



Project Summary

Analysis System for Total Sulfuric Acid in Ambient Air—Development and Preliminary Evaluation

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A total sulfuric acid analysis (TSAA) system was developed and shown to provide quantitative determinations of sulfuric acid in air at concentrations as low as $0.26 \mu\text{g}/\text{m}^3$. Quantitation at lower concentrations appears to be possible. The general approach in the design and development effort emphasized sample conditioning, rather than detector selectivity, to provide unambiguous detection. Separation of the acid from other sample components was accomplished by stagewise condensation and revaporization; therefore particulate filters were not required. Effects of major potential interferences (SO_2 , NH_3 , and ammonium sulfates) apparently were eliminated by the addition of a small amount of hydrogen chloride to the sample.

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

Introduction

The increase in damage to properties and crops in the United States by fall-out effects of "acid rain" has brought about a greater need for instrumentation to monitor airborne H_2SO_4 . To date, the determination of ambient concentrations of H_2SO_4 is based on exposing a screen-type filter to large quantities of air and analyzing from the filter the total quantity of collected SO_4^{2-} , by x-ray diffraction, and H^+ , by pH measurement. Although this method appears to be the most valid technique currently available, it does suffer from serious limitations. For example, although forced passage of large volumes of air through a screen-type filter appears to be an efficient method of removing H_2SO_4 droplets from the air, the airflow itself adversely affects the stability of the collected H_2SO_4 . Due to the nature of the filtration technique, the local concentrations of H_2SO_4 and other collected particulates on the surface of the filter are increased by several factors (relative to their respective concentrations in the ambient); the surface of the filter thus can serve as a site for enhanced chemical and physical reactions which can take place between the collected H_2SO_4 and such ambient compounds as NH_3 , SO_2 , H_2O , metal oxides and metal salts.

An alternative approach to sampling and analyzing airborne H_2SO_4 has been developed and a pre-prototype instru-

ment incorporating these alternative methods has been fabricated and preliminarily tested. The design, mode of utilization and preliminary results from efficiency tests and interference evaluations that were conducted on the pre-prototype instrument are discussed herein.

H₂SO₄ Analyzer System Design and Operation

The instrumental system is based on the use of stagewise condensation and revaporization to separate H₂SO₄ from other components of an ambient air sample. Following the separation step, potential interferents in the sample (NH₃ and SO₂ in particular) can be eliminated through the action of gaseous HCl added to the sample. Unambiguous detection is thus effected by the sample conditioning steps rather than detector selectivity. A schematic of the overall system is shown in Figure 1. The two major subsystems, i.e., the H₂SO₄ sampler and the FPD analyzer, are described below.

H₂SO₄ Sampler — Sampling Mode

There are two operating modes of the system: the sampling mode and the analysis mode. At initiation of the

sampling mode, a sample stream is drawn into and out of the H₂SO₄ sampler by a vacuum pump, as illustrated by Figure 1. The method by which H₂SO₄ is removed from the sample stream is based on condensation of the H₂SO₄. As the sample gas enters the hot inlet transport tube of the sampler during the sampling mode, the sample gas is rapidly heated to a temperature exceeding the dew point temperature of the H₂SO₄. Within the hot transport tube (before entering the collector tube), the H₂SO₄ thus is believed to be in a vapor state. The H₂SO₄ vapor is then condensed on the cold walls of the collector tube. The remaining gas is ejected from the sampler through the vacuum pump.

It should be noted that H₂SO₄ is not removed from the sample gas through the utilization of a screen-type filter, but, rather, is collected on the cold wall of the tubular collector. Therefore, the non-condensable particulates should not be collected along with the H₂SO₄.

In addition to segregating H₂SO₄ from the non-condensable particulates, the H₂SO₄ sampler appears to be free of NH₃ and SO₂ interferences. This is accomplished through the addition of HCl gas upstream of the hot inlet transport tube and the subsequent reaction of the potential interferents with the HCl. These reactions appear to be preferen-

tial to reaction of the interferents with the H₂SO₄.

The actual mechanisms involved in the reactions of SO₂ and NH₃ with HCl have not been determined, but HCl gas will readily react with NH₃ to form particulate NH₄Cl which would be ejected from the sampler during the H₂SO₄ condensation step. With regard to SO₂, there are several possible reactions which might proceed in the sampler. One possibility is the formation of SOCl₂ which might also be ejected as a solid particulate.

It should be pointed out that if the H₂SO₄ collector in the sampler were a screen-type filter (the conventional collector) in place of a cold condensation surface, the elimination of SO₂ and NH₃ interference in the analysis of H₂SO₄ by the introduction of HCl gas into the sample might *not* occur because particulate reaction products would be collected by the filter.

