APPENDIX 3A: Description of Sample Collection and Analysis

3A.1 IMPROVE Sampler

General Description

The IMPROVE Sampler is a cyclone-based modular unit designed for the NPS/IMPROVE particulate monitoring networks.[1] The units were used in the WHITEX study prior to their deployment in these networks.

The IMPROVE samplers in the WHITEX study consisted of a series of nearly identical filter modules. A typical module is shown in Figure 3A.1. The air enters via an inlet designed to eliminate rain, bugs and particles larger than around 20 μm. The air then passes through a 1 meter aluminum tube into a cyclone. This tube differed for the two nitrate modules, as discussed below. The cyclone is designed to provide a 50% collection efficiency for particles of 2.5 μm. The airstream passes through one of the filters, determined by which solenoid is open. The air finally passes through a critical orifice between the filter and pump. Note that each module has its own inlet, cyclone and critical orifice.

Denuder

Different inlets were used in the two nitrate modules at Canyonlands, Hopi Point, Bullfrog, and Page. In the denuder module E, the air passed through 5 parallel aluminum tubes inserted inside the main tube. In the nondenuder module D, the aluminum stack was completely removed, so that the only denuding would be due to contact with the aluminum cyclone.

The surface area of the denuder was 0.25 m^2. The IMPROVE sampler now uses a slightly more efficient design with four concentric aluminum tubes coated with K_2CO_3 and a surface area of 0.3 m^2. The efficiency of the current design in removing nitrate gases is estimated to be greater than 99.9%. A comparison between the WHITEX and IMPROVE configurations was made in July 1987 during the Southern California Air Quality Study (SCAQS). Figure 3A.2 indicates that the WHITEX and IMPROVE configurations give equivalent results. A second test, conducted at Davis in July 1988, indicated that the bare inlet pipe is a fairly efficient denuder even without adding the parallel or concentric tube inserts. In this test, the bare tube gave 5% higher nitrate values than the IMPROVE denuder.

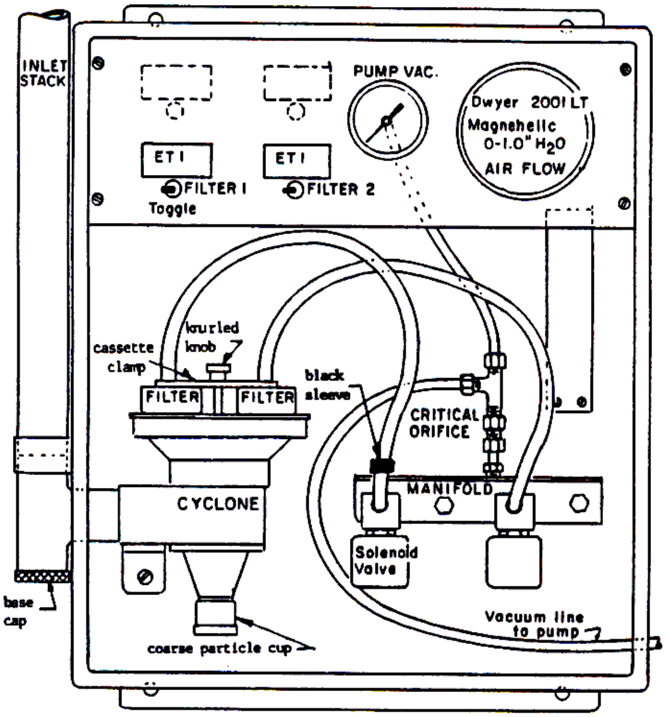

Figure 3A.1: Layout of IMPROVE filter module.

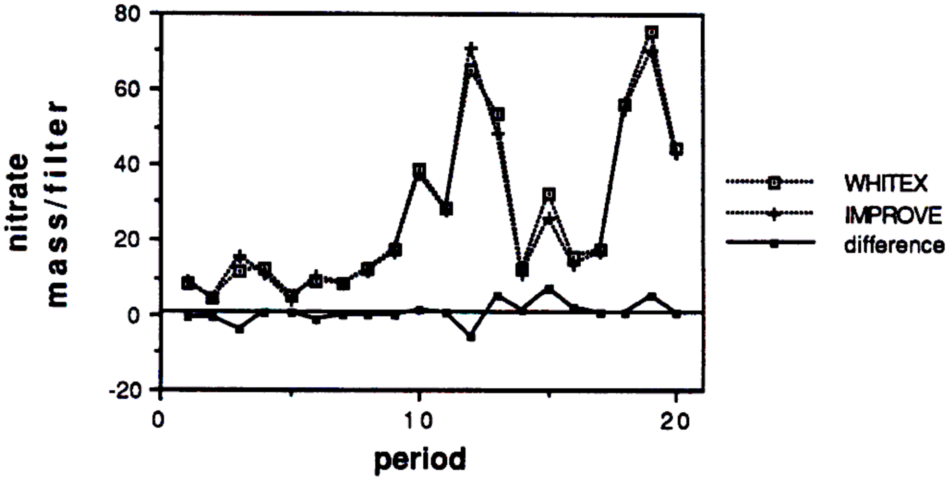

Figure 3A.2: Comparison of nitrate mass at SCAQS for denuders of WHITEX and IMPROVE configurations.

