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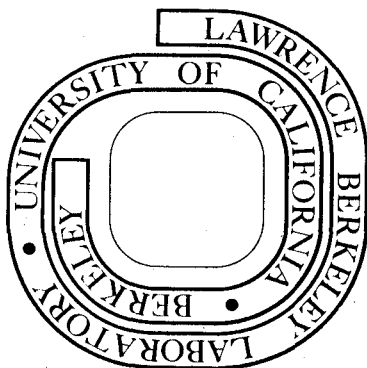
Billy W. Loo, Ray C. Gatti, Fred S. Goulding, and
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LARGE-SCALE MEASUREMENTS OF AIRBORNE PARTICULATE
SULFUR BY X-RAY FLUORESCENCE*

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ABSTRACT

A large-scale aerosol sampling program has now been continuously operating in the St. Louis Regional Air Monitoring System (RAMS) network for a period approaching two years. During that time we have collected approximately 30,000 aerosol samples at ten selected RAMS sites. These samples were collected by automated dichotomous virtual impactors in two particle size fractions of above and below 2.4 μm .¹ Measurements are being performed at LBL for total mass with beta attenuation and elemental compositions with an energy dispersive X-ray fluorescence analyzer.²

In order to evaluate the effectiveness of this approach to large scale monitoring, extensive checks have been made regarding the validity of the sample, the precision, accuracy and long-term stability of the instrument. The accuracy of X-ray fluorescence method itself has been demonstrated by intercomparison studies.³ Special emphasis has been placed on the elemental sulfur determination. Absolute calibration was first performed for copper using accurately known uniform evaporated standards. Calibrations for other elements, excepting aluminum and silicon, were obtained by measuring laboratory aerosol depositions of known elemental ratios. In particular, the calibrations for sulfur were compared using 0.3 μm $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and K_2SO_4 particles deposited on the surface of Nuclepore filters. The two independent bootstrap calibrations agreed to within 1%.

The analysis of fine particle sulfur was much facilitated by the removal of coarse particle interference in the collection process. X-ray attenuation effects due to particle size, particle layer and filter penetration have all been assessed to be typically under a few percent.⁴ Accurate corrections for sulfur in the coarse particle mode generally require detailed characterization of the aerosol.

Interference in the sulfur X-ray intensity caused by the presence of lead has been determined to be $40 \pm 1\%$ using a thin lead polymer standard. The magnitude of this well defined correction factor can be reduced if necessary by modifying the method of spectral reduction.

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To illustrate the precision of the XRF measurement technique, a typical St. Louis fine aerosol sample has been measured repeatedly. Table 1 lists, for each element measured, the mean values and standard deviations of six periodic measurements over a two month period. The minimum detectable limits (MDL)⁵ for a typical analysis time of 1.2 minutes in each of the three excitation energies used for each sample are also listed for comparison. It is seen that for major elements such as sulfur and lead, the reproducibility was about one percent.

In order to express the measured quantities as aerosol concentration in the atmosphere, the performance of the samplers must also be included. Three automated dichotomous virtual impactors were used to collect 12 hour samples side by side at LBL. The sampler calibrations were last set two years ago and two of the samplers (ADAS 4 and ADAS 11) were pulled from the RAMS network after one and a half years of continuous field service. The results are listed in Table 2 and are illustrative of the uniformity and long term stability of the sampler characteristics.

Results from the ten sampling sites in the RAMS network will be presented. Limitations and desirable future technique improvements will be discussed. In particular, the development of an on-line sulfur monitor and the use of more sensitive X-ray techniques for the non-destructive identification of the chemical form of the aerosol species will also be discussed.

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ELEMENT	MEAN AREAL CONCENTRATION (ng/cm ²)	STANDARD DEVIATION (ng/cm ²)	MINIMUM DETECT. LIMIT (ng/cm ²)
Al	226	150	153
Si	214	37	63
P	44	41	40
S	11675	121	34
Cl	224	24	28
K	222	8	12
Ca	196	41	62
Ti	26	19	31
V	11	6	21
Cr	10	6	16
Mn	16	9	13
Fe	337	9	11
Ni	6	2	6
Cu	91	21	7
Zn	495	7	6
Ga	0	0	4
As	3	4	3
Se	6	2	3
Br	84	2	3
Rb	1	1	3
Sr	1	1	4
Hg	0	0	7
Pb	632	3	10
Cd	24	4	4
Sn	30	8	5
Sb	2	2	5
Ba	5	6	22

TABLE 1

ELEMENT	PART. SIZE FRACT.	12 HR SAMPLING PERIOD NUMBER	MEAN CONCENTRATION (ng/m ³)	STAND. DEVIATION (ng/m ³)
S	F	1	771	3
		2	1145	6
		3	1738	9
	C	1	109	11
		2	231	5
		3	269	7
Pb	F	1	632	6
		2	1716	22
		3	1114	15
	C	1	229	6
		2	501	11
		3	378	15
Fe	F	1	67	4
		2	230	5
		3	186	4
	C	1	1015	42
		2	2113	113
		3	1737	79

TABLE 2

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