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Precision of an Ambient Sequential Acid Aerosol Sampling System

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The repeatability (i.e., precision) of an automated sequential acid aerosol sampling system was investigated by collocating two identical systems on the roof of an air monitoring site in White Plains, New York (a suburb north of New York City) to collect 6 weeks of daily samples during August and September 1989. The variance of the resulting 41 paired samples was derived for each ion measured. The overall coefficients of variation for SO_4^{2-} and NH_4^+ were 7.7 percent and 13 percent, respectively, while estimates for H^+ ranged from 13 percent to 19 percent. Linear regressions relating data from the paired systems resulted in high coefficients of determination ($R^2 > 0.93$) for all ions. Also, time series plots of the daily ion differences indicated no significant difference between the systems for SO_4^{2-}, NH_4^+, and H^+. Paired t-tests of the daily differences affirmed the intersystem agreement for SO_4^{2-} and NH_4^+; however, this test also indicated a paired difference that was statistically significant but small, when compared to the percent coefficient of variation (%C.V.) for H^+. Overall, these results demonstrate and quantify the reliability of this sampling system for characterizing the strong acid content of fine particulate matter. Jaques, P.A.; Thurston, G.D.; Kinney, P.L.; Gorczynski, J.E.: Precision of an Ambient Sequential Acid Aerosol Sampling System. Appl. Occup. Environ. Hyg. 8(4):313-316; 1993.

Introduction

Acidic aerosols containing the unneutralized hydrogen ion (H^+) are normally found in the submicrometer particle fraction (primarily as H_2SO_4 and NH_4HSO_4).(1,2) Particles in this size range can penetrate to the bronchial region of the lung and potentially alter bronchial mucociliary clearance.(3,4) Because of the ubiquitous nature of acid aerosols, the U.S. Environmental Protection Agency (EPA) Clean Air Scientific Advisory Committee (CASAC) recommended that an acid aerosol issue paper be prepared to address the need to list acid aerosols as a separate criteria pollutant for regulation under the Clean Air Act.(1) This provided impetus for an examination of the performance of monitoring systems suitable for acid aerosol measurements in the field. One that is consistent, reliable, relatively easy to handle, and cost efficient would be ideal for this purpose. However, according to the 1989 U.S. EPA Acid Aerosol Issue Paper, no assessments had been completed on the reliability of methods used in field measurements of acid aerosols.(1)

The study reported here assesses the repeatability (i.e., precision) of one acid aerosol measurement method which has seen wide application in the research community and which may be suited to regulatory purposes. The precision of a sampling method has been defined as "a measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions and is best expressed in terms of the standard deviation."(5) Chester(6) described the precision of measurements as an indicator of the repeatability of measurements made within a restricted set of conditions, for example, for individual operators. This current article reports on the repeatability, or precision, of the entire measurement process (including sample flow, extraction, and analysis) for the New York University (NYU) Sequential Acid Aerosol Sampling System. It is based on an analysis of analytic data from duplicate samples collected simultaneously in the same ambient environment with two identical units (i.e., side by side).

Methods and Approach

Two identical, automated, ambient, sequential acid aerosol sampling systems were placed side by side on the roof of a New York State Department of Environmental Conservation (N.Y. DEC) air monitoring site located in a residential part of White Plains, New York. One system was already in place as part of an ongoing epidemiologic study on the health effects of acid aerosols.(7) A second (collocated) sampling system was set up and operated from August 3 to September 12, 1989, for the purposes of this precision study.

Figure 1 presents a schematic of the pneumatic and electronic configuration of the NYU sequential sampling system employed in this research. The impactor-filter unit within the system was originally designed by Marple *et al.*(8) and has been previously used for manual sampling of acid aerosols.(9) The design and application of the entire automated sequential system is described in more detail by

