in a sample of  $n$  components,  $k_i$  is the reference intensity constant for component  $i$  (defined earlier), and  $I_i$  is the absolute intensity of an X-ray beam diffracted from the component in the mixture. Chung has shown that the presence of amorphous or unidentified components may alter the absolute weight fractions obtained with Equation (1), but that the relative weight fractions of the identified materials will not be affected.

Davis<sup>6</sup> has shown that the Chung equation cannot be used directly in the analysis of samples which do not approximate infinite thickness characteristics.<sup>a</sup> Thus high volume air filter samples (hereafter termed Hi-Vol samples), which rarely satisfy the infinite thickness criterion, cannot be analyzed by direct

<sup>a</sup>In practise, a sample is said to have infinite thickness characteristics if no more than 0.1% of an incident X-ray beam intensity is transmitted by the sample.

Table V. Linear Regression Correlations for TSP  
Loading by Site and Wind Direction

Site	Wind Direction											
	Northerly				Southerly				All			
	2	3	4		2	3	4		2	3	4	
1	-0.43	-0.02	-0.27		0.34	0.93	0.01		0.24	0.76	-0.19	
2	-	-0.02	0.88		-	0.26	0.15		-	0.20	0.35	
3	-	-	0.72		-	-	0.87		-	-	0.62	



application of Equation (1). The problem is that X-ray beam penetration of the sample varies with the angle at which the beam strikes the sample. A correction must be applied to the diffraction intensities of a thin sample to use the Chung equation.<sup>6</sup>

In a theoretical treatment of a Hi-Vol sample as three distinct layers, one of pure filter material, one of filter-sample composite, and one of pure sample, Davis has derived an equation which allows the correction of diffraction intensities from a thin layer sample to values approaching those from an infinitely thick sample. The working equation for obtaining the corrected intensity ( $I_c$ ) is

$$I_c = \frac{I_i \mu_H^*}{W_B^H \mu_B^* \left( 1 - e^{-2\mu_H^* (\bar{M}_B / W_B^H / \sin \theta)} \right)} \quad (2)$$

where  $\mu_H^*$  is the mass absorption coefficient for the composite (hybrid) layer of material,  $W_B^H$  is the weight fraction of the sample, B, in the composite layer, and  $\mu_B^*$  is the overall mass absorption coefficient for the sample. The quantity  $\bar{M}_B$  is the sample mass divided by the filter area ( $\text{g}/\text{cm}^2$ ) and  $\theta$  is the diffraction angle ( $\frac{1}{2}$  of  $2\theta$ ). A detailed derivation of this equation is available in the literature.<sup>6</sup>

The use of Equation (2) required the calculation of  $\mu_f^*$ ,  $\mu_H^*$ ,  $W_B^H$ , and  $\mu_B^*$ . The mass absorption coefficient for the filter material,  $\mu_f^*$ , was given by

$$\mu_f^* = -\frac{1}{M_f} \ln \left( \frac{I_f}{I_o} \right) \quad (3)$$

using  $I_f/I_0$ , the intensity ratios for blank filters discussed in Chapter II.  $\bar{M}_f$  is the mass of filter material divided by the filter area.  $I_f/I_0$  values are given in Table VI. Glass-fiber TSP filters used in the study were assumed to be identical and thus a mean value for  $\mu_f^*$  was determined and used in all X-ray diffraction analyses. The data used to determine the mean value of  $39.34 \text{ cm}^2/\text{g}$  are available in Table VII.

The parameter  $W_B^H$  is dependent on filter characteristics and on the sample loading of the filter ( $\bar{M}_B$ ); its value is given by

$$W_B^H = \left( 1 + \frac{t_g \rho}{\bar{M}_B} \right)^{-1} \quad (4)$$

$t_g$  is the depth of penetration of sample into the filter matrix and  $\rho$  is the density of the filter material. The values for  $t_g$  and  $\rho$  have been determined for binderless glass-fiber filters to be  $2.6 \times 10^{-4} \text{ cm}$  and  $2.42 \text{ g/cm}^3$  respectively.<sup>12,24</sup>

$\mu_B^*$ , corrected intensities, and weight percentages were calculated by means of an iterative correction procedure to be described. The basic equation for  $\mu_B^*$  is

$$\mu_B^* = \sum_{i=1}^n \mu_i^* W_i \quad (5)$$

for a sample of  $n$  components.  $\mu_i^*$  values have been determined for many substances (See Table I).<sup>6,21</sup> The iteration process began with the determination of provisional weight percentages ( $W_i$ ) using Equation (1). The provisional weight percentages were then used in Equation (5) to determine an approximate  $\mu_B^*$ . This value

Table VI. Transmission Ratios for Glass-Fiber Air Filters<sup>a</sup>

Trial Number	Blank 1	Blank 2	Blank 3	Blank 4
1	0.7444	0.7363	0.7569	0.7484
2	0.7443	0.7450	0.7473	0.7360
3	0.7234	0.7386	0.7345	0.7248
4	0.7382	0.7506	0.7343	0.7218
5	-	0.7486	0.7262	-
			Mean	0.7389
			$\sigma$	.0102

<sup>a</sup>Ten-second counting; Cu K<sub>α</sub> 35 kV, 15 mA; 1° - 0.1° slits

Table VII

## Mass Absorption Measurements for Glass-Fiber Filters

Mass Absorption* Coefficient, $\mu_f$ ( $\text{cm}^2/\text{g}$ )	Filter (and $\bar{M}_f$ ) <sup>a</sup>			
	1 (0.007708)	2 (0.007623)	3 (0.007765)	4 (0.007684)
38.29	40.15	35.87	37.71	
38.31	38.61	37.51	39.89	
42.00	39.75	39.75	41.88	
39.38	37.64	39.77	42.43	
	37.98	41.21		
		mean		39.34
		$\sigma$		1.77

<sup>a</sup> $\bar{M}_f$  is the filter mass divided by its area ( $\text{g}/\text{cm}^2$ ). All filters had areas of  $526 \text{ cm}^2$ .

of  $\mu_B^*$  was used to generate corrected intensities with Equation (2). These intensities were used to calculate corrected weight percentages. The iteration was continued using corrected weight percentages until constant values for  $\mu_B^*$ ,  $I_C$ , and  $W_i$  were obtained. A computer program was written to handle the calculations needed and a listing is included in Appendix B. A sample printout of the data generated by the computer is shown in Figure 6.

Detailed analyses were performed on six series of samples chosen according to wind direction. Of the 24 filters included in the series, three were not useable for X-ray analysis because peaks in their diffraction patterns were either too small or too few. Tabulations of data collected are shown in Tables VIII-X.



---

 FILTER #4J
 

---

 u\*b= 47.1424555 mass/area= 731.ug/cm<sup>2</sup>
~~THE FINAL WEIGHT PERCENTS ARE~~

<u>component</u>	<u>weight %</u>	<u>intensity</u>
MUSC	80.52	.14733
SELEN	1.530	.01573
CHLORITE	11.01	.03432
QZ	6.928	.02394

---

 FILTER #3K
 

---

 u\*b= 73.4670218 mass/area= 400.ug/cm<sup>2</sup>
~~THE FINAL WEIGHT PERCENTS ARE~~

<u>component</u>	<u>weight %</u>	<u>intensity</u>
BIOT	1.916	7.9970
MUSC	24.46	.02932
HORN	65.42	.06099
QZ	7.212	.01633
PHLOGOPIT	.9818	.01024

---

 FILTER #4K
 

---

 u\*b= 55.8420623 mass/area= 646.ug/cm<sup>2</sup>
~~THE FINAL WEIGHT PERCENTS ARE~~

<u>component</u>	<u>weight %</u>	<u>intensity</u>
MUSCOVITE	77.61	.23952
HORNBLEND	3.822	9.1746
SELENITE	.6693	.01161
CHLORITE	6.107	.03211
NATROJAR	7.173	.09371
QUARTZ	1.684	.05468
FLUORITE	2.928	.11948

---

Figure 6. Computer printout for Filters 4J, 3K, and 4K

Table VIII  
 Components Identified on Sample Filters<sup>a</sup>

Site	Series <sup>b</sup>				
	I	J	L	C	M
1	M, H, Q, B, S	M, H, B, N, S	M, H, Ha, Q, C, S	M, H, By, N, S	M, Q, B, K, S
2	M, H, Q	M, Q, S	M, Q, C, S	M, C, Ca, N, G, B, F	-
3	M, Q, B, C, By, F	M, Q, N, B, S	M, H, C, S, Ha, N, B	M, H, S	H, M, Q, B, P M, By, Q, S
4	M, Q, C, S	M, C, Q, S	M, H, Q, C, S, By, Si	M, H, C, He, S	M, N, C, H, F, Q, S M, B, H, C, S, N

<sup>a</sup>Abbreviations are noted in Table I; components listed in order of decreasing weight percent.

<sup>b</sup>Series I, J, and L sampled during northerly wind; series C, K; and M sampled during southerly winds.

Table IX

Weight Percentages of Eight Most Frequently Identified Components<sup>a</sup>

## A. Samples Collected During Northerly Winds

Series	Site	Component						
		M	S	Q	H	C	B	N
I	1	74	1	7	16	-	1	-
	2	41	-	19	40	-	-	-
	3	59	-	14	-	8	11	-
	4	89	1	5	-	5	-	-
J	1	68	2	-	16	-	10	4
	2	61	7	32	-	-	-	-
	3	50	1	43	-	-	2	5
	4	81	2	7	-	11	-	-
L	1	47	2	10	17	8	-	-
	2	57	9	23	-	11	-	-
	3	38	8	-	24	13	4	5
	4	50	2	14	21	8	-	-

<sup>a</sup>Percentages may add to more than 100% due to rounding

Note: Weight percents reported are calculations based on the crystalline fraction of the sample identified. Amorphous or unidentified components preclude the possibility of absolute weight percentages.

