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June 20, 2000

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June 13, 2000. Prepared for the American Petroleum Institute.**

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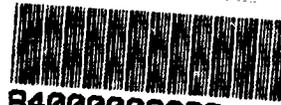
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"Hydrogen Sulfide Ambient and Human Breath Study, Phase 1: Literature Review"

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Hydrogen Sulfide Ambient and Human Breath Study

Phase I: Literature Review

June 13, 2000
Version 2.0

Prepared for the
American Petroleum Institute
Project # DB-08300-83C61

McDaniel Lambert, Inc.



Syngas Sulfide Ambient and Human Breath Study

Phase I: Literature Review

Version 2.0

Prepared for the American Petroleum Institute

George Woodall, Ph.D.

Project No. DB-08300-83C61

June 13, 2000

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SECTION 1. INTRODUCTION

This review discusses the literature from January 1964 to January 2000 concerning the sources of hydrogen sulfide, including the human body, natural, biogenic, and anthropogenic sources. The scope of this search did not include literature on the health effects of hydrogen sulfide. Our objective was to identify measured concentrations of hydrogen sulfide that have been reported in the literature. For all studies, we evaluated the analytical techniques used to measure hydrogen sulfide.

Prior to commencing the current study, our preliminary field measurements indicated that biogenic and other natural sources far exceed industrial contributions. In a rural community on the Central Coast of California, we found average ambient concentrations of approximately 2.0 ppbv, three times the USEPA RfC of 0.7 ppb. Human breath measurements of area residents averaged 48 ppbv. This study was completed to support one of the largest community monitoring plans ever undertaken for a petroleum remediation site.

We conducted the hydrogen sulfide literature review as the first step in a program proposed to the American Petroleum Institute in September 1999. The objectives of the program as a whole are to determine if: 1) low ambient concentrations are ubiquitous and not restricted to downwind of industrial sources and 2) natural and biogenic sources predominate.

The literature review was conducted to determine what is currently known about concentrations of hydrogen sulfide in the human body and the environment. The results of this review will serve to establish a baseline for the next phase of the project, which involves measurements of human and ambient levels of hydrogen sulfide.

The literature review is divided into seven sections. Section 1, Introduction, provides an overview. Section 2, Hydrogen Sulfide in the Human Body, discusses those studies focusing on hydrogen sulfide in the human breath and human gut as well as endogenous hydrogen sulfide. Section 3, Ambient Measurements of Hydrogen Sulfide, focuses on three main sources of hydrogen sulfide: natural atmospheric, biogenic, and anthropogenic. Section 4, Sampling and Analytical Methods, is divided into four main categories: 1) gas chromatography/flame photometric detection, 2) derivatization/fluorimetry, 3) electrochemical sensors, and 4) miscellaneous. Section 5, Literature Search Conclusions, summarizes our findings to date. Section 6 consists of the Bibliography.

We have summarized the more noteworthy papers and have presented the general findings of a number of papers. We have not attempted to summarize each study individually. The Analytical Methods section includes studies that also appear in the other categories, but emphasizes the major techniques that have been used to measure hydrogen sulfide in the human body and the environment. We have presented the analytical data in special detail because of its importance in determining the methods and approach to be used in the next phase of the program.

Following the discussion of the literature, we provide an assessment of the current state of the literature, including data gaps, and offer our conclusions regarding future research needs.

SECTION 2. HYDROGEN SULFIDE IN THE HUMAN BODY

2.1. Human Breath

We found 41 references to reduced sulfides in human breath. All of these studies were conducted by dental researchers who were investigating the causes of breath malodor. The studies looked at both normal populations and those suffering from halitosis. Two main analytical approaches were used in the human breath studies: 1) gas chromatography (GC) with flame photometric detection (FPD) and 2) a portable monitor with an electrochemical sensor. With one exception (Miyazaki, 1995), the studies used relatively small sample populations ranging from 15 to 52 subjects. Studies identified levels of hydrogen sulfide in the human breath ranging from 1 ppbv to 34 ppmv. Below we have discussed some of the more noteworthy papers in more detail.

Blanchette (1976) investigated the use of gas chromatography with flame photometric detection for analysis of hydrogen sulfide and methylmercaptan in mouth air. The study was well conducted. The protocol involved measuring mouth air of ten subjects (unknown sex and unknown health status). Subjects closed their mouths for one minute and nose-breathed. Mouth air measurements ranged from 65 to 698 for hydrogen sulfide and 10 to 188 ppbv for methylmercaptan. The limit of detection using this approach was 7 ppbv for hydrogen sulfide, and 15 ppbv for methylmercaptan.

