Chapter 3

Optical, Particulate, SO_2, and CD_4 Measurements

3.1 Introduction

The purposes of this chapter are to summarize the optical, particulate, SO_2, and CD_4 measurements and characterize their precision and accuracy. The details of the measurements are included in Appendices 3A to 3G. The specific topics of the Appendices are:

3A. Description of Sample Collection and Analysis

3B. Precision and Accuracy of CD_4 Injection and Measurement

3C. Precision and Accuracy of Particulate Measurements

3D. Particulate Concentration Intercomparisons

3E. Precision and Accuracy of SO_2 Measurements and Intercomparisons

3F. Precision and Accuracy of Optical Measurements

3G. Description of Regression Plots

Most of the samples were collected by instruments from three monitoring networks. Measurements of b_{ext} were made using transmissometers from the IMPROVE (Interagency Monitoring of Protected Visual Environments) network.[1] Government agencies participating in this program are the National Park Service (NPS) and the Environmental Protection Agency (EPA). Particulate samples were collected at nine sites using the fine particle modules of the IMPROVE samplers.[2] Particulate samples were collected at three sites using the stacked filter unit (SFU) while the SCISAS (Size-Classifying Isokinetic Sequential Aerosol Sampler) was employed at four SCENES (Subregional Cooperative Electric Utilities, NPS, Department of Defense and EPA Study) sites.[3, 4, 5]

The measurements of variables used in the model analyses are:

- optical: Extinction coefficients, b_{ext}, were measured using transmissometers. Scattering coefficients, b_{scat}, were measured using unheated integrating nephelometers. Absorption coefficients, b_{abs}, were measured using the integrating plate method to determine the absorption by the fine particles collected on Teflon filters by IMPROVE samplers.

- fine particles: Fine particles (smaller than 2.5 μm) were collected on Teflon, nylon, and quartz filters by IMPROVE,[2] SFU,[4] and SCISAS samplers. These filters were analyzed by a variety of methods: gravimetric analysis, particle induced x-ray emission (PIXE), x-ray fluorescence (XRF), proton elastic scattering, ion chromatography, and thermal carbon methods. Concentrations were determined for mass, major and trace elements, hydrogen, sulfate, nitrate, nitrate plus nitric acid vapors, and organic and elemental carbon. Comparisons were made between IMPROVE and SCISAS samples at Page. The model analyses were based primarily on the measurements of the IMPROVE sampler.

- coarse particles: Coarse particles (2.5 μm to 15 μm) were collected on Nuclepore filters by SFU samplers at four sites and analyzed by gravimetric analysis. Total particles (smaller than 15 μm) were collected on Teflon filters by SCISAS samplers at four other sites and analyzed by gravimetric analysis; the coarse mass was estimated by subtraction.

- particles in multiple size ranges: Particles in nine size ranges were collected by the DRUM (Davis Rotating Unit for Monitoring) sampler and analyzed by PIXE.[6]

- SO_2: SO_2 was measured by the IMPROVE sampler using the impregnated-filter method; in this method, SO_2 was converted to sulfate on K_2CO_3–impregnated filters and analyzed for sulfate by ion chromatography. Results were compared with measurements on impregnated-filter and annular denuder samplers operated at Page by Brigham Young University (BYU).[7]

- CD_4: CD_4 was released from the Navajo Generating Station. Air samples were collected in 60 liter bottles at the sampling sites and analyzed for CD_4 by gas chromatography/mass spectrometry.[8]

3.2 CD_4 Tracer Injection

During the WHITEX period, 4.9 kg of CD_4 was released through the stacks of the Navajo Generating Station. A manifold and valve system permitted the release through any of the three stacks. Preliminary experiments determined that the CD_4 was well-mixed and conserved in the stack. The release rate was based on the power output of the station. From January 7 to 30, the ratio of tracer released to the power output was held between 2.0 to 2.5 mg CD_4/MW. Beginning on January 30, the rate was increased to approximately 3.5 mg CD_4/MW. However, between February 6 and 10, the ratio rose because of an unanticipated outage (to nearly 5 mg CD_4/MW), and on February 13, the ratio decreased to 2.5 mg CD_4/MW, because of an unanticipated early restart. The details of the injection are discussed in Appendix 3B. The analysis of the samples is discussed in section 3.5 and in Appendices 3A and 3B.