Table IX

Continued

## B. Samples Collected During Southerly Winds

Series	Site	Component						
		M	S	Q	H	C	B	N
C	1	57	1	-	29	-	-	1
	2	82	-	-	-	8	1	3
	3	68	3	-	29	-	-	-
	4	76	1	-	15	6	-	-
K	3	24	-	7	65	-	2	-
	4	78	1	2	4	6	-	7
M	1	77	1	13	-	-	6	-
	3	75	2	9	-	-	-	-
	4	58	3	-	13	10	15	2

Table X  
 Relative Weight Percentages of Eight Components  
 A. Samples Collected During Northerly Winds (Wt % M=100)

Series	Site	Component						
		M	S	Q	H	C	B	N
I	1	100	1.4	9.5	21.6	-	1.4	-
	2	100	-	46.3	97.6	-	-	-
	3	100	-	23.7	-	13.6	18.6	-
	4	100	1.1	5.6	-	5.6	-	-
J	1	100	2.9	-	23.5	-	14.7	5.9
	2	100	11.5	52.5	-	-	-	-
	3	100	2.0	86.0	-	-	4.0	10.0
	4	100	2.5	8.6	-	13.6	-	-
L	1	100	4.3	21.3	36.2	17.0	-	-
	2	100	15.8	40.4	-	19.3	-	-
	3	100	21.1	-	63.2	34.2	10.5	13.2
	4	100	4.0	28.0	42.0	16.0	-	-



Table X  
Continued

B. Samples Collected During Southerly Winds (Wt % M=100)

Series	Site	Component						
		M	S	Q	H	C	B	N
C	1	100	1.8	-	50.9	-	-	1.8
	2	100	-	-	-	9.8	1.2	3.7
	3	100	4.4	-	42.6	-	-	-
	4	100	1.3	-	19.7	7.9	-	-
K	3	100	-	29.2	271	-	8.3	-
	4	100	1.3	2.6	5.1	7.7	-	9.0
M	1	100	1.3	16.9	-	-	7.8	-
	3	100	2.7	12.0	-	-	-	-
	4	100	5.2	-	22.4	17.2	25.9	3.4

## CHAPTER IV

### DISCUSSION

The ambient TSP data of Tables III and IV show distinct differences in the averages TSP concentrations among the four sampler sites. Site 2, established at the most remote location of the four sites, proved to have consistently low levels of TSP. Sites 1 and 4, located in areas with considerable human activity, display substantially higher average TSP levels. When winds are northerly, sites 2 and 3 maintain rather consistent loading characteristics while the levels at sites 1 and 4 vary markedly. The changes for sites 3 and 4, which for each site are very near 32% of the overall mean loading, occur in opposite directions. It is reasonable to assume that the area between the two sites contains one or more major TSP sources. This is an interesting possibility because the bulk of industry in Spruce Pine lies closer to site 3 than to either site 1 or 4. A clay mining operation between the sites may be discounted as the possible source in light of the fact that kaolinite, a clay mineral comprising a major portion of the clay being mined, was identified as a component of only one TSP sample during analysis.

A comparison of TSP components collected at different times at the sites in question shows no great difference between average compositions during southerly and northerly winds. More

marked differences due to wind direction were found for sites 2 and 3. During southerly air flow, the TSP at those sites contained small amounts of quartz (<10%) or none at all; during northerly winds the quartz content of the samples averaged 41%. It is interesting that even during significant changes in composition, mass loadings at those sites remained relatively constant.

Another interesting point is found in the linear regression analysis of TSP data correlations between sites (See Table V). Site 4 shows rather good data correlation with sites 2 and 3 when the wind direction is northerly; when the wind is southerly site 4 maintains good correlation with site 3, but shows virtually none with site 2. Similarly, site 1 shows close data correlation with site 3 during southerly air flow though virtually no correlation exists under reversed conditions.

During the X-ray diffraction analyses of samples it was thought probable that relatively large amounts of the feldspar minerals would be detected. In fact, the opposite was found. The common feldspar minerals orthoclase, microcline, albite, and oligoclase, mined in large quantities near Spruce Pine, were either absent, or present in undetectable quantities in the samples analyzed. The one feldspar which was present in appreciable amounts, bytownite, was identified in filters 1C, 3I, 4L, and 3M in concentrations of 12, 4, 2, and 14 percent respectively. The absence of mining products in the samples collected during this study implies that the mining industry may contribute significantly less to ambient TSP than is commonly believed.

The mineral muscovite, a mica, was found to be the major component in all but one of the samples analyzed. This finding was not unexpected since the mineral is found virtually everywhere in the area. Muscovite, along with two other common minerals, quartz and hornblende, frequently made up 80 weight percent or more of the total amount of identified crystalline material.

An initially troublesome finding, later explained, was the presence of selenite, a close relative of gypsum, in all but four samples. Selenite is not native to the Spruce Pine region and its presence was highly suspect. Further investigation uncovered the fact that a large, heavily mined deposit of selenite and gypsum lies north of Spruce Pine in southern Virginia. It is very likely that selenite, which is easily and finely divided, is blown into the region. This supposition is supported by evidence drawn from the data in Table IX for site 2. The sampler at the Spruce Pine fire tower was sited at a higher and more remote location than the other samplers and was therefore less subject to locally originating TSP. The site showed high average selenite concentrations with respect to the other samplers during northerly air flow. Southerly winds at the same site reduced the amount of selenite beyond detectable limits.<sup>a</sup> This is exactly what would be expected if the selenite source was located north of the Spruce Pine region.

<sup>a</sup>Although analytical data are not presented for filter 2K, a diffraction pattern was run. The pattern showed several small peaks, but the major peak for selenite was totally absent.

A detailed error analysis for this experiment is far beyond the scope of this report. A study of errors associated with the X-ray diffraction method used here has been published and offers a reasonable estimate of analytical accuracy.<sup>13</sup> Errors as high as 50% of weight percentages determined have been reported for certain minerals. The large errors are principally due to variations in the  $k_j$  values for some minerals. Problem minerals during this experiment include biotite and calcite with  $k_j$  values that deviate by 37% and 57% from mean values. Only the biotite is of significant importance here. In general,  $k_j$  values used in this study had standard deviations between 10% and 25% of  $k_j$ . It is believed that a 10 to 25 percent range of error should be assumed for the weight percentages reported.



CHAPTER V  
SUMMARY AND CONCLUSIONS

A network of high volume air samplers was established around Spruce Pine, N. C. to collect suspended airborne particles for analysis. Samples were collected using wind activated electric switches which allowed sampling only from certain wind directions. The switches sometimes malfunctioned due to temperature fluctuations and sampling was continued without them.

Analysis of the samples began with determinations of sample masses and ambient particulate loading. Chemical analysis, using X-ray diffraction patterns of the collected samples and a method for correcting intensities to infinite thickness values, was performed. Weight percentages based on the corrected intensities calculated were determined for all identified components in a sample.

Based on mass and chemical analysis several possibilities are suggested. It was inferred from the quantities and compositions of TSP samples from the four sites that the mining industry may be an unlikely suspect for apportionment of ambient TSP. Other data imply that a source of selenite, probably located north of Spruce Pine, generates an airborne suspension of selenite which is carried into the Spruce Pine region.

Further work should involve the design and construction of wind directional switches based on a non-mechanical switching apparatus such as photoelectric relays or magnetic reed switches. The accuracy of X-ray diffraction analysis would be greatly improved by using samplers which would pull a large volume of air through a smaller filter, enhancing the sensitivity to less abundant materials. Samplers installed in a grid pattern around the area (as opposed to a perimeter pattern) would allow a much more detailed analysis of factors and sources in the transport of airborne particle suspensions.

## REFERENCES

- (1) "Cleaning Our Environment: A Chemical Perspective", 2nd ed.; American Chemical Society: Washington, D. C., 1978 p. 118.
- (2) Van Horn, E. C. "Position Statement by Mitchell County Environmental Quality Committee", Spruce Pine Economic Development Commission, Spruce Pine, N. C., 1981; p. 1.
- (3) Kolak, Nicholas P.; Visalli, Joseph R. Environmental Science & Technology, 1981, 15, 219-24.
- (4) Liu, Benjamin Y. H.; Raabe, Otto G.; Smith, Wallace B.; Spencer, Herbert W., III; Kuykendal, William B. Environmental Science & Technology, 1980, 14, 392-7.
- (5) Fox, Donald L.; Jeffries, Harvey E. Analytical Chemistry, 1981, 53, 3R-13R.
- (6) Davis, Briant L.; Cho, Nam-Kun. Atmospheric Environment, 1977, 11, 73-85, (Great Britain).
- (7) Davis, William D. Environmental Science & Technology, 1977, 11, 587-92.
- (8) Chung, Frank H. Journal of Applied Crystallography, 1974, 7, 519-31.
- (9) Chung, Frank H. Journal of Applied Crystallography, 1975, 8, 17-19.
- (10) Davis, Briant L. Atmospheric Environment, 1978, 12, 2403-6, (Great Britain).
- (11) Davis, Briant L. Atmospheric Environment, 1980, 14, 217-20, (Great Britain).
- (12) Davis, Briant L.; Johnson, L. Ronald. Atmospheric Environment, 1982, 16, 273-82.
- (13) Davis, Briant L. Atmospheric Environment, 1981, 15, 291-96.
- (14) Davis et al. Journal of Applied Meteorology, 20, 922-33.

