# SAMPLING HYDROGEN SULFIDE IN AIR USING

# DIRECT-READ DIFUSSIVE SAMPLERS

## Data Report

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## Introduction

Hydrogen Sulfide ($H_2S$) is a toxic gas that is produced naturally from decomposition of organic matter. Individuals may be exposed to $H_2S$ released from oil and gas production facilities, petroleum refineries, sewage treatment plants, hot asphalt paving, landfills, animal containment and handling facilities, agricultural pits, iron smelting, pelt processing facilities, and paper production operations [1].

Symptoms of exposure to $H_2S$ include irritation of the eyes, nose, throat and respiratory systems, and death may occur upon exposure to high concentrations of $H_2S$ [2]. Most individuals can detect the characteristic smell of $H_2S$ at concentrations of 0.01 to 1.5 ppm. $H_2S$ has a characteristic smell of "rotten egg"; however, smell alone cannot be used to identify dangerous levels of $H_2S$ because it causes olfactory fatigue [3]. Individuals exposed to $H_2S$ at concentrations between 2 – 5 ppm may experience nausea, tearing of the eyes, headaches and loss of sleep. Symptoms of exposure to 20 ppm $H_2S$ include fatigue, headache, irritability, poor memory and dizziness. At 100 ppm, $H_2S$ causes loss of smell within minutes of exposure and death may occur. Individuals exposed to 700 – 1,000 ppm experience rapid unconsciousness ("knockdown") within 1 to 2 breaths and death within minutes [3].

The U.S. Occupational Safety and Health Administration (OSHA) mandates that exposure to $H_2S$ for general industry workers do not exceed a ceiling limit of 20 ppm anytime during an 8-hour shift, or a peak limit of 50 ppm over a 10-minute period [3]. For workers in construction or shipyard operations, OSHA mandates that exposure to $H_2S$ should not exceed 10 ppm time weighted average (TWA) over an 8-hour shift [3]. The National Institute of Occupational Safety and Health (NIOSH) recommends that exposure to $H_2S$ do not exceed 10 ppm over a 10-minute period (Recommended Exposure Limits, REL), and at 100 ppm $H_2S$ is considered immediately dangerous to life and health (IDLH) [2]. The American Conference of Governmental Industrial Hygienists (ACGIH) established a threshold limit value (TLV) for $H_2S$ of 1 ppm TWA over 8 hours, and a short-term exposure limit (STEL) of 5 ppm [3].

In this report, we describe a new method for monitoring personal exposure to $H_2S$. The method utilizes two components: (1) diffusive ("passive") badges to sample $H_2S$ in air, and (2) an electronic reader to analyze the diffusive sampling badges and provide a TWA value of the concentration of $H_2S$ in air.

## Overview of Method

The method presented here enables rapid and accurate determination of personal exposure to $H_2S$. The method utilizes the following equipment:

1. Diffusive sampling badges to collect $H_2S$ in air;
2. Electronic reader for analyzing sampling badges;
3. Personal computer with operating system Windows Vista or newer version;
4. USB cord to connect personal computer and electronic reader
5. Software CD for first-time installation of reader software;
6. Reference piece for calibration of electronic reader.

