

6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting, and/or measuring, and/or monitoring sulfur trioxide and sulfuric acid, its metabolites, and other biomarkers of exposure and effect to sulfur trioxide and sulfuric acid. The intent is not to provide an exhaustive list of analytical methods. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Many of the analytical methods used for environmental samples are the methods approved by federal agencies and organizations such as EPA and the National Institute for Occupational Safety and Health (NIOSH). Other methods presented in this chapter are those that are approved by groups such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). Additionally, analytical methods are included that modify previously used methods to obtain lower detection limits, and/or to improve accuracy and precision.

6.1 BIOLOGICAL SAMPLES

No methods for determining sulfur trioxide or sulfuric acid in biological materials were located. Studies in which plasma sulfate was measured after exposure to sulfuric acid were not identified. Sulfate is a normal constituent in the blood found at concentrations of 0.8-1.2 mg/dL in humans (Hensyl 1990). Increases in blood sulfate would result in increased sulfate excretion in the urine. Therefore, the measurement of plasma sulfate would not be a very useful indicator of sulfuric acid exposure.

A decrease in saliva pH has been observed in persons occupationally exposed to sulfuric acid (El-Sadik et al. 1972). However, a decrease in saliva pH is not specific to sulfuric acid exposure.

6.2 ENVIRONMENTAL SAMPLES

Methods for measuring sulfur trioxide and sulfuric acid in air, and sulfate in water, are summarized in Table 6-1. Sulfuric acid in air is usually measured as H_2SO_4 or as titratable hydrogen ion (Lioy and Waldman 1989). Measurements are usually made by the collection of aerosols on filters, with subsequent analysis of the concentration of sulfate and other ions, or by continuous analysis. A cascade impactor, which has stages to separate aerosols of different sizes, is often used to measure aerosol size.

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Because of the reactive nature of sulfuric acid, air sampling poses some unique challenges. Difficulties encountered in collecting samples for acid measurements include reversible or irreversible sorption losses onto filters, and equilibrium-driven loss or gain of species as a result of nonsteady-state conditions in the atmosphere of the time period of measurement (Lioy and Waldman 1989). To help avoid sorption losses, treated quartz and teflon filters are recommended rather than glass-fiber filters, which contain a larger number of free basic sites. The loss of strong acid by reactions between co-collected basic and acidic particles can be eliminated by using a coarse particle separator (e.g., a cyclone or impactor inlet) or by sampling for shorter time periods. To prevent neutralization, a denuder is used to scavenge neutralizing species.

Following collection of the sample, acid aerosols are most often quantitated by extracting the aqueous particles from the filter and then measuring levels of ions in the extract by methods such as ion chromatography, pH measurement, or titration (Lipfert et al. 1989). NIOSH recommends ion chromatography (Method 7903) for the determination of sulfuric acid in ambient air (NIOSH 1994a). Method 7903 is a method for the determination of inorganic acids. This method measures the total concentration of six airborne anions. Particulate salts of all of the acids will give a positive interference (NIOSH 1994a). The working range is approximately 0.01-5 mg/ m³ for a 50-L air sample (NIOSH 1994a).

Most of the acid aerosol measurements are completed on a 12- or 24-hour basis. With 24-hour sampling, peaks may be underestimated by as much as 50%, and Lipfert et al. (1989) recommend that ambient sampling be conducted for the shortest practical averaging times on an every-day basis.

Sulfuric acid in air may also be determined using a continuous flame photometric detector with a diffusion denuder tube for sulfur dioxide removal before the detector (Appel et al. 1987). The time resolution for this method is about 6-8 minutes (Lioy and Waldman 1989). The sensitivity of this method is enhanced if sulfur hexafluoride-doped hydrogen gas is used (Lioy and Waldman 1989). The advantages of using flame photometric detector analysis include low maintenance, high sensitivity, fast response, and no interference from nonsulfur species. However, this method is unable to discriminate between sulfur species.

A method has been developed for measuring personal exposure to sulfate, strong acidity (strong H⁺), as well as other gases including sulfur dioxide and ammonia (Brauer et al. 1989; Koutrakis et al. 1988, 1989). In this method, air is collected by a pump at a rate of 4 L/minute and passes through a borosilicate glass impactor that collects coarse particles, through two glass denuders that collect the gases, and through a Teflon

TABLE 6-1. Analytical Methods for Determining Sulfur Trioxide and Sulfuric Acid in Environmental Samples