- (15) "High Volume Air Sampler". Manual for recommended sampler operation. General Metal Works, Inc.; Cleves, Ohio.
- (16) Local Climatological Data. A monthly summary climatic data. National Oceanic and Atmospheric Administration; National Climatic Center; Asheville, N. C.; 7/81-2/82.
- (17) "Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)", Federal Register, Friday, April 30, 1971.
- (18) "Operations Manual for SPG-2 X-Ray Spectrogoniometer", Direction 11690 E, General Electric Company.
- (19) "Operations Manual for XRD-5", Direction 12129 C, General Electric Company.
- (20) "Operations Manual for SPG-3 Detector", Direction 12727 A, General Electric Company.
- (21) Davis, Briant L., South Dakota School of Mines and Technology, "Component Table", personal communication, 1981.
- (22) Borg, I. Y.; Smith, D. K. "Calculated X-Ray Powder Patterns for Silicate Minerals"; memoir 122; The Geological Society of America, Inc.: Boulder, Colorado, 1969.
- (23) "Powder Diffraction File - Inorganic", Joint Committee on Powder Diffraction Standards: Swarthmore, Pennsylvania.
- (24) Davis, Briant L. "Practical Suggestions of Measurement of Various Parameters Required for Reference Intensity Analysis", personal communication.

APPENDIX A  
Calibration Curves for High Volume  
Air Samplers



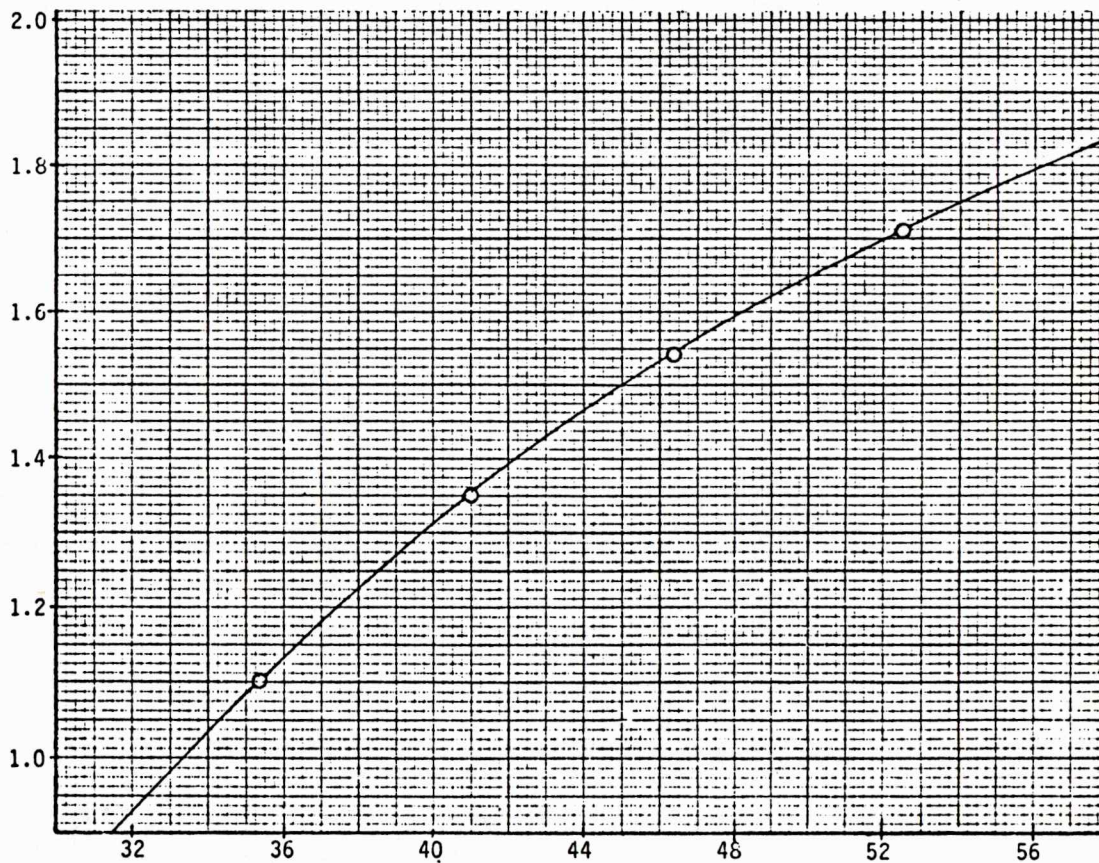
Hi-Vol serial number 12366 Located at Site # 1

Calibration date 10/10/81 Orifice Number 10651

Temperature 22.0°C Barometric Pressure 686mm

Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>18</u>	<u>10.23</u>	<u>52.5</u>	<u>1.71</u>
<u>13</u>	<u>8.28</u>	<u>46.3</u>	<u>1.54</u>
<u>10</u>	<u>6.42</u>	<u>41.0</u>	<u>1.35</u>
<u>7</u>	<u>4.29</u>	<u>35.3</u>	<u>1.10</u>
<u>5</u>	<u>2.60</u>	<u>29.0</u>	<u>&lt; 0.9</u>

TRUE FLOW RATE VS. ROTAMETER READING



Calibration curve for Filter 1A

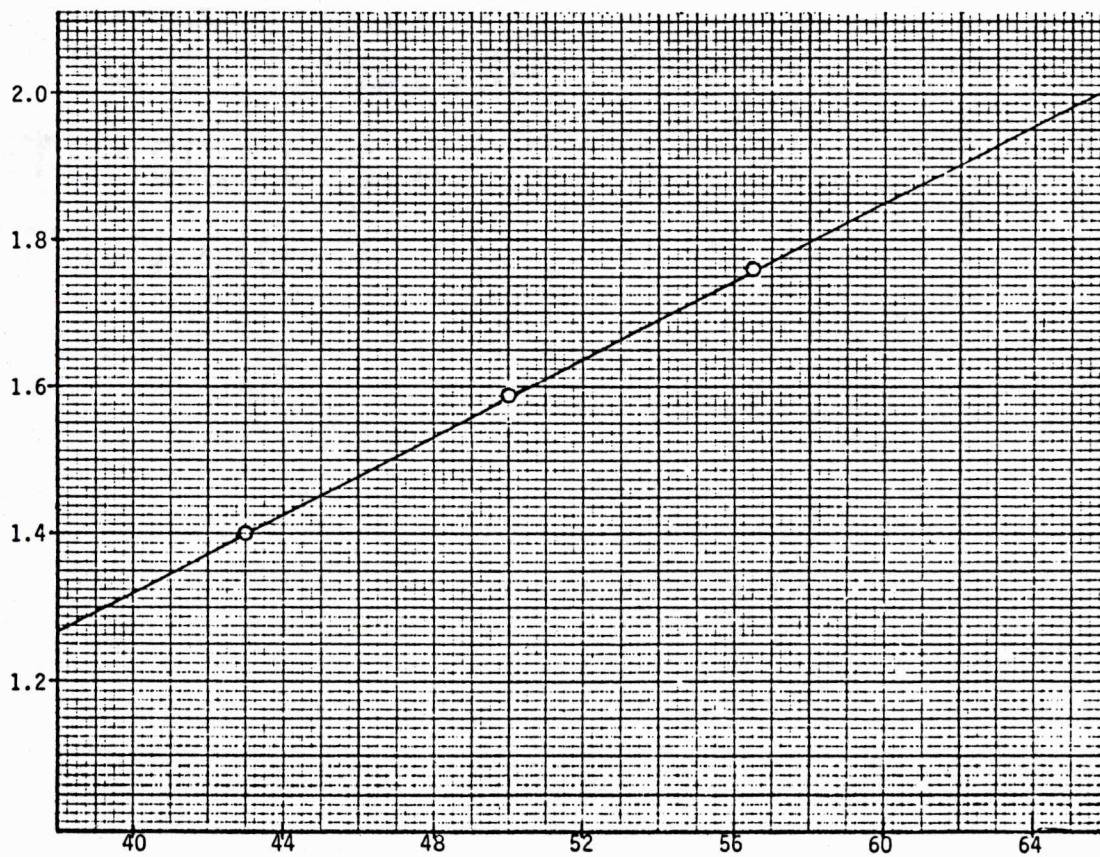
Hi-Vol serial number 12369 Located at Site # 2

Calibration date 10/10/81 Orifice Number 10651

Temperature 22.0°C Barometric Pressure 686mm

Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>18</u>	<u>10.86</u>	<u>56.5</u>	<u>1.76</u>
<u>13</u>	<u>8.85</u>	<u>50.0</u>	<u>1.59</u>
<u>10</u>	<u>6.85</u>	<u>43.0</u>	<u>1.40</u>
<u>7</u>	<u>4.92</u>	<u>35.5</u>	<u>1.18</u>
<u>5</u>	<u>2.81</u>	<u>31.0</u>	<u>&lt;0.9</u>