Kozlovsky (1994) measured levels of reduced sulfide compounds (hydrogen sulfide and mercaptans) using a portable Interscan electrochemical monitor together with a disposable plastic straw connected to inlet of the monitor. The study involved a group of 52 patients, aged 11 to 63 years (35 females) of whom 43 complained of bad breath. Each patient was instructed to bring his/her slightly opened mouth over the straw so that it extended approximately 4 cm into oral cavity. The monitored population included no smokers, no systemic disease, no antibiotic use, and no dentures. The peak volatile reduced sulfide compound concentration was 155 ppbv (mean), and the steady state was 103 ppbv.

Shimura (1996) used a gas chromatograph with detector along with the Interscan electrochemical monitor to identify concentrations of volatile sulfur compounds in 21 volunteers. In those subjects with halitosis, the following mean measurements were made by GC for individuals with halitosis and normal breath respectively: 177.6 and 13.2 ppbv hydrogen sulfide, 251.5 and 4.7 ppbv methylmercaptan, and 57.7 and 7.2 ppbv dimethylsulfide. According to the researchers, there was good general correlation between the GC and the portable monitor.

Another study by Shimura (1997) measured reduced sulfide compounds using the portable Interscan monitor. As a result, all data were presented on logarithmic graph with poor ability to distinguish among individual measurements. The study does show positive correlation between breath malodor and increased reduced sulfur concentrations. Bosy (1994), Miyazaki (1995), Quirynen (1998), and Rosenberg (1991) also used the Interscan portable monitor to measure reduced sulfides in human breath with most results ranging from ~ 40 to ~150 ppbv.

Tonzetich has done the most research on reduced sulfides in breath. In a 1971 study, Tonzetich used gas chromatography with flame photometric detection for analysis of hydrogen sulfide and methylmercaptan in mouth air in 15 non-smoking subjects, aged 10-50. More than 90% of the volatile sulfide compounds measured consisted of hydrogen sulfide and methyl mercaptan, while less than 1 % consisted of dimethylsulfide, with no dimethyldisulfide measured.

In 1977, Tonzetich put together one of the best review articles on reduced sulfides in breath. A review of 54 papers led Tonzetich to conclude that GC/FPD is the most sensitive analytical method for measuring hydrogen sulfide and methylmercaptan in human breath. Some studies under review involved organoleptic evaluation, which demonstrated that 118 ppbv hydrogen sulfide and 25 ppbv methylmercaptan are objectionable concentrations in human breath (Tonzetich, 1964). Other studies showed that these "objectionable" concentrations were exceeded by the early morning mouth air in 50% of population. Hydrogen sulfide and methylmercaptan are produced by decreased saliva flow, decreased drinking of fluids, and proteolytic activity in the oral cavity.

2.2. Human Gut

We found 12 studies that investigated the formation and/or presence of hydrogen sulfide in the human gut. Most of these studies concerned the production of hydrogen sulfide and other reduced sulfide compounds in human flatus. Most of the malodor associated with the human flatus was determined to result from the reduced sulfides, hydrogen sulfide, methyl mercaptan, and dimethylsulfide, with hydrogen sulfide being the largest component. In one of the most comprehensive studies to date, Suarez (1998) measured the concentrations of sulfides in 16 healthy volunteers (6 women and 10 men). Limits of detection for the analytical procedure were not provided in the paper. It was noted, however, that glass, some plastics, and rubber all reacted with sulfur-containing gases, making polypropylene syringes the best alternative for gas collection. The average concentration of hydrogen sulfide measured in flatus using GC/FPD was 25.5 ppmv. The malodor of flatus correlated significantly with the hydrogen sulfide concentration. Suarez (1998) is one of the only studies identified in which concentrations of reduced sulfides were measured directly from human flatus produced *in vivo*. Most of the studies under review investigated the *in vitro* production of gases from fecal material.

2.3. Endogenous Hydrogen Sulfide

We identified six studies in which hydrogen sulfide was measured in normal human tissue and/or found to have a possible role as a neuromodulator in brain and other tissues. The most interesting of these was Abe (1996). The results of this study help support the argument that the body has evolved mechanisms not only to metabolize low concentrations of hydrogen sulfide but also to utilize this chemical as a neuromodulator. Hydrogen sulfide is produced in the brain largely by the metabolism of L-cysteine through the actions of the enzyme cystathionine b-synthase (CBS). CBS is highly expressed in the hippocampus. Physiological concentrations of hydrogen sulfide (50-160 μ M) selectively enhance receptor-mediated responses and facilitate the induction of hippocampal long-term potentiation.

Hosoki (1997) found that endogenous hydrogen sulfide acts as a smooth muscle relaxant by itself, and greatly enhances smooth muscle relaxation induced by nitric oxide. In this study the production of hydrogen sulfide and its ability to act as a smooth muscle relaxant were studied in the ileum, the portal vein, and the thoracic aorta.