Cyclone

The cyclone follows the AIHL design of John and Reischl.[2] The AIHL design provides a 50% collection efficiency for 2.5 μm particles with a flow rate of 21.7 l/min. This was chosen as the desired nominal flow rate for the WHITEX study. Preliminary tests show that the IMPROVE cyclone does not precisely follow the characteristics of the AIHL design, because of the wide manifold following the cyclone, required to accommodate multiple filters. As shown in Figure 3A.3, the 50% efficiency for 2.5 μm particles requires a flow rate of 22.8 l/min. The 21.7 l/min flow rate gives a 50% efficiency for 2.8 μm particles. The average flow rate during WHITEX of 20.9 l/min corresponds to a 50% efficiency for 3.1 μm particles. The average flow rates for the six modules at Canyonlands, Hopi Point, Bullfrog, and Page are shown in Table 3A.1.

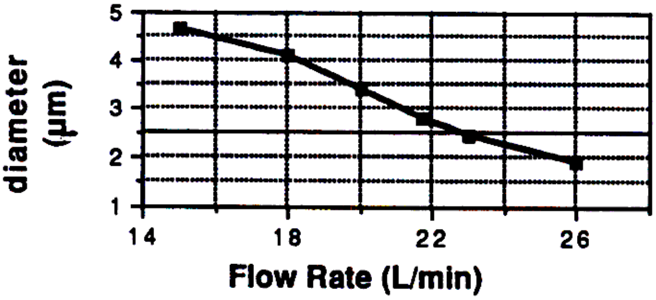

Figure 3A.3: Diameter of 50% capture efficiency versus flow rate for IMPROVE cyclone.

Table 3A.1: Average flow rates, in l/min.

Site	Module A	Module B	Module C	Module D	Module E	Module F
Canyonlands	20.7±0.5	21.4±2.5	21.2±1.1	21.0±0.9	20.6±0.8	21.3±0.8
Hopi Point	20.9±0.7	19.7±3.7	20.7±0.3	22.1±2.7	22.8±2.6	20.5±0.9
Bullfrog	20.4±0.7	21.6±2.3	20.6±0.6	20.3±0.8	20.8±1.0	20.5±1.0
Page	21.8±0.9	19.8±1.3	21.4±0.8	20.2±1.0	20.8±0.7	20.4±0.8

Flow Control

Flow control is provided by a critical orifice located between the filter and the pump. The equation for the flow rate is given by

$$Q = Q_o \left(1 - \frac{\Delta P}{P}\right) \left(\frac{T}{T_o}\right)^{\frac{1}{2}},$$

where ΔP is the pressure drop across the filter, P is atmospheric pressure (assumed to be constant for a given site), T is the absolute temperature at the orifice, and Q_o is the flow rate with no filter at temperature T_o. The constant Q_o depends on the geometry of the orifice, primarily the diameter.

For a given orifice the flow rate will depend on the pressure drop across the filter and on the temperature. The temperature variation is generally small over a short duration study, such as

WHITEX. For example, a 1% increase in flow rate requires a temperature increase of 6°C. The major cause of flow rate variation is the pressure drop across the filter, due to variations between clean filters or to filter loading during collection. Filter loading was never a problem during WHITEX. The variation in flow rate due to pressure drop across clean filters was significant for module B, with Teflon followed by impregnated Whatman, and to a smaller degree for the nylon modules D and E. For the Teflon and nylon modules (A, F, C) the variation in flow rate was around 3%, for the nylon modules it was 8%, for the Teflon impregnated Whatman it was 13%. This variation in flow rate will change the outpoint, but has no effect on the uncertainties in the flow rate and volume.

Flow Rate Measurement

The flow rate was determined before and after collection by measuring the pressure drop across the cyclone and inlet using a magnehelic gauge. This internal orifice-meter system is similar to those used to calibrate and audit most samplers. The precision and accuracy of the internal system are comparable to those of typical audit devices and considerably better than those of the traditional rotameter. Each internal system was calibrated using an external orifice-meter system that had been in turn calibrated at Davis using a spirometer and corrected for temperature and elevation. In the calibration procedure, the pressure drop across the filter is varied using a special valve system, and the magnehelic gauge and orifice meter are both measured. A calibration curve for the internal system is determined of the form

$$Q = a(\Delta P)^b.$$

In general, b is around 0.45 and a is around 30. This equation is independent of the critical orifice, so that changing the critical orifice will change the normal flow rate, but not this calibrating equation. At a different absolute temperature T the flow rate is

$$Q = a(\Delta P)^b \left(\frac{T}{T_c}\right)^{\frac{1}{2}},$$

where T_c is the temperature at calibration.

The volume is calculated from the average flow rate over the duration of the sample. If ΔP_1 and ΔP_2 are the readings before and after collection, the average flow rate is

$$Q_{avg} = \frac{a}{2}\left[(\Delta P_1)^b + (\Delta P_2)^b\right]\left(\frac{T_{avg}}{T_c}\right)^{\frac{1}{2}},$$

where T_{avg} is the average temperature over the duration of the collection. The average temperature for each sample was determined from the meteorological measurements made at the site.

Sample Handling

The filters were stored in Petri dishes until loaded into cassettes and again stored in Petri dishes after unloading. The filters remained in cassettes for around 24 hours at the primary sites and around 72 hours at the secondary sites. The Petri dishes for the quartz and impregnated Whatman filters were kept refrigerated.

Sample changing involved reading the magnehelic and elapsed timers for the exposed filters, removing the exposed cassettes, inserting the clean cassettes and reading the magnehelic. At the primary sites, all the filters were changed at 8 am. The 6-hour filters were also changed at 8 pm. At the secondary sites, the filters were changed every other day.