An overview of the method for detection and characterization of $H_2S$ exposure is presented in Figure 1. In summary, a sampling badge is placed near the breathing zone of the worker for a well-defined time interval. Appropriate areas for attaching the sampling badge include (i) the lapel or collar of shirt, jacket or coat, (ii) the outside of a breast pocket, or (iii) the brim of hat or helmet. The operator must record the time at which sampling begins and the time at which sampling ends. The total sampling time is necessary to calculate a time-weighted average of the exposure concentration. Following sampling, the badge can be removed from the worker and analyzed using the electronic reader connected to a personal computer. Before inserting the badge in the electronic reader, the protective plastic cover of the badge must be removed. The software installed in the personal computer guides the user to input the sampling time, and outputs the exposure dose (defined as $H_2S$ concentration multiplied by exposure time) and the TWA concentration of $H_2S$. The output TWA concentration is the average concentration of $H_2S$ estimated over the measured sampling time.
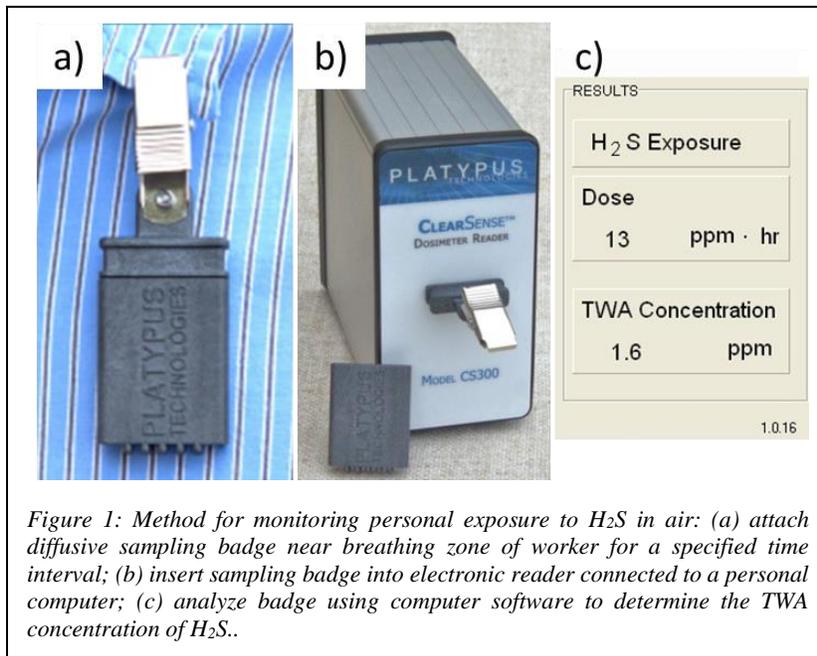
*Figure 1: Method for monitoring personal exposure to H₂S in air: (a) attach diffusive sampling badge near breathing zone of worker for a specified time interval; (b) insert sampling badge into electronic reader connected to a personal computer; (c) analyze badge using computer software to determine the TWA concentration of H₂S..*

This method can be used to determine exposure to $H_2S$ at the recommended or regulatory limits established by NIOSH, OSHA, or ACGIH. This method for monitoring $H_2S$ exposure has an accuracy well below the ±25% of the target concentration, and thus meets OSHA requirements for air monitoring. The advantages of this method are as follows:
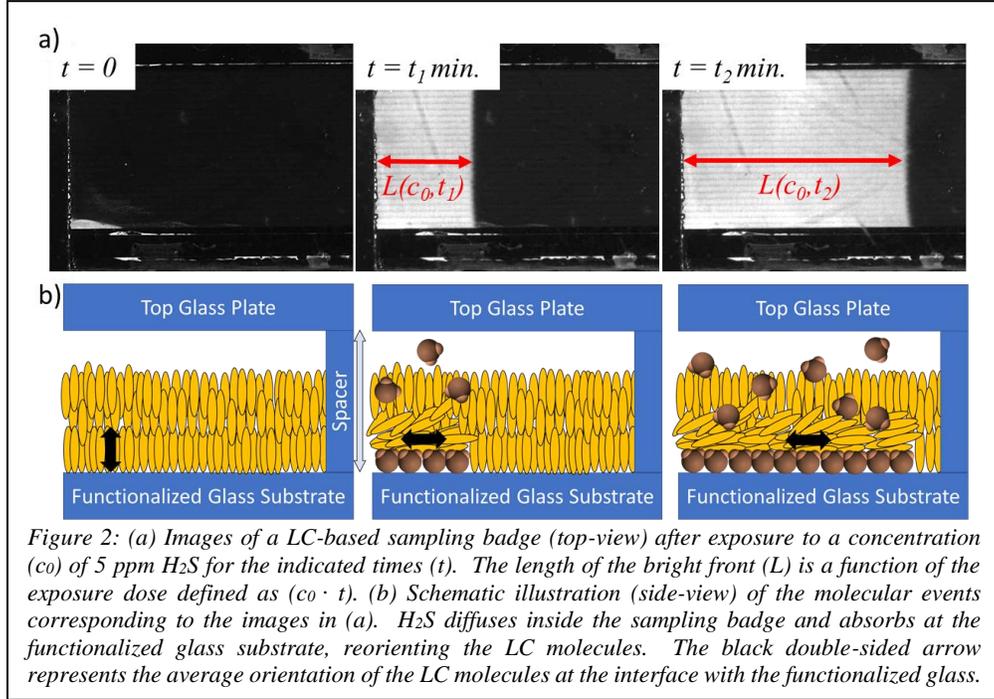
- No laboratory analysis is required;
- No sampling pumps are required;
- Sampling badges do not require calibration or electric power, do not generate noise, and do not require monitoring;
- Sampling badges are inexpensive, small, lightweight, and wearable;
- Sampling badges can be used under a wide range of environmental conditions, and in the presence of hazardous gases;
- TWA concentration of $H_2S$ can be obtained promptly on-site;
- Minimum training is necessary to accurately sample and characterize exposure to $H_2S$;

