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Development and field evaluation of a new diffusive sampler for hydrogen sulfide in the ambient air

Abstract A diffusive sampler for the determination of hydrogen sulfide (H_2S) was developed based on collection on a paper filter coated with silver nitrate followed by optical densitometric determination of the metal sulfide. Laboratory tests were conducted in controlled atmosphere to evaluate linearity, uptake rate, face velocity effects, sample stability, precision, accuracy, and influence of relative humidity and interferents. The measured uptake rate for H_2S was determined in experiments involving sampling at different concentration levels in comparison to a wet standard colorimetric technique. The precision of the measurements for co-located passive samplers was lower than 15%. The accuracy of the data collected is within 20% of the actual value measured by the wet method. The sampler is capable of reliable measurements of H_2S at common levels of a polluted atmosphere in urban settings yielding average concentration levels over one month and beyond. Diffusive sampling can be adopted to analyze in detail the temporal and spatial trends of H_2S concentration in ambient air and in specific historic buildings or museums.

Keywords Atmospheric pollution · Diffusive sampling · Hydrogen sulfide

Introduction

Hydrogen sulfide (H_2S) is one of the principal compounds involved in the natural cycle of sulfur in the environment [1, 2]. H_2S constitutes a serious pollutant in ambient air because of its malodor and toxicity. Concerns about chronic, low-level emissions of H_2S are based on its toxicity even at low concentrations and its widespread

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occurrence in the diverse industries that rely on processes using sulfur and sulfur compounds as a natural contaminant. Some medical evidence suggests that even low level exposures can cause irreversible damage to the brain and central nervous system [3, 4]. Besides its health effects, H_2S has adverse effects on lead-based pigments and some metals such as silver and copper [5]. Because catalyst-equipped vehicles are known to emit H_2S [6], there is now a concern that the introduction of catalytic converters, as a consequence of new legislation, could entail the preferential production of H_2S over sulfur dioxide [7]. In view of this possibility the quantification of ambient H_2S is important and a number of methods can be considered. Stationary automatic analyzers for H_2S are expensive and require calibration as well as periodic maintenance. Benner and Stedman [8] evaluated the performance of available commercial instruments and concluded that reliable measurement at the sub ppb level was not possible with such instruments. The standard wet method involves collection of H_2S on $Cd(OH)_2$ suspension followed by colorimetry through formation of the dye methylene blue [9]. The methylene blue method is sensitive and specific but requires too much laboratory analysis time which limits its utility as a general sampling procedure and is inconvenient for field work. Colorimetric tubes based on a silver–gelatin complex have also been used to sample urban air [10]. They are easy to handle and convenient for storage but they are sensitive to photoreduction. The lead acetate tape method for continuous sequential sampling of hydrogen sulfide has also been commonly used to measure hydrogen sulfide [11]. However, it has been found that ozone, sulfur dioxide, and light strongly faded the PbS stain, resulting in lower absorbances. To avoid the limitations posed by the lead acetate reagent, a mercuric chloride impregnated tape method was developed [12] and modified by Hochheiser and Elfers [13]. The mercuric chloride reagent is more specific than lead acetate but the procedure requires an additional color development step and furthermore working with mercuric chloride is cumbersome. Natusch et al. [14], who investigated the collection of H_2S on paper tapes impregnated with silver