SECTION 3. AMBIENT MEASUREMENTS

A total of 52 references were found relating to the measurement of hydrogen sulfide from various sources in the environment in addition to a few papers focusing specifically on analytical methodologies themselves. The types of measurements reported in these papers can be broken down into three categories: 1) natural atmospheric emissions, which involve global cycling, 2) biogenic atmospheric emissions, which look at emission factors from plants and animals, and 3) anthropogenic, which concern man-made emissions. This last category includes a limited number of urban sites but also any activity that generates hydrogen sulfide as a result of human activity, such as livestock farming and landfills.

Ambient measurements of hydrogen sulfide included measurements in a number of diverse locations from various sources, including mobile sources (Watts, 1999), trees (Kindermann, 1995), museums (Hisham, 1991), marine environments (Cutter, 1999), oil fields (Tarver, 1997), wetlands (Cooper, 1987), landfills (Fairweather, 1998), pulp and paper mills (Shooter, 1995), a bird sanctuary (Siegel, 1986), geothermal areas (Shooter, 1995), volcanoes (Bandy, 1982), and wastewater treatment facilities (Devai, 1999). The major sources of global hydrogen sulfide are biogenic (Aneja, 1986; Bates, 1992). Hydrogen sulfide is released from vegetation and produced by the decomposition of organic matter or from bacterial sulfate reduction in the biosphere (Aneja 1986; Brown, 1986).

3.1. Natural Atmospheric

A natural atmospheric emission is defined in this report as an emission that is generated from geological, thermal, hydrothermal, aquatic, volcanic, or other non-biological sources. While some aquatic emissions may result from biological activity or as a secondary breakdown product from biological organisms, we focus on the emissions directly from the water itself.

Ambient air measurements of hydrogen sulfide have often focused on the atmospheric sulfur cycle, primarily in remote locations such as the open ocean. Studies conducted by Andreae (1993), Cutter (1999), Davison (1994), and Shooter (1999) all centered on the emission of hydrogen sulfide or other reduced compounds (primarily dimethyl sulfide, the dominant emittent) from oceanic sources.

The sulfur cycle has been extensively studied over the last few decades, a process that has been accelerated in recent years due to concern about the role of sulfate in global warming (Sze, 1980). Until the 1960s, the question of the role of reduced sulfur in the global sulfur cycle was open (Shooter, 1999), when it was shown that the combined effects of hydrogen sulfide, dimethyl sulfide, carbonyl sulfide, and carbon disulfide were minor in relation to the oxidized forms of sulfur represented in sulfur dioxide and sulfates (Andreae, 1991; Cooper, 1993). Furthermore, hydrogen sulfide is now believed to be nearly non-existent as a component of marine atmospheres, with dimethyl sulfide being the primary source of reduced sulfur (Moller, 1983; Shooter, 1999). Shooter (1999) also suggests that any hydrogen sulfide measured in the marine atmosphere is the result of continental air masses.

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Measurements of hydrogen sulfide in the remote ocean have reported concentrations ranging from 30 pptv (Delmas, 1983) to up to 200 pptv (Shooter, 1999). Detection limits for the methods cited were as low as 0.4 pptv. However, Shooter (1999) also presents strong arguments that weaknesses in the silver nitrate fluorescence quenching analytical method have compromised past measurements, so many of these data points are not useful for accurate calculations.

Most of the natural atmospheric studies consisted of reviews of emission factors from various sources. Bates (1992a, 1992b), Berresheim (1995), Shooter (1999), and Sze (1980) all examined various literature data in attempts to sort out the various components of the natural oceanic atmospheric sulfur emissions. Spiro (1992) presents a high resolution global inventory of sulfur sources. Few of these papers present gas phase concentration values, but cite flux or emissions in mass per unit area per unit time, or in a global atmospheric mass emission rate such as Tg/year.

There were two studies of volcanic emissions of hydrogen sulfide. Mount St. Helens is a major source of sulfur dioxide (900 tons per day); hydrogen sulfide was emitted at 65 tons per day, 7.2 percent of the sulfur dioxide emissions (Bandy, 1982). In a study of passive samplers, Shooter (1995) detected an average of 21 ppbv of hydrogen sulfide at a distance of 1-2 km from both a geothermal field and a pulp and paper mill.

One of the most interesting ambient measurement studies was conducted at a bird sanctuary on Lake Rotorua in New Zealand (Siegel, 1986). The area has significant geothermal activity and sulfur emissions. It is also adjacent to the town of Rotorua. The analytical method (lead acetate type method) was not very sophisticated and had a high limit of detection (5 ppbv). Average concentrations as high as 105 ppbv were measured in the town itself. Average concentrations at some locations in the bird sanctuary were as high as 3.9 ppmv. Given the higher respiration rate of birds and the likely higher exposure than humans to hydrogen sulfide the biologists were surprised at the flourishing and abundant bird life in the area and conclude that "exposures to relatively low hydrogen sulfide concentrations may be less hazardous than has hitherto been assumed". The major problem with this study is that it used the relatively poor method based on lead acetate which has been shown to be inadequate due to photochemically-induced losses of the sulfide reaction product, thereby underestimating actual ambient concentrations.