In addition, this method can be used for area or site monitoring of "hotspots" for $H_2S$ using various badges places in several locations in and around the target area.

## Technology

In this section, we describe the technology and mechanism of $H_2S$ sampling using the method described in this report. The passive sampling badge that collects $H_2S$ consists of a thin film of liquid crystal (LC) enclosed between two parallel rectangular glass plates separated by a U-shaped spacer. Three of the four edges of the rectangular plates are sealed, while the fourth edge is open to atmospheric air. $H_2S$ diffuses through the gap of the inlet between the glass plates and absorbs at the functionalized glass substrate, leading to a change of the optical properties of the LC. When viewed with crossed-polarized light, an unexposed badge appears dark but a badge that has been exposed to $H_2S$ exhibits a bright band whose length depends on the exposure time and concentration of $H_2S$. In Figure 2a we present photographs of the sampling badge exposed to 5 ppm of $H_2S$ at three different time intervals. The length of the bright band (response length) in the exposed sampling badges increases with increasing exposure time or increasing concentration of $H_2S$. For this reason, in Figure 2a the response length is denoted as $L(c_0, t)$, where $c_0$ is the concentration of $H_2S$ and $t$ is the exposure time.
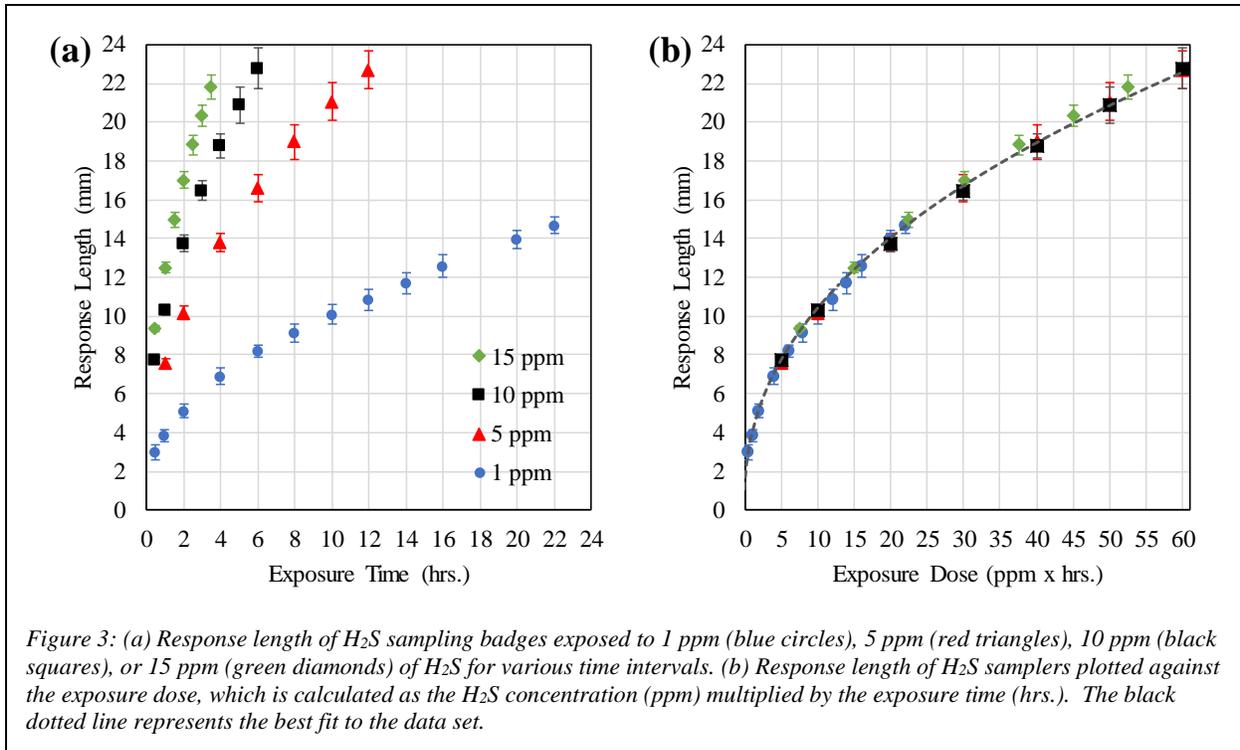
The images in Figure 2b illustrate the molecular mechanism of $H_2S$ detection using the sampling badges described herein. The LC film enclosed in the sampling badges is composed of rod-shaped molecules that align perpendicular to the supporting glass substrate, which is functionalized with a proprietary layer that selectively absorbs molecules of $H_2S$. When $H_2S$ diffuses inside the badge, it quickly absorbs at the LC-glass interface. The LC molecules immediately change orientation, from perpendicular to parallel to the surface, in response to the presence of the absorbed $H_2S$. This change in organization of the LC molecules at the interface with the functionalized glass results in a change in the optical properties of the LC film. As more $H_2S$ diffuses inside the sampling badge and absorbs at the functionalized glass surface, more LC molecules re-orient and the observed response length of the sampling badge increases.