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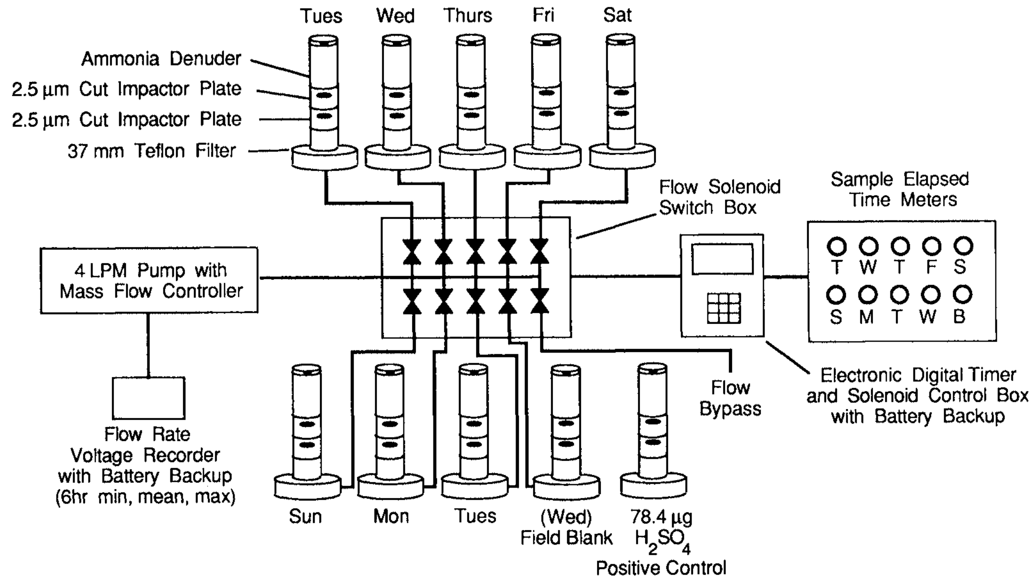

FIGURE 1. Schematic of the NYU sequential acid aerosol sampler.(7)

Thurston *et al.*(10) The impactor of the sequential acid aerosol sampling system selects particles less than 2.5 μm in aerodynamic diameter, where acid particles are predominately found and which can penetrate the bronchial mucociliary region of the lung.

During the 6 weeks of field sampling, 41 pairs of daily filter samples were collected. However, only 40 pairs could be analyzed for H^+ because one of the two pH samples collected on September 10 was voided.

The precision of the collocated systems was estimated from the variation of daily paired differences(11) and was reported as the percent coefficient of variation (%C.V.):

$$\mathrm{C.V.} = \frac{s_{\mathrm{adjusted}}}{\bar{x}_{\mathrm{diff}}} \tag{1}$$

where:

$$s_{\mathrm{adjusted}} = (s^2_{\mathrm{diff}}/2)^{1/2} \tag{2}$$

$$s_{\mathrm{diff}} = \{[1/(n-1)]\Sigma x^2_{\mathrm{diff}} - (\bar{x}_{\mathrm{diff}})^2\}^{1/2} \tag{3}$$

= standard deviation of paired daily differences over 6 weeks of sampling

x_{diff} = difference between individual pairs

$\bar{x}_{\mathrm{diff}}$ = overall mean of paired differences

Results

Correlation of the analytic data from the two systems resulted in very high R^2 values for H^+ (0.93), NH_4^+ (0.97), and SO_4^{2-} (0.99) and align well along a 1:1 line, as displayed in their scatterplots (Figure 2). The close agreement between the paired samplers for all ions can also be seen by inspecting their time series plots (Figure 3), which indicate very little difference between pairs at all concentrations measured. Paired *t*-tests of the overall results clearly indicated no significant difference between the two sampling systems for SO_4^{2-} and NH_4^+ ($p \gg 0.05$), while the difference was small, but significant, for H^+ (mean = 6nm/m³; $p = 0.01$). As summarized in Table I, the overall ion uncertainties (%C.V.) of the paired sequential samplers were calculated, per Equation 1, to be 7.7 percent (SO_4^{2-}), 13 percent (NH_4^+), and 19 percent (H^+).

Discussion

In this study an estimate of precision for particulate acid aerosol measurement by the pH method was made from repeated, collocated measurements with the same sampling system. The Electric Power Research Institute (EPRI) has previously conducted such a precision analysis of repeated Hi-Volume (Hi-Vol) particulate measurements (aerodynamic particle diameter, d_{ae}, < 15 μm, at a 50% cut point) for nine different sites.(12) The mass, sulfate, nitrate, ammonium, and total noncarbonate carbon data were separated into different concentration ranges to account for any concentration-dependent measurement variability. At mean SO_4^{2-} concentrations of 6.8 and 15.8 μg/m³, the EPRI measurements resulted in SO_4^{2-} coefficients of variation of 7 percent and 8 percent, respectively. This compares well with the sulfate results of this study wherein, for the mean of the sampled concentration (87 nmol/m³, or about 8.2 μg/m³ SO_4^{2-}), the estimated coefficient of variation was 7.7 percent (Table I). However, the results for ammonium did not compare as favorably. In the 1.1 to 2.6 μg/m³ range for NH_4^+, the coefficients of variation were 7 percent and 8 percent, respectively, whereas the uncertainly in NH_4^+ measurement for the NYU system was 13 percent at the mean sample concentration of 111 nmol/m³ (or 2.0 μg/m³ NH_4^+). This may be due to the fact that the EPRI Hi-Vol samplers collected a much larger mass, perhaps resulting in less measurement variability on days of low concentration.