3.2. Biogenic

Biogenic sources of hydrogen sulfide included vegetation (Brown, 1986), microbes in soil (Adams, 1979), forests (Delmas, 1983; Kinderman, 1995), and wetlands (Cooper, 1987). Two reviews on the topic covered the full range of literature (Aneja, 1986; Berresheim, 1995).

A study of Florida wetlands demonstrated concentrations as high as 62 ppbv using the method of collection on a silver nitrate filter with subsequent extraction of the silver sulfide and detection by fluorescence (Cooper, 1987). Another study of wetlands used cryogenic collection with GC/FPD analysis to examine dimethyl sulfide, finding it at levels from 0.09 ppbv to 0.2 ppbv, with a brief maximum of 0.56 when influenced by polluted air from a nearby paper mill (Berresheim, 1993).

3.3. Anthropogenic

The work done on anthropogenic sulfur sources covers primarily sulfur dioxide and a variety of the reduced sulfur compounds. Of 16 papers found relating to anthropogenic contributions, 6 were on sulfur dioxide and 10 were related to various reduced sulfur compounds, with 7 of those containing discussions of hydrogen sulfide. Specific measurements of general urban hydrogen sulfide are limited mainly to source-impacted sites such as waste water treatment plants, with levels around the plant reaching into the hundreds of ppbv (Devai, 1999). Samples collected around a dairy showed levels ranging from 28-47 ppbv (Clanton, 1999). Measurements in rural West Texas oil production fields showed a range of 1-2 ppbv (Tarver, 1995). Measurements near a pulp mill averaged 10 ppbv (Shooter, 1995).

Data collection studies in general background urban areas used different methods. One limited study provided just two data points from urban areas, showing levels of 0.3 ppbv in Oxford, and 0.05 to 0.26 ppbv in Los Angeles. A study in France used silver nitrate filters with fluorescence detection (Servant, 1982) and reported 0.022 to 0.647 ppbv with the higher concentrations observed in more urbanized areas. Another study by Shooter (1995) using a similar analytical method found levels as high as 0.660 ppbv inside a museum. A study inside a museum (Hisham, 1991) used commercial passive colorimetric samplers, finding up to 1.4 ppbv. However, as discussed below, these methods suffer from interference by other sulfides.

Unpublished data collected by the project team during a large scale petroleum remediation project suggest ambient levels in the 2-4 ppbv range in a small coastal town heavily influenced by diesel and automotive exhaust as well as emissions from the contamination. Several hundred samples collected using Tedlar bags did not detect (<1 ppbv sensitivity), while a hand-held real-time instrument (a gold-film sensor, the Jerome 631-X) with 1 ppbv sensitivity showed detectable levels for nearly all sample sites. The lack of detectable results with the Tedlar bag was attributed to losses during the sampling time (10 hours), and from the delay in sampling until the time of analysis (up to 24 hours).

The research data citing non-remote hydrogen sulfide data suggest an average of less than 1 ppbv of hydrogen sulfide. However, the recent data cited above using the gold-film sensor contradicts this data set. In addition, the California Air Resource Board's data base of statewide air quality data from 1980 to 1997 shows that concentrations in various regions are commonly in the 4-10 ppbv range.

SECTION 4. SAMPLING AND ANALYTICAL METHODS

According to our literature review, three main sampling and analytical methods have been used with varying degrees of success: 1) gas chromatography with flame photometric detection, 2) derivatization with fluorimetric detection (formation of stable derivatives on filters or other media), and 3) sensors of various types. Other analytical methods were used in some special cases and are discussed below under the heading, Miscellaneous. The choice of analytical methods varies widely, depending on the purpose of the study and the detection limit desired. In addition, much of the literature, particularly in the dental arena, shows a lack of sophistication in the application of consistent methods and good laboratory practice. These instances will be discussed in detail.

4.1. Gas Chromatography/Flame Photometric Detection

For the separation and detection of mixtures of chemicals, gas chromatography is the method of choice. However, its correct use requires a consistent high level of attention and experience, attributes that several of the studies cite as reasons for rejecting this method (e.g., Nausch, 1972). A total of 49 papers in our review cited the use of gas chromatography with flame photometric detection. A variety of sample introduction schemes, chromatographic materials, and detection schemes were used, depending on the application.

For sulfur analysis, the application of the selective flame photometric detector (FPD) has the advantage that it allows the detection of only the compounds of interest (i.e., sulfur-containing compounds). The principle of the FPD is based on the formation of chemiluminescent sulfur radical species in a hydrogen-rich flame. Oxygen and hydrogen are added as make-up gases to support combustion with helium or nitrogen typically used as carrier gases. As the compound is eluted from the column and combusted, the constituent elements are excited by the process into higher energy states. When the higher energy states relax to equilibrium, the atoms emit light of a characteristic wavelength. Sulfur emits at 394 nm, and phosphorus at 526 nm. An appropriate interference filter is placed in the radiation path to select the wavelength of light directed to a photomultiplier tube. The interference filter provides the elemental selectivity.