*Figure 2: (a) Images of a LC-based sampling badge (top-view) after exposure to a concentration ($c_0$) of 5 ppm $H_2S$ for the indicated times (t). The length of the bright front (L) is a function of the exposure dose defined as ($c_0 \cdot t$). (b) Schematic illustration (side-view) of the molecular events corresponding to the images in (a). $H_2S$ diffuses inside the sampling badge and absorbs at the functionalized glass substrate, reorienting the LC molecules. The black double-sided arrow represents the average orientation of the LC molecules at the interface with the functionalized glass.*

The data plot in Figure 3a depicts the measured response length of the sampling badges (in units of millimeters) as a function of exposure time to $H_2S$ at concentrations of 1 ppm, 5 ppm, 10 ppm, or 15 ppm (ppm = parts per million of $H_2S$ in air). As demonstrated in this plot, for a fixed concentration of $H_2S$ the response length increases with increasing exposure time (units of hours). Similarly, for a fixed exposure time the response length is larger for higher concentrations of $H_2S$ than for lower concentrations of $H_2S$ (units of ppm). These two observations demonstrate that the response length, denoted as $L(c_0, t)$ in Figure 2a, is a function of the concentration of $H_2S$, $c_0$, and the exposure time, $t$. The explicit function of $L(c_0, t)$ can be deduced by plotting the response length against the exposure dose, which is defined as the product of the concentration of $H_2S$ (in ppm) multiplied by the exposure time (in hours). When data for the response length is plotted as a function of the exposure dose, as presented in Figure 3b, the data sets for the four concentrations collapse into a single continuous function. Using the least square method, the line of best fit for the data in Figure 3b was identified as a power function with the following form:

*Equation 1:* $$L(c_0,\ t) = \alpha(c_0 \cdot t)^\beta$$

where $\alpha = 3.8163$ and $\beta = 0.4335$ are the best-fit parameters.

*Figure 3: (a) Response length of H₂S sampling badges exposed to 1 ppm (blue circles), 5 ppm (red triangles), 10 ppm (black squares), or 15 ppm (green diamonds) of H₂S for various time intervals. (b) Response length of H₂S samplers plotted against the exposure dose, which is calculated as the H₂S concentration (ppm) multiplied by the exposure time (hrs.). The black dotted line represents the best fit to the data set.*

Using Equation 1, the response length of the sampling badge can be estimated from a known concentration of H₂S and a known exposure time:

**Example #1**: A sampling badge has been exposed continuously for 4 hours to a known concentration of 2 ppm H₂S in air. In this case, $t = 4$ hours and $c_0 = 2$ ppm. The exposure dose is then calculated as $c_0 \cdot t = 2$ ppm x 4 hours = 8 ppm-hr. The estimated response length of the sampling badge is calculated using Equation 1: $L(c_0, t) = \alpha(c_0 \cdot t)^\beta = 3.8163$ (8 ppm-hr)^(0.4335) = 9.4 mm.

