

APPENDIX J

Results of Annular Denuder Sampling
During the December 1990 El Paso Study

Introduction

This appendix summarizes the annular denuder measurements of ambient air taken at the Texas Air Control Board's (TACB's) continuous air monitoring station (CAMS) 6 in the City of El Paso (El Paso) during the winter of 1990-1991. These measurements were a portion of the joint El Paso/Ciudad Juarez inhalable particulate matter (PM_{10}) Receptor Modeling Scoping Study performed by the TACB, United States Environmental Protection Agency, El Paso City-County Health District, Secretariat of Urban Development and Ecology, Sandia National Laboratories, and others. Findings of the preliminary data analyses of the denuder samplers are also presented.

The annular denuder system allows for the accurate measurement of several important, reactive species in polluted urban air. More conventional sampling techniques such as size-selective high volume samplers and dichotomous samplers are subject to substantial measurement errors, due to the interaction of the reactive species on the filter media used to collect these samples. The reactive species which can be more accurately measured by annular denuders include:

- o Gaseous nitrous acid ($HONO$)
- o Gaseous nitric acid (HNO_3)
- o Sulfur dioxide (SO_2)

- o Fine particulate matter sulfates (SO_4^{-2})
- o Fine particulate matter nitrates (NO_3^{-1})

The system is designed to minimize or account for the reactions of these pollutants on the filter media. The TACB publication entitled Report on the Development of the Annular Denuder for Routine Unattended Sampling for Use in Visibility Studies (1989) has a more complete description of the annular denuder system.

Description of the Sampling

The TACB has modified the design of the commercially available annular denuder system produced by University Research Glass of Carrboro, North Carolina. These modifications consist of controlling the flow and sample selection with a Campbell data logger, which regulates the mass flow controllers to maintain a constant flow as well as recording the flow. Eight complete denuder trains are placed in a single box. Each train is connected to one of two sets of manifolds, the flow of which is controlled by solenoids and mass flow controllers. At any given time, either zero, one, or two denuder trains collect samples from ambient air.

The denuder sampling trains consist of a linear array of the following components, which are listed in the order that the air flows through them.

- a. At the inlet, a cyclone sampler which has a size cut point of 2.5 micrometers (μm). This cut point means that particles significantly larger than 2.5 μm are stopped by the cyclone.
- b. One annular denuder coated with a solution of sodium chloride and glycerin in distilled water.
- c. Two annular denuders coated with a solution of sodium carbonate and glycerin in distilled water.
- d. A filter pack containing first a 47-millimeter (mm) teflon filter and then a 47-mm nylon filter. The nylon filters are first cleaned to eliminate sulfur contamination so that the nylon filter can also be used to measure sulfur.

In preparation for the December 1990 study, the staff of the TACB's central laboratory in Austin coated the denuder sections and loaded the filters into the filter packs. After samples were obtained, the denuder trains were disassembled and returned to Austin. The denuders' coatings and filters were extracted in the TACB Laboratory and analyzed by ion chromatography (IC).

Presentation of Results

The results of the denuder analyses are reported in Table J-1. The concentrations are based on flows measured by a mass flow controller/meter. Flows have been corrected for the blank contamination by subtracting the average of the concentrations of ions of three field blanks which were handled in the same manner as the normal sample train, except that no air was pulled through the field blanks. In general, the contamination of the field blanks was relatively small.

The last two columns of Table J-1 are the fraction of the element in gaseous form. These fractions indicate the amount of conversion of gas to particulate matter that has occurred in the air sampled at CAMS 6.

Table J-2 presents the results of collocated samples collected during the study. These samples were collected to estimate the precision of the denuder and IC system. The standard deviation (SD) is the measure of the variability of the measurements. The resultant standard deviation (RSD) is the SD divided by the average of the observation. The RSD is a measure of the relative precision of the denuder systems. A small value of the RSD indicates a precise number. If the RSD is greater than 0.33, then the observation was below the detection limit.