TRUE FLOW RATE VS. ROTAMETER READING



Calibration curve for Filter 2A

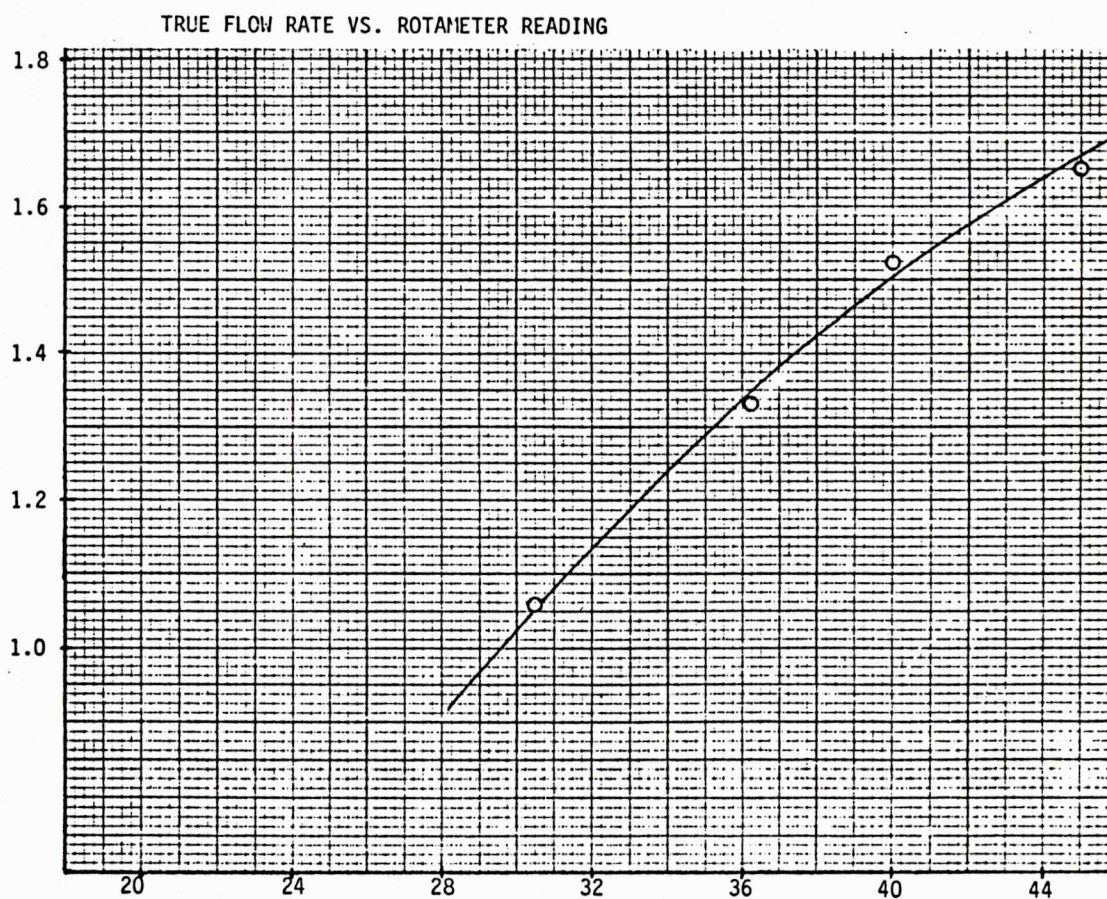


Hi-Vol serial number 12368 Located at Site # 3

Calibration date 10 / 10 / 81 Orifice Number 10651

Temperature 22.0°C Barometric Pressure 686mm

Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>18</u>	<u>9.52</u>	<u>45.0</u>	<u>1.65</u>
<u>13</u>	<u>8.04</u>	<u>40.0</u>	<u>1.52</u>
<u>10</u>	<u>6.26</u>	<u>36.2</u>	<u>1.33</u>
<u>7</u>	<u>4.00</u>	<u>30.5</u>	<u>1.06</u>
<u>5</u>	<u>2.52</u>	<u>25.9</u>	<u>&lt; 0.9</u>



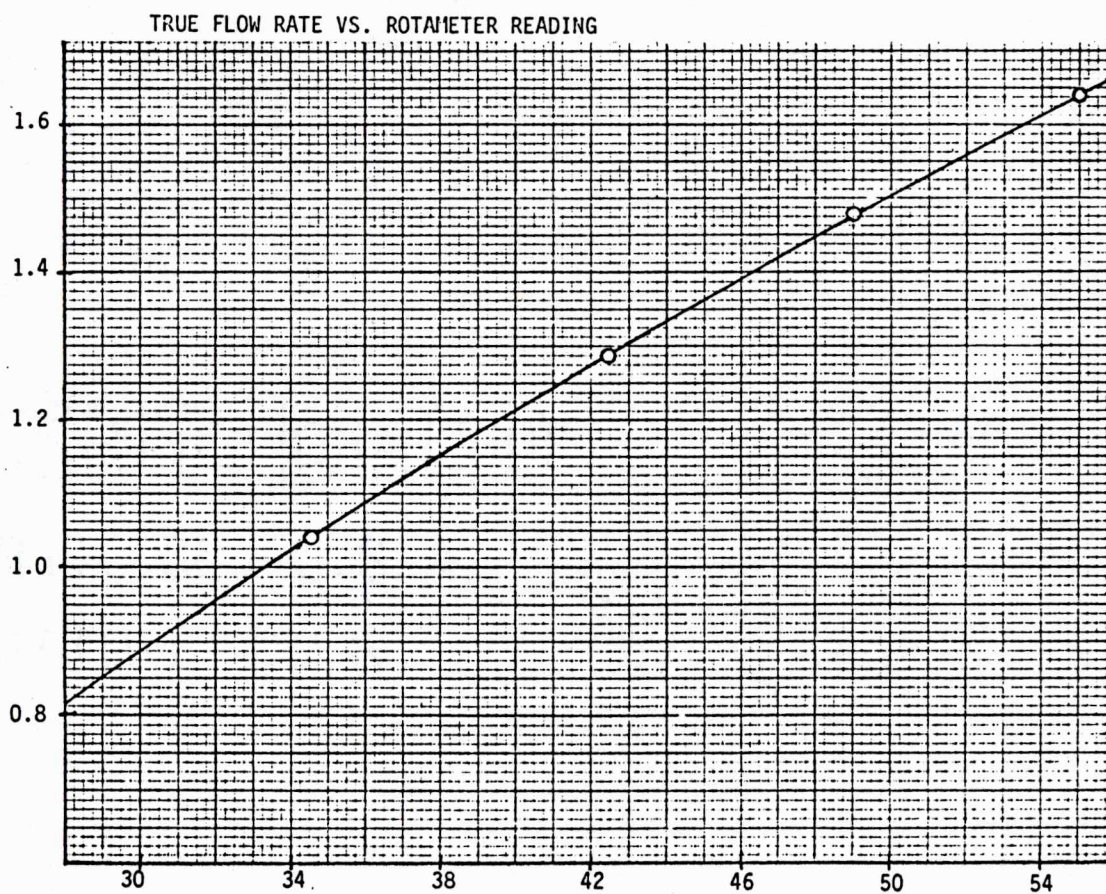
Calibration curve for Filter 3A

Hi-Vol serial number 12370 Located at Site # 4

Calibration date 10 / 10 / 81 Orifice Number 10651

Temperature 22.0°C Barometric Pressure 686mm

Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>18</u>	<u>9.42</u>	<u>55.0</u>	<u>1.64</u>
<u>13</u>	<u>7.59</u>	<u>49.0</u>	<u>1.48</u>
<u>10</u>	<u>5.89</u>	<u>42.5</u>	<u>1.29</u>
<u>7</u>	<u>3.80</u>	<u>34.6</u>	<u>1.04</u>
<u>5</u>	<u>2.38</u>	<u>28.0</u>	<u>&lt; 0.9</u>