Gravimetric Analysis (Mass)

The mass concentration of the fine particles on Teflon filters was determined for modules A and F at the primary sites and for all samples at the secondary and tertiary sites.[3] The mass of coarse particles on the SFU Nuclepore filter was also measured. The analysis involved weighing the clean filters at Davis before loading into the Petri dishes and then weighing the exposed filters after the Petri dishes returned to Davis. All analyses were performed on a Cahn 25 electromicrobalance.

Because of the low ambient concentrations during WHITEX, the material collected by the IMPROVE sampler was generally small. The mass of the average 12-hour filters ranged from 25 μg at Hopi Point to 60 μg at Page. The 6-hour filters had one-half as much material. The small amount of material made gravimetric analysis especially difficult. Masking the area of deposit on the filter benefited PIXE, but not gravimetric analysis. Table 3A.2 compares the A and F samples to those for the standard IMPROVE, the stacked filter units (used at national parks through 6/86), and the SCISAS. The SCISAS sampler has approximately 5 times the flow rate of the IMPROVE. The table gives the mass of material on the filter for an ambient concentration of 3 $\mu g/m^3$, typical for the primary sites in WHITEX.

Table 3A.2: Air volumes and typical masses for various samplers.

Sampler		Volume (m^3)	Mass in μg giving 3 $\mu g/m^3$
WHITEX–A	(6h)	7.5	23
WHITEX–F	(12h)	15	45
IMPROVE	(24h)	33	100
SFU	(72h)	43	130
SCISAS	(12h)	81	244
SCISAS	(24h)	163	488

PIXE Analysis (Elements Na to Pb)

Particle Induced X-ray Emission (PIXE) measured the concentrations of elements from Na to Pb on IMPROVE filters A, F, and X, on the SFU fine filters, and on the DRUM strips and afterfilters.[3] A 4.5 MeV proton beam induced atoms to emit characteristic x-rays, which were collected by an energy-dispersive $Si(Li)$ detector system. By counting the x-rays at the characteristic energy, the concentration of each element was determined. The system was calibrated using a series of 60 elemental standards.

One of the features of PIXE is its ability to analyze deposit areas smaller than 2 cm^2. By concentrating the particles with a mask behind the filter it is possible to reduce the minimum detectable limits of trace elements in ng/m^3. The reduction in area is limited by the pressure drop across the filter during collection. The 6-hour A and the 12-hour X filters were masked to an area of 1.1 cm^2, while the 12-hour F filters were masked to 0.7 cm^2. This latter area is the smallest permitted by the IMPROVE system for operation at 22 l/min.

In order to maximize the sensitivity for both light and heavy elements, the UCD PIXE system uses two detectors. For most aerosol samples, there are far more x-rays from the light elements;

if accepted directly, the detector system would be overwhelmed by these low-energy x-rays and the sensitivity for heavier trace elements would suffer. The solution is to use filters to reduce the number of low-energy x-rays compared to the high-energy ones. The first detector (PIXE–1) is used for elements Na to Mn; this detector is far from the sample and has a minimum filter. The second detector (PIXE–2) is as close to the sample as possible and has a filter to attenuate most x-rays below those of Fe. The conditions are set so that each detector operates at its optimum count rate for a typical aerosol sample. In the analysis of the WHITEX F samples, the PIXE–1 detector was in the process of failing, although the PIXE–2 detector was good. The A filters were analyzed after a new detector system had been installed. As a result, we invalidated all 12-hour F filter data for elements lighter than Fe. In the original study design, the F filters were intended to provide data on the trace elements, such as Se; therefore no projected data were lost.

PESA Analysis (Hydrogen)

The hydrogen concentration of the sample was measured using Proton Elastic Scattering Analysis (PESA).[3, 4] Some of the protons in the 4.5 MeV proton beam used for PIXE are elastically scattered by the nuclei of the various atoms in the sample. The lowest energy recoil protons will result from scattering from a hydrogen nucleus (a single proton). A solid state detector at 30° separates this proton from all protons scattered by other nuclei. By counting the number of protons at this energy and subtracting the background, we determined the areal density of hydrogen in the sample. As with PIXE, the system is calibrated by elemental standards, in this case mylar foils. The method works best with Teflon filters because the CF_2 material has very little hydrogen.

Quality assurance procedures include measuring several standards, and reanalyzing a series of filters from previous analytical sessions.

Hydrogen is used as a quality assurance check of gravimetric mass and as a measure of organic mass. Hydrogen correlates well with mass because hydrogen is present as a 5–10% component of ammonium sulfate, ammonium nitrate and organics. As long as soil and elemental carbon are not significant components of the mass, hydrogen will be around a 5% component of mass. For the NPS SFU network from 1984 to 1986, the correlation between hydrogen and mass was 0.82, with an average contribution of 4.3%. As discussed later, the correlation for the WHITEX data was 0.90 and the ratio was 4.7%.

The second application of hydrogen is as an alternative measure of organic mass.[5] The problem with the quartz-thermal method is that the minimum detectable limit and uncertainty are relatively large so that with low air volumes in pristine conditions, the method is inadequate. For example, at Hopi Point, the measured OC was above the mdl (defined as 2σ) on only 5% of the samples and above the uncertainty on only 24% of the samples. At Canyonlands and Bullfrog the situation was only slightly better, with 36% above the mdl. Only at Page was the ambient level high enough to be consistently above the mdl. Even at Page, the mean OC concentration of 892 ng/m^3 was less than twice the mdl of 482 g/m^3. On the other hand, the excess hydrogen after subtracting the sulfate contribution, was above the minimum detectable limit on 63% of the Hopi Point samples and 91% of the samples at other sites. The difference is that the mdl for organic mass by excess hydrogen is around 14% of that by quartz/thermal analysis.