3.3 Sample Collection

A complete suite of measurements were made at the three receptor sites: Canyonlands National Park, Hopi Point (Grand Canyon National Park), and Page (Glen Canyon National Recreation Area). Each site had (1) a multimodule version of the IMPROVE sampler that collected fine particles on 6 filters and SO_2 on another filter, with durations ranging from 6 to 24 hours; (2) a DRUM sampler that collected particles in nine size ranges; (3) a system to collect 6-hour air samples for CD_4 analysis; and (4) a transmissometer to measure b_{ext}, an integrating nephelometer to measure b_{scat}, and a meterological package. SCISAS samplers operated at Hopi Point and Page as part of the SCENES network, with the sampler at Page following the time schedule of the

IMPROVE sampler. BYU operated an annular denuder and a HiVol sampler at Page for SO_2 and SAS cenosphere concentrations.

All of the above measurements except b_{ext} were made at the gradient site of Bullfrog in Glen Canyon National Recreation Area. Particulate and CD_4 samples were collected at the other gradient site (Hite) and at four satellite sites: Green River, Cisco, Monticello, and Mexican Hat. These five sites had less elaborate versions of the IMPROVE sampler, consisting of four identical fine particulate modules that operated sequentially, collecting 12-hour samples for gravimetric and elemental analysis. Air samples of 48-hour duration were collected at each of the five sites for CD_4 analysis.

Particulate samples of 24-hour duration were collected by SFU's at two additional satellite sites: Navajo National Monument and Wupatki National Monument. No samples of CD_4 were collected there. A SCISAS sampler collected 24-hour samples at the final satellite site, Lake Mead.

Particulate samples of 24-hour duration were collected by an SFU and a SCISAS at the background site in Bryce Canyon National Park; these samplers operated on a different start-time schedule. An annular denuder and a HiVol sampler were operated by BYU.

The nominal numbers of measurements at each site are shown in Table 3.1. The sampler collection is described in detail in Appendix 3A.

Table 3.1: Nominal number of 6 and 12-hour measurements. Real-time measurements were averaged in 6-hour segments.

	IMPROVE	DRUM	SCISAS	SFU	BYU	CD_4	Optical
Primary							
Canyonlands[1]	882	1386		84	168	168	336
Hopi Point	798	1386	168			168	336
Page	882	1386	336		168	168	336
Gradient							
Bullfrog	798	1386				168	168
Hite	84					21	
Satellite							
Green River	84					21	
Cisco	84					21	
Monticello	84					21	
Mexican Hat	84					21	
Navajo				84			
Wupatki				84			
Lake Mead			168				
Background							
Bryce Canyon			168	84	252		

[1]Canyonlands: also SO_2 gas chromatography measurements

3.4   Sample Analysis

The coefficients of extinction and scattering and the meteorological parameters were measured in real-time and telemetered to the central data-processing facility of Air Resources Specialists. The extinction coefficients were obtained by OPTEC LPV–2 transmissometers, which measure the amount of light transmitted from an optically focused incandescent light source to a computer-controlled receiver. The light beam was 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, allowed a direct calculation of the average atmospheric extinction along the light path of 5–15 km. The scattering coefficients were determined by unheated MRI 1560 integrating nephelometers. The site of the transmissometer receiver and the nephelometer was not always precisely collocated with the particulate/SO_2/CD_4 sampling site.

Selected 60 liter samples of air were analyzed for CD_4 at Los Alamos National Laboratory using the following process. First, the sample was spiked with normal methane, and the methane concentration determined by gas chromatography. Second, the methane fraction of the sample was separated by a preparative-scale gas chromatographic method. Third, the CD_4/CH_4 ratio was determined by isotopic-ratio mass-spectrometric techniques. The concentration of CD_4 was determined from the product of the CH_4 concentration from step 1 and the CD_4/CH_4 ratio from step 2.

The particulate and SO_2 samples collected on the IMPROVE, DRUM, and SFU samplers were analyzed by the Air Quality Group at the University of California, Davis (UCD)[9] for mass, elements, and absorption; by Research Triangle Institute (RTI)[10] for ion; and by Desert Research Institute (DRI)[11] for carbon. The SCISAS samples were analyzed by NEA for mass and elements, ERT for carbon, and Combustion Engineering for nitrate ion. BYU analyzed the samples from their annular denuder and HiVol samplers.