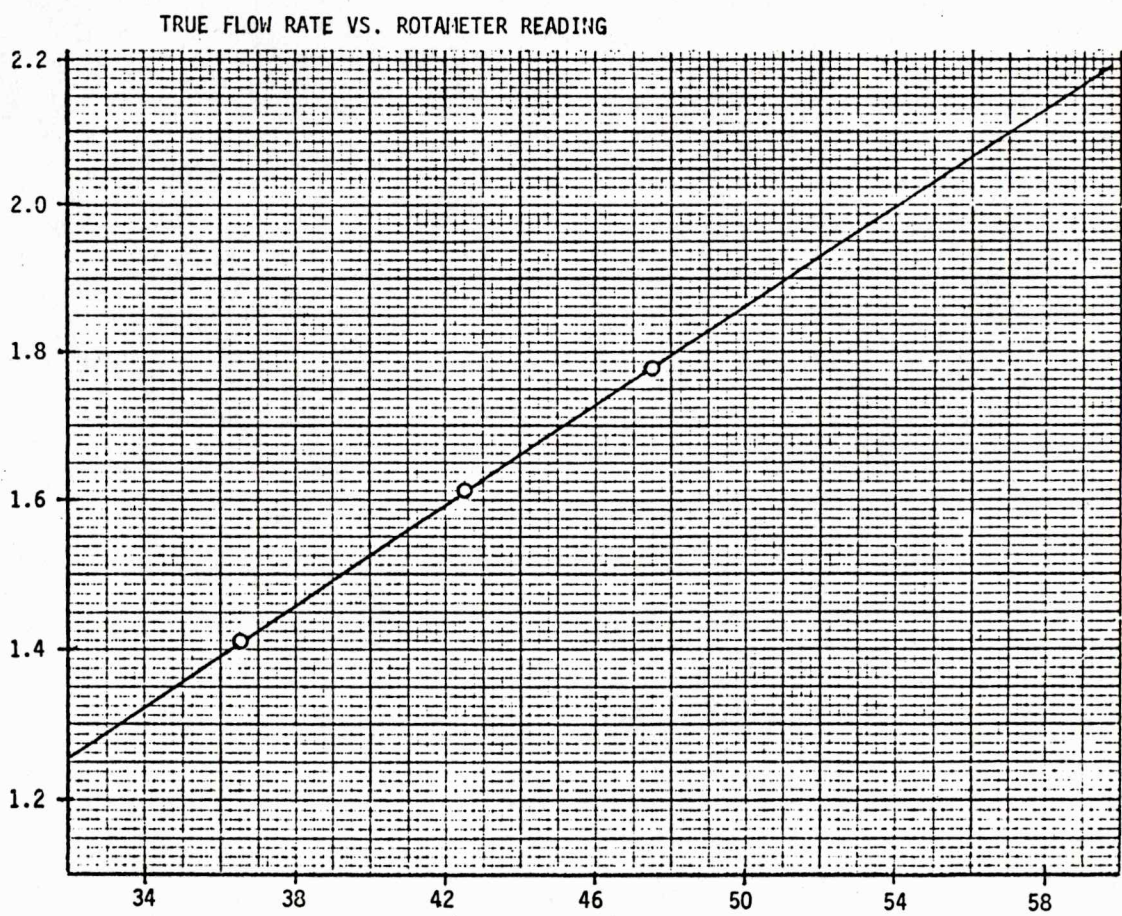


Calibration curve for Filter 4A



Hi-Vol serial number 12366 Located at Site # 1  
 Calibration date 12/ 7 / 81 Orifice Number 10651  
 Temperature 7.2°C Barometric Pressure 704mm

Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>18</u>	<u>11.95</u>	<u>47.5</u>	<u>1.78</u>
<u>13</u>	<u>9.75</u>	<u>42.5</u>	<u>1.61</u>
<u>10</u>	<u>7.45</u>	<u>36.5</u>	<u>1.41</u>
<u>    </u>	<u>    </u>	<u>    </u>	<u>    </u>
<u>    </u>	<u>    </u>	<u>    </u>	<u>    </u>



Calibration curve for Filters 1A - 1H

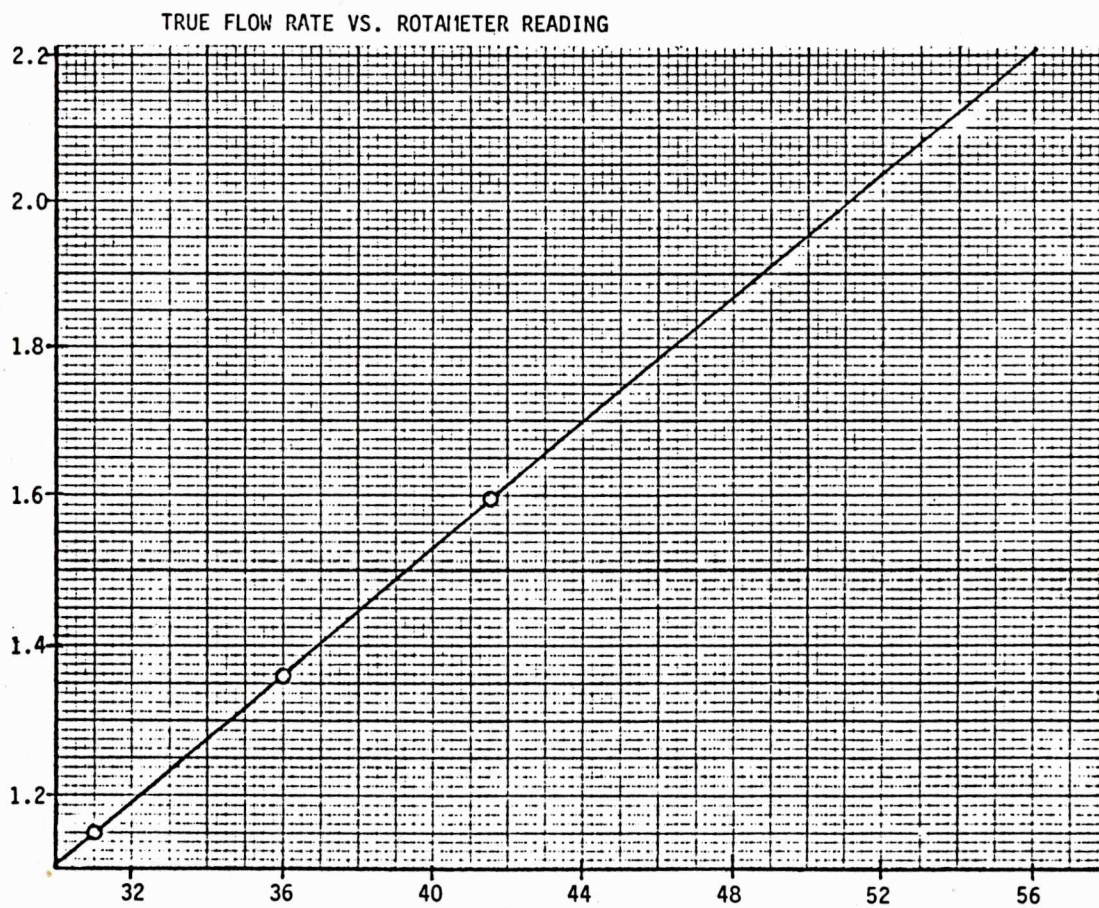


Hi-Vol serial number 12369 Located at Site # 2

Calibration date 12/ 7 / 81 Orifice Number 10651

Temperature 7.2°C Barometric Pressure 704mm

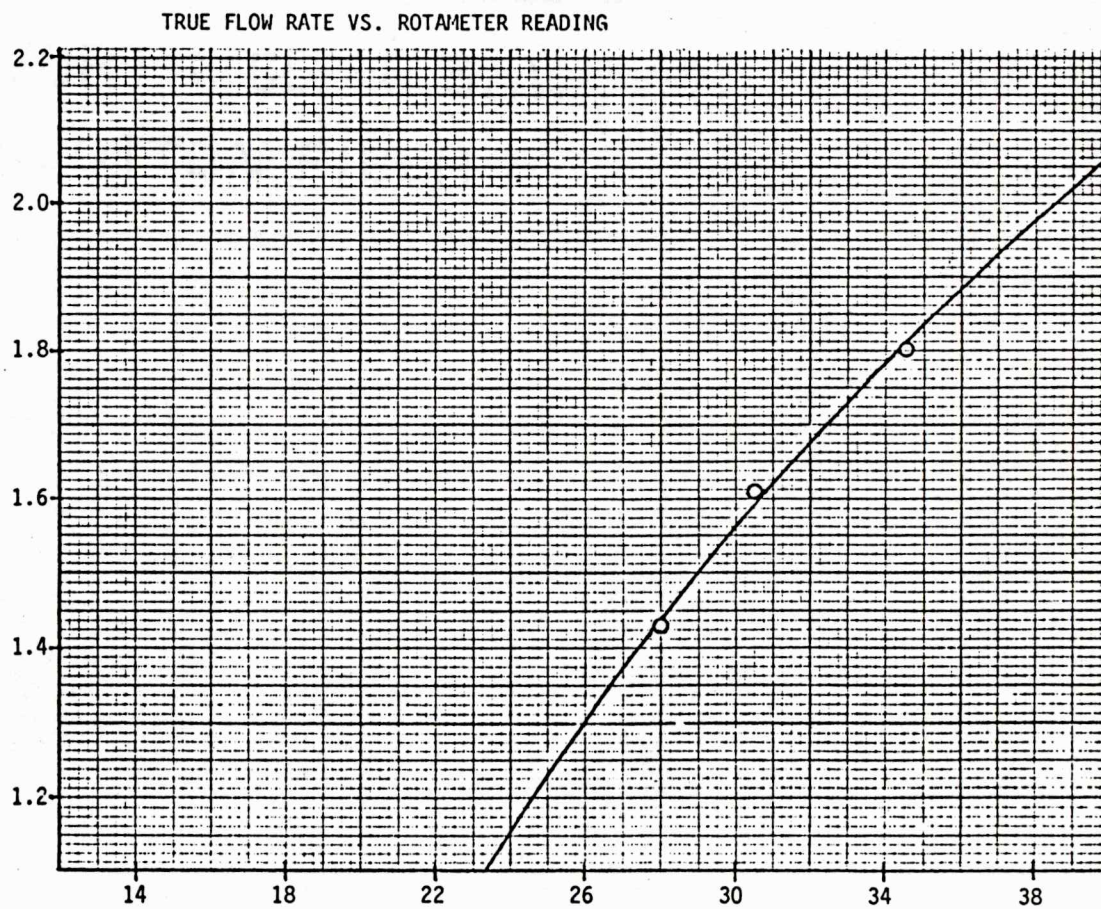
Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>18</u>	<u>9.55</u>	<u>41.5</u>	<u>1.59</u>
<u>13</u>	<u>6.95</u>	<u>36.0</u>	<u>1.36</u>
<u>10</u>	<u>5.05</u>	<u>31.0</u>	<u>1.15</u>
<u>    </u>	<u>    </u>	<u>    </u>	<u>    </u>
<u>    </u>	<u>    </u>	<u>    </u>	<u>    </u>