nitrate, dicyanoargentate (I), mercuric chloride, and lead acetate, demonstrated that tapes impregnated with silver nitrate are the only ones that are very suitable for the determination of H_2S from some $\mu g\ m^{-3}$ to $mg\ m^{-3}$ levels. The silver nitrate is converted into silver sulfide, which is then quantified by its quenching effect on the fluorescence of fluorescein mercuric acetate [15, 16]. None of these methods are suitable for sub-ppb H_2S determinations. In contrast to active samplers in which air is brought into contact with a detector or collector device by means of a pump, diffusive (or passive) sampling relies on diffusion to bring the pollutant into contact with the collector. Compared with the pump-dependent active sampling procedure, the main advantages of the method are the cost effectiveness, the simplicity, and the potential for large-scale measurements carried out at the same time. The silver nitrate/fluorescein mercuric acetate fluorimetric method (FMA) has been used by Shooter et al. [17] for a passive sampler based on Palmes' original design for diffusive samplers. At neutral or acidic values, silver ion is present in the trapping media and this rapidly reacts with H_2S (but not COS) to form the sulfide. In the procedure of Ankersmith et al. [18] the tubes were analyzed using an autoanalyzer and because the FMA system is sensitive to oxygen the entire sample train was analyzed under nitrogen. This method is sensitive and specific but requires too much laboratory analysis time thus limiting its utility as a general sampling procedure. This paper describes the development and field trials of a diffusive method for determining the concentration of H_2S by measuring the decrease in reflectance of an $AgNO_3$-impregnated paper filter resulting from the formation of silver sulfide on a proper filter surface.

Experimental

The device developed in this study is a variation of that described by De Santis et al. in previous laboratory and field studies of atmospheric NO_x and NO_2 [19]. The body of the sampler is a cylindrical black polyethylene vial with threaded caps of different colors at both ends. The sampler is schematically shown in Fig. 1 closed, before sampling.

H_2S is collected on a disc of $AgNO_3$-impregnated paper filter placed at the bottom of the vial facing one of the threaded caps (cap 2 in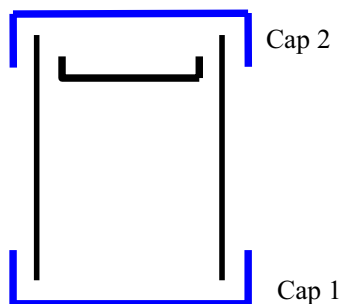 Fig. 1) and held in position by a stainless steel ring. The absorbing pad faces the bottom of the device and air is sampled through three small sectors. The measurement of optical density is simply carried out at the end of the sampling period by removing the gray cap (cap 2 in Figs. 1 and 2) and placing the sampler in a specially developed densitometer derived from the principle of a classic black-smoke reflectometer.

The measurement of the optical density is converted to concentration from a standardized curve. Laboratory tests were conducted in a 15-L glass test chamber closed with a removable leak-proof cap, in which air flow, humidity, temperature, and gas concentration were controlled. The diffusive samplers were placed in the chamber and held in position, so that the air flow was at right angles to the face of the sampler. The exposure chamber could hold up to six samplers. A minimum distance of about 5 cm between samplers was used to minimize concentration gradients. To avoid turbulent diffusion inside the vessel the open end (cap 1) was protected using a windscreen made of white fine stainless steel net which supports a fine plastic net (Sefar PET 1000, 250 mesh) (Fig. 3).

Before and after sampling the windscreen is replaced with the black polyethylene cap (cap 1 in Fig. 1). Silver nitrate impregnated filters were prepared by soaking paper filters in 2% $AgNO_3$, 8% glycerol in a solution 20/80 of H_2O/HNO_3 0.01 M. After 5 min of immersion in the solution, the filters were removed and horizontally supported at the edges on parallel glass rods glued to a glass plate and then dried in an oven at 70°C. The filters were then stored in a desiccator and protected from light until use. To calibrate the sampler, air streams containing known H_2S concentrations, generated by a permeation tube, were diluted with clean air at controlled relative humidity (Humicon-D.A.S., Palombara Sabina, Italy). The permeation tube was placed in a thermostatic bath at controlled temperature to within ±1°C in the range 20–40°C. By varying the operating conditions (e.g., type of permeation tube, temperature) concentrations ranging from about 50 to 1,300 $\mu g\ m^{-3}$ could be obtained. The mean concentrations of H_2S during the different exposure times