Seven analytical methods were used on the samples collected by UCD. Filters A through F were collected at Canyonlands, Hopi Point, Bullfrog, and Page; filter X was collected at Hite, Green River, Cisco, Monticello, and Mexican Hat.

- Gravimetric analysis measured the mass concentrations on IMPROVE filters A, F, and X and on the coarse and fine SFU filters.

- Proton Induced X-Ray Emission (PIXE) measured the concentrations of elements Na to Pb on IMPROVE filters A, F, and X, the fine SFU filters, and on the strips and afterfilters of the DRUM sampler.[3]

- Proton Elastic Scattering Analysis (PESA) measured the concentration of hydrogen on IMPROVE filters A, F, and X, and the fine SFU filters.[12]

- Forward Alpha Scattering Technique (FAST) measured the concentration of hydrogen, carbon, nitrogen, and oxygen on IMPROVE filter F.[13]

- Laser Integrating Plate Method (LIPM) measured the coefficient of optical absorption on IMPROVE filters A and X and the fine SFU filters.[14]

- Ion Chromatography (IC) measured the concentration of sulfate and nitrate on Teflon filter B, nylon filters D and E, and impregnated Whatman filter S.

- Thermal Optical Reflectance (TOR) measured the concentration of organic and elemental carbon on quartz filter C.[15]

Four analytical methods were used on the SCISAS samples.

- Gravimetric analysis measured the fine and total mass concentrations on filters W and Y.

- X-Ray Fluorescence (XRF) measured the concentrations of elements Al to Pb on the fine and total filters W and Y.

- Ion Chromatography (IC) measured the concentration of nitrate on the nylon filter.

- Thermal MnO_2 Oxidation (TMO) measured the concentration of organic and elemental carbon on the quartz filter.

Two analytical methods were used on the BYU samples. Other analyses were performed but not included in the data base.

- Ion Chromatography (IC) measured the concentration of sulfate on the Teflon and impregnated filters.

- Scanning Electron Microscopy (SEM) measured the number of SAS cenospheres on the fine HiVol filter.[16]

The particulate and SO_2 samples collected, and the corresponding measured variables, are given in Table 3.2. The analytical methods are described in detail in Appendix 3A.

3.5   Internal Precision and Accuracy

The particulate and SO_2 concentrations were calculated from the measured mass A, the artifact mass B, and the volume V by

$$c = \frac{A - B}{V}. \tag{3.1}$$

The artifact B was found to be negligible for PIXE and PESA analyses. For other analyses B was determined from field blanks and second filters. Second filters were necessary for organic carbon on quartz and sulfate on nylon, since one source of artifact was the adsorption of gases during collection. To improve the statistics of the estimate of B, laboratory and control blanks were used when appropriate. Values of B/V are listed in Table 3.3 for selected variables.

The propagated precisions of the concentrations were determined by combining the flow rate, artifact, and analytical precisions. The analytical precision may include calibration and statistical components. The precision factors always add quadratically, so small factors may be safely neglected.

The flow rate precision of the IMPROVE sampler was estimated from the standard deviations of the ratios of IMPROVE to ERT audit flow rates to be between 1 and 3%, depending on how the precision of the audit device was treated. The largest estimate of 3% was chosen for the propagation calculations. The flow rate accuracy of the IMPROVE sampler was estimated from the mean ratio to be less than 1%.

The measurements for the WHITEX study fell into one of two categories, depending on the roles of artifact subtraction and statistics. The first category is appropriate for measurements in which artifact subtraction is important and statistical precision is small. This includes IC, TOR, and gravimetric analysis. For these measurements, the concentration precision was calculated using the equation

$$\sigma(c) = \sqrt{\sigma^2 + (f_v \cdot c)^2 + (f_m)^2 \cdot (c + B/V)^2}, \tag{3.2}$$

Table 3.2: Particulate and SO_2 measurements.