4.1.1. Introduction and Preconcentration of Sample

In general chromatography, the use of direct injection of the sample with a syringe is the most common method of introducing the sample onto the column. A technique related to direct injection is the use of calibrated loops, which was reported in four studies. Nearly half of the studies used simple gas-tight syringes to inject the sample onto the column. The advantage of this approach is the ease of use; however, the potential disadvantage is that the mass of compound applied to the column may be low due to the limited volume that can be injected. Consequently, the detection limit may be high. For the work related to breath analysis, the majority of the papers cited the use of direct injection techniques.

The detection limit can be decreased (i.e., sensitivity increased) by the use of preconcentration approaches to increase the amount of material collected prior to injection onto the GC column. This is typically done with various solid sorbents or cryogenically. The use of sorbents is

problematic due to the high volatility of hydrogen sulfide and its reactivity. MacTaggart (1999) discusses the weaknesses of various sorbents along with their development of a direct measurement system. Davison (1994) presents a list of several sorbents tested for the preconcentration of oceanic air in the determination of dimethyl sulfide, concluding that Molecular Sieve 5A was the most effective, while Steudler (1985) used the same sorbent with Tenax to determine emissions from a New England marsh. Devai (1999) used an unspecified sorbent with thermal desorption to measure reduced sulfur species around waste water treatment plants. However, Tarver (1997) stated that after testing these same sorbents and many others, the researchers were unable to obtain quantitative and reproducible recoveries over tens of cycles. Their approach was to utilize a diffusion denuder followed by desorption onto the GC column.

An alternative to sorbents for preconcentration was the use of cryogenic sample collection or metal foils. Cryogenic sample collection consists of pulling air through a trap immersed in a cryogen such as liquid argon or nitrogen. Seven papers cited the use of cryogenic sample collection, followed by thermal desorption onto the GC column. This approach is effective, but is limited by the cumbersome use of the cryogens and the need for effective water management, as water vapor in the air is the major component of the trapped mixture. Berresheim (1993) used a Nafion dryer upstream of the cryotrap to remove water vapor in a study of wetland regions in the Southwestern U.S. Detection limits down to 3 pptv were achieved through the use of this technique. Goldan (1987) also used Nafion to dewpoints of -25°C , but suffered the loss of analyte, ranging from 1% of COS and CS₂, and up to 30% for hydrogen sulfide and other species. Hoyt (1993) used cryofocus GC/MS to achieve detection limits of 1 ppbv for a list of 20 reduced sulfur species.

Three papers cited the use of gold metal foils as a preconcentration step. These applications were limited to remote oceanic atmospheres where either hydrogen sulfide was ignored, or alternative methods were used to detect it. In these atmospheres, dimethyl sulfide is the dominant material. The metal foil technique is dependent on the formation of a surface metal-sulfur complex. When the metal is heated, the sulfur is desorbed as sulfur dioxide which is subsequently injected onto the GC for detection. This method achieves a very low detection limit but is hindered by a lack of specificity as all sulfur compounds are converted to sulfur dioxide similarly.

4.1.2. Chromatography

A variety of chromatographic columns were used in the literature reviewed, but these consisted primarily of packed columns rather than capillary columns. This preference appears to be due to three factors: 1) many of the papers were not recent enough to reflect the current common use of capillary columns; 2) the simple low resolution analysis of only 3-4 compounds can be easily performed using the older packed column technology, especially since the development of effective capillary coatings specific to sulfur compounds has been a recent phenomenon, and 3) the use of packed columns allows the injection of larger volumes of gas, thus lowering the possible detection limit. Furthermore, a packed column for a limited number of compounds makes for a rapid analysis, often in just a few minutes.

The use of capillary columns for sulfur analysis is now being addressed mainly by column manufacturers who have developed sulfur-specific stationary phases. For example, Supelco has

introduced the SPB-1 capillary column for sulfur species, which has a very low phase ratio of 20 (compared to values of 100 to 400 for typical columns), making it well-suited for analyses of gaseous sulfur compounds.

4.1.3. Detection

The standard flame photometric detector (FPD) was used in the majority of the studies reviewed. Its popularity is mainly due to its position as the only selective detector available for sulfur compounds, at least until recently.

The standard sensitivity of an FPD is generally thought to be on the order of 50 ppbv for a direct injection gas sample. Dominguez (1993) cites detection limits of 40 to 120 ppbv for a standard flame photometric detector for a variety of reduced sulfur compounds, including some industrially important alkyl sulfides. The detection limit is affected by the inherent flame noise (Farwell, 1976). However, preconcentration of the sample can significantly lower the actual detection limit for the sample. In addition, doping (Hill, 1992) of the make-up gas has been used in several studies. Goldan (1987) used SF₆, and Davis (1994) used COS as dopants to achieve detection limits significantly lower than standard approaches, often down to the low pptv range.