H₂SO₄ Sampler-Analysis Mode

The analysis of collected H₂SO₄ takes place immediately upon completion of sampling. In the analysis mode, clean air saturated with moisture is drawn into the inlet of the sampler (in place of the sample gas) and is ejected by a vacuum pump downstream of the FPD analyzer. In other words, the FPD analyzer receives *all* the gas swept through the collector tube during the analysis mode. As the moist air passes through the sampler to the FPD analyzer, the internal walls of the collector tube are rapidly heated to drive the H₂SO₄ off the walls of the collector tube to the FPD analyzer for subsequent analysis.

The data representing the analysis of H₂SO₄ from a sample stream are in the form of a chromatogram as shown in Figure 2.

In operation of the H₂SO₄ sampler and FPD analyzer, it is observed that some residual HCl gas will also come off the walls of the collector tube. However, the HCl gas comes off the walls much earlier than H₂SO₄ response in the presence of HCl. In addition, the component (NH₄)₂SO₄, if artificially introduced into the front end of the H₂SO₄ sampler, will come off the walls of the collector tube at a later time than the H₂SO₄. The H₂SO₄ resolution in this case is shown in Figure 3, which is a traced copy of an actual chromatogram.

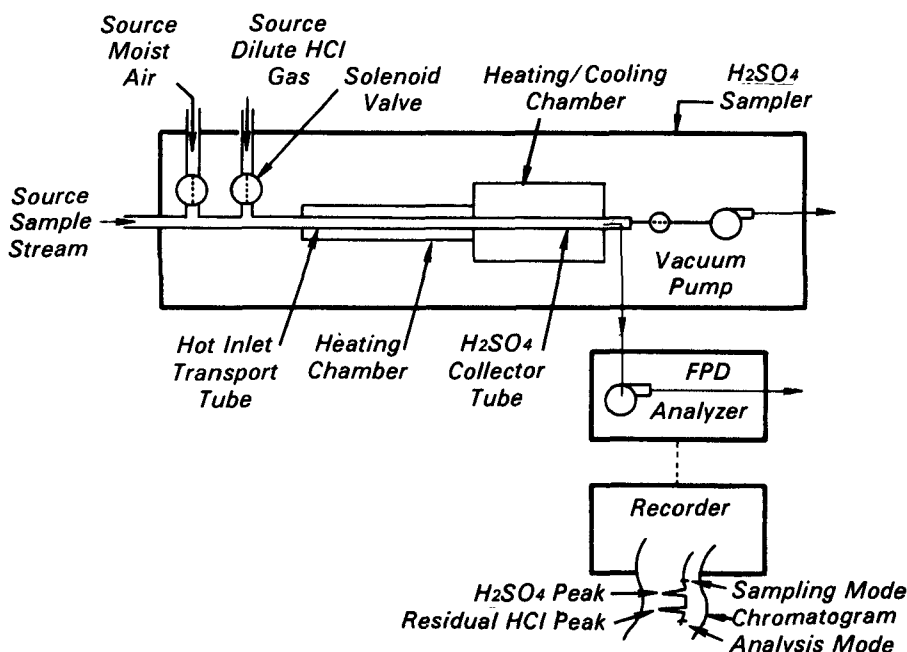


Figure 1. H₂SO₄ Sampler and FPD Analyzer.

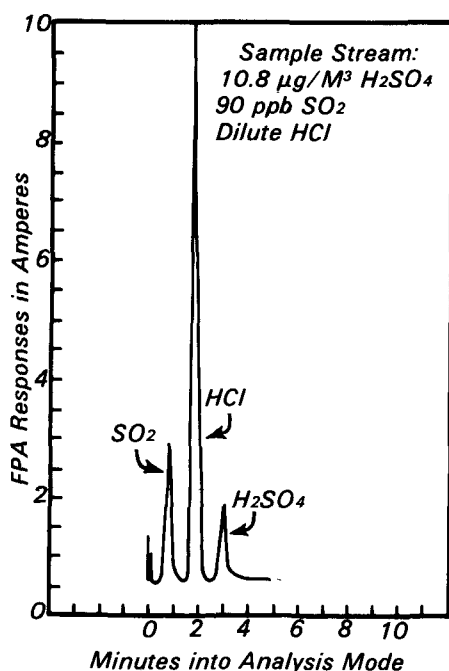


Figure 2. Elimination of SO_2 interference.