SAMPLER Module	Substrate	Duration	Size (μm)	Deposit (cm^2)	Measured Variables
IMPROVE					
A	Teflon	6h	0–2.5	1.1	absorption, Na to Fe
B	Teflon	6h	0–2.5	3.8	sulfate, nitrate
S	impregnated	6h	gas	3.8	SO_2
C	quartz	12h	0–2.5	3.8	organic and elemental carbon
D	nylon	12h	0–2.5	13.8	total nitrate, sulfate
E	nylon	24h	0–2.5	13.8	particulate nitrate, sulfate
F	Teflon	12h	0–2.5	0.7	mass, H, Fe to Pb
X	Teflon	12h	0–2.5	1.1	mass, absorption, H, Si to Pb
DRUM					
2–8	mylar	6h	**	0.02	Al to Pb
AF	Teflon	12h	0–.07	1.1	Al to Pb
SFU					
1	Nuclepore	24h	2.5–15	13.8	mass
2	Teflon	24h	0–2.5	1.1	mass, absorption, H, Na to Pb
SCISAS					
W	Teflon	12h,24h	0–2.5	13.8	mass, Al to Pb
Y	Teflon	12h,24h	0–15	13.8	mass, Al to Pb
U	quartz	12h,24h	0–2.5	13.8	organic and elemental carbon
V	nylon	12h,24h	0–2.5	13.8	total nitrate
BYU					
AD		12h			SO_2, sulfate
HV	Teflon	12h	0–3.5		SO_2, sulfate, SAS cenospheres

**DRUM size cuts: 8, 4, 2, 1, .6, .3, .2, .07 μm.

where c is the concentration, σ is a sum of all constant absolute precisions (independent of the magnitude of the concentration), f_v is the constant relative precision of flow rate, (f_m) is the constant relative precision of analysis, and B is the artifact. The constant absolute precision, σ, is the quadratic sum of the precision of the artifact subtraction and any constant analytical precision. The analytical precision was found to be constant for gravimetric analysis and TOR and relative for IC. Thus f_m is zero for gravimetric and TOR analyses. The B/V term is generally negligible for IC; dropping it never changes $\sigma(c)$ more than 5%. Thus for any method, the precision of the concentration is approximately a combination of a constant term and a relative term:

$$\sigma(c) = \sqrt{\sigma^2 + (f * c)^2}, \tag{3.3}$$

where

$$f = \sqrt{f_m^2 + f_v^2}. \tag{3.4}$$

For small concentrations, the precision in the concentration is approximately constant; for large concentrations, the precision increases linearly with concentration.

Table 3.3 lists selected precision factors for typical flow rates to be used in Equation 3.3. The specific factors used for the data base are listed in Table 3C.7 of Appendix 3C. Table 3.3 shows that the average relative precisions for SO_4 and SO_2 were only slightly larger than f; generally the concentrations of these two variables were large enough to be in the region where the precision varies linearly.

Table 3.3: Average artifact and precision for selected key variables. The second and third columns give average input values for Equation 3.3. The last two columns give the results for all the data.

Module Variable	Artifact B/V (ng/m^3)	Input Variables σ (ng/m^3)	f (%)	Average Precision $\sigma(c)$ (ng/m^3)	$f(c)$ (%)
B–SO_4	16	11	4%	35	5%
D–NO_3	88	40	6%	46	16%
E–NO_3	44	20	6%	24	13%
S–SO_2	102	90	8%	137	11%
C–OC	967	239	3%	246	41%
C–LAC	141	133	3%	137	39%
F–mass and X–mass					
Page	1000	600	3%	645	17%
Others	600	400	3%	420	16%

In the second category of measurements, the artifact subtraction is negligible and the statistical precision is important; this is applicable for PIXE, XRF, PESA, and CD_4–mass spectrography. For these methods, the constant precision term is replaced by one of statistical precision; the statistical precision increases with concentration, but more slowly than the relative precision. A relative analytical precision of 4% was used for PIXE analyses and 10% for PESA and FAST. As in the first category, the relative precision is dominant for large concentrations. The statistical precision is dominant for low concentrations.

The minimum detectable limit (mdl) is defined separately for the two categories. In the first category, the mdl is defined as 2σ in the limit of a lightly loaded sample. The variable is generally measurable well below this limit, but the concentration is not statistically significant. In the second category, the mdl is defined from the background in the spectrum and the relationship between real counts and concentration. The variable cannot be observed by the analysis much below this value. In both categories, the uncertainty at the mdl is approximately 50%.