Two steps are required to estimate organic mass from hydrogen. The first step is to subtract the hydrogen that is not associated with organics. The major source of this hydrogen is sulfate, which is generally present as fully neutralized $(NH_4)_2SO_4$.[6] We assume that the hydrogen associated with water is removed from the sample when it is placed in vacuum prior to the PESA analysis of hydrogen. A study of 24 samples collected in Davis during humid winter conditions in February 1988 showed that samples lost and gained 2% of their mass when taken from the laboratory to a vacuum and back. This indicates that at least some of the water is volatilized in vacuum. Finally, we assume that the hydrogen associated with ammonium nitrate is negligible. If we use the nitrate concentrations measured on Teflon filter B by ion chromatography and assume that no nitrate is volatilized in vacuum, the estimate of organic hydrogen is changed by only 4%. However, since ammonium nitrate is highly volatile, the actual change will be much less than 4%.

The second step in the calculation of organic mass requires an estimate of the composition of an average organic molecule. A similar estimate must also be made is calculating organic mass from organic carbon. A typical estimate for OC analysis is that organics are 71% carbon by weight, which is what we will use in this report for OC. Most organic molecules lie between CH and CH_2 so that there are approximately 1.5 hydrogen atoms for every carbon atom. Combining the 71% estimate and the estimate that there are 3 hydrogen atoms for every 2 carbon atoms yields the estimate that organics are 9% hydrogen by weight. The remaining 20% of organics is composed of oxygen and nitrogen.

FAST Analysis (H, C, N, O)

The module F filters were analyzed for light elements (H, C, N, and O) using Forward Alpha Scattering Techniques (FAST).[7] Thirty MeV particles were scattered by nuclei in the sample and detected by two detectors, at 62° and 74°. The 62° detector was used to measure hydrogen and give confirmatory values for the other elements, while the 74° detector provided the primary data for C, N, and O. Carbon is especially difficult because it is present in the substrate (CF_2). The substrate contribution is removed by determining the C to F ratio for blank Teflon filters and using these ratios to estimate the C in the substrate. N and O are more straightforward since Teflon does not have either of these elements; however, care must be taken to remove contributions from inelastic scattering of the fluorine.

Ion Chromatography (Nitrates, Sulfates)

The masses of nitrates and sulfates were measured at Research Triangle Institute for particles on the module B Teflon filters and on the module D and E nylon filters.[8] Chloride and nitrite were also measured but because of low ambient levels and high minimum detectable limits the analyses are not reported. (The minimum detectable limit of chloride ion is 2 orders of magnitude higher than that of chlorine by PIXE, and only one PIXE sample had a concentration above mdl.)

The material on the filters was desorbed in 15 ml of aqueous solution with sodium carbonate prior to IC analysis. Redesorbing selected filters showed that no further material can be desorbed.

Quality assurance procedures included daily analysis of two standards, one commercial and the other EPA, routine reanalysis of desorbed samples, and routine analysis of the desorbing solution.

Thermal Optical Reflectance (TOR) Analysis for Carbon

The 12-hour quartz filters (module C) at the primary sites were analyzed at Desert Research Institute for organic and light absorbing carbon (OC, LAC) using the thermal optical reflectance (TOR) method.[9] The term "light-absorbing carbon" is used to distinguish elemental carbon determined by TOR from the elemental carbon determined by another carbon combustion method, thermal manganese dioxide oxidation (TMO). As will be seen in Appendix 3D, the concentrations of elemental carbon by TOR are much closer to the estimates from the coefficient of optical absorption than they are to the concentrations by TMO.

In the TOR method, the sample is heated in five temperature steps (250°C, 450°C, 550°C, 700°C, and 800°C), with the first two and half the third in He atmosphere and the remainder in a

He/O_2 atmosphere. The analysis records the reflectance of the filter and the response of a flame ionization detector (FID). the following steps occur during the 30 minute cycle:

- The system is purged in He for 120s prior to sample injection.
- The sample is injected and the temperature raised to 250°C (He atmosphere) for 180s. The peak in FID is recorded.
- The temperature is raised to 450°C for 200s. The reflectance is reduced because of pyrolysis of organics to elemental carbon. A second FID peak is observed.
- The temperature is raised to 550°C for 250s. A third FID peak is observed.
- A He/O_2 atmosphere is introduced at 550°C for 170s. A rise in FID and reflectance occurs. Any FID values occurring before the reflectance rises to its original value is included in OC along with the first three peaks. All later FID responses are included in LAC.
- The temperature is raised to 700°C for 190s.
- The temperature is raised to 800°C for 220s.
- CH_4 is injected as a system calibration and the temperature reduced to ambient in 260s.

Laser Integrating Plate Method (Coefficient of Absorption)

The coefficient of absorption for fine particles was determined from the Teflon filters of the IMPROVE and SFU samplers using a Laser Integrating Plate Method (LIPM).[3] Light of wavelength 633 nm from $He(Ne)$ laser was diffused and collimated to provide a uniform beam of less than 1 cm^2 at the sample. The light transmitted through the sample is collected with an ORIEL photodiode detection system. The intensity of the transmitted light will depend on the absorption of particles in the sample and on large-angle scattering. The blank Teflon filter does not absorb light but does decrease the transmitted light by scattering; this varies from filter to filter. It is therefore necessary to determine the amount of transmitted light for every blank filter before collection. The exposed filters are arranged so that the side with sample is toward the detector. With this arrangement, the light transmitted through the blank filter is equal to the light incident upon the sample. The absorption of the particles are determined from the ratio of the intensity of transmitted light for the blank filter to that for the filter plus sample.

