PMTACS-NY 2001
Data and QA Summary Report for the
Harvard School of Public Health (HSPH)/Allen Sulfate Instrument
February 2002

Overview of Instrument Operation and Data Generation:

- Ambient air stream passes through 5 LPM sharp-cut cyclone, then sodium carbonate denuder, carbon monolith denuder, and Nafion dryer.
- About 0.5 LPM passes through an 8-10 foot long coil of 1/8" O.D. SS tubing heated to 900°C in a tube furnace , then a PTFE filter.
- The sulfate converted to SO_2 in the sample is detected in a low-level pulsed fluorescence SO_2 analyzer.
- Once each hour for 10 minutes, the ambient air stream is diverted through a capsule filter, then through the oven and into the analyzer. This provides a continuous measure of the zero response of the instrument.
- The SO_2 analyzer was operated on the 20 ppbv full scale range. If there is 100% conversion of SO_4 to SO_2, 20 ppbv SO_2 corresponds to nearly 80 ug/m3 of SO_4 at 1 atmosphere and 25°C.
- Data is generated continuously by the TEI Model 43S SO_2 analyzer. The instrument time constant is set to 60 seconds, and the analog output terminals of the analyzer are connected to an ESC Model 8816 data logger.
- The data logger stores the data as minute and hour averaged values. A computer at the site running EDAS Ambient software downloads data from the data logger to the computer each hour.

Data Reduction:

- Minute data stored on the computer is "exported" to an ASCII file in one day increments. These ASCII files are imported into EXCEL for further manipulation. The EXCEL worksheet begins with columns for 1) time; and 2) minute averaged analyzer signal.
- Within EXCEL, the data from 4 to 10 minutes past each hour is used to calculate the zero response signal for that hour. Five three minute averages (4-6, 5-7, 6-8, 7-9, and 8-10) are computed, and the minimum from these three minute averages is taken as the zero. A new zero value is computed for each hour.
- The zero correction signal is subtracted from all of the minute averaged data points for each hour. This results in minute averaged difference signals.
- The minute averaged data is collected in ten minute periods and averaged to yield ten minute averaged data. Each hour yields up to five 10 minute averaged data points, the first ten minute period having been used for the zero correction.
- The difference signals were multiplied by 3.93 to convert from ppbv SO_2 gas concentration to ug/m3 SO_4 concentration.
- Based on a zero air gas replacement test on July 25, 2001 (described below), an additional zero offset of 1.03 ug/m3 was measured. This zero offset was subtracted from the final data.

Period of Operation and Operations Log:

- Instrument began operation on July 21, 2001 at 16:00. The SO_2 analyzer had been calibrated earlier in the day. There was a large (offscale) signal as the SS coil was heated to 900°C for the first time.
- Initially the zero response was measured every 90 minutes.
- On July 23, 2001 the flow demand of the SO_2 analyzer was checked, and the PTFE filter was changed.
- On July 24, 2001 at 12:00 the zero checks were reprogrammed to occur every 60 minutes.
- July 25, 2001: The SO_2 analyzer was calibrated through the heated SS coil. Zero air was directed through the coil and into the analyzer for about 90 minutes. This provided the basis for the "additional zero offset" described above. Following the zero air, a flow containing 10 ppbv of SO_2 was introduced to the heated coil/analyzer system for two hours.
- July 27, 2001: Sodium carbonate denuder in the inlet sample train was changed. The bypass flow was checked and determined to be 4.6 LPM.
- August 5, 2001: Instrument was turn off (oven only initially).

Data Flagging:

The following flags are used for the data generated by this instrument during this campaign:

- V0 Valid Value
- V1 Valid Value, but wholly or partially below the detection limit (se below)
- M2 Missing Value because invalidated by data originator (i.e., zero checks, calibrations, and instrument maintenance.)

The detection limit was determined to be 0.80 ug/m3 SO_4, which was calculated as 3* standard deviation of the blank signal determined in the July 25 zero check period. (As noted above, the mean signal during this period was 0.26 ppbv SO_2, which corresponds to 1.03 ug/m3 SO_4. Thus the detection limit measures the ability to detect signals above the 1.03 ug/m3 zero offset.)

Summary Statistics:

Data from the eight hour warm up period from 16:00 to 23:59 on July 21, 2001 is considered pre-deployment. Deployment period is from 00:00 on July 22, 2001 to 18:00 on August 5, 2001. This makes 2124 ten minute averaging periods, and 354 hour averaging periods. Completeness statistics will be calculated using these totals.

	10 minute averages	Hour averages
Number of unqualified valid values	1656 (78%)	336 (94.9%)
Number of MDL valid values	109 (5.1%)	14 (4.0%)
Total valid values	1765 (83.1%)	340 (98.9%)
Number of missing values	359 (16.9%)	4 (1.1%)

Data Summary:

Summary of SO_4 concentrations measured during period of operation (all data in ug/m3):

	10 minute averaged data	Hour averaged data
Minimum	-.30	.25
25th percentile	1.55	1.54
Median	3.10	3.18
75th percentile	5.19	5.04
Maximum	19.98	18.93
Mean	3.88	3.89

Quality Assurance Experiments:

- SO_2 analyzer was calibrated with a mixture of SO_2 in air 1)directly (through PTFE filter only); and 2)through the zero valve and heated SS coil. The SO_2 came from a NIST certified reference standard cylinder from Scott-Marrin. This was dynamically diluted with UHP zero air using an Environics S100 calibrator.
- Instrument flow and bypass flow were checked with a BIOS DryCal Lite to assure a total flow of 5 LPM for the cyclone.
- Processed data was compared with data from filters, R&P 8400S, PILS, and AMS (ongoing work).

Problems or Issues with the Instrument and/or Data:

- The zero check valve arrangement uses a solenoid pinch valve to cut off the flow of ambient air with particles, while at the same time opening a PFA solenoid valve downstream of a Balston capsule filter. This arrangement substitutes particle free ambient air to the oven and analyzer during the zero check. One possible problem with this set up is that a roughly four inch long piece of latex tubing was used in the pinch valve. It was necessary to use latex because the conductive rubber tubing was too stiff for the solenoid to effectively pinch it shut.
- The data from the instrument showed a characteristic “waveform” pattern that was quite clearly instrumental, and not environmental in nature. Namely, at the end of each “zero period” the analyzer signal would rebound to a higher level, and invariably decay as the hour progressed; until the next “zero period” began and the signal dropped sharply. No good explanation has been discovered for this behavior. It is recommended that the zero check valve arrangement be modified to see if it is responsible for the waveform pattern of the data.