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### Title

SPURIOUS SULFATE FORMATION ON COLLECTED AMBIENT AEROSOL SAMPLES

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B. W. Loo, R. C. Gatti, A. J. Ramponi,  
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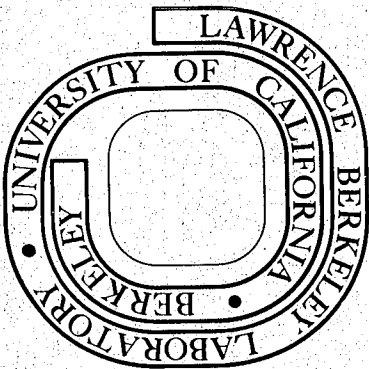
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SPURIOUS SULFATE FORMATION ON COLLECTED AMBIENT AEROSOL SAMPLES\*

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It is known that ambient  $\text{SO}_2$  may be oxidized to  $\text{SO}_4$  on air filters.<sup>1</sup> The amount of such spurious sulfate depends on the alkalinity and hygroscopicity of the filter material. The question still remains whether spurious sulfate may also be formed on the collected aerosol during the sampling period. Serious concerns arose when as much as 40% spurious sulfate was reported to be found from the comparison of parallel samples collected with and without a  $\text{SO}_2$  denuder tube in an airstream prior to filtration.<sup>2</sup>

To investigate the possibility of spurious sulfate formation under field conditions, three similar experiments have been carried out. The first was conducted on the roof of the Federal Building in Charleston, West Virginia. Two identical samplers, each equipped with a flow controller and a 152 cm aluminum inlet tube of 2.8 cm bore were calibrated to sample side-by-side at 5 l/m. The inner surface of one of the tubes was coated with  $\text{MgO}$  to remove  $\text{SO}_2$  from the inlet airstream. The efficiency of such a  $\text{SO}_2$  denuder has been measured by EPA's Environmental Sciences Research Laboratory (RTP, N.C.) to be 99.5% at 50% relative humidity and at an inlet  $\text{SO}_2$  level of 400 ppb ( $1044 \mu\text{g}/\text{m}^3$ ). Samples collected on 37 mm Teflon filters (1  $\mu\text{m}$  pore size) were then analyzed by x-ray fluorescence at Lawrence Berkeley Laboratory (LBL) for sulfur and lead concentrations. Teflon filters, which have excellent resistance to spurious sulfate formation, were chosen such that the effect of  $\text{SO}_2$  on the aerosol particles may be unambiguously studied.<sup>3</sup>

The sampling periods were approximately 12 hours starting at 8 a.m. except for the least two periods which were 24 hours each. The mean 12 hour total particulate S concentration was  $7.88 \mu\text{g}/\text{m}^3$  while the mean  $\text{SO}_2$  concentration as measured 5 km away was  $99.5 \mu\text{g}/\text{m}^3$  (38.1 ppb). Assuming that Pb and S, which are usually found in fine particles, are collected with the same sampling efficiency, then the S to Pb ratios of the parallel samplers can be compared independent of any sampler asymmetry that might exist. The data showed that both the relative S concentration and the relative S/Pb ratio were within 1% from unity, proving the absence of any detectable spurious sulfate formation on the samples.

\*Footnotes.

This experiment was repeated at the Illinois Institute of Technology (IIT). The data on 24 hour samples shown in Table 2 indicates similar results. The comparison of the S concentration in the case of an open filter without an inlet tube shows that an insignificant amount of particle loss occurred in the denuder tubes.

A third experiment was also conducted at IIT. Parallel 24 hour samples were collected with Fluoropore filters (37 mm dia.) at slightly under 5  $\mu$ /m. Various denuder tubes and coating techniques were employed. The IIT denuder was a 122 cm polyethylene tube with a 2.5 cm bore. It also contained a center partition web to enhance the SO<sub>2</sub> removal efficiency. The data summarized in Table 3 reveals no spurious sulfate formation.