Sample Stream: $10.8 \mu\text{g}/\text{M}^3 \text{H}_2\text{SO}_4$
 52 ppb NH_3
 NO HCl
 Sample Volume: 31.3 Liters
 Amperes Full Scale: $1.0 \times 10^{-6} \text{ AFS}$

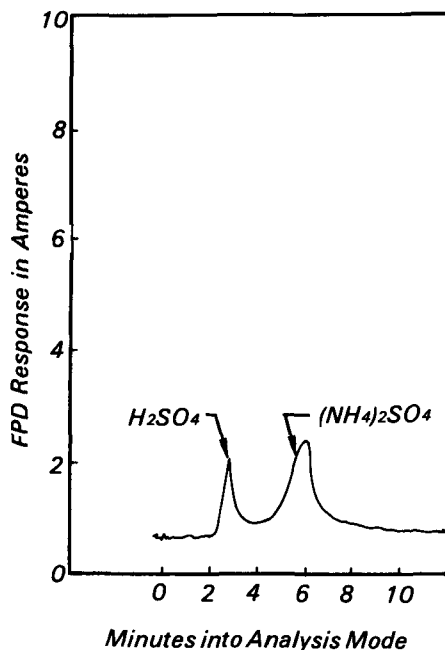


Figure 3. Elimination of NH_3 interference.

FPD Analyzer Operation

An FPD analyzer is basically a flame photometric detector (FPD) with appended supporting sample handling and signal conditioning subsystems. Constant operation conditions are maintained at the FPD and the photomultiplier tube to provide the noise and drift characteristics required for ppb sensitivity and unattended long-term operation.

Hydrogen and sample air are continuously supplied to the analyzer at 140 and 200 ml/min, respectively. The analyzer sample line is connected directly to the downstream side of the H_2SO_4 collector tube in the H_2SO_4 sampler. The pneumatic network maintains precise control of the flow rate of the gas streams leading to and away from the burner block. Since the exhaust gas flow rate is the sum of the hydrogen and sample gas flow rates, indirect control of sample flow rate is achieved by virtue of mass conservation.

Results of Evaluative Tests

The H_2SO_4 sampler/FPD analyzer system described above was evaluated experimentally with a series of laboratory tests. The efficiency of the system in its measurement of H_2SO_4 in air was compared to a more conventional method, which involved collecting H_2SO_4 aerosol on a glass fiber filter and analyzing the filter for H^+ concentration by pH determination. H_2SO_4 aerosol was produced by a nebulizer. Throughout the comparison test the nebulizer was operated with all conditions constant with the exception of the concentration of H_2SO_4 in the nebulizer solution. Solutions containing 1.0N H_2SO_4 were used in the nebulizer to produce levels of collected H_2SO_4 aerosols sufficiently high to allow measurement of H^+ concentration on the glass fiber filters by pH determination. The output (H_2SO_4 concentration in air) of the nebulizer using 1.0N H_2SO_4 as measured by the conventional method, was divided by 1000 to provide an extrapolative comparison with the output from a 0.0001N H_2SO_4 solution used with the new system.

On the above basis, the output of the nebulizer during sampling as determined by conventional filtration was $11.1 \text{ mg}/\text{m}^3$. The standard deviation for 6 data points was 26.7%. The output of the nebulizer from analysis by the developed system was determined to be $11.8 \mu\text{g}/\text{m}^3$, and the standard deviation for 8 data points was 1.8. In addition to

the comparison test, the sampler was challenged by the nebulizer to a level as low as $0.24 \mu\text{g}/\text{m}^3 \text{H}_2\text{SO}_4$ in air, as determined by appropriate dilution of the nebulizer (H_2SO_4) solution. The analyzer measured the output to be $.26 \mu\text{g}/\text{m}^3$.

The sampler was also challenged with significant levels of SO_2 and NH_3 which without the presence of HCl gas in the sample stream would have resulted in extensive analytical interference. The levels of SO_2 and NH_3 in the sample air were 90 ppb and 52 ppb, respectively, and the H_2SO_4 concentration were of the order of $11 \mu\text{g}/\text{m}^3$ throughout the interference tests. There was no measurable interference by the SO_2 and NH_3 when HCl gas was introduced into the sample stream of the sampler/FPD analysis system.

Recommendations

Further development and evaluative testing of the general system and technique described herein are strongly recommended, based on the results obtained to date. Specific recommendations include construction and optimization of several prototype units for field evaluation, extensive testing of the effects of solid particulates on the system, and design and implementation of field evaluation experiments.

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The complete report, entitled "Analysis System for Total Sulfuric Acid in Ambient Air: Development and Preliminary Review," (Order No. PB 81-159 139;

Cost: \$8.00, subject to change) will be available only from:

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