Table 3.4 lists average concentrations, precisions, and minimum detectable limits for the major and trace variables for the IMPROVE samplers at Canyonlands, Hopi Point, Bullfrog, and Page. The major variables directly affect visibility and are the major components of the particulate mass. The trace variables do not directly influence visibility because of the low concentrations, but can be used to separate sources.

An important test of quality assurance is whether the reconstructed mass agrees with the gravimetrically measured mass. For WHITEX, the reconstructed mass was calculated in two ways. The first way was to add the major components of sulfate, soil, organics, soot carbon, and nitrate, using the measurement of select key variables. The second way was to simply add all elements measured by PIXE, PESA, and FAST. The two scatterplots are shown in Figure 3.1. In both cases, it is evident that all of the mass is being accounted for.

Several IMPROVE modules were operated side-by-side to verify the precision estimates. At Canyonlands, there was a second undenuded module with nylon filter, which permitted a check of sulfate and nitrate by ion chromatography. At Page, a second quartz module permitted a check of the organic and light-absorbing carbon measurements. At Page and three other sites, two Teflon filters routinely collected samples of 6-hour and 12-hour durations. Iron and mass were the two common measurements of these filters. We will define the measured difference as

$$\text{measured difference} = \frac{1}{n} \sum \sqrt{(y-x)^2}. \tag{3.5}$$

The average predicted difference was estimated from the propagated precisions for the variables using the equation

$$\text{predicted difference} = \frac{1}{n} \sum \sqrt{(\sigma_y)^2 - (\sigma_x)^2}. \tag{3.6}$$

Table 3.5 compares the measured and predicted differences. In most cases, the measured difference was smaller than the predicted difference (ratios less than 1.0), indicating that the propagation estimates were conservative.

In addition, sulfate was measured on Teflon filters by both ion chromatography and PIXE. The comparison assumes that all of the elemental sulfur is in the form of SO_4. The measured difference of 113 ng/m^3 was slightly larger than the predicted difference of 71 ng/m^3. In this case the predicted difference is based only on precision, while the measured difference may include accuracy components.

The details of the precision and accuracy calculations are discussed in Appendices 3B (CD_4), 3C (particles), 3E (SO_2), and 3F (optical coefficients).

3.6   Intercomparison of Optical Data

The collocated SCISAS and IMPROVE samplers at Page were operated on the same time schedule and permit intersampler comparisons. Two 6-hour IMPROVE measurements were averaged to compare with the 12-hour SCISAS. The details of this particulate comparison are given in Appendix 3D. Table 3.6 compares the measured difference (Equation 3.5) to the predicted difference (Equation 3.6) for several variables. The precision for SCISAS mass was calculated using Equation 3.3 with

Table 3.4: Average concentrations, precisions, and minimum detectable limits in ng/m^3 for the IMPROVE sampler at Canyonlands, Hopi Point, Bullfrog, and Page.

Variable	Time	Filter	Method	Mean Concentration	Mean Precision	%	Mean mdl	% Samples above mdl
				Major Variables				
mass	12h	Teflon	grav	2833	477	17%	934	89%
H	12h	Teflon	PESA	131	15	12%	6	100%
Al	6h	Teflon	PIXE	40.8	4.7	12%	2.9	81%
Si	6h	Teflon	PIXE	44.2	3.3	8%	2.0	100%
S	6h	Teflon	PIXE	262	13.9	5%	2.0	100%
SO_4	6h	Teflon	IC	742	35	5%	22	100%
K	6h	Teflon	PIXE	29.3	2.6	9%	1.7	100%
Ca	6h	Teflon	PIXE	12.5	1.5	12%	1.4	94%
Fe	6h	Teflon	PIXE	13.0	1.0	8%	1.0	96%
Fe	12h	Teflon	PIXE	11.3	0.6	6%	0.24	100%
abs[1]	6h	Teflon	LIPM	4.23	0.38	9%	0.42	97%
pNO_3 [2]	24h	nylon	IC	187	24	13%	38	86%
tNO_3 [3]	12h	nylon	IC	293	46	16%	79	85%
OC	12h	quartz	TOR	606	246	41%	489	40%
LAC	12h	quartz	TOR	348	137	39%	272	48%
SO_2	6h	impreg	IC	1246	137	11%	136	84%
				Trace Variables				
Ni	12h	Teflon	PIXE	0.45	0.10	23%	0.24	29%
Cu	12h	Teflon	PIXE	0.46	0.09	19%	0.17	48%
Zn	12h	Teflon	PIXE	1.26	0.13	11%	0.15	96%
As	12h	Teflon	PIXE	0.68	0.14	20%	0.16	56%
Se	12h	Teflon	PIXE	0.85	0.14	17%	0.18	49%
Br	12h	Teflon	PIXE	1.08	0.18	17%	0.21	75%
Pb	12h	Teflon	PIXE	2.13	0.41	19%	0.48	27%

