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 dioxide, its metabolites, and other biomarkers of exposure and effect to sulfur dioxide. 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 dioxide in biological materials were located. Most studies concerning human health effects measure the concentrations of sulfur dioxide in the air or in the water which surrounds the subject. The measurement of sulfur dioxide in biological materials is not a method commonly used because of the rapid conversion of sulfur dioxide to sulfur-containing metabolites. Biomarkers can be used to indirectly measure sulfur dioxide exposure. In a study by Gunnison and Palmes (1974), *S*-sulfonate levels in human plasma showed a positive correlation with atmospheric sulfur dioxide. However, the methods for detecting *S*-sulfonates in human plasma lacked sensitivity and precision (Gunnison and Palmes 1974). If *S*-sulfonate is confirmed as a biomarker of exposure to sulfur dioxide and as methods for determining Ssulfonate in human plasma become more sensitive, detection of S-sulfonates in human plasma may serve as an adequate method for determining exposure to sulfur dioxide.

6.2 ENVIRONMENTAL SAMPLES

Sulfur dioxide has been measured in air, in water, and in food and beverages. Methods for determining levels in the air include ion chromatography, titration, calorimetry, mass spectrometry, conductimetry, amperometric detection, flame photometric detection, and turbidimetry (see Table 6-l). Ion chromatography seems to be the most sensitive of these methods with a detection limit of 3 μg/sample for sulfur dioxide (NIOSH 1994a). Sulfur dioxide has also been measured in stack gases. Methods for measuring sulfur dioxide in stack gases

Table 6-1. Analytical Methods for Determining Sulfur Dioxide in Environmental Samples

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Collect on cellulose filter saturated with Na_2CO_3 preceded by a cellulose ester membrane; oxidize sulfite to sulfate with H_2O_2; elute with $NaHCO_3/NaCO_3$.	IC	3 µg/sample	NR	NIOSH 1994a (Method 6004)
	Absorb in 0.3N H_2O_2; titrate using bromocresol green and methyl red solution.	Titration	Range 0.026–26 mg/m^3 (0.01–10 ppm)	NR	NIOSH 1977 (Method 146)
	Draw air through bubbler containing H_2O_2; add isopropanol; adjust pH with dilute HCl; titrate using 0.01M $Ba(ClO_4)_2$ and Thorin indicator.	Titration	3.4 mg/m^3 (1.3 ppm)	NR	EPA 1995k
	Absorb in potassium or sodium tetrachloro-mercurate; complex heavy metals with EDTA; treat with 0.6% sulfamic acid; treat with formaldehyde and para-rosaniline; read maximal absorbance at 548 nm.	Colorimetry	26 µg/m^3 (0.01 ppm)	NR	Kok et al. 1987b
	Adsorb onto Molecular Sieve 5A; desorb with heat.	MS	2 mg/m^3 (0.8 ppm)	NR	NIOSH 1977 (Method 146)

Table 6-1. Analytical Methods for Determining Sulfur Dioxide in Environmental Samples (*continued*)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
	Remove particles by filtration; impinge air onto surface of hydrogen peroxide solution; record conductivity.	Conductimetry	139 µg/m^3 (~0.05 ppm)	>99	Adams et al. 1971; Nash et al. 1961
	Maintain constant current as sulfur dioxide reduces halogen to halide; measure current.	Amperometric detection	Range 26–5200 µg/m^3) (0.01–2 ppm)	NR	Kok et al. 1987c
	Collect on filter paper saturated with triethanolamine aqueous solution. Convert sulfur dioxide to sulfate.	IC	3.3 µg/m^3	NR	Dariusz et al. 1997
	Collect on fluoro-(aerosol) pore and Na_2CO_3 cellulose (gas) filter in tandem. Collect in bucket. Collect on filters and extract H_2O.	IC and colorimetry	–	–	Okita et al. 1996
	Collect on sodium carbonate treated filter and teflon particulate filter	IC uv/vis	0.14 µg/m^3	>95%	Karakas and Tuncel 1997
	Collect in a dilute solution of H_2O_2. Oxidize SO_2 to sulfate with H_2O_2.	IC	0.44 µg/mL	99%	Velasquez et al. 1996