Inspection of Figure 3 indicated that one day (August 16) was an outlier and may have overly influenced the analysis. To test this, the precision analysis was repeated after dropping that day's sample pair. This resulted in an increased R^2 (0.97), a substantially reduced coefficient of variation (13%),

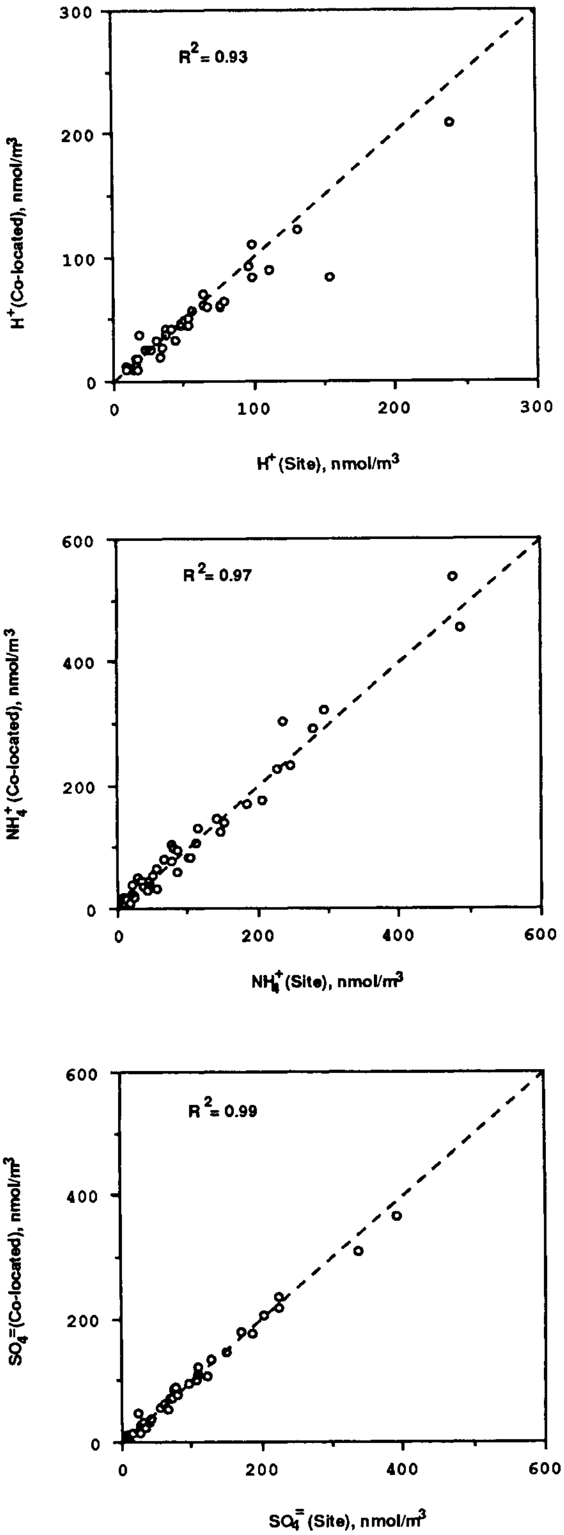

FIGURE 2. Site versus collocated scatterplots of H^+, NH_4^+, and SO_4^{2-} ions (with 1:1 reference line) for 6 weeks (August 3 to September 12, 1989) at White Plains, New York.

and a smaller mean difference between samplers (4.3 nm/m³) for H^+; however, this did not significantly affect the statistics for the other measured ions.