[1]abs: coefficient of absorption, in units of $10^{-6}m^{-1}$.
[2]pNO_3: particulate nitrate, collected with denuder.
[3]tNO_3: total nitrate, collected without denuder.

N = 258   x̄=3024.23
R = 0.94 R² = 0.88   ȳ=2861.77
  RNH   =   0.94*FFPM   +   17.64   z̄=-162.46
±σ_a =   0.04   ±σ_b =   131.35   z̄/x̄=-.054

$$RNH = 0.94 * FFPM + 17.64$$

N = 190   x̄=3272.64
R = 0.84 R² = 0.70   ȳ=3172.04
  ELEM   =   1.12*MASS   +   -482.82   z̄=-100.60
±σ_a =   0.12   ±σ_b =   384.86   z̄/x̄=-.031

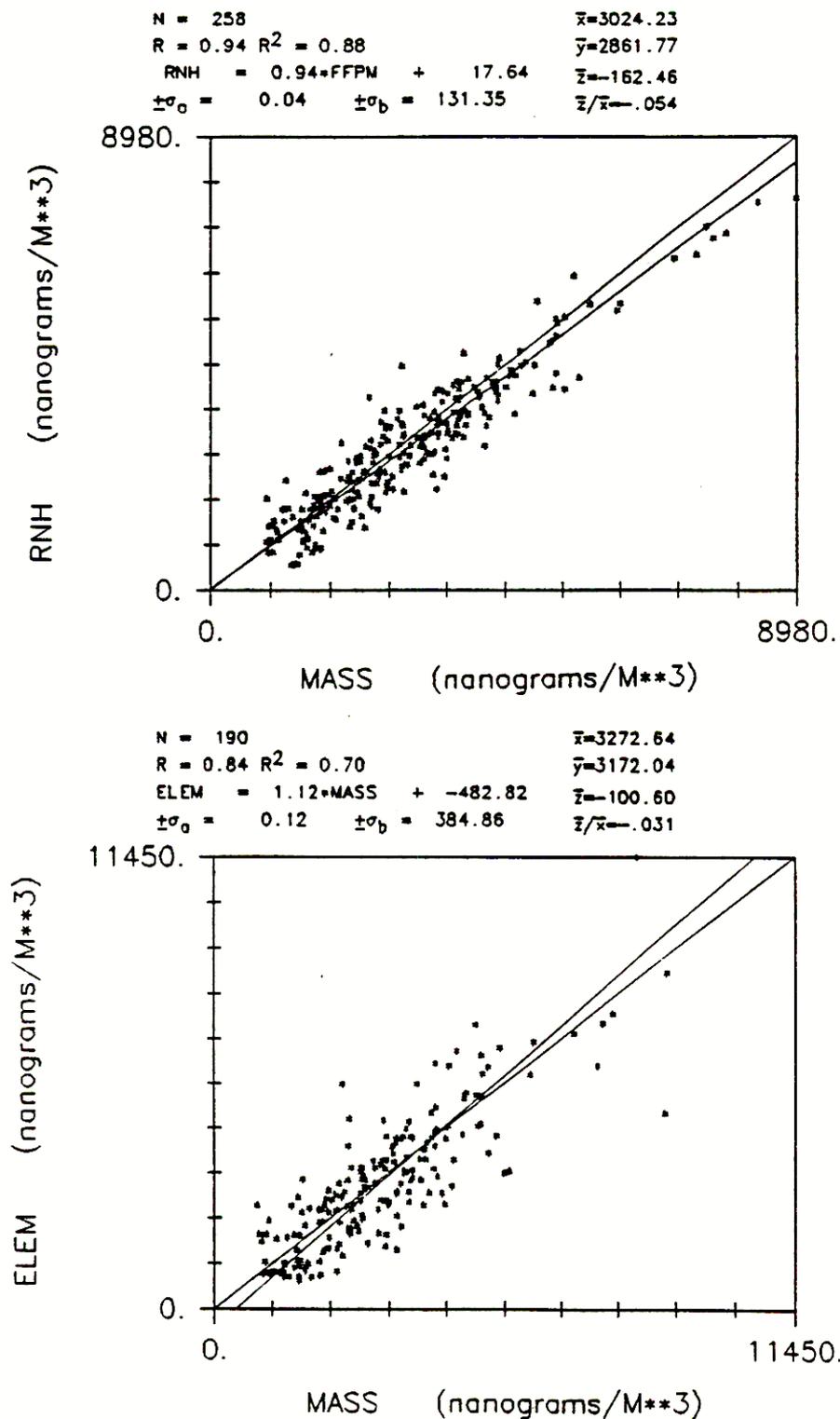$$ELEM = 1.12 * MASS + -482.82$$

Figure 3.1: Comparison of reconstructed and gravimetric mass for samples collected on Teflon filters at Canyonlands, Hopi Point, Bullfrog, and Page. The reconstructed mass in the upper plot is the sum of ammonium sulfate (from S), organics (from hydrogen), soil, soot (from absorption), and nitrate. The reconstructed mass on the lower plot is the sum of all elements from PIXE, PESA, and FAST.

Table 3.5: Average measured and predicted differences in ng/m^3 for the IMPROVE sampler at Canyonlands and Page.

Variable	Site	Filter	Analytical Method	Measured Difference	Predicted Difference	Ratio
SO_4	Canyonlands	nylon	IC	54	84	0.7
NO_3	Canyonlands	nylon	IC	39	58	0.7
OC	Page	quartz	TOR	167	270	0.6
LAC	Page	quartz	TOR	115	151	0.8
Fe	Page	Teflon	PIXE	2.3	1.5	1.5
mass	Page	Teflon	gravimetric	821	1256	0.7

$\sigma = 7$ μg and $f = 7\%$; the precision for all other SCISAS variables was assumed to be a constant 8%. In this comparison, the predicted difference is based only on precision, while the measured difference may include accuracy components. The agreement for the first seven variables was consistent with the predicted precisions, indicating no major accuracy problems. The measured difference is much larger than the predicted difference for the second group of variables, with ratios of 3–4 for soil elements and elemental carbon, 6 for total nitrate, and 11 for copper. The copper concentrations were much higher