The results of these three field experiments indicate, within the uncertainty of a few percent, that no evidence exists for significant spurious sulfate formation on collected ambient aerosols.

### References

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### Footnotes

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Table 1 Results of LBL Samples Collected in Charleston, West Virginia with Aluminum SO<sub>2</sub> Denuder Tubes

Day (May 1977)	Mean Sulfur ( $\mu\text{g}/\text{cm}^2$ )	Mean S/Pb Ratio	Relative S/Pb Ratio	
			with MgO	without MgO
12 (D)	1.96	4.9	.99	1.01
12 (N)	2.45	3.8	.99	1.01
13 (D)	3.36	6.4	1.00	1.00
13 (N)	4.38	5.4	1.00	1.00
14 (D)	3.96	10.3	.99	1.01
14 (N)	4.60	7.2	.99	1.01
15 (D)	1.81	15.0	1.00	1.00
15 (N)	1.15	2.5	1.06	.94
16 (D)	2.90	4.1	1.00	1.00
16 (N)	2.78	5.5	1.00	1.00
17	9.08	8.3	1.01	.99
18	9.30	10.3	.99	1.01
Ave. relative S/Pb Ratio →			1.00	1.00
Ave. relative S Conc. →			.99	1.01

Table 2 Results of LBL Samples Collected in Chicago, Illinois with Aluminum SO<sub>2</sub> Denuder Tubes

Day (Oct. 1977)	Mean Sulfur ( $\mu\text{g}/\text{cm}^2$ )	Mean S/Pb Ratio	Relative S/Pb Ratio		
			with MgO	without MgO	Open Face
3	2.52	.79	.99	.99	1.03
4	2.21	2.41	.98	.97	1.05
5	.75	.69	1.03	1.01	.96
6	1.16	2.10	.98	1.01	1.01
10	1.66	2.94	.94	1.08	.98
12	1.90	.65	.93	.93	1.14
13	1.71	1.28	.99	.96	1.05
17	1.08	1.09	.97	1.02	1.01
18	.94	.85	1.01	.95	1.04
19	2.41	1.42	.97	1.00	1.03
20	2.57	2.64	.99	1.00	1.01
24	4.36	5.59	1.00	.98	1.02
Ave. relative S/Pb Ratio →			.98	.99	1.03
Ave. relative S Conc. →			.99	.99	1.02



Table 3 Results of IIT Samples Collected in Chicago, Illinois, with Various SO<sub>2</sub> Denuder Tubes

Mo./Day (1977)	Mean Sulfur ( $\mu\text{g}/\text{cm}^2$ )	Mean S/Pb Ratio	Relative S/Pb Ratio					
			A*	B*	C*	D*	E*	F*
9/6	1.97	2.48	1.04	.98	1.02	1.05	.95	.98
9/7	2.10	5.12	1.02	1.02	1.00	1.06	.98	.92
9/8	2.74	4.12	1.01	.96	1.21	.96	.94	.92
9/28	1.15	.69	1.03	.98	.95	1.11	.93	1.00
9/29	2.57	1.60	1.08	1.01	.74	1.19	.99	1.00
10/19	1.67	1.01			1.00		1.00	
10/20	1.96	2.01			1.02		.98	
10/24	3.44	3.97			1.08		.92	
Ave. relative S/Pb Ratio →			1.04	.99	1.00	1.07	.96	.96
Ave. relative S Conc. →			1.04	.99	1.01	1.05	.91	1.00

A\* = IIT polyethylene tube with vaseline coating only.

B\* = IIT polyethylene denuder with alcohol dispersed MgO coating.

C\* = IIT polyethylene denuder with MgO on vaseline coating.

D\* = LBL aluminum denuder tube with MgO coating.

E\* = Open face filter.

F\* = Same as B\* except tube was coated over half its length and with center partition plate removed.

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