Besides the sensitivity, the weaknesses in the FPD have been known for some time. Farwell (1976) cites the following critical difficulties with the FPD: 1) non-linear concentration response; 2) non-uniform sulfur atom response factor; 3) dependence on burner designs for compound specific response factors; 4) quenching by other species present, especially hydrocarbons.

These weaknesses were addressed in the development of an alternative detector, the pulsed flame photometric detector (PFPD), developed and described by Amirav and Jing (1995). This detector relies on the time-dependence of the various elemental emissions as the combustion occurs in the chamber. The gas flow is too low to sustain a continuous flame, which results in a pulsed flame on the order of 0.1 ms. A gated detection scheme coupled with more efficient glass filters allows a greater optical throughput to the photomultiplier. The advantages of this detector are the following: 1) higher sensitivity; 2) improved selectivity; 3) uniform molar response; 4) reduced quenching; 5) wider dynamic range; and 6) lower gas consumption.

Another recent development has been the sulfur chemiluminescence detector (Dominguez, 1993). This detector exploits the chemiluminescence reaction of sulfur monoxide with ozone following combustion (MacTaggart, 1999). The advantages to this detector are 1) sensitivity; 2) linearity; 3) equimolar response; 4) lack of interference. Detection limits have been cited as down to 1 ppbv for a direct analysis of gases (Dominguez, 1993).

A number of other chromatographic methods were found to have been used in the analysis of reduced sulfur compounds.

4.2. Derivatization/Fluorimetry

Another class of sampling and analysis approaches relies on the use of an *in-situ* reaction of hydrogen sulfide with other reagents (mainly metallic salts) to form a stable derivative. These methods can achieve very low detection limits but are constrained by the need to sample the air over an extended period, as well as interference from other common contaminants and the instability of the resultant reaction product. A total of 22 papers using various aspects of this technique were found.

Prior to the development of the more sensitive preconcentration/gas chromatographic approaches to hydrogen sulfide detection, various schemes of integrated sampling on filter substrates were used to achieve sufficiently low detection limits. The majority relied on an *in-situ* derivatization of hydrogen sulfide with various metals such as silver, zinc, cadmium, and lead.

Early methods to capture and analyze hydrogen sulfide relied on its collection into a cadmium hydroxide suspension followed by reaction with p-amino-N,N-dimethylaniline to produce the dye methylene blue. However, this procedure suffered from interference from sulfur dioxide and losses of the collected sulfide (Natusch, 1972). The use of lead acetate to form stable compounds with sulfides was used in several studies, but was discredited by the finding that the lead sulfide decomposed in the presence of light (Natusch, 1974).

The most common derivatization method appears to be the collection of hydrogen sulfide on filter papers impregnated with a solution of silver nitrate, with half of the 22 papers describing its use. In this method, sulfides in the air react with the silver to produce silver sulfides (Ag_2S), which then are analyzed to determine the amount of quenching of fluorescein mercuric acetate. This method has been used in a number of studies to measure low pptv concentrations of hydrogen sulfide. Shooter (1999) presents an analysis of the method, finding that there are three problems with its use: 1) much of its application is near the detection limit, and little uncertainty analysis of this concentration region has been done; 2) other compounds present such as dimethyl sulfide and sulfur dioxide can interfere with the process; and 3) an artifact from the presence of carbonyl sulfide interferes with the analysis. Natusch (1972) also states that mercaptans and ozone cause interferences. Cooper (1987) concluded that all measurements made before 1987 using this method may be in error due to the production of an artifact sulfide.

Similar problems were found using impregnated filter schemes with alternative reactants. A zinc acetate/EDTA spectrophotometric method was found to be susceptible to sulfur dioxide interference, although it detected 44-222 ppbv of hydrogen sulfide in a laboratory (Balasubramanian, 1990). Various other unusual combinations were used in a number of papers, but have not found widespread use.

Overall, the impregnated filter sample collection methods appear attractive due to their simplicity and ability to provide extremely low detection limits, but the inherent lack of selectivity from ubiquitous interferences hinders their use unless knowledge of the other compounds' presence is available. Consequently, accurate quantitative data will always be difficult to achieve when using these approaches.

4.3 Electrochemical Sensors

There are literally dozens of sensors available for the detection of hydrogen sulfide in ambient air at typical health and safety levels of 1-10 ppmv. These detectors are intended for area monitoring for detection of gas concentrations approaching the threshold limit value (TLV) of 10 ppmv and can be as small as a belt clip-on device. However, these sensors cannot achieve the sensitivity required for ambient air concentrations, even less than 100 ppbv.