on the SCISAS, suggesting a copper contaminant in the SCISAS system. The soil elements, such as Ca and Fe, were also much larger on the SCISAS fine filters. The comparison of fine and total soils on the SCISAS sampler indicates that many of the SCISAS fine particle samples were contaminated with artifactual soil. This is discussed in Appendix 3D. The ratio of fine IMPROVE to total SCISAS soil concentrations were in the normal range for airborne soils. The SCISAS copper and soil concentrations were not used in the model calculations. The difference for elemental carbon reflects analytical difference between TOR and TMO. The total nitrate concentrations on the SCISAS are larger than those on the IMPROVE; the most probable reason is that the IMPROVE total nitrate module denuded more nitric acid vapors than the SCISAS did. The overall conclusion is that the comparison showed no major accuracy problems for most variables.

SO_2 measurements were made by three samplers at Page: an IMPROVE impregnated filter, a BYU HiVol impregnated filter, and a BYU annular denuder. The agreement for all three methods, discussed in detail in Appendix 3E, is good, with correlations of $r^2 = 0.9$ and slopes near 1. This comparison was the first validation of the impregnated filter method at remote western sites.

The accuracy of the extinction measurements on the transmissometer was examined prior to WHITEX by three comparisons and during WHITEX by comparison to the integrating nephelometer. Two transmissometers with different path lengths were compared prior to WHITEX in order to investigate the effects of atmospheric turbulence. Under a variety of turbulence conditions and time of day, the extinction measurements were almost identical. The average relative difference between the two instruments was 12%. The conclusion is that either turbulence does not affect the measurements, or that turbulence effects on measured irradiance is a simple exponential function of the path length.

