



Project Summary

Intercomparison of Periodic Fine Particle Sulfur and Sulfate Concentration Results

David C. Camp, Richard J. Paur, and Robert K. Stevens

A one-week study was conducted in August 1979 to evaluate the comparative ability of representative aerosol sampling systems to monitor fine particulate sulfur and sulfate concentrations periodically *in situ*. Participants in the study operated their samplers simultaneously in the same location for the duration of the study. Samplers tested included five modified flame photometric detection instruments and two dichotomous samplers, including one sampler designed to yield near-real-time sulfur concentrations from on-line, wavelength dispersive x-ray fluorescence analysis of fine particles collected on Teflon substrate. All but one of the samplers were operated from a common duct located within the same laboratory; the other was operated on the roof of the building.

Normalized results of all sulfur concentration levels measured for five of the six samplers were 1.0 ± 0.05 . The sixth set gave a result of 0.60 ± 0.14 . After revised results were resubmitted for the sixth set, normalized results for the six sets of hourly sulfur results agreed to within $\pm 8\%$ of their composite-mean values, with standard deviations varying from 9 to 22%. One participating group operated three similar samplers, each calibrated by a different method, that gave normalized results of 1.06 ± 0.12 , 0.93 ± 0.22 , and 1.54 ± 0.25 ; these results point out the need for a standard calibration procedure.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully docu-

mented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In August 1979, a one-week study was conducted at Washington University, St. Louis, to compare a family of air pollution monitoring instruments that are capable of measuring in near-real-time atmospheric concentrations of aerosol sulfur. The main objective of this study was to compare different procedures to measure aerosol sulfur that use flame photometric detectors (FPD's) and an automated semi-real-time x-ray fluorescence (XRF) aerosol sample-analyzer. The instruments that use the FPD's have been used in a variety of air pollution studies, but because each instrument uses a different method of sample conditioning prior to the sulfur measurement, bias in the measurements may exist. This study compared measurements of different automated aerosol sulfur monitors on both simulated and real ambient air samples over a period of 7 days to establish the range of differences between instruments and the basis for variations in response characteristics.

Procedure

Analyzers brought to Washington University by the seven participating groups included five modified FPD instruments and two dichotomous samplers. One dichotomous sampler was designed to report near-real-time sulfur concentrations from an on-line, wavelength dispersive, XRF analysis of the fine particles collected on a filter substrate. All sam-

plers were operated simultaneously, and all but one operated from a common duct leading to a common laboratory. The inlet to the common duct contained an impactor plate particle-sizing device that rejected all particles greater than $3.0 \mu\text{m}$ in aerodynamic diameter. The sampler not using the common duct was operated on the roof above the laboratory.

Results

Concentration of the sulfur measured during the study by the participants consisted of eight sets of hourly fine particulate sulfur values. Only six of eight sets were intercompared. One of the participating groups reported three sets of sulfur data based on three different calibrations methods. Ambient sulfur concentrations measured during the study ranged from just below $1 \mu\text{g}/\text{m}^3$ to $9 \mu\text{g}/\text{m}^3$. Above $6 \mu\text{g}/\text{m}^3$ the five FPD instruments and the automated XRF sulfur analyzer intercompared agreed to within $\pm 25\%$ of their combined composite-mean concentrations. Five of the six agreed to within $\pm 5\%$ of the composite-mean values. All of the automated FPD instruments were able to resolve and measure the relatively sharp sulfur concentration peaks that occurred daily. The source and nature of these short, sometimes multi-peaked, excursions were not investigated.

Three sets of 6-h sulfate concentrations were reported and intercompared. Their concentrations varied from about $2 \mu\text{g}/\text{m}^3$ to $20 \mu\text{g}/\text{m}^3$. At relatively high sulfate concentrations ($\geq 14 \mu\text{g}/\text{m}^3$) all three samplers agreed to within $\pm 10\%$ of their composite 6-h means. Regression analysis of 6-h composite-mean sulfate concentrations, derived from ion chromatographic analysis of fine particles collected with a dichotomous sampler, vs. equivalent 6-h averages for the hourly

sulfur composite-mean values gave a sulfate-to-sulfur ratio of 2.2 for the St. Louis study vs. 3.0 observed in two earlier studies. This ratio remained at 2.2 for both clean and stagnant air and during the transient sulfur excursions. Thus, either all of the sulfur did not occur in sulfate form or the sulfate could not be extracted completely from the filter-types used by all three independent groups.

Three sampling systems operated by the host institution provided results based on three different calibration methods. Their results based on an $(\text{NH}_4)_2\text{SO}_4$ calibration were closest to the composite mean average (1.06 ± 0.12 —an average of all hourly results normalized to the hourly composite-mean values); whereas the sulfur monitors that used SO_2 for calibration differed substantially from the composite mean (1.54 ± 0.25). If either of the two worst-result sets of the eight sets submitted had been the *only* set of sulfur

concentrations measured, the reported hourly sulfur concentrations would sometimes have been as much as a factor of higher or lower than the consensus composite-mean concentrations from the six sets intercompared.

Conclusions and Recommendations

Measurements obtained from FPD systems modified to measure aerosol sulfur and calibrated by appropriate procedure agreed within $\pm 8\%$ with the composite mean. Data from FPD's calibrated using $(\text{NH}_4)_2\text{SO}_4$ had less scatter and were in closer agreement to the composite mean average than data from FPD analyzer calibrated using SO_2 . A standard ASTM type aerosol calibration procedure needs to be developed and documented for routine calibration of instruments used to measure in near-real-time ambient concentrations of aerosol sulfur.

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The complete report, entitled "Intercomparison of Periodic Fine Particle Sulfur and Sulfate Concentration Results," (Order No. PB 84-119 940; Cost: \$10.00, subject to change) will be available only from:

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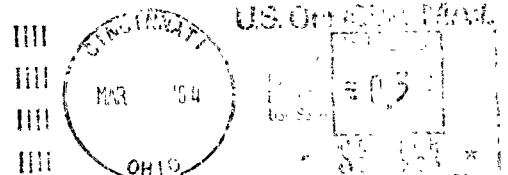
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