TABLE J-1

Denuder Results for CAMS 6, Winter 1990

START		CONCENTRATION $\mu\text{g}/\text{m}^3$					GAS FRACTION	
DAY	TIME	HNO_3	HONO	SO_2	SO_4^{-2}	NO_3^{-1}	S	N
901202	1705	0.95	0.03	8.20	1.05	1.10	0.92	0.47
901203	505	1.95	-0.48	0.25	0.60	1.70	0.38	0.43
901203	1705	0.88	1.98	9.15	0.68	0.76	0.95	0.82
901204	505	2.80	1.08	1.94	0.69	1.17	0.81	0.78
901204	1705	0.36	2.47	10.79	0.92	7.91	0.95	0.31
901205	505	1.78	-0.41	24.28	1.60	2.57	0.96	0.32
901205	1705	1.31	1.63	13.64	1.37	6.14	0.94	0.36
901206	505	3.47	3.16	29.99	2.60	5.77	0.95	0.57
901206	1705	0.39	1.84	8.57	0.57	2.82	0.96	0.50
901207	505	1.31	2.10	107.64	2.09	3.48	0.99	0.54
901212	1705	0.39	8.60	32.10	2.58	1.57	0.95	0.88
901213	505	0.44	8.08	28.77	1.71	2.56	0.96	0.81
901213	1705	0.16	3.18	13.45	1.55	1.84	0.93	0.70
901214	1705	0.34	8.38	3.44	2.15	0.59	0.71	0.95
901215	505	0.38	14.96	24.80	3.03	3.17	0.92	0.86
901215	655	0.52	8.07	29.36	2.53	0.42	0.95	0.96
901215	1705	0.09	4.62	14.14	1.72	1.11	0.92	0.85
901216	505	0.13	8.07	11.78	0.75	0.90	0.96	0.92
901216	1705	0.08	1.53	20.48	0.63	0.39	0.98	0.84
901217	505	0.98	0.92	11.32	0.80	0.56	0.96	0.80
901217	1705	0.63	9.06	48.81	1.93	1.43	0.97	0.90
901218	505	0.25	3.47	22.60	1.98	2.04	0.94	0.70
901218	1705	0.61	1.61	10.55	1.38	0.64	0.92	0.81
901219	1700	0.18	0.74	10.48	0.38	0.16	0.98	0.88
901221	1705	0.31	1.37	24.77	1.68	0.37	0.96	0.85

TABLE J-1 (continued)

Denuder Results for CAMS 6, Winter 1990

START		CONCENTRATION $\mu\text{g}/\text{m}^3$					GAS FRACTION	
DAY	TIME	HNO_3	HONO	SO_2	SO_4^{-2}	NO_3^{-1}	S	N
901222	505	0.44			1.32	0.79		
901223	505	0.34	0.69	6.54	0.66	0.51	0.94	0.71
901223	1705	1.14	1.04	9.30	0.88	0.62	0.94	0.80
901224	505	0.41	0.09	34.30	1.55	2.08	0.97	0.20
901224	1705	0.62		1.07	0.72	1.37	0.69	0.31
901225	505	0.84	-0.39	186.01	1.45	1.04	0.99	0.23
901225	1705	0.47	4.02	43.89	1.49	1.82	0.98	0.76
901226	505	0.48	4.50	46.86	1.31	3.39	0.98	0.65
901226	1705	0.50	6.59	47.83	1.66	6.04	0.98	0.60
910115	1705	0.52	3.00	32.19	1.08	0.32	0.98	0.93
910116	505	0.68	2.22	12.92	0.73	0.80	0.96	0.82
910116	1705	0.27	1.31	4.79	0.68	0.56	0.91	0.78
910117	505	0.42	2.95	6.41	0.67	0.48	0.93	0.90
AVERAGE		0.73	3.21	25.09	1.35	1.87	0.90	0.67
MAXIMUM		3.47	14.96	186.01	3.03	7.91	0.99	0.96
MINIMUM		0.08	-0.48	0.20	0.38	0.16	0.38	0.20

$\mu\text{g}/\text{m}^3$ - micrograms per cubic meter

S - sulfur

N - nitrogen

TABLE J-2

Precision Data

START	START	CONCENTRATION $\mu\text{g}/\text{m}^3$					GAS FRACTION	
DAY	TIME	HNO_3	HONO	SO_2	SO_4^{-2}	NO_3^{-1}	S	N
901212	1700	0.36	7.82	29.91	2.57	1.77	0.95	0.86
901212	1815	0.41	9.38	34.11	2.59	1.36	0.95	0.90
AVERAGE	1740	0.39	8.60	32.01	2.58	1.57	0.95	0.88
SD		0.03	0.78	2.10	0.01	0.21	0.00	0.02
RSD		0.07	0.09	0.07	0.00	0.13	0.00	0.03
901217	1705	0.69	16.79	54.28	2.62	2.22	0.97	0.91
901217	1705	0.58	1.33	43.35	1.25	0.64	0.98	0.79
AVERAGE	1705	0.63	9.06	48.81	1.93	1.43	0.98	0.85
SD	1705	0.05	7.73	5.46	0.68	0.79	0.01	0.06
RSD	1705	0.09	0.85	0.11	0.35	0.55	0.01	0.07
901224	1705	0.61	-1.22	1.04	0.74	1.41	0.68	-2.50
901224	1705	0.63	-1.58	1.10	0.71	1.33	0.70	10.04
AVERAGE	1705	0.62	-1.40	1.07	0.72	1.37	0.69	3.77
SD	1705	0.01	0.18	0.03	0.02	0.04	0.01	6.27
RSD	1705	0.01	-0.13	0.03	0.02	0.03	0.02	1.66
910115	1705	0.58	3.25	32.11	1.15	0.31	0.98	0.94
910115	1705	0.45	2.75	32.27	1.02	0.33	0.98	0.93
AVERAGE	1705	0.52	3.00	32.19	1.08	0.32	0.98	0.93
SD	1705	0.06	0.25	0.08	0.07	0.01	0.00	0.01
RSD	1705	0.12	0.08	0.00	0.06	0.02	0.00	0.01

