APPENDIX 3E: Precision and Accuracy of SO_2 Measurements and Intercomparisons

3E.1 Internal Precision and Accuracy

IMPROVE Impregnated Filter Sampler

The precision of the air volume for the impregnated filter is the same as for other filters, 3%.

The sulfate mass on the impregnated Whatman samples was measured by IC at RTI and converted to ng/m^3 of SO_2. Two special problems were encountered for the impregnated filters not met with the nylon and teflon filters. For the impregnated Whatman filter it was necessary to add 50 μl of hydrogen peroxide to the desorbing solution, in order to convert any sulfite and sulfide to sulfate. The problem is that the hydrogen peroxide contained a small amount of sulfate. (This is apparently a problem with all peroxides.) The 50 μl addition introduced an artifact of 0.67 ± 0.68 μg of sulfate. In the analysis of the first 50 filters from Canyonlands (through January 19), the amount of peroxide was less carefully monitored and approximately 100-150 μl of peroxide was added. To account for this, two analytical artifacts and associated uncertainties were applied to the data. For the first 50 Canyonlands filters, the total artifact (field blank including desorbing solution) was 2.296 ± 1.352 μg. For the majority the artifact chosen was 1.148 ± 0.676 μg.

The second problem was that the potassium carbonate in the impregnated material caused the sulfate peak to broaden. Because of the way the spectrum was analyzed this broadening produced an additional uncertainty of 6%. When this uncertainty was combined with the analytical uncertainty determined from the standards, the total analytical uncertainty for SO_2 was set at 7%.

With the definition of minimum detectable limit as twice the uncertainty of the artifact, the average minimum detectable limit is 136 ng/m^3 and 84% of samples had values above the mdl.

Drexel SO_2 Gas Chromatograph

The published precision of the system[1] for both wet and dry air is 5 pptv (parts per trillion by volume) out of 540 pptv, or 1%. The Drexel group has not provided estimates of accuracy.

BYU HiVol and Annular Denuder[2]

The denuder data from BYU indicates that the efficiency of the carbonate denuder surface for the collection of SO_2 is above 95% per denuder section. Replicate data for the annular denuder for

SO_2 indicates that the accuracy and precision are better than 10%. The accuracy of the HV data can be determined by comparison with the denuder data.

Figure 3E.1 compares the HV and AD data for SO_2 for 20 samples. The correlation is excellent, with $r^2 = 0.9$. The slope is close to unity and the intercept is small.

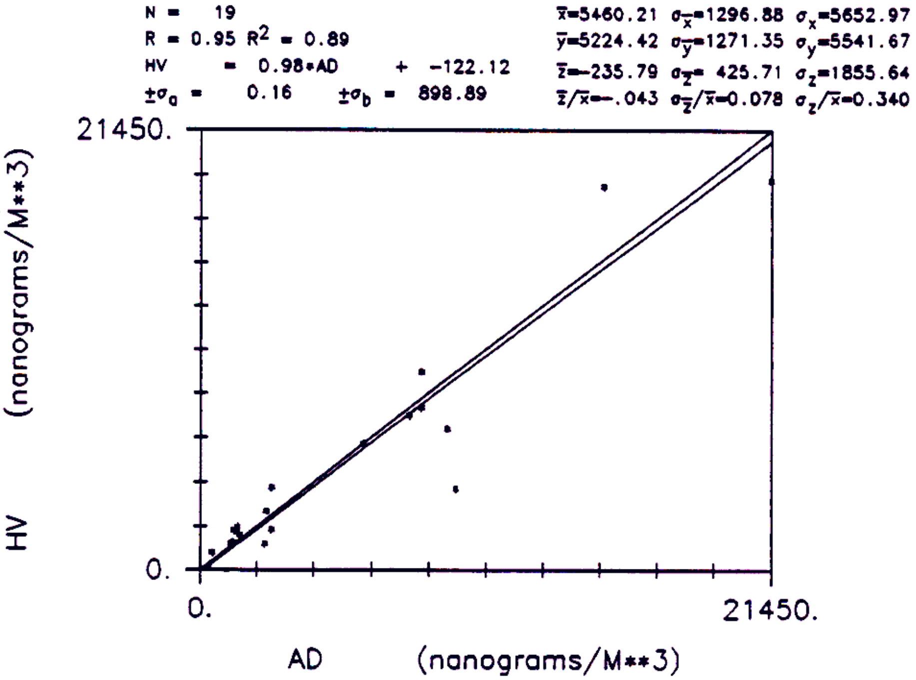

Figure 3E.1: Comparison of SO_2 by HiVol and by annular denuder at Page, February 5–15.