Calibration curve for Filters 2A - 2H

Hi-Vol serial number 12368 Located at Site # 3  
 Calibration date 12 / 7 / 81 Orifice Number 10651  
 Temperature 7.2°C Barometric Pressure 704mm

Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>18</u>	<u>12.35</u>	<u>34.5</u>	<u>1.80</u>
<u>13</u>	<u>9.85</u>	<u>30.5</u>	<u>1.61</u>
<u>10</u>	<u>7.65</u>	<u>28.0</u>	<u>1.43</u>
<u>      </u>	<u>      </u>	<u>      </u>	<u>      </u>
<u>      </u>	<u>      </u>	<u>      </u>	<u>      </u>



Calibration curve for Filters 3A - 3H



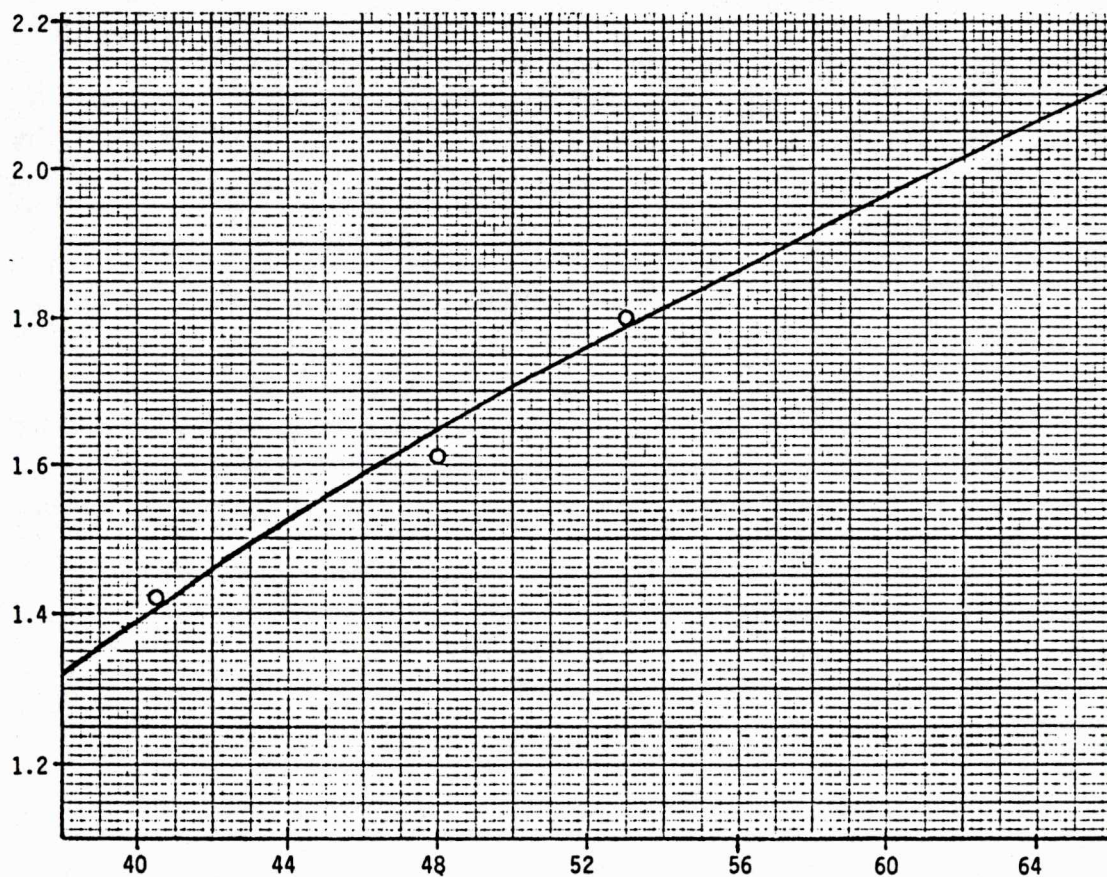
Hi-Vol serial number 12370 Located at Site # 4

Calibration date 12 / 7 / 81 Orifice Number 10651

Temperature 7.2°C Barometric Pressure 704mm

Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>18</u>	<u>12.30</u>	<u>53.0</u>	<u>1.80</u>
<u>13</u>	<u>9.80</u>	<u>48.0</u>	<u>1.61</u>
<u>10</u>	<u>7.60</u>	<u>40.5</u>	<u>1.42</u>
<u>    </u>	<u>    </u>	<u>    </u>	<u>    </u>
<u>    </u>	<u>    </u>	<u>    </u>	<u>    </u>

TRUE FLOW RATE VS. ROTAMETER READING



Calibration curve for Filters 4A - 4H

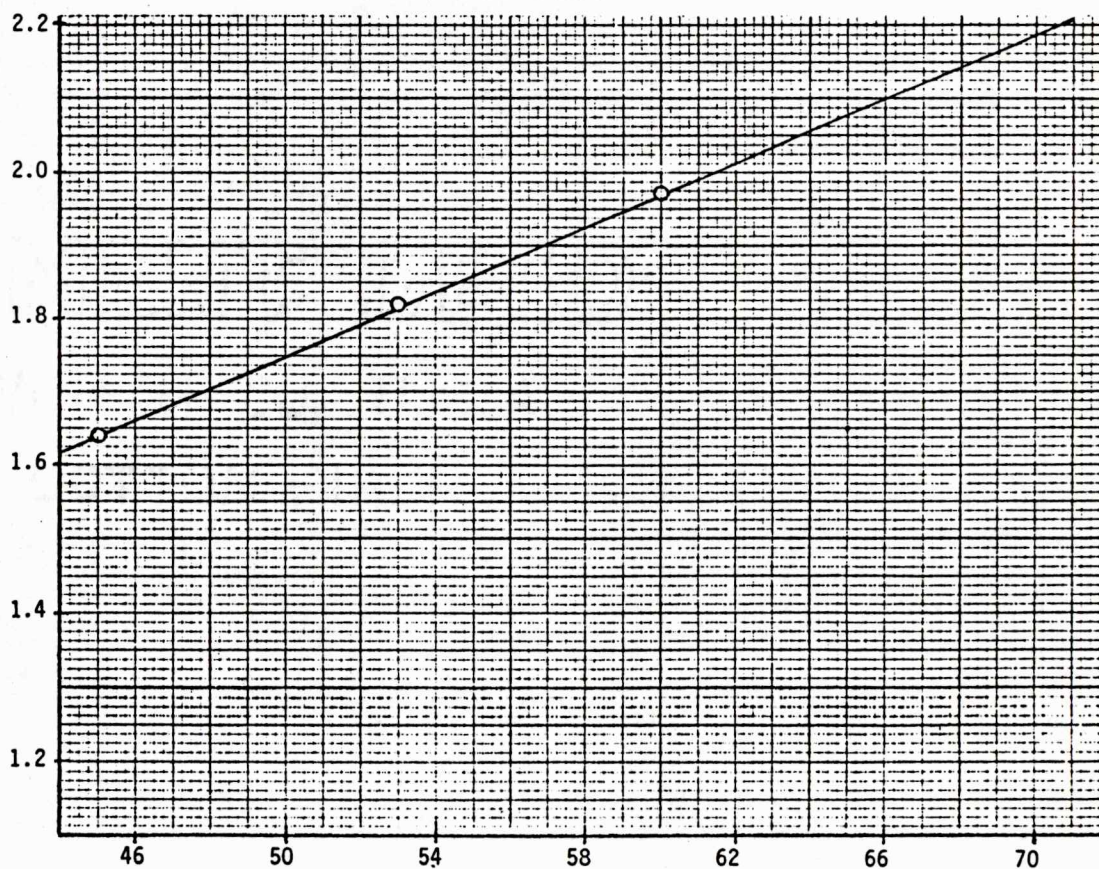
Hi-Vol serial number 12366 Located at Site # 1

Calibration date 2 / 3 / 82 Orifice Number 10651

Temperature 23.0°C Barometric Pressure 679mm

Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>26</u>	<u>13.43</u>	<u>60.0</u>	<u>1.97</u>
<u>18</u>	<u>11.45</u>	<u>53.0</u>	<u>1.82</u>
<u>13</u>	<u>9.35</u>	<u>45.0</u>	<u>1.64</u>
<u>10</u>	<u>6.80</u>	<u>38.5</u>	<u>1.40</u>
<u>7</u>	<u>4.32</u>	<u>30.5</u>	<u>1.11</u>