TABLE J-2 (continued)

Precision Data

START		CONCENTRATION $\mu\text{g}/\text{m}^3$					GAS FRACTION	
TIME	DAY	HNO ₃	HONO	SO ₂	SO ₄ ⁻²	NO ₃ ⁻¹	S	N
910116	505	0.67	2.02	12.56	0.72	0.79	0.96	0.81
910116	505	0.69	2.42	13.27	0.74	0.81	0.96	0.83
AVERAGE	505	0.68	2.22	12.92	0.73	0.80	0.96	0.82
SD	505	0.01	0.20	0.35	0.01	0.01	0.00	0.01
RSD	505	0.01	0.09	0.03	0.01	0.01	0.00	0.01
910116	1705	0.34	1.61	4.88	0.66	0.51	0.92	0.83
910116	1705	0.20	1.01	4.70	0.71	0.61	0.91	0.72
AVERAGE	1705	0.27	1.31	4.79	0.68	0.56	0.91	0.77
SD	1705	0.07	0.30	0.09	0.02	0.05	0.00	0.06
RSD		0.26	0.23	0.02	0.03	0.08	0.00	0.07
910117	505	0.49	3.14	6.43	0.67	0.46	0.94	0.91
910117	505	0.34	2.75	6.39	0.67	0.49	0.94	0.89
AVERAGE	505	0.42	2.95	6.41	0.67	0.48	0.94	0.90
SD	505	0.08	0.19	0.02	0.00	0.02	0.00	0.01
RSD		0.19	0.07	0.00	0.00	0.03	0.00	0.01

Samples Corrected for Field Blank

In general, the SO₂ measurements were the most precise. This is to be expected, since SO₂ concentrations were highest and the sensitivity of the IC is concentration dependent. The concentrations of HONO were the least precise. This is expected, since the HONO concentration is determined by subtracting two measurements, each of which is a relatively small quantity.

One pair of samples, collected on December 6, 1991, was deleted from the precision table. A very large difference in the individual observations was noted for this pair. When this problem was identified, a TACB engineer from Austin visited the monitoring site to determine the cause of the erratic data. The cause was a faulty power supply to the mass flow controllers. The power supply was replaced on December 12, 1990. The power supply problem caused the invalidation of the samples collected during the period of December 6 to 10, 1990. Data for these samples are not included in Table J-1.

An erratic flow was detected with the invalid samples discussed above. An erratic flow may cause turbulent motion in the denuder. The turbulence deposits particulate matter on the denuder, thus rendering the observations invalid. Since the particle size cut of the cyclone inlet is flow dependent, a low-flow velocity related to an erratic flow will allow particles larger than 2.5 μm to penetrate the sampler.

Discussion Of Results

In general, SO_2 was the species present in highest concentration during the December 1990 study. The concentration tended to peak during the daytime. This suggests that high SO_2 concentrations may be related to inversion breakup conditions during mid-morning and subsequent fumigation from a polluted layer above the ground inversion layer. The high fraction of sulfur in SO_2 , averaging about 0.9, suggests that the emissions were relatively fresh since there was little time for the gaseous sulfur to oxidize to sulfur trioxide (SO_3), combine with water molecules, and accumulate as particulate sulfate.

An important consideration in the proper operation of the annular denuder is the gaseous breakthrough capacity. The breakthrough capacity is the measure of the denuder's capacity to collect a sample. When the denuder's breakthrough capacity for SO_2 is exceeded, some of the gaseous material reaches the filters instead of being collected by the denuder coatings. It would then be erroneously reported as SO_4^{2-} . Once breakthrough occurs, the instrument is no longer operating properly, and the sample data must be invalidated. The sample collected on the morning of December 25, 1990 had the largest SO_2 concentration, about 186 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$). It also had a relatively small SO_4^{2-} concentration, about 1.45 $\mu\text{g}/\text{m}^3$. This data suggests that the breakthrough concentration for SO_2 in this denuder

system is greater than about 1,000 μg of sample, which indicates that the system is useful in areas with large SO_2 concentrations.