3E.2 Intersampler Comparisons

IMPROVE *vs* Drexel (Canyonlands)

The IMPROVE sampler with impregnated filter and Drexel gas chromatograph were run in parallel at the Canyonlands site for the duration of the study. The IMPROVE sampler collected integrated 6-hour samples, while the Drexel gas chromatograph made a series of approximately 3 measurements over a period of 1-hour at the start of the 6-hour period.

The Drexel data indicate that the 3-minute concentrations varied widely over each 1-hour sampling period. The average standard deviation for each 1-hour period averaged 1/3 of the mean concentration for that period. If the SO_2 concentrations varied this widely over the 1-hour period, the variation over 6-hours should be even larger. Thus a close correlation between the two methods cannot be expected.

The plot of the SO_2 values of impregnated filter (designated "S") *vs* Drexel (designated "L") is shown in Figure 3E.2. The correlation of 0.72 is good considering the differences in air volume sampled. The surprising relationship is that the Drexel average values are approximately one-half those of the IMPROVE sampler. If the ambient concentrations are log normal, one would expect an arithmetic mean of instantaneous values to be higher that an integrated sample, which is completely arithmetic. Time plots of the two variables are shown in Figure 3E.3.

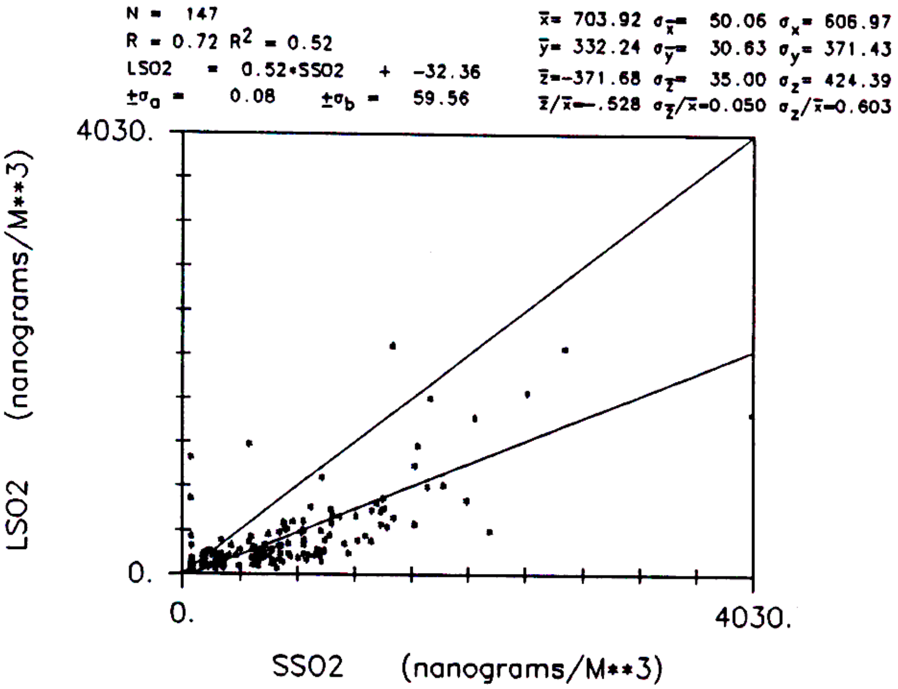

Figure 3E.2: Comparison of SO_2 by Drexel (LSO2) and by IMPROVE (SSO2) at Canyonlands.