Table 6-1. Analytical Methods for Determining Sulfur Dioxide in Environmental Samples (*continued*)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
	Filter disks inserted into gas cell. Gas circulation on both sides. Fill cell with test gas.	FTIR	0.5 ppm	NR	Batterman et al. 1997
	Filter extracted in H_2O_2 ultrasonically. Filter and inject solution.	IC	10 ppb	–	Santis et al. 1997
Stack gases	Irradiate sample with pulsed ultraviolet light; pass emitted fluorescent light through broad-band optical filter; detect by photomultiplier tube	PFD	Range 2.6–13,000 mg/m^3 (1.0–4,962 ppm)	NR	Adams et al. 1987
	Collect via impinger (using controlled condensation method); titrate using sodium hydroxide and bromophenol blue indicator	AT	Range 26–15,600 mg/m^3 (10–6,000 ppm)	NR	Knapp et al. 1987
	Extract isokinetically; separate sulfuric acid mist (including sulfur trioxide) and sulfur dioxide; add isopropanol; titrate using 0.01M $Ba(ClO_4)_2$ and Thorin indicator	Titration	1.2 mg/m^3 (0.46 ppm)	NR	EPA 1995c

Table 6-1. Analytical Methods for Determining Sulfur Dioxide in Environmental Samples (*continued*)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Gases	Sample drawn though filter and injected into an evacuated Saran gas bag	GC/TCD	125 ppm	–	Endecott et al. 1996
Gas (flue)	SO_2 removed when flue gas passes.	SNAP (SO_2/NO_2 adsorption process)	–	99	Anonymous 1996a
Gas	Filter pack- collected on NaOH (1% in MeOH) filters.	IC	0.1 µg S/m^3	NR	Makkonen and Juntto 1997
	Absorption solution - air drawn in prefilter and bubbled through 0.3% H_2O_2 solution (solution acidified by perchloric acid).	IC	0.02 µg/m^3	NR	
	Passive sampler - collected on 1% NaOH in MeOH filter.	Molecular diffusion	NR	NR	
Beer	Add mercury stabilizing solution and 0.1N H_2SO_4; add 0.1N NaOH; add para-rosaniline and formaldehyde solutions	Colorimetry	NR	NR	Helrich 1990
Food	Heat in refluxing HCl; add nitrogen gas stream; condense gas into 3% H_2O_2 solution; titrate with NaOH and methyl red indicator	Titration	10 ppm (26.2 mg/m^3)	NR	Kim et al. 1990

Table 6-1. Analytical Methods for Determining Sulfur Dioxide in Environmental Samples (*continued*)

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
	Heat in refluxing HCl; add nitrogen gas stream; condense into Na_2HPO_4/ D-mannitol solution; dilute	AD/IEC-EC	<10 ppm (26.2 mg/m^3)	NR	Kim et al. 1990
	Homogenize with buffer (pH 9) for 1 minute using Polytron; filter extract and immediately inject	AE/IEC-EC	<1 ppm (2.62 mg/m^3)	NR	Kim et al. 1990

AD = acid distillation; AE = alkali extraction; AT = alkalimetric titration; IC = ion chromatography; IEC-EC = ion exclusion chromatography with electrochemical detection; MS = mass spectrometry; NR = not reported; PFD = pulsed fluorescence detection; S = sulfur

include pulsed-fluorescence detection and titration (Adams et al. 1987; EPA 1995k). Sulfur dioxide is not found in water because it is reduced to sulfuric acid in water. Colorimetry, titration, and either acid distillation (AD) or alkali extraction (AE) ion exclusion chromatography (IEC) with electrochemical detection (ED) can be used to measure sulfur dioxide in food and beer (Helrich 1990; Kim et al. 1990). These methods are summarized below.

NIOSH recommends ion chromatography (Method 6004) for the determination of sulfur dioxide in ambient air (NIOSH 1994a). Method 6004 is specific for sulfur dioxide and is applicable to STEL samples; the working range is 0.5-20 mg/m^3 (0.2-8 ppm) for a 100-L air sample (NIOSH 1994a). Sulfur trioxide may give a positive interference for sulfur dioxide.