Alternatively, Equation 1 can be used to estimate the exposure dose if the response length of a sampling badge is known:

**Example #2**: A sampling badge exhibits a response length, $L(c_0, t)$, of 10.0 mm. To solve for the exposure dose, Equation 1 must be inverted as follows: $c_0 \cdot t = (L(c_0, t)/\alpha)^{\wedge}(1/\beta)$. Using a known value of $L(c_0, t) = 10.0$ mm, the exposure dose is then estimated as (10.0 mm/3.8163)^(1/0.4335) = 9.2 ppm-hr.

Once the dose has been calculated, the concentration of H₂S can be readily calculated if the exposure time is known.

**Example #3**: A sampling badge was exposed to an unknown concentration of $H_2S$ for 2 hours continuously, and after analyzing the badge the response length was measured as $L(c_0, t)$ 10.0 mm. As shown in Example #2, the exposure dose corresponding to a response length of 10.0 mm is 9.2 ppm-hr. The concentration of $H_2S$ is then calculated using the stated definition of the exposure dose: $c_0 = (c_0 \cdot t) / t = 9.2$ ppm-hr / 2 hours = 4.6 ppm.

As shown in the previous examples, Equation 1 enables interpretation of the response length of sampling badges exposed to $H_2S$ in terms of the exposure time and concentration of $H_2S$ in air. This equation is pre-programmed in the computer software program used for analyzing the sampling badges (Figure 1). The estimate for the response length is provided by the electronic badge reader, which contains advanced optical devices to accurately measure the response length in each sampling badge. The user must input the exposure time for the software to calculate the TWA concentration of $H_2S$

## Method Evaluation

This method has been described by Robinson et al. [4]. The method was evaluated in the laboratory using sampling badges exposed to air streams containing $H_2S$ at concentrations in the rage of 1 to 15 ppm. Field evaluations of the method were conducted on personnel working in an oil refinery. The key elements of method validation including bias, precision, accuracy, specificity, and limit of detection have been investigated during this method's development. The accuracy and precision were determined by exposing sampling badged at four different concentration levels and are described in detail later in this report. The other elements are also described in detail with their respective results within this report.

Sampling badges were exposed to air streams containing $H_2S$ inside a custom-built plastic (polyethylene terephthalate ethylene) exposure chamber (8.5 cm $\times$ 6.5 cm $\times$ 4 cm) containing an inlet and an outlet and equipped with cross-polarizers. A digital cameral was placed directly above the exposure chamber to image the response length of the sampling badges during exposure to $H_2S$ as a function of time. The exposure chamber was placed between a diffuse light box and a digital camera (Basler, Ahrensburg, Germany). The digital images (8 bit) of the badges were captured every 10 seconds using StreamPix 4 software (Norpix Inc., Montreal, Quebec, Canada). As detailed previously, unexposed sampling badges appear dark when viewed with cross-polarized

light. Upon exposure to $H_2S$, a bright band grows at the inlet of the sampling badges (See Figure 2). The optical response from the badge was then quantified by measuring the length of the bright front in the digital image (captured by the digital camera) using ImageJ image analysis software (National Institutes of Health, Bethesda, Md.). The measured concentration of $H_2S$ was calculated from the response length of the sampling badges and the exposure time according to Equation 1.

To generate the desired concentrations of $H_2S$, a custom-built gas delivery system was built comprising of a gas dilution system (Sabio Instruments, Georgetown, Texas), a zero air [dry air free of $NO_x$, $SO_2$, $O_3$, and $H_2S$] source (Sabio Instruments, Georgetown, Texas), solenoid valves (Parker, Cleveland, Ohio), and certified $H_2S$ gas cylinders containing 100 ppm of $H_2S$ in nitrogen (Air Gas North Central, Chicago, Ill.). A humidified gas stream was generated by bubbling zero air through water and mixing it, at appropriate ratios, with the dry stream containing $H_2S$ gas. The total flow rate of gas into the exposure chamber was maintained at 1 litter per minute (L/min.). The total humidity in the air stream containing $H_2S$ was 60% R.H. All exposures were carried at 22 °C (71.6 °F). The concentration of $H_2S$ in the gas streams was set to 1, 5, 10, or 15 ppm. Five sampling badges were tested independently at each concentration of $H_2S$. The badges were exposed continuously to a constant concentration of $H_2S$ for up to 22 hours.