| Sample matrix | Preparation method | Analytical method | Sample detection limit | Percent recovery | Reference |
|--------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|-------------------------------------------------------------------------|------------------------------------------|-------------------------------------------------|
| Air (H ₂ SO ₄) | Pass through a heater (120° C); then through a diffusion denuder; then through a detector | Continuous FPD | 1–2 µg/m ³ | NR | Appel et al. 1987 |
| | Draw through silica gel tube; desorb with NaHCO ₃ /NaCO ₃ and heat | IC | 0.9 µg/sample | NR | NIOSH 1994a (Method 7903) |
| | Collect on cellulose filter paper; heat for 72 hours; compare charring coloration to standard | Colorimetry | 15 µg/sample (≈0.2 mg/m ³) | NR | NIOSH 1979 (Method 267) |
| | Absorb in water in midjet impinger; precipitate as barium sulfate; measure turbidity at 420 nm | Turbidimetry | 10 µg (0.1 mg/m ³) | NR | NIOSH 1977 (Method 187) |
| | Air collected into mixing chamber; mixed with superheated steam; enters a maze where it is cooled; inertial air/liquid separator separates dissolved and insoluble particles | IC | 2.2 ng/m ³ sulfate | 96.97%, MMAD 0.5 µm; 99.95%, MMAD 0.7 µm | Simon and Dasgupta 1995 |
| | Collection on Chemcassette | Colorimetry | 26 ppb | NR | Zeilweger Analytics 1996 |
| Air—personal exposure (SO ₄ ²⁻ , strong H ⁺) | Air collected through a borosilicate glass impactor, two glass annular denuders, and a Teflon filter pack | IC | 12.7 nmol/m ³ sulfate; 49 nmol/m ³ H ⁺ | NR | Brauer et al. 1989; Koutrakis et al. 1988, 1989 |
| Stack gases | Collect via impinger (using | AT | 40–24,250 mg/m ³ | NR | Knapp et al. 1987 |

TABLE 6-1 Analytical Methods for Determining Sulfur Trioxide and Sulfuric Acid in Environmental Samples (continued)

| Sample matrix | Preparation method | Analytical method | Sample detection limit | Percent recovery | Reference |
|-----------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|----------------------------------------------------------------------------|------------------|-----------|
| (H ₂ SO ₄) | controlled condensation method); titrate using NaOH and bromophenol blue indicator | | | | |
| Stack gases (SO ₃ , H ₂ SO ₄) | Extract isokinetically; separate sulfuric acid mist (including sulfur trioxide) and sulfur dioxide; add isopropanol, titrate using 0.01 M Ba(ClO ₄) ₂ and Thorin indicator | Titration | 0.05 mg/m ³ SO ₃ ; NR H ₂ SO ₄ | NR | EPA 1988 |
| Water, wastes (sulfate) | Pass through a sodium-form cation-exchange column; react with ethanol solution of barium chloride and methylthymol blue at pH 2.5–3.0; raise to pH 12.5–13.0; measure color intensity | Automated colorimetry | 0.5 mg sulfate/L | 90–110% | EPA 1993 |
| Water, wastes (sulfate) | Separate ions of interest on an ion chromatograph; then pass through a conductivity detector | IC | 2.85 mg/L | 75–125% | EPA 1993 |

AT = alkalimetric titration; Ba(ClO₄)₂ = barium perchlorate; FPD = flame photometric detection; H⁺ = hydrogen ion; H₂SO₄ = sulfuric acid; IC = ion chromatography; M = molar; MMAD = mass median aerodynamic diameter; NaCO₃ = sodium carbonate; NaHCO₃ = sodium bicarbonate; NaOH = sodium hydroxide; NR = not reported; SO₃ = sulfur trioxide; SO₄²⁻ = sulfate

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filter pack that collects the fine aerosols. The filters are then analyzed for ions using ion chromatography. The personal monitors can be worn in a backpack with a total weight of about 5 pounds (Suh et al. 1992). In water, sulfate can be measured by calorimetry anion chromatography (EPA 1993). Sulfur trioxide is not found in water because it is hydrated to sulfuric acid in water. Calorimetric analyzers are simple and highly sensitive. Calorimetric analyzers measure a solutions optical absorbance spectrophotometrically; the absorbance is proportional to the concentration of the colored species. However, color intensity is sensitive to temperature, pH, development time, purity of reagents, and age of solutions. Specificity may improve with development time but does not allow a fast response. EPA (1993) recommends that for the ion chromatography method, the samples be stored at 4°C for a maximum of 28 days before analysis.

6.3 ADEQUACY OF THE DATABASE

Section 104(I)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of sulfur trioxide and sulfuric acid is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of sulfur trioxide and sulfuric acid.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.3.1 Identification of Data Needs

Methods for Determining Biomarkers of Exposure and Effect. Biomarkers that show a concentration-related response have not been developed for exposure to sulfuric acid. The pH of saliva is decreased in persons occupationally exposed to sulfuric acid (El-Sadik et al. 1972). Further studies to examine the relationship between air concentrations of sulfuric acid and saliva pH are not needed because such saliva tests are not specific for sulfuric acid.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Methods are available for measuring sulfur trioxide and sulfuric acid in air (Appel et al. 1987; Knapp et al. 1987; NIOSH 1977, 1979, 1994a; Simon and Dasgupta 1995) and sulfuric acid in water (EPA 1993). The development of additional methods to distinguish between sulfuric acid in air and ammonium bisulfate (sulfuric acid partially neutralized by ammonia) are needed (Lioy and Waldman 1989).

6.3.2 Ongoing Studies

Dr. Beverly S. Cohen's group at New York University Medical Center is developing a method to measure ambient acidic particles with a diameter less than 0.05 μm (Cohen 1997).