A second study prior to WHITEX compared the extinction by the transmissometer with that of a teleradiometer with a black target. Using a truly black target eliminated the error associated with

Table 3.6: Average measured and predicted differences in ng/m^3 for comparison of IMPROVE and SCISAS samplers at Page.

Variable	Filter	Analytical Methods	Measured Difference	Predicted Difference	Ratio
S	Teflon	PIXE, XRF	50	36	1.4
SO_4	Teflon	IC, XRF	191	104	1.8
Zn	Teflon	PIXE, XRF	.37	.23	1.6
Se	Teflon	PIXE, XRF	.30	.20	1.4
Pb	Teflon	PIXE, XRF	.99	.69	1.7
OC	quartz	TOR, TMO	272	260	1.0
mass	Teflon	gravimetric	520	709	0.7
Cu	Teflon	PIXE, XRF	7.0	.62	11
Ca	Teflon	PIXE, XRF	12	2.7	4
Fe	Teflon	PIXE, XRF	5.8	1.8	3
total NO_3	nylon	IC	511	135	6
EC	quartz	TOR, TMO	533	94	4

inherent contrast. The two extinction measurements correlated very well and there was very little apparent bias. The linear regression line between the two variables was not statistically different from one. The average relative difference was 15%.

Comparisons were also made between extinction measurements by the transmissometer and the scattering measurements by an unheated integrating nephelometer. The extinction coefficient is the sum of the scattering and absorption coefficients. Comparisons made during WHITEX agreed with those made during a prior study. Below relative humidities of around 60%, the two measurements were in good agreement. Above around 80% relative humidity, the nephelometer measurements were considerably smaller than the transmissometer measurements. For the 6–hour average values at the three WHITEX receptor sites when the average relative humidity was below 60%, the correlation coefficient was $r = 0.82$. The slope of the perpendicular regression line was 0.80; the remaining 20% could be accounted for by the absorption coefficient. The intercept was within 2σ of zero, indicating that atmospheric turbulence was not affecting the transmissometer readings. (If the transmissometer measurements were biased toward larger extinctions by atmospheric turbulence, the offset would be apparent at low as well as high extinctions.) The average difference between the transmissometer and nephelometer measurements when corrected for the slope was 15%. Appendix 3F discusses possible mechanisms for bias in the integrating nephelometer at high relative humidity.

3.7 Summary of Results

CD_4 injection, collection, and analysis:

- The CD_4 was well-mixed and conserved in the stack.

- The ratios of the CD_4 release rate and the power output of NGS was usually, but not always, held fixed.

- The major source of analytical imprecision was associated with counting statistics in the mass spectrographic analysis; precision values were provided for all measurements in the data base.

IMPROVE particulate and SO_2 samples:

- An external flow rate audit was conducted by ERT. The flow rate precision determined from the standard deviation of the ratios of flow rate to be less than 3%; the value of 3% was used in the precision estimates. The flow rate accuracy determined from the average ratio was less than 1%.

- Artifact masses and precisions were determined using field blanks and second filters.

- Analytical precisions were determined from replicate analyses.

- Propagated precisions were calculated for every measurement, based on flow rate, artifact, and analytical precisions.

- Collocated comparisons between IMPROVE filters during WHITEX indicated that the propagated precisions were reasonable. For most variables, the collocated precision was slightly less than the predicted precision.

- Collocated comparisons between IMPROVE, SCISAS, and BYU samplers at Page indicated that the IMPROVE concentrations had no major accuracy problems. Except for soil elements and copper, which were contaminated in the SCISAS samples, and for total nitrate, the measured differences were only 40% larger than the differences predicted from the propagated precisions.

- Comparison of gravimetric mass and two estimates of reconstructed mass indicated that all of the mass was accounted for, and there were no major inconsistencies in the data.

Optical Measurements:

- The extinction measurements by the transmissometer were not biased by atmospheric turbulence.

- At relative humidities below around 60%, the integrating nephelometer gave reliable measurements of the scattering coefficient.

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