Results of sampling for the nitrogen compounds are more complex than for the sulfur compounds. Diurnal trends were not as clear as they were for sulfur compounds. It is surprising that there was not a strong diurnal pattern in HONO concentrations, since HONO rapidly photo disassociates in the presence of ultraviolet sunlight. This may be explained by the fact that the sampling was performed at essentially the winter solstice. The hours that the sun was high enough to allow ultraviolet radiation to reach the ground may have been relatively small.

In general, the measured nitrogen compounds were mostly in the gaseous phase. The average gaseous fraction was about 0.67. As in the case of sulfur compounds, these results suggest that the air parcels were relatively fresh on the days that the samples were collected.

It is assumed that, since the measured HONO and HNO_3 concentrations were significantly less than the SO_2 concentrations, no significant breakthrough has occurred with the gaseous nitrogen compounds.

The highest contribution to the total PM_{10} by sulfates and nitrates, as measured by the annular denuders, occurred on the

night of December 4, 1990. The measured concentration of SO_4^{2-} was about $1 \mu\text{g}/\text{m}^3$, while the concentration for NO_3^{-1} was about $8 \mu\text{g}/\text{m}^3$. Including the associated basic ions and water, the concentration of this inorganic material in PM_{10} should be about $10\text{-}12 \mu\text{g}/\text{m}^3$. This small amount of fine secondary particulate matter would be a small fraction of the PM_{10} standard. This suggests that at this site the contribution of reacted sulfur and nitrogen compounds to PM_{10} was only a small fraction of $150 \mu\text{g}/\text{m}^3$ standard.

The high gaseous concentrations of sulfur and nitrogen compounds not only suggest that the emissions are fresh, but also suggest the possibility of significant positive artifact formation on samples obtained with dichotomous and PM_{10} high volume samplers. A positive artifact is a sampling error where the measurement technique produces more of some pollutant than is actually present in the air. This is likely to occur with the gaseous SO_2 , since both the particles on the filter and filter media itself (such as teflon or quartz) are efficient reaction sites for the conversion of SO_2 to SO_3 , which then rapidly combines with water vapor to form particulate SO_4^{2-} . The positive sampling artifact which can occur without the removal of the SO_2 before the air reaches the filter can be substantial. For example, the sample with the greatest SO_2 concentration was the morning sample of December 25, 1990. The SO_2 concentration was about $186 \mu\text{g}/\text{m}^3$, while the particulate SO_4^{2-} concentration was only about $1.5 \mu\text{g}/\text{m}^3$.

If only 20 percent of the gaseous SO_2 reacted, then the positive artifact could be about 50 to 70 $\mu\text{g}/\text{m}^3$ which would be a significant fraction of the short-term PM_{10} standard. This SO_4^{2-} sampling artifact then could cause an erroneously high PM_{10} measurement.

A comparison between collocated denuder, PM_{10} dichotomous samplers, and PM_{10} size-selective high volume samplers should be made to determine what possible sampling artifacts may be present on measurements made by the latter two samplers. Sulfur is an element which X-ray fluorescence can measure on either dichotomous sampler filters or high volume filters. It is also possible to analyze some of the PM_{10} filters for SO_4^{2-} and NO_3^{-1} by IC. A select set of dichotomous and size-selective high-volume samples will be analyzed by the above techniques to estimate the magnitude of the possible sampling artifact on the samples. The days chosen for the analysis will be those days when the SO_2 concentrations are large. If the sampling artifacts are substantial, then the PM_{10} mass estimates may have to be modified to correct for sampling artifacts.

Conclusions and Recommendations

Based on the analysis of valid denuder measurements, the following conclusions and recommendations can be made.

1. During most of this period, the high gaseous to particle ratios of sulfur and nitrogen suggest that the pollutants in the air parcels are from relatively recent emissions. Significant long-range transport was unlikely. Therefore, the monitoring of background PM_{10} concentrations related to secondary particulate formation may not need to be a high priority in the El Paso area.
2. Positive SO_4^{2-} artifact formation in particulate matter sampling is likely. Artifact formation could result in a substantial increase in "apparent" PM_{10} mass measured during periods of significant SO_2 concentrations. Therefore, annular denuder systems should be deployed during future studies in El Paso to reduce sampling artifact errors. If funds are available, denuders should be located at each intensive PM_{10} monitoring site. This is particularly crucial for the Advanced Transformer site, which typically had the highest fine particulate mass of the five special sites during the December study period.