A major assumption in the derivation is that the large-angle scattering from the particles in the sample is small. This assumption was tested by comparing the results from the LIPM system to those obtained from an integrating sphere system.[10] Since the integrating sphere system measures both transmittance and reflectance, it measures absorption directly without the scattering assumption. The results, discussed in Appendix 3F.2, show that the scattering effect is small, causing approximately a 3% increase in the absorption estimate. This 3% correction is included in the reported data.

A second important assumption is that the absorption by the particles in the atmosphere equals the absorption by the particles on the filter.[10] In the atmosphere the light wave reforms after interacting with a particle, so the absorption by a given particle does not depend on the concentration of other particles. The situation is different for particles on a filter; here the absorbing particle might be shielded from the incident light by other scattering and absorbing particles. The effect will increase with the areal density of scattering and absorbing particles. The magnitude of this effect was determined in a series of tests of measuring the same ambient coefficient on filters with different areal densities. The empirical relationship is discussed in Appendix 3F.2. For the average WHITEX 6-hour filter, the effect was to increase the coefficient by 25%.

3A.2 DRUM Sampler

General Description

The Davis Rotating Unit for Monitoring (DRUM) sampler is an eight stage Lundgren-type rotating drum cascade impactor using a series of single round jets for each stage including low-pressure stages.[11] The DRUM has eight orifices of decreasing size, ranging from Stage 1 (8.54 *μm* aerodynamic diameter) to Stage 8, the finest orifice (0.069 *μm* aerodynamic diameter). This last orifice serves to provide flow control at about 1.1 *l/min* by operation at sonic velocity as a critical orifice. A two-stage 25 *mm* filter cassette holds two Teflon filters that follow the last stage; the first collects the particles smaller than 0.069 micrometer aerodynamic diameter that pass the last stage and the second serves as a backup. These filters were typically changed every 12-hours in WHITEX.

The particles were collected on greased-mylar substrates of slowly rotating cylindrical drums (2 *mm* in 6 hours for WHITEX). The sample trace obtained for each 3-week period was 16.8 *cm* long. The mylar collection strips are 17.6 *cm* long by 1.6 *cm* wide. Because the sample size is small, the analytical methods determine the resolution of the deposit. The resulting narrow linear deposit for each stage was evaluated with time resolution of 6 hours using PIXE.

After exhaustive theoretical and experimental analysis, the orifices were revised in 1986, prior to WHITEX.[12] The operational characteristics are summarized in Table 3A.3. Monodisperse fluorescent polystyrene latex particles of various sizes were aerosolized and sampled with the DRUM impactor to observe the collection efficiencies of the stages with particles of known aerodynamic size.

The problem of bounce-off is minimized in the DRUM during collection of environmental samples by three factors: (1) environmental aerosols tend to be hygroscopic and stick upon contact with surfaces, (2) the DRUM substrate is coated with an oily film that prevents bounce, and (3) the turning of the drums prevents excessive build-up of deposited material on the substrate, spreading out the deposit along a 16.8 *cm* long trace rather than keeping it at a single spot.

PIXE Analysis (Elements)

The DRUM strips were analyzed using a special PIXE system that analyzes the strips in 2 *mm* increments. For WHITEX, this corresponded to 6-hour resolution. Sulfur was the element of primary concern because of its effect on visibility.

3A.3 SFU Sampler

The Stacked Filter Unit (SFU) is a 2-stage sampler that uses the collection properties of 8m Nuclepore material to separate the particles into coarse (2.5 to 15 *μm*) and fine (0–2.5 *μm*) ranges.[13] The sampler operates at a flow rate of 10 *l/min*. The sampler was used at the three tertiary sites and at Canyonlands for QA. The samples were analyzed using the gravimetric, PIXE, and PESA systems described for the IMPROVE sampler.

A second purpose for the SFU sampler at Canyonlands was to evaluate the effect of large particles on visibility. In addition to the fine stage information for QA, the sampler also provided mass and major (PIXE) elements in the 15 *μm* to 2.5 *μm* size range with 24-hour samples.

Table 3A.3: Drum impactor design criteria (Sampling rate = 1.1 l/min; conditions ambient sea level, 23°C.

Stage No.	Impactor Jet (cm)	Diam. (mil)	S/W	T/W	Inlet Pressure $(cm\ Hg)$	Outlet Re	Outlet u_o (cm/s)	Cutoff ECD_{ar} (m)	Diam. ECD_{ae} (m)
1	0.373	147	0.5	2.0	76	407	167	8.62	8.54
2	0.236	93	1.0	1.1	76	642	419	4.34	4.26
3	0.150	59	1.0	1.4	76	1010	1040	2.20	2.12
4	0.102	40	2.0	1.9	75.9	1500	2260	1.23	1.15
5	0.066	26	3.0	2.5	75.5	2310	5470	0.63	0.56
6	0.051	20	3.0	2.6	73.4	3050	9870	0.41	0.34
7	0.046	18	3.0	2.8	67.6	3490	13900	0.33	0.24
8	0.041	16	3.0	3.0	55.7	4510	31500	0.19	0.069
9	filter				<29.4			–0–	–0–

3A.4 SCISAS Sampler

The size classifying isokinetic sequential aerosol sampler (SCISAS) is the standard SCENES monitoring sampler, and has been used at 7 SCENES sites since 1984.[14] The sampler is similar to the IMPROVE in that it uses a cyclone to define the 2.5 μm fine particle upper cut point and it collects samples on several substrates. The primary difference is that the flow rate for each of the fine filters is 113 l/min rather than 22 l/min.