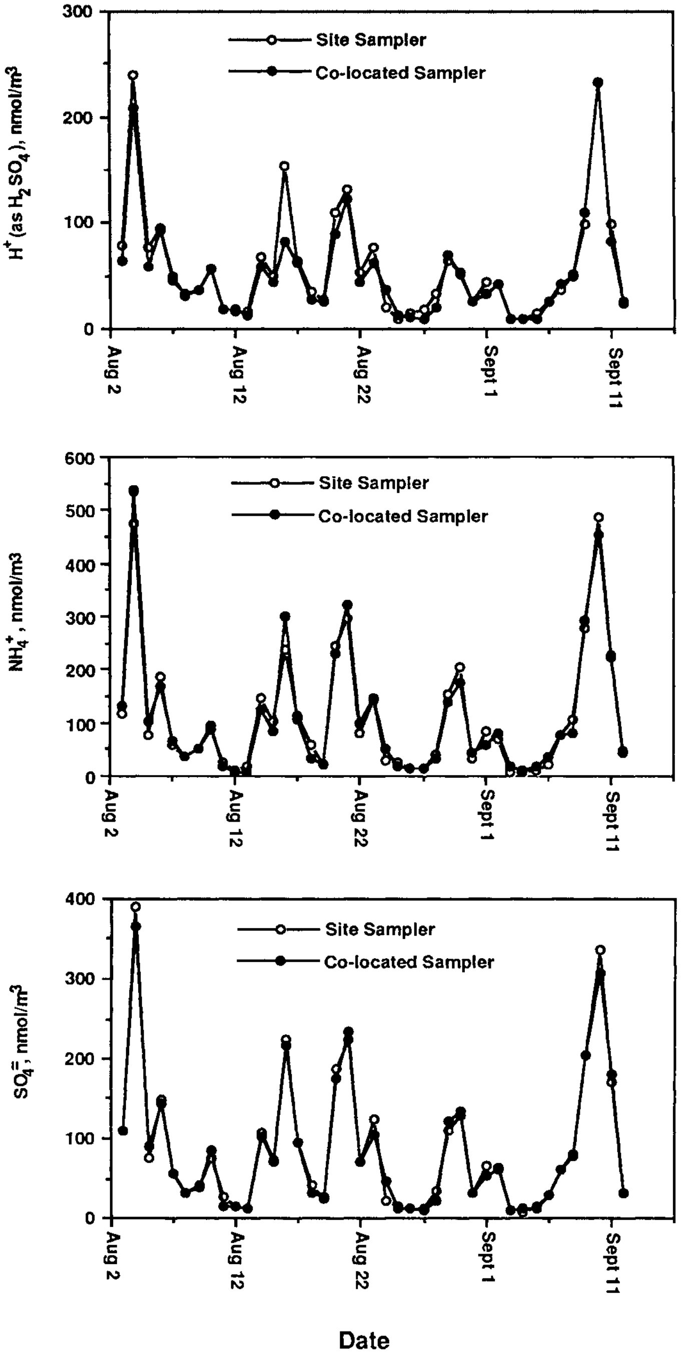

FIGURE 3. Time series plots of H^+, NH_4^+, and SO_4^{2-} for each impactor over the 6-week period (August 3 to September 12, 1989).

The sequential acid aerosol sampling system appears to be a reliable method for determining particulate ion concentrations in ambient environments. The paired systems were highly correlated for all the ions considered ($R^2 \geq 0.93$). Paired *t*-tests for SO_4^{2-} and NH_4^+ similarly indicated that the sequential sampling systems were not different from one another, although this particular test also indicated that they were different for the H^+ ion. However, this H^+ mean difference was small in absolute terms (6.0 nm/m³ for n = 40, and 4.3 nmol/m³ for n = 39), especially when it is compared with the H^+ uncertainty (i.e., C.V. = 13% to 19%).

TABLE I. Mean, Standard Deviation, and Coefficient of Variation as a Percent of Each Ion Measured

	H^+ (as H_2SO_4) (n = 40 pairs)	Sulfate (n = 41 pairs)	Ammonium (n = 41 pairs)
Mean ion concentration (nmol/m^3)	51.2	87.0	111
Mean paired difference (nmol/m^3)	6.0	1.9	−1.5
$S_{adjusted}$ (Equation 2)	9.7	6.7	14.5
C.V. (%)	19	7.7	13

Overall, the calculated uncertainties were relatively low (<20%) for all these ions, with the %C.V. being lowest for sulfate.

Acknowledgments

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