## Precision, Accuracy and Bias

Following exposure, the average and standard deviation of the $H_2S$ concentration measured using the sampling badges were calculated at each concentration. The bias and precision of each measurement was also calculated using the method defined in Ref. [5]. The results are presented in Table 1:

*Table 1: Calculated Bias and Precision of method for TWA concentrations of $H_2S$ measured between 1 ppm and 15 ppm.*

| Known Concentration | Measured TWA Concentration (ppm) | | | |
| --- | --- | --- | --- | --- |
| | Average | Standard Deviation | Bias | Precision |
| 1 ppm | 0.97 | 0.04 | -2.8% | 0.037 |
| 5 ppm | 4.95 | 0.14 | -0.9% | 0.028 |
| 10 ppm | 9.92 | 0.26 | -0.8% | 0.026 |
| 15 ppm | 15.73 | 0.18 | 4.9% | 0.012 |

The overall bias and precision for the entire data set were calculated as -0.3% and 0.026, respectively. Using these values, the overall accuracy at the 95% confidence interval was calculated as 5.0% using the following equation:

*Equation 2:* $A = 1.57 (B + 1) S_{rT} + sqrt( (0.39(B + 1)S_{rT})^2 + B^2 )$

where $B$ and $S_{rT}$ are the estimates for the bias and precision, respectively, and $A$ is the estimate for the accuracy at the 95% confidence interval. These results as summarized in Table 2:

*Table 2: Calculated Method Statistics.*

| Method Statistics | | |
|---|---|---|
| **Bias** | **Precision** | **Accuracy** |
| -0.30% | 0.026 | 5.0% |

## Specificity

To determine the specificity of the method, the sampling badges were exposed to air streams containing various compounds that could produce a false-positive measurement. The list of compounds tested is presented in Table 3. Three identically prepared badges for $H_2S$ sampling were exposed to the air streams flowing at 1 L/min and containing a single non-target compound at the concentration listed in Table 3. The sampling badges were subsequently analyzed to determine the response length and measured concentration. As detailed in Table 3, the sampling badges did not respond to air streams containing carbon monoxide, nitrogen dioxide, sulfur dioxide, methane, ammonia, and other hydrocarbons. In this case, the measured TWA concentration was 0 ppm. We note that the sampling badges are not affected by the presence of $SO_2$ and $NO_2$, two common interferents for other $H_2S$ sensing technologies. However, compounds containing mercaptan functional groups (-SH) elicited a measurable response in the sampling badges. For example, when the badges were exposed to 1 ppm of ethyl mercaptan in air for 2 hours, the measured TWA concentration was $0.8 \pm 0.1$ ppm; and when exposed to 1 ppm of methyl mercaptan in air for 2 hours, the badges reported a reading of $2.4 \pm 0.1$ ppm. These results demonstrate that the method presented herein exhibits specificity for $H_2S$ against various organic and inorganic compounds, except compounds containing mercaptan functional groups.

*Table 3: List of gases used to study the selectivity of the direct-read sampling badges.*

