Measurement and Evaluation of Acid Air Pollutants in Chicago Using an Annular Denuder System

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**ABSTRACT**

Filter techniques have commonly been used to collect acidic gases and aerosols of interest in the past. However, an important disadvantage of such a collection procedure is the interaction of gases and aerosols while the sample is on the filter. Recently, an annular denuder system (ADS) has been developed, which selectively removes gases of interest before the respirable particles ($d_{50}$ < 2.5um) are deposited.

The cyclone/annular denuder/filter pack sampling system was used to collect and evaluate an urban ambient data set of pollutants in Chicago. Eighty-one 12-hour average samples, equally divided into day/night intervals, were collected during eight months in spring/summer/fall 1990 and winter 1991. The chemical species measured were $SO_2$ and $NH_3$ in the gas phase and $SO_4^{2-}$, $NO_3^-$, $NH_4^+$ and $H^+$ in the particulate phase. In addition, by using a NaCl-coated denuder, we were able to decouple the collection of $HNO_3$ from $HNO_2$.

Mean concentrations and the range in ( ) were: 0.81 ug/m$^3$ (0.00-4.85) for $HNO_3$; 0.99 ug/m$^3$ (0.16-2.57) for $HNO_2$; 21.2 ug/m$^3$ (1.37-81.2) for $SO_2$; 1.63 ug/m$^3$ (0.11-8.20) for $NH_3$; 4.21 ug/m$^3$ (0.00-19.1) for $NO_3^-$; 5.55 ug/m$^3$ (0.26-34.8) for $SO_4^{2-}$; 2.74 ug/m$^3$ (0.17-12.6) for $NH_4^+$; and 7.70 nmole/m$^3$ (0.00-78.0) for $H^+$. The highest values occurred in the summer except for $HNO_2$ and $NO_3^-$ which had the highest values in the winter. These levels were in the same range as observations in other urban areas.

As checks on the performance of the ADS, $SO_2$ concentrations using the ADS were in excellent agreement (slope of the least squares fit line=1.07, r=0.96) with a calibrated $SO_2$ chemiluminescent analyzer. $SO_4^{2-}$ concentrations from the ADS were also well correlated (r=0.97) with S concentrations from the proton induced x-ray emission (PIXE) analysis of the particulate matter ($d_{50}$<10um). From the linear regression equation between $SO_4^{2-}$ and S, the slope was 3.2 (where the theoretical ratio of molecular weights for $SO_4^{2-}$/S is 3.00). This suggests that the majority of the particulate S in Chicago is in the form of $SO_4^{2-}$.

Sulfate data fell into two groups defined by the absolute humidity and temperature. On days with low humidity (<0.0075 g-water/g-dry air) or low temperature (<14.75 °C), $SO_4^{2}$ concentrations were linearly related to $SO_2$ concentrations (r=0.77 and r=0.75, respectively). This relationship probably reflects primary source contributions, defined as sulfate directly emitted or formed relatively soon after discharge from local $SO_2$ sources. The average primary source contribution to $SO_4^{2-}$ concentration was estimated to be 3.70 ug/m$^3$ which

represents 66% of the average sulfate concentration.

As expected, $H^+$ and $NH_4^+$ were highly related to $SO_4^{2-}$ for all seasons. The measured molar ratios of $H^+/SO_4^{2-}$ suggested that sulfates might be in the composition range of ammonium sulfate ($[NH_4]_2SO_4$) to letovicite ($[NH_4]_3H[SO_4]_2$). However, the molar ratios of $NH_4^+/SO_4^{2-}$ did not directly correspond to these compounds.

The ADS data were collected simultaneously with $PM_{10}$ samples. The particulate matter was analyzed for elemental composition. These composition were combined with the ADS observations and subjected to evaluation using a chemical mass balance receptor model (CMB). From the CMB analysis, the contributions from soil, mobile, coal, steel, refinery and incinerator were 14.6%, 13.9%, 2.3%, 0.6%, 0.3% and 0.2% of the $PM_{10}$. $NO_3^-$ represented an additional 8.8% of the $PM_{10}$. Residual $SO_4^{2-}$ and OC represented an additional 21.8% and 20.4% of the $PM_{10}$, respectively. Other unidentified sources constituted the remaining 17%. From the standpoint of source contributions of sulfur and nitrogen compounds, coal combustion (22.5%) and refinery emissions (22.6%) are the major contributors of ambient sulfur. Mobile sources (87.4%) contributed most of the ambient nitrogen. From the residual analysis of the CMB coefficients, only 51% of the sulfur is accounted for by sources included in the CMB model. In contrast, 98% of the nitrogen is explained by the sources included.