TRUE FLOW RATE VS. ROTAMETER READING



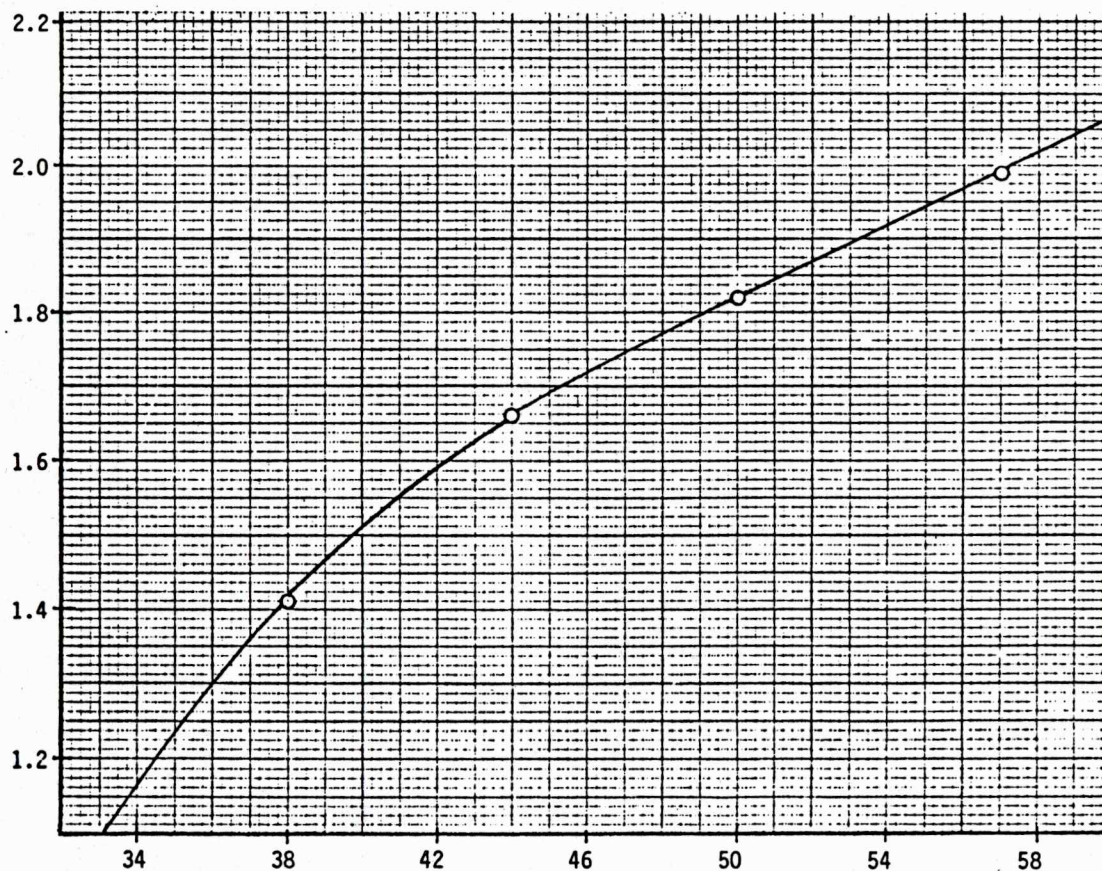
Calibration curve for Filters 1I - 1M



Hi-Vol serial number 12369 Located at Site # 2  
 Calibration date 2 / 3 / 82 Orifice Number 10651  
 Temperature 23.0°C Barometric Pressure 679mm

Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>26</u>	<u>13.70</u>	<u>57.0</u>	<u>1.99</u>
<u>18</u>	<u>11.50</u>	<u>50.0</u>	<u>1.82</u>
<u>13</u>	<u>9.55</u>	<u>44.0</u>	<u>1.66</u>
<u>10</u>	<u>6.94</u>	<u>38.0</u>	<u>1.41</u>
<u>7</u>	<u>4.44</u>	<u>30.0</u>	<u>1.13</u>

TRUE FLOW RATE VS. ROTAMETER READING



Calibration curve for Filters 2I - 2M



Hi-Vol serial number 12364 \*\* Located at Site # 3

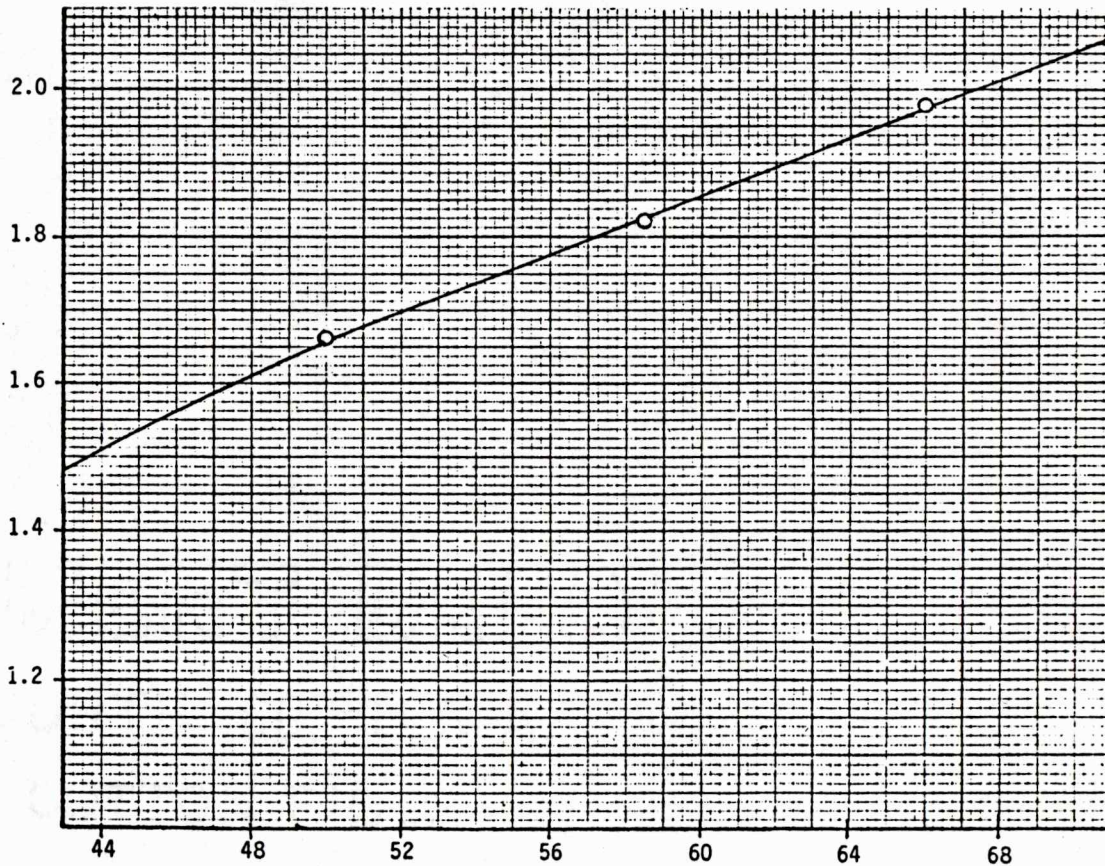
Calibration date 2 / 3 / 82 Orifice Number 10651

Temperature 23.0°C Barometric Pressure 679mm

\*\*This was a new sampler for this location

Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>26</u>	<u>13.65</u>	<u>66.0</u>	<u>1.98</u>
<u>18</u>	<u>11.50</u>	<u>58.5</u>	<u>1.82</u>
<u>13</u>	<u>9.47</u>	<u>50.0</u>	<u>1.66</u>
<u>10</u>	<u>7.02</u>	<u>42.0</u>	<u>1.43</u>
<u>7</u>	<u>4.46</u>	<u>34.5</u>	<u>1.13</u>

TRUE FLOW RATE VS. ROTAMETER READING



Calibration curve for Filters 3I - 3M

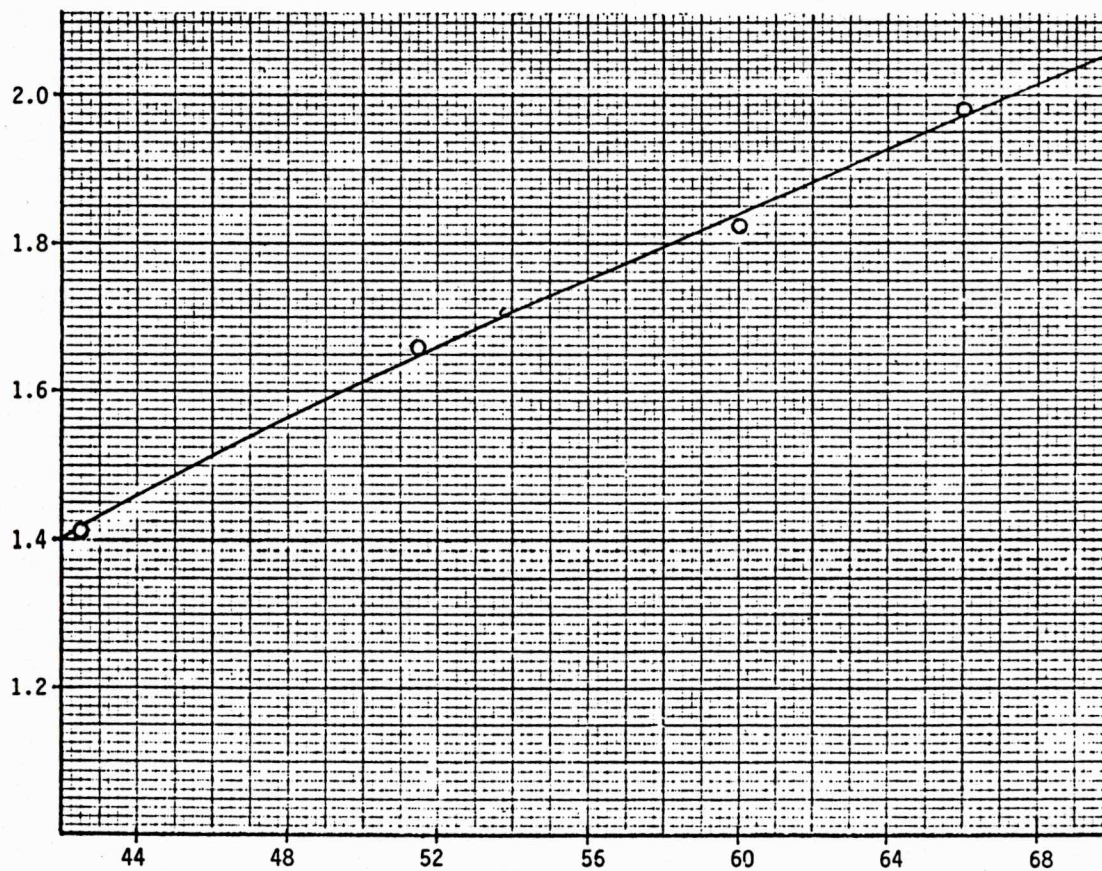
Hi-Vol serial number 12370 Located at Site # 4