| Name | Formula | Exposure Concentration | Exposure Time | Measured TWA Concentration |
|---|---|---|---|---|
| Carbon Monoxide | $CO$ | 1,000 ppm | 2 hrs. | 0 ppm |
| Carbon Dioxide | $CO_2$ | 5,000 ppm | 20 min. | 0 ppm |
| Hydrogen | $H_2$ | 1,000 ppm | 2 hrs. | 0 ppm |
| Nitrogen Dioxide | $NO_2$ | 2 ppm | 2 hrs. | 0 ppm |
| Nitrogen Dioxide | $NO_2$ | 5 ppm | 20 min. | 0 ppm |
| Carbon Disulfide | $CS_2$ | 500 ppm | 2 hrs. | 0 ppm |
| Sulfur Dioxide | $SO_2$ | 2 ppm | 2 hrs. | 0 ppm |
| Ammonia | $NH_3$ | 50 ppm | 20 min. | 0 ppm |
| Methane | $CH_4$ | 1.0 vol % | 20 min. | 0 ppm |
| Hexane | $C_6H_{14}$ | 500 ppm | 2 hrs. | 0 ppm |
| Octane | $C_8H_{18}$ | 0.2 vol % | 20 min. | 0 ppm |
| Toluene | $C_6H_5\text{-}CH_3$ | 0.2 vol % | 20 min. | 0 ppm |
| Toluene | $C_6H_5\text{-}CH_3$ | 500 ppm | 2 hrs. | 0 ppm |
| Xylene | $C_6H_4\text{-}(CH_3)_2$ | 0.2 vol % | 20 min. | 0 ppm |
| Water | $H_2O$ | 90% R.H. | 20 min. | 0 ppm |
| Ethyl Mercaptan | $C_2H_5\text{-}SH$ | 1 ppm | 2 hrs. | $0.8 \pm 0.1$ ppm |
| Methyl Mercaptan | $CH_3\text{-}SH$ | 1 ppm | 2 hrs. | $2.4 \pm 0.1$ ppm |

## Range

This method should be considered accurate for measuring $H_2S$ at exposure doses between 1 ppm x hr. to 60 ppm x hr. which correspond to TWA concentrations between 1 ppm to 15 ppm measured over an exposure time in the range of 1 – 22 hrs. Exposure doses and TWA concentrations outside this range have been measured with this method (see "Field Validation"), but the accuracy, precision and bias have not been evaluated outside the cited range.

## Limit of Detection (LOD)

The minimum dose that was measured during evaluation of the method was 1 ppm-hour, obtained by exposing the sampling badges to 1 ppm $H_2S$ for 1 hour. At this dose, the response length of the sampling badges is 3.81 mm. This minimum dose is programmed into the electronic reader used in the method described here. In principle concentrations as low as 0.2 ppm have been measured with this method, provided that the sampling is performed for long enough time (>5

hours) (see "Field Validation"), but the accuracy, precision and bias at concentrations below 1 ppm have not been evaluated.

## Field Validation

Field evaluations of the method were carried as described in Ref. [4]. Briefly, passive sampling badges were used to monitor $H_2S$ exposure of workers at the Shell Martinez Refinery in California. The sampling badges were placed in the breathing zones for full-shift TWA and STEL measurements. For comparison, air samples were simultaneously collected from the breathing zone using ORBO-34 (Sigma Aldrich) tubes and an air pump (PAS 500, Spectrex Corporation, Redwood City, Calif., for long sampling, and AirCheck 2000, SKC Inc., Eighty Four, Pa., for short air sampling). The sorbent tube sampling was performed according to NIOSH Method 6013. Workers typically wore the pump with tube within inches of the breathing zone (Figure 4). For the samples when particulate sulfate could be present, i.e., handling molten sulfur, the ORBO-34 tube was preceded by a 1 $\mu$m PTFE particulate filter to reduce positive interference from particulate sulfate. The sampling badge uses no such filtering.



*Figure 4: Image of refinery worker wearing devices for monitoring personal exposure to $H_2S$, including $H_2S$ diffusive samplers (blue badge) and ORBO-34 sampling tubes.*

The pump flow rates for the TWA samples were set at ~150 – 200 ml/min and at ~1,000 ml/min for the STEL samples. The flow rate of the pump was checked before and after each sample using a primary airflow measuring device (BIOS Defender 510, Mesa laboratories, Lakewood Colo.). Immediately at the end of the sample period, the sampling badge was analyzed on-site. The ORBO-34 sample tubes were stored and shipped cold overnight to BureauVeritas (Novi, Mich.) for analysis following the NIOSH Method 6013 for $H_2S$. The laboratory has American Industrial Hygiene Association (AIHA)-Industrial Hygiene Laboratory Accreditation Program (IHLAP) accreditation for this analysis.