However, the same company, Interscan Corporation of Chatsworth, California, that has modified its volumetric detector to achieve adequately low detection limits for breath measurements. This device is called the Halimeter, and relies on a small internal pump to pull sample into the single detector chamber for a measurement of what is termed volatile sulfur compounds (VSC). The cited detection limit is 40 ppbv, although some works discussed below have measured lower concentration levels.

The halimeter was used in 9 breath studies to measure VSC as an indication of malodor or halitosis. The largest study reported an average of 46.9 ppbv from a group of 2,672 subjects (Miyazaki, 1995); no range of individual was provided. Bost (1994) detected an average of 39 ppbv in patients without halitosis, but an average of 136 for patients with halitosis. The range for all patients was from ~15 to ~325 ppbv. Kozlovsky (1994) detected concentrations ranging from 102 to 155 ppbv.

Most of these studies showed a lack of good laboratory practices related to measurement accuracy and precision. For example, Rosenberg (1991) reports that better data may have been achieved if daily calibration was performed. In addition, it was noted that methyl mercaptan (the dominant gas present other than hydrogen sulfide) and dimethyl sulfide (present in some ill individuals) can cause significant interferences.

The interference from other sulfides is well known, with response factors from methyl mercaptan cited from 70% of hydrogen sulfide (Rosenberg, 1991) to 50% (personal communication, M. Shaw, Interscan Corp.). This interference is a well recognized phenomenon of electrochemical sensors since the detection chemistry utilizes the production of sulfide anions in a conductive electrolyte matrix.

A zinc oxide sensor was reported in two studies (Shimura, 1996, 1997), which detected from 12 to 100 ppbv in mouth air and gave a moderate correlation with GC/FPD and an odor panel. However, the same limitations for a general sensor of a lack of specificity was noted.

While only two papers were found with reported data (Clanton, 1999; Winegar, 1998), another sensor that produces sufficiently low detection is the Jerome 631-X. This sensor is based on the adsorption of reduced sulfur species on the surface of a gold film, with changes in its resistivity being proportional to the concentration of the adsorbate which is converted into a concentration. This instrument is widely used in the wastewater treatment and petroleum industries for screening for hydrogen sulfide. While it is adequately sensitive to provide levels at and below the odor threshold of approximately 10 ppbv, it too suffers from the same problems with

interferences from other reduced sulfur compounds. The response factors for other common reduced sulfur compounds compared to hydrogen sulfide are up to 40% (Winegar, 1998).

4.4. Miscellaneous Methods

A small number of papers used miscellaneous methods for the measurement of reduced sulfur compounds. Goodwin (1989) used gas dialysis to determine hydrogen sulfide in brain tissue, and Taucher (1996) used proton-transfer mass spectrometry to measure reduced sulfur compounds in human breath. Although most remote sensing systems have poor response to hydrogen sulfide, one study did report its use in determining sulfur gases from a wetland environment (Hines, 1993). Many other papers were found that discussed the use of various methods for the determination of hydrogen sulfide in water, but were deemed not relevant to this report.

One of the more sophisticated approaches that has been used in the past is isotope dilution GC/MS. This method can achieve very low detection limits and high accuracy. Two particular examples are Bandy (1993) and Blomquist (1993). Both reports, however, focus on atmospheric measurements of sulfur compounds, primarily other than hydrogen sulfide.

Besides the methods cited in the research literature, there are a number of other methods used by governmental agencies and industry organizations. However, these methods are primarily directed toward point source sampling and analysis, or occupational settings. Since there is no Federal ambient air quality standard for hydrogen sulfide, EPA has not developed methods for its analysis, although there are methods for measuring point source emissions.

EPA Methods 15 and 16 are described for the point source collection and on-site analysis of hydrogen sulfide and total reduced sulfur. The California Air Resources Board (CARB) has methods 11, 15, and 16 for point source analysis. The analysis method for all these is GC/FPD. OSHA cites its method ID-141, which uses silver nitrate impregnated filter followed by differential pulsed polarography. NIOSH has method 6013 which uses collection onto a charcoal sorbent tube, followed by laboratory desorption and conversion to sulfate and analysis by ion chromatography.

In California, hydrogen sulfide is a criteria air pollutant with a standard of a 1-hour average of 30 ppbv. CARB measures hydrogen sulfide with an automated continuous analyzer based on thermal oxidation to sulfur dioxide, followed by detection of the sulfur dioxide by pulsed UV-fluorescence. In addition, an older wet chemistry method, the cadmium hydroxide method, is cited but is considered obsolete.

The National Council of the Paper Industry for Air and Stream Improvement (NCASI) published a method based on the use of Tedlar bags for the determination of workplace concentrations of reduced sulfur compounds (NCASI, 1993). Weaknesses of this method were noted, such as the relatively low stability of the target species and the activity of metallic fittings.

NCASI also reported on the use of passive card monitors in workplace monitoring (NCASI, 1998). The detection levels were focused on concentrations above 0.1 ppmv, far above ambient

levels, but typical of workplace exposure considerations. Relatively rapid responses were reported, as well as good accuracy at moderate levels, and overall good functionality for the intended use.