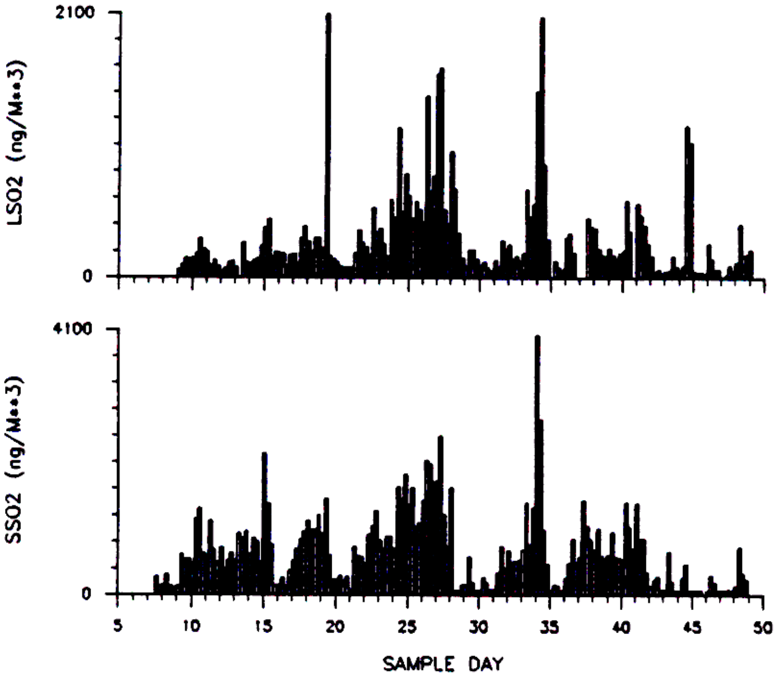

Figure 3E.3: Time plots of SO_2 by Drexel (LSO2) and SO_2 by IMPROVE at Canyonlands.

IMPROVE *vs* BYU (Page)

The IMPROVE and BYU samplers took samples in parallel for an 11-day period from February 5–15. Figure 3E.4 shows the temporal behavior of the three measurements. Figure 3E.5 compares the three individual measurements with the mean. The correlations between any two methods are approximately $r^2 = 0.9$.

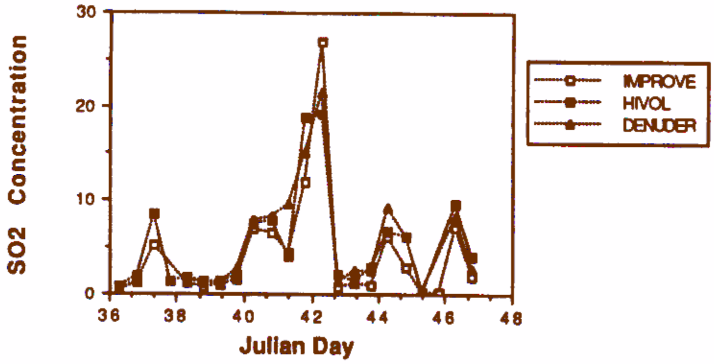

Figure 3E.4: Time plot of IMPROVE, BYU HiVol, and BYU annular denuder samplers for SO_2.

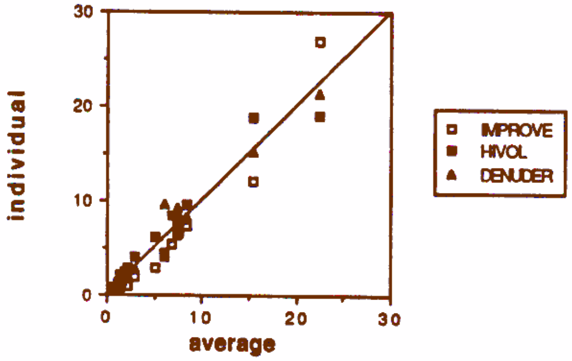

Figure 3E.5: Comparison of SO_2 by IMPROVE, BYU HiVol, and BYU annular denuder samplers at Page for February 5–15.

References

[1] Thornton, D.C., A.R. Driedger, and A.R. Bandy, 1986: Determination of part-per-trillion levels of sulfur dioxide in humid air, *Anal. Chemistry*, **58**, 2688.

[2] Lewis, E.A., C. Benner, L. Lewis, M. Olsen, L.D. Hansen, D.L. Eatough, N.L. Eatough, and P.S. Bhardwaja, 1990: Sulfur and nitrogen oxi-acids present during the WHITEX study as determined by using filter pack and diffusion denuder sampling systems, *Proceedings of the AWMA/EPA International Specialty Conference: Visibility and Fine Particles*, Estes Park, CO, October 15–19.