The workers participating in this field validation included molten sulfur truck drivers, process operators, inspectors, and pipe fitters. The workers wore the sampling devices for various time intervals between 0.5 to 12 hrs. The field validation tests were carried from April to July,
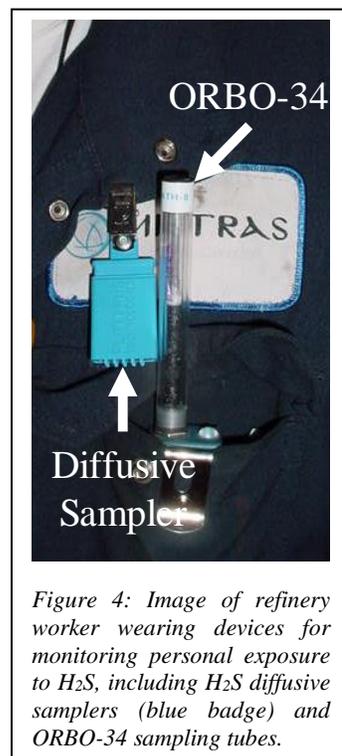
2013.  During the tests, the environmental temperature was 15.5 °C to 32.3 °C (65 – 90 °F), and the environmental humidity was 20% RH to 60% RH.

In total thirty-nine (39) exposures to $H_2S$ were recorded, but only sixteen (16) produced a measurable response in both the diffusive sampling badges and the sorbent tubes analyzed by an external laboratory.  Eighteen (18) samples revealed that the workers were exposed to $H_2S$ at concentrations below the limit of detection for both methods, while the remaining five (5) exposures did not produce results that could allow for comparison between the sampling badge and the sorbent tubes.  The TWA concentration of $H_2S$ measured with the diffusive sampling badges and NIOSH method 6013 are compared in Figure 5.  The results show that the TWA concentrations of $H_2S$ measured with the diffusive sampling badges are qualitatively similar to those measured using the NIOSH 6013 method.  A simple regression analysis was performed between the TWA concentrations obtained by two methods using the model y = mx.  The fit yields a straight line with m = 0.919 and $R^2$ = 0.845, suggesting a moderate correlation between TWA values measured by the sampling badges and the NIOSH 6013 method.  Additional statistics were calculated to establish the correlated between the two methods:  Lin's Concordance Correlation Coefficient (LCCC) was calculated as 0.924; the Asymptotic Standard Error (ASE) was calculated as 0.038; the Asymptotic interval (AI) at the 95% confidence level was calculated as 0.850 – 0.998.  These statistics demonstrate that the TWA concentration measured by the sampling badges exhibits correlation with concentrations measured with sorbent tubes analyzed according to NIOSH Method 6013.
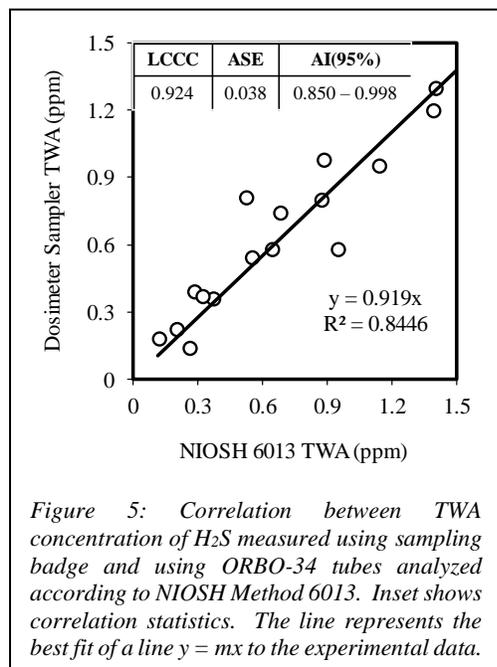


*Figure 5: Correlation between TWA concentration of $H_2S$ measured using sampling badge and using ORBO-34 tubes analyzed according to NIOSH Method 6013.  Inset shows correlation statistics.  The line represents the best fit of a line y = mx to the experimental data.*

## Summary

The data generated during the development of this method meets NIOSH criteria for bias precision, accuracy.

# References

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[5] National Institute for Occupational Safety and Health (NIOSH). A NIOSH Technical Report: Guidelines for Air Sampling and Analytical Method Development and Evaluation. By Kennedy ER, Fischbach TJ, Song R, Eller PM, Shulman SA.  Cincinnati, OH.: NIOSH, 1995