Most commercial laboratories suggest the use of Tedlar bags with GC/FPD analysis for ambient air analysis, notwithstanding the known stability issues (Parmar, 1991, 1996). Most laboratories have adapted the EPA point source method for ambient air, although this mainly means that GC/FPD is used for analysis. This recommendation is made primarily because there is no commonly accepted and easily used method for adequately low detection limits for ambient air measurements such as in relation to odor or corrosion studies. One laboratory cites ASTM Method 5504-96 for ambient air. However, this method is described for fuels analysis. The common element is the use of GC with a sulfur chemiluminescence detector.

SECTION 5. LITERATURE SEARCH CONCLUSIONS

The literature search leads to a number of conclusions about human and ambient sources of hydrogen sulfide. While the studies provide some useful baseline information about levels of hydrogen sulfide that have been measured in the human body and the environment, there remain a number of data gaps requiring further research. In addition, the analytical methods used have varied widely in quality and reliability.

Our review of the literature concerning human and ambient sources of hydrogen sulfide has resulted in the following conclusions about results and methods:

Human Body

- Hydrogen sulfide is produced in the human body as a by-product of protein metabolism and is therefore present throughout the human alimentary tract. Breath concentrations of hydrogen sulfide cited in the dental literature ranged from 1 ppbv to 34 ppmv.
- While the dental literature has addressed the level of hydrogen sulfide in the human breath in connection with studies of breath malodor, these studies have not addressed levels of hydrogen sulfide in the human breath in a reliable, consistent manner that would be acceptable to the environmental and toxicological communities.
- Variations of hydrogen sulfide in human breath between individuals have not been analyzed nor have temporal variations over the course of a day and their causes (e.g., hygiene, food intake, exercise). Further, the studies to date tend, on the whole, to be poorly documented.
- Hydrogen sulfide is naturally present in the human body at measurable endogenous levels. There is some evidence to support the role of hydrogen sulfide as both a neuromodulator and smooth muscle relaxant.

Ambient Sources

- Most ambient hydrogen sulfide is a naturally occurring biogenic product.
- Biogenic hydrogen sulfide is released from vegetation, produced by the decomposition of organic matter, and from bacterial sulfate reduction in the biosphere.
- Ambient measurements of hydrogen sulfide have concentrated on remote areas, with little work completed in urban and suburban areas where most people live. The range of concentrations measured in various ambient locations is quite large (low pptv to high ppmv).

In Table 1.0, we have summarized some of the hydrogen sulfide measurements that have been made for human breath and various ambient sources demonstrating the large variability in measurements.

Table 1.0 Reduced Sulfide Concentration (ppbv)

Author/Date/Sample	Analysis Method	Reduced Sulfide	Hydrogen Sulfide	Methymercaptan
Richter, 1964 Breath	MS		3,000 to 34,000	4,000 to 9,000
Blanchette, 1976 Breath	GC/FPD		65 to 698	10 to 188
Miyazaki, 1995 Breath	Electrochemical Sensor	58.6 (mean)		
Suarez, 1998 Flatus	GC/FPD		25,500 (mean)	
Cooper, 1987 Wetland	Derivatization and fluorimetry		62 (max)	
Shooter, 1995 Museum	Derivatization and fluorimetry		0.66 (max)	
Siegel, 1986 Geothermal site	Lead acetate		3,900 (max)	

Analytical Methods

- The analytical techniques used, particularly to gather ambient data, vary widely in their level of sensitivity and repeatability.
- While the ability to analyze hydrogen sulfide at concentrations of 100 ppbv and higher has been demonstrated, the quality of measurements taken at lower levels has been compromised or biased because of the instability of hydrogen sulfide at low levels and through interference from other reduced sulfur species.
- GC/FPD appears to be the most reliable and sensitive of the techniques for measuring hydrogen sulfide in both human breath and the environment.

The literature review has demonstrated some very significant data gaps including the underreporting of urban and suburban hydrogen sulfide concentrations. In addition, the absence of a consistent and reliable analytical methods has left lingering questions about the reliability of the measurements made.

SECTION 6. BIBLIOGRAPHY

Note: All entries have been coded according to subject matter and/or techniques used. The following abbreviations appear at the end of entries to indicate which categories apply:

- A** Measurement of hydrogen sulfide in the ambient environment from various sources, both natural and manmade
- B** Measurement of hydrogen sulfide in human breath
- D** Analytical measurement of hydrogen sulfide by use of derivatization and fluorimetry
- E** Use of electrochemical sensor to measure hydrogen sulfide
- EN** Endogenous measurements of hydrogen sulfide
- G** Measurement of hydrogen sulfide in human gut
- GC** Analytical measurement of hydrogen sulfide by gas chromatography
- M** Miscellaneous analytical paper (e.g., analytical methods, stability, preconcentration)

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