Fig. 1 Schematic view of the H_2S sampler

Fig. 2 At the end of sampling cap 2 is removed and optical density is measured

Fig. 3 Cap 1 is removed when in operation and substituted by a windscreen

of the diffusive samplers were independently measured by active sampling. For this purpose, H_2S from the permeation tube was collected in a midget impinger containing 10 mL of an alkaline suspension of cadmium hydroxide. CdS was converted to methylene blue for spectrophotometric analysis according to Vasireddy et al. [20]. To each sample, 0.5 mL of amine-sulfuric acid test solution and 1 drop of ferric chloride solution was added: the solution was mixed, adjusted to 15 mL with distilled water and left for 30 min to allow full color development. The μg of H_2S in each sample was read at 670 nm from a standard curve and the concentration of H_2S was calculated in μg m^{-3}. By measuring standard samples of sulfide obtained by exposition at different H_2S concentrations, the relationship between the percentage optical density and the sulfide concentration is determined and a calibration curve is obtained. Optical density of the brown stain that developed on the impregnated filter was determined with a specially designed portable reflectometer Model UNIVAR available from DAS (Palombara Sabina, Rome, Italy). The interference of ozone, nitrogen dioxide, and sulfur dioxide was studied by exposing diffusive samplers previously loaded with H_2S in the exposure chamber to ozone obtained by using an ozone generator, to nitrogen dioxide and sulfur dioxide obtained from permeation tubes. Ozone was measured by using a UV absorption analyzer (API 400A, San Diego, USA), nitrogen dioxide by using a chemiluminescence analyzer (API 200, San Diego, USA), and sulfur dioxide using a fluorescence analyzer (API 100A, San Diego, USA). The performance of the sampler was evaluated in the field by comparing results from co-located samplers for different lengths of time (self-consistency test). The self-consistency of the method was evaluated by carrying out simultaneous field sampling (twelve samplers plus six field blanks) of different time durations: two subsequent fifteen-day samplings and one simultaneous one-month sampling for each test. The samplers were deployed with their open ends down to exclude dust. They were positioned under an aluminium rain shelter at a height of 1.9 m above the ground.

Results and discussion

Linearity and uptake rate

Linearity of response (i.e., the extent to which response is directly proportional to input) was evaluated by exposure to known concentrations of H_2S mixtures with purified air at 50% relative humidity. In each trial, six samplers were exposed simultaneously in the glass chamber to H_2S levels up to about 300 μg m^{-3} generated by a permeation tube. Figure 4 shows the relationship between the optical density and the concentration of H_2S equivalent to an exposure length of one month.

It is clear that the length of the sampling period may be varied according to the anticipated sulfide dose. The reflectance drop of the filter is a function of the sample size and the unit selected for expressing results is the loss of reflectance. Figure 4 indicates that the sampler shows very good linearity characteristics up to a concentration of H_2S corresponding to 4 μg m^{-3} for one month exposure. The values lie on straight lines with a correlation coefficient equal to 0.988. It should be stressed that the issue of linearity is one of the most important aspects that must be considered when evaluating a new passive sampler. The diffusion sampling rate at which the analyte is transferred through the vial depends on the average concentration in the ambient air according to the Fick's equation [21]. Because of the complex geometry of the sampler (see Figs. 1 and 2) it is difficult to calculate the sampling rate for H_2S as it could be simply done on the basis of Fick's equation. Therefore, the sampling rate of the diffusive sampler was determined in experiments involving side-by-side sampling with the wet impinger method. The H_2S concentrations were in the range 20–300 μg m^{-3} and sampling duration ranged from 4 to 12 h. The results for 6 sets of experiments yielded a measured diffusion sampling of 7.5±1.2 mL min^{-1}. Within the range of conditions studied, measured sampling rates were not affected by H_2S concentration or by sampling duration. The operative limits of diffusive samplers, as is the case of other enrichment devices, are determined by the detection limits and the operative capacity of the system, that is, the maximum loading that the device will accept without decreasing its
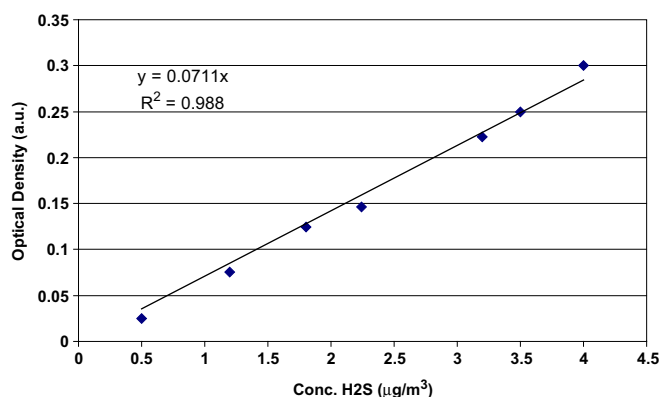