During the WHITEX study, the SCISAS samplers collected PM_{15} particles (0 to 15 μm) on Teflon filters and $PM_{2.5}$ particles (0 to 2.5 μm) on three filters, Teflon, nylon, and quartz. The nylon filter was not preceeded by a denuder. The Teflon filters were analyzed for mass and elemental composition using gravimetric analysis and x-ray fluorescence (XRF). The nylon filter was analyzed for total nitrate (fine particulate and vapor) by ion chromatography. The quartz filter was analyzed for organic and elemental carbon by TMO.

XRF differs from PIXE in using x-rays to induce the x-ray emission rather than a charged particle beam. The XRF system of NEA, Inc. uses multiple x-ray anodes to optimize sensitivity over the range of elements from Al to Pb. The system is calibrated by a series of elemental standards. Because of errors in the elemental standards and calibration techniques, the calibration for elements Al and Si was incorrect by a factor of 2.0.[15] These incorrect values were used in the draft final report. The revised models indicate that soil is a smaller contributor to the mass balance than was originally calculated.

The TMO method measures the carbon evolved from the sample during temperature steps using a flame ionization detector. In the TMO method there are three temperature steps: 400s at 125°C, 200s at 550°C and 120s at 850°C. The sample is oxidized in a reaction with MnO_2 in a He atmosphere. Carbon released in the first step is designated volatile organic carbon (VOC) and acid released carbon (ARC). That released in the 500°C step is residual organic carbon (ROC) and that released at the highest temperature is considered elemental carbon (EC). For the WHITEX study, SCENES reported ROC and EC. They are compared to OC and LAC from the IMPROVE sampler in this report.

The SCISAS sampler was run on a cycle compatible with the IMPROVE samplers, namely 12-hour samples beginning at 0800 and 2000 hours. At the other sites (Hopi Point and Bryce) the SCISAS samplers operated on their normal 24-hour sequence beginning at midnight. For this reason only the Page SCISAS data is used for comparison with the IMPROVE. The only SCISAS data used directly in the model calculation was selenium from Hopi Point.

3A.5 Brigham Young University Samplers

Cascade High Volume Sampler

Two samplers were operated at Page and Bryce Canyon by Brigham Young University (BYU).[16] Samples were collected for the entire period, but analyzed only for a 10-day period from February 5–15. The most important measurements were for spherical aluminosilicate (SAS) particles, which are associated with emissions of coal-fired power plants.[17] Particulate SO_4 and gaseous SO_2 were also measured. The first sampler is a cascade HiVol unit with three analyzed stages:

1. A 0.5 to 3.5 μm paraffin coated stage analyzed for spherical aluminosilicate (SAS) and sulfate particles.
2. A 0 to 0.5 μm stage analyzed for sulfate particles.
3. A $NaCO_3$ impregnated quartz filter analyzed for SO_4 to give SO_2.

All analyses were performed at BYU. The number of SAS particles was counted using a scanning electron microscope. The SO_4 concentrations were determined by ion chromatography.

Annular Denuder

The second sampler was a two-stage annular denuder. The air first passed through an annular denuder impregnated with carbonate to remove SO_2 gas; this denuder was washed out at BYU. The air then passed through a bubbler that collected the particles. The contents of the denuder and the bubbler liquid were both analyzed for SO_4.

3A.6 Drexel Gas Chromatography (SO_2)

Measurements of SO_2 were taken at Canyonlands by a team from Drexel University, using a high sensitivity gas chromatograph system.[18] In order to achieve the desired sensitivities of around 20 ng/m^3 of SO_2 in a short (3 minute) sample, the air was preconcentrated using liquid argon before being introduced to a flame photometric detector.

In the WHITEX protocol, a series of measurements were taken every six hours, at the 0200, 0800, 1400, and 2000 start time of the 6- hour IMPROVE sample. In general, at least three measurements were taken during a one-hour interval. Each measurement sampled $2\times10^{-3}m^3$ of air, which was collected in less than three minutes. The various measurements in a given series were averaged to compare with the 6-hour IMPROVE impregnated-Whatman SO_2 sample.

3A.7 Giant Particle Sampler

A giant particle sampler was operated under the direction of K. Noll at Canyonlands National Park to ascertain the potential role played by large particles in visibility. Data have not yet been received for this instrument.

3A.8 Transmissometer

General Description

The coefficient of extinctions was measured by LPV–2 transmissometers from OPTEC, Inc.[19, 20] These instruments, used in the IMPROVE network, measure the amount of light transmitted from an optically focussed incandescent light source to a controller-controlled receiver. The light beam is chopped to minimize the effect of background illumination. Knowing the intensity of the light source, the distance between the source and the receiver, and the intensity of the received light, allows a direct calculation of the average atmospheric extinction along the light path of 5–15 km. The extinction coefficients were telemetered to a data collection center operated by Air Resource Specialists, Inc.