Calibration date 2 / 3 / 82 Orifice Number 10651

Temperature 23.0°C Barometric Pressure 679mm

Orifice Plate	Manometer Inches of H <sub>2</sub> O	Flow Meter (ft <sup>3</sup> /min)	Actual Flow (m <sup>3</sup> /min)
<u>26</u>	<u>13.50</u>	<u>66.0</u>	<u>1.98</u>
<u>18</u>	<u>11.45</u>	<u>60.0</u>	<u>1.82</u>
<u>13</u>	<u>9.50</u>	<u>51.5</u>	<u>1.66</u>
<u>10</u>	<u>6.95</u>	<u>42.5</u>	<u>1.41</u>
<u>7</u>	<u>4.43</u>	<u>32.0</u>	<u>1.13</u>

TRUE FLOW RATE VS. ROTAMETER READING



Calibration curve for Filters 4I - 4M

## APPENDIX B

Computer Listing of Program to Calculate  
Weight Percent



```

10 PRINT"THIS PROGRAM WILL CALCULATE THE COR-
20 PRINT"RECTED INTENSITIES FOR THIN FILM DIF-
30 PRINT"FRACTION PEAKS"
35 GOSUB 4000
40 CLR:PRINT"WHAT IS THE FILTER ID NUMBER";
42 INPUTNU#
45 PRINT"SHOW MANY COMPONENTS";
50 INPUT N
60 PRINT"MASS OF FILTER";:INPUT M1
70 PRINT"MASS OF FILTER + SAMPLE";:INPUT M2
80 M3=M2-M1:REM** M3=SAMPLE MASS
90 M4=M3/410:REM**M4=SAMPLE MASS/AREA
100 PRINT"UM=SAMPLE MASS/UNIT AREA"
110 PRINT"U=";M4;"G/CM^2"
120 UF=39.34
125 REM***MAC FOR FILTER
130 TG=2.6E-4
140 REM***DEPTH OF PENETRATION
150 R=2.42
160 REM***DENSITY OF FILTER MATERIAL
170 WH=1/(1+TG*R/M4)
180 REM***WH=SAMPLE FRACTION IN HYBRID
185 PRINT"WBH=SAMPLE FRACTION IN HYBRID"
190 PRINT"   =" ;WH
205 GOSUB 5000
210 DIM DA(N,8),NA$(N,3)
220 PRINT"PLEASE ENTER DATA REQUESTED"
230 FOR I=1 TO N
240 PRINT"NAME OF COMPONENT";I;:INPUT NA$(I,1)
245 NA$(I,1)=LEFT$(NA$(I,1),9)
250 PRINT"2 THETA OF PEAK";I;:INPUT DA(I,1)
260 PRINT"MU STAR OF COMPONENT";I;:INPUT DA(I,2)
270 PRINT"RAW INTENSITY OF PEAK";I;:INPUT DA(I,3)
273 DA(I,6)=DA(I,3)
275 PRINT" "
280 NEXT I
290 GOSUB 4500
300 PRINT"PLEASE CHECK THE DATA"
310 PRINT"COMPONENT","2-THETA","MU*","INTENSITY"
315 PRINT"-----","-----","-----","-----"
320 FOR I=1 TO N
330 PRINT" ";NA$(I,1),DA(I,1),DA(I,2),DA(I,3)
340 NEXT I
350 PRINT"IS A CORRECTION NEEDED?"
360 GET Q$
370 IF Q$="" THEN GOTO 360
380 IF Q$<>"Y" THEN GOTO 400
390 GOTO 220

```

```

400 REM*** DA1=2-THETA
405 REM*** DA2=MU STAR OF COMPONENT
410 REM*** DA3=RAW INTENSITY
415 REM*** DA4=KI
420 REM*** DA5=PROVISIONAL WT%
425 REM*** NA$=NAME
440 PRINT"NOW ENTER KI VALUES"
450 FOR I=1 TO N
460 PRINT" ";NA$(I,1);:INPUT DA(I,4)
470 NEXT I
480 GOSUB 6500
490 UH=WH*UB+(1-WH)*UF
500 Q=Q+1
510 GOSUB 6000
520 ON (P+1) GOTO 523,523,527
523 GOSUB 5000
527 GOSUB 6500
530 P=P+1
540 ON P GOTO 490,490,550
550 PRINT"IS THE AGREEMENT GOOD ENOUGH?"
560 GET A$
570 IF A$="" GOTO 560
580 IF A$="Y" GOTO 600
590 P=0:GOTO 490
600 PRINT"THE FINAL WEIGHT FRACTIONS ARE:"
605 GOSUB 6100
610 PRINT"....."
615 PRINT"WOULD YOU LIKE A HARD COPY  ",",",
616 PRINT"OF THIS TABLE?"
620 GET A$
630 IF A$="" GOTO 620
640 IF A$<>"N" GOTO 8000
650 PRINT"DO YOU WISH TO RUN THE PROGRAM AGAIN?"
660 GET A$
670 IF A$="" GOTO 660
680 IF A$<>"N" GOTO 040
690 END
4000 FOR L=1 TO 2000
4010 NEXT L
4020 RETURN
4500 FOR L=1 TO 500
4510 NEXT L
4520 PRINT" "
4530 RETURN
5000 PRINT"PRESS RETURN TO CONTINUE"
5010 GET Q$
5020 IF Q$="" GOTO 5010
5030 RETURN

```



```

5500 FOR I=1 TO N
5510 DA(I,8)=π/360*DA(I,1)
5520 NEXT I
5530 RETURN
6000 FOR I=1 TO N
6010 DA(I,8)=π/360*DA(I,1)
6020 NEXT I
6040 FOR I=1 TO N
6045 A=(-2*UH*M4)/(WH*SIN(DA(I,8)))
6050 A=EXP(A)
6055 A=1-A
6060 A=WH*UB*A
6065 A=1/A
6070 DA(I,6)=DA(I,3)*UH*A
6080 NEXT I
6090 PRINT"COMPUTATION #";Q;" "
6100 PRINT"UB=";UB
6110 PRINT"COMPONENT","WEIGHT %","INTENSITY"
6115 PRINT"-----"
6120 FOR I=1 TO N
6130 NA$(I,2)=STR$(DA(I,5)*100)
6140 NA$(I,3)=LEFT$(STR$(DA(I,6)),7)
6150 FOR J=1 TO 3
6160 PRINT NA$(I,J),
6170 NEXT J
6180 NEXT I
6190 RETURN
6500 SU=0
6510 FOR I=1 TO N
6520 SU=SU+DA(I,6)/DA(I,4)
6530 NEXT I
6540 FOR I=1 TO N
6550 DA(I,5)=1/((DA(I,4)/DA(I,6))*SU)
6560 NEXT I
6570 UB=0
6580 FOR I=1 TO N
6590 UB=UB+DA(I,2)*DA(I,5)
6600 NEXT I
6610 RETURN
8000 OPEN 2,4
8010 M$=LEFT$(STR$(M4*1000000),5)
8030 PRINT#2,"FILTER #";NU$;" "
8035 PRINT#2," "
8040 PRINT#2,"UB=";UB,"MASS/AREA=";M$;"UGO/CMO12"
8050 PRINT#2,"THE FINAL WEIGHT PERCENTS ARE:"
8060 PRINT#2,"COMPONENT","WEIGHT %","INTENSITY"
8070 PRINT#2,"-----"
8080 CLOSE2,4

```

```
8090 OPEN 1,4,2:OPEN2,4,1:OPEN5,4
8100 PRINT#1,"AAAAAAAAAAAAA      AAAAA
8110 FOR I=1 TO N
8120 PRINT#2,NA$(I,1)CHR$(29)NA$(I,2)CHR$(29)NA$(I,3)
8130 NEXT I
8140 PRINT#5,"_____ "
8150 CLOSE2,4:CLOSE1,4:CLOSE5,4
8160 GOTO 650
READY.
```

## VITA

Steven Jay Breiner was born in Atlanta, Georgia, on August 11, 1953. After attending a bilingual grammar school in that city, he attended Cross Keys High School. During his senior year he attended courses at the Georgia Institute of Technology for high school and college credit leading to a graduation in June, 1970. He later attended Antioch College in Yellow Springs, Ohio for three years, including nine months of service as a crisis intervention counselor in Boston, Massachusetts. After a several year interval during which he worked and traveled, Mr. Breiner entered Appalachian State University in January, 1977 and received a Bachelor of Science degree in Chemistry in August, 1979 and a Master of Science degree in Chemistry in August, 1982.