Sulfur dioxide can also be measured in the air and in stack gases by titration. After separation of sulfur dioxide and sulfuric acid, the quantity of sulfur dioxide can be measured by barium-thorin titration (EPA 1995k). Possible interferents are free ammonia, water-soluble cations, and fluorides.

Colorimetry has been used to measure sulfur dioxide in air and beer (EPA 1986a, 1986b; Kok et al. 1987a, 1987b). Calorimetric analyzers are simple and highly sensitive (Hollowell et al. 1973). Calorimetric analyzers measure a solution's 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, age of solutions, and some atmospheric interferents. Specificity may improve with development time but does not allow a fast response (Hollowell et al. 1973).

Conductimetric analysis measures the increase in conductivity as sulfur dioxide is absorbed into a hydrogen peroxide solution. This method has also been used to measure sulfur dioxide in the air (Adams et al. 197 1). Conductimetric analysis is popular because it of its high sensitivity, fast response, minimal maintenance, and simple operation. The major disadvantage to conductimetric analysis is its susceptibility to interference by nonsulfur dioxide gases that form or remove ions (Hollowell et al. 1973).

Amperometric analyzers can also be used to measure sulfur dioxide in air. Amperometric analyzers measure the current necessary to maintain a constant concentration of titrant as sulfur dioxide reduces the titrant. This method needs minimal maintenance; however, this method is limited by interference from compounds that

react with the titrant (Hollowell et al. 1973). It is applicable to the determination of sulfur dioxide when other sulfur compounds or other interferents do not exceed 5% of the sulfur dioxide concentration (Kok et al. 1987c).

Sulfur dioxide emissions can be continuously detected and determined in stack gases by pulsed fluorescence (Adams et al. 1987). Sample gas is irradiated by pulsed ultraviolet illumination that has passed through an interference filter, while the 90° emitted fluorescent light is passed through a broad band optical filter (240-420 nm) and is detected by a photomultiplier tube. The emitted light is proportional to the concentration of the sulfur dioxide in the sample. Interference may be caused by a build-up of particulate matter and condensed water on all the surfaces in contact with the sample.

Alkalimetric titration is another method for the determination of sulfur dioxide in stack gases (Knapp et al. 1987). This method is applicable to the determination of sulfur dioxide in the range of 26-15,600 mg/m^3 (or 10-6000 ppm). Below these levels, the color change at the end point cannot be visually detected. This lack of sensitivity and the possible interference caused by ammonia, ammonia compounds, and fluorides limit the use of this method. Ion chromatography is much more sensitive and allows much lower detection limits for equivalent sample volumes or better time resolution (shorter sampling times) at the same detection limits.

Sulfur dioxide is used as a fungicide on grapes. Sulfite residues from this use are tolerated up to 10 ppm; however, it is important that adequate methods are available to measure levels that exceed 10 ppm. Three methods have been suggested for the determination of sulfite residues on grapes; however, AE/IEC-ED is the recommended method because it is rapid, straightforward, free from interference, and able to detect sulfite residues at levels far below the limit of tolerance (Kim et al. 1990).

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 dioxide 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 dioxide.

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. No specific methods for determining biomarkers of exposure and effect were identified. Potential biomarkers include plasma S-sulfonate levels and urinary levels of sulfate (Balchum et al. 1960a; Frank et al. 1967; Kleinman 1984; Speizer and Frank 1966; Yokoyama et al. 1971). Further studies examining the accuracy and reliability of these potential biomarkers would be useful.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Methods are available for measuring sulfur dioxide in air (EPA 1995k; NIOSH 1994a; WHO 1979). One difficulty in measuring environmental levels of sulfur dioxide is the interference from other air pollutants, in particular, other sulfur-containing compounds. Accurate methods that are specific to sulfur dioxide and that minimize interference from other sulfur-containing compounds would be useful. Also, research investigating the relationship between observed health effects and levels measured in air, water, soil, and sediment could increase our confidence in existing methods and/or indicate where improvements are needed.

6.3.2 Ongoing Studies

No ongoing studies of improved analytical methods were located for sulfur dioxide.