Theory[21]

Historically, transmissometry has been thought of as teleradiometric measurements of the intensity of a light source placed at some distance r from an observation point.[22] The equation governing the amount of radiant energy received at the observation point is

$$H = \frac{I_o}{r^2} e^{-b_{ext} r}, \tag{3A.1}$$

where H is irradiance at some distance r from the light source, I_o is radiant intensity and b_{ext} is the atmospheric extinction coefficient. I_o/r^2 is essentially a calibration term that can be determined by comparison of transmission measurements to other optical measurements such as teleradiometer measurements made under "standard" lighting conditions or to integrating nephelometer measurements made on days that are near the Rayleigh scattering limit. A second calibration technique utilizes measurement of a signal proportional to H at two different distances:

$$H_1 = \frac{I_o}{r_1^2} e^{-b_{ext} r_1} \tag{3A.2}$$

$$H_2 = \frac{I_o}{r_2^2} e^{-b_{ext} r_2}. \tag{3A.3}$$

Measuring r_1, r_2, and a signal proportional to H_1 and H_2, and assuming the atmosphere is homogeneous over distances r_1 and r_2 allows Equations 3A.2 and 3A.3 to be solved for I_o.[23] A third calibration technique and the one used in all field studies involves measuring H when the receiver and light source (transmitter) are placed within a few hundred feet of each other and assuming $e^{-b_{ext} r} \approx 1$. Then $I_o = Hr^2$ where r is the distance between the teleradiometer and transmitter.

Effect of Turbulence

If it is assumed that the effect of atmospheric turbulence on measurement of H is to modify Equation 3A.1 in a multiplicative way, and that it is some function of transmitter-receiver distance, then

$$b'_1 = -\frac{1}{r_1} \ln \frac{f(r_1) H_1 r_1^2}{I_o} = -\frac{1}{r_1}\left[\ln \frac{H_1 r_1^2}{I_o} + \ln f(r_1)\right] \tag{3A.4}$$

and

$$b'_2 = -\frac{1}{r_2} \ln \frac{f(r_2) H_2 r_2^2}{I_o} = -\frac{1}{r_2}\left[\ln \frac{H_2 r_2^2}{I_o} + \ln f(r_2)\right]. \tag{3A.5}$$

Since $b = -\frac{1}{r_1} \ln \frac{H_1 r_1^2}{I_o} = -\frac{1}{r_2} \ln \frac{H_2 r_2^2}{I_o}$, subtracting Equation 3A.5 from 3A.4 yields

$$b'_1 = b'_2 + a_o, \tag{3A.6}$$

where

$$a_o = \frac{1}{r_2} \ln f(r_2) - \frac{1}{r_1} \ln f(r_1). \tag{3A.7}$$

a_o is the difference between derived extinction associated with atmospheric turbulence for two transmissometric measurements over different path lengths.

In order for $b'_1 = b'_2$ requires $a_o = 0$. a_o is zero if $\frac{1}{r_2} \ln f(r_2) = \frac{1}{r_1} \ln f(r_1)$. $\frac{1}{r_2} \ln f(r_2) = \frac{1}{r_1} \ln f(r_1)$ requires that $\frac{1}{r} \ln f(r) = c$ where c is a constant. Therefore

$$f(r) = e^{cr}. \tag{3A.8}$$

If $c = 0$ then $f(r) = 1$ and $b'_1 = b'_2 = b$. Under these circumstances, turbulence would not affect the measured irradiance, and true extinction will be measured. If, however, $c \neq 0$ and the turbulence effect on measured irradiance takes on the functional form of Equation 3A.8, the effect of atmospheric turbulence would not be detected by comparing transmissometric measurements of different path lengths.

Design Considerations

To minimize the effect of background or ambient illumination, the transmitted light beam is modulated from on to off while the receiver electronics are designed to measure the difference between background radiance (transmitter off) and background plus transmitter radiance (transmitter on). The difference between the two signals is proportional to the irradiance associated with the radiant energy from the transmitter light source.

To achieve modulation of transmitter light source, a four blade "chopper" is mounted near a condenser lens and rotated at an exact speed of 19.53125 revolutions per second. This results in a 78.125 cycle per second modulated signal. To maintain the lamp output constant to better than 1%, an optical feedback unit is used. Approximately 8% of lamp output is optically diverted to a photo diode over which a narrow, 550 nm band pass interference filter has been placed. The output from this diode is used to control voltage applied to the transmitter lamp.

The receiver optics consist of a 125 mm refractor lens with a focal length of 629 mm mounted in a heavy walled aluminum tube. The transmitter (light source) image is focussed on a photo diode detector with an interference filter placed directly in front of it. The interference filter has a band pass centered at 550 nm, a 10 nm band width and a peak transmission of 60%. Characteristics of the receiver interference filter are nearly identical to the one used in the transmitter optical feedback system.

The processing of the signal received at the transmitter is schematically shown in Figure 3A.4. The transmitter signal at $t = 0$ is shown in Figure 3A.4a. The "on-off" cycle time is 12.8 ms. Figure 3A.4b, the output from the receiver 12 bit A/D converter, shows the effect of atmospheric

The processing of the signal received at the transmitter is schematically shown in Figure 3A.4. The transmitter signal at $t = 0$ is shown in Figure 3A.4a. The "on-off" cycle time is 12.8 ms. Figure 3A.4b, the output from the receiver 12 bit A/D converter, shows the effect of atmospheric turbulence and attenuation on the transmitted signal after the modulated light beam has transversed some path length r. To determine the difference between lamp on and off voltage, the receiving computer must accurately determine the time at which the transmitted signal is sampled. That is, the voltage must be extracted from the transmitted signal that corresponds to when the light is on and when it is off. This is achieved by using a phase-sensitive detection scheme. A high Q ($Q = 32$) band pass amplifier centered at the chopper frequency 78.125 CPS allows the fundamental frequency of the chopped signal to be passed to a zero crossover detector. The output of the high Q band pass amplifier is shown in Figure 3A.4c, while the output from the zero cross detector is represented in Figure 3A.4d. By knowing the time associated with zero cross point, an algorithm can be used to determine the time at which the incoming signal is sampled. The signal is sampled for 0.4 ms and consists of eight separate readings.

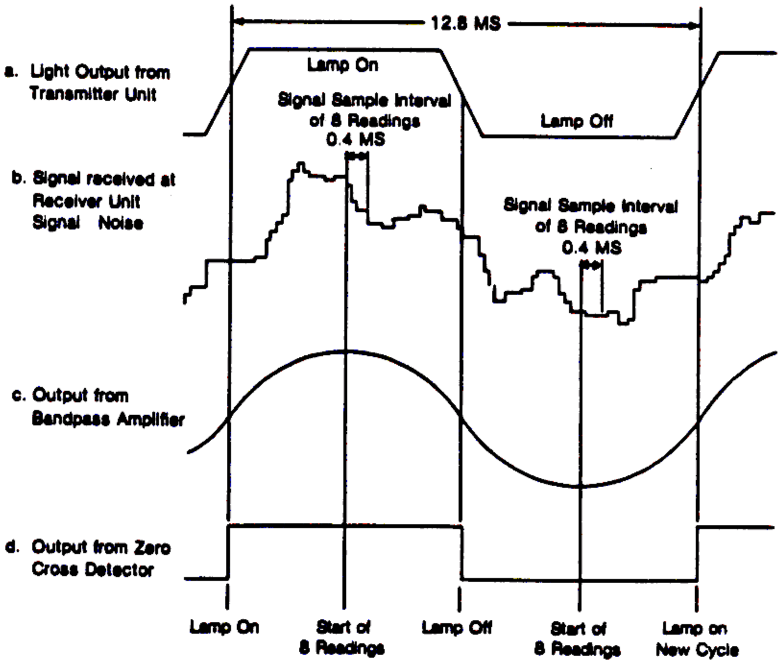

Figure 3A.4: Schematic for processing the transmissometer signal.

If the effect of atmospheric turbulence on the signal is random, averaging many radiance difference measurements will yield a "true" value. Figure 3A.5 shows an example of how the receiving electronics is designed to yield a 10 minute average transmitter irradiance signal. A ten minute reading is the average of ten one-minute readings. A one-minute reading consists of ten six-second sampling intervals where the initial second is used to establish the "phase" of the signal and the subsequent five seconds are used to obtain 6250 samples of the signal. The receiver electronics is designed to average over any time period selected by the operator. Once the receiver has been calibrated, the averaged signal can be used directly in Equation 3A.1 to calculate atmospheric extinction.

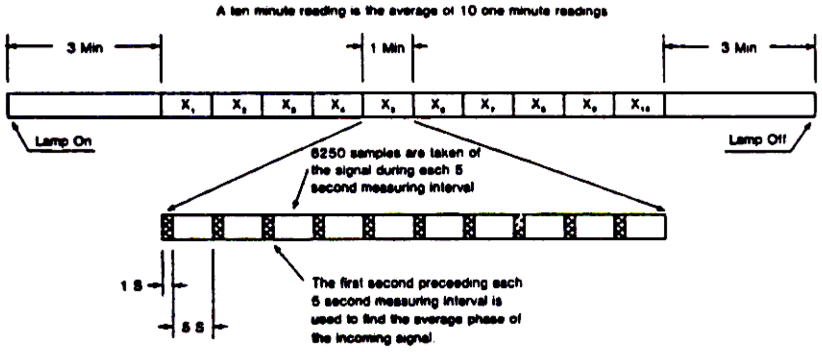

Figure 3A.5: Example of a ten minute integration.

3A.9 Integrating Nephelometer

The coefficient of scattering was measured with MR1 1560 integrating nephelometers operated according to standard procedures. The span of the instrument was set using Freon 12, while the zero point was monitored at least every 6 hours by pumping clean air through the sampling chamber. Typical temperature differences between the nephelometer inlet and outlet were approximately 5°C.

3A.10 CD_4 Collection and Analysis

Ambient samples of CD_4 were obtained by pumping approximately 60 liters of air into large mylar/polyethylene bags. At the end of the sampling period the air was transferred to pressurized steel containers. These containers were stored at Los Alamos National Laboratory until analysis.

The analysis of selected samples was performed in three steps.[24] The first step was to spike the sample with approximately 0.3 cm^3 of normal methane in order to provide a sufficient amount of methane for separation. The next part of this first step was to measure the concentration of the normal methane by gas chromatography using a flame ionization detector (GC/FID). The response factor for the FID was calibrated with NBS SRM 1658(a,b) Methane in Air.

The second step was to separate the methane (both normal and deuterated) by gas chromatography.[24]

The third step was to determine the ratio of deuterated to normal methane using mass spectrometry. This requires determining the ion currents for both CD_4 and CH_4. The CH_4 ions were focused into a Faraday cup and the collected charge measured by the voltage drop across a precision resistor. A high-sensitivity system is needed to collect the much less abundant CD_4 ions. The Faraday cup is retracted from the beam line and the CD_4 ions are focused on a 17-stage electron multiplier, with a gain of greater than 10^8, connected to a pulse height discriminator and a scalar. The relationship between the CH_4 signal from the Faraday cup and the CD_4 signal from the multiplier system is calibrated using standard of known ratios of CD_4/CH_4. The calibration procedures were performed daily.

The concentration of CD_4 was determined from the product of the CH_4 concentration from step one and the CD_4/CH_4 ratio from step two.

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