Fig. 4 Calibration curve

collection efficiency below a given value (typically 95%). A series of laboratory experiments showed that the sampling range for H_2S varies between 400 μg m^{-3} per hour and 250,000 μg m^{-3} per hour. The lower limit (limit of detection, LOD) of the sampling range was a function of the blank value (the LOD corresponds to the blank value plus three times the standard deviation of blank values). The maximum limit represents the point at which the uptake is no longer a linear function of the concentration to which the sampler is exposed. In consideration of this upper limit value, an exposure time for H_2S as large as 1 month can be expected at an average concentration up to 3–4 μg m^{-3}. Higher concentrations can be measured by reducing the sampling time.

Effects of face velocity on the sampling rate

Face velocity is an important factor to consider when developing a diffusive sampler due to a relatively large variation in face velocity during ambient sampling. A series of preliminary experiments were carried out to check the degree of attenuation for the face velocity effect as a result of the use of the stainless steel net placed at the sampler inlet. Two sets of devices, one set protected only with the stainless steel net and the other protected by the stainless steel and the plastic net, have been exposed in a vessel in which turbulence was created by operating a small fan under the lid of the vessel. The effect of face velocity on the sampler for H_2S was determined by studying the percentage recovery of H_2S from air after 5-h exposures at face velocity ranging from 20 to 200 cm s^{-1}. at chamber concentrations of 400 μg m^{-3}. Experiments in triplicate have shown that at the maximum speed provided by the fan the H_2S overestimation was more than 70% for the partially protected device, whereas it was 5±1% for the protected device. The response of the H_2S passive sampler was similar to that previously observed for NO_x samplers having similar geometry [19] and did not show starvation effects at face velocity of 20 cm s^{-1}.

Field sampling

To determine whether a diffusive sampler can be used for ambient monitoring it is necessary to investigate whether samplers exposed for extended periods (weeks and months) give the same integrated response as a series of short-term samplers run side-by-side. The ratio of a 4-week average concentration computed from the sum of three subsequent 2-week samples to the corresponding monthly samplers was used to indicate the self-consistency of the method. Results obtained in 3 subsequent tests showed a very good agreement between the monthly and the sum of the bi-weekly samples. A ratio of 1.05±0.1 was measured. The results were very satisfactory: the sum of H_2S collected during the fifteen-day sampling and the H_2S collected during the long-term 30-day sampling was between −5.6% and 4.7% in the three different separate experiments.

Precision is a measure of the variability of response expected at any given concentration. The coefficient of variation (standard deviation of repeated measurements divided by the mean) is a common indicator of precision. The standard deviation of the six samplers was between 3.8% and 6.2%, largely within the limit of 10% which is normally accepted for this type of sampler.

Storage of the exposed sampler

The stability of the sample was studied by collecting H_2S with a number of samplers and by analyzing some of them immediately and the other after storage in different conditions. A batch of 15 samplers was exposed in the chamber to a concentration of 380 μg m^{-3} for 9 h. The exposed samplers were divided into three groups. Five samplers were analyzed immediately, whereas the other were stored for two months either at room temperature on the bench or in a refrigerator at 4°C. At the end of this period the 10 samplers were analyzed. No significant sample loss was detected. The mean value of the sulfide recovered after storage either at room temperature or in the refrigerator does not differ by more than 5±0.5% from the value before storage.

Influence of humidity

To study the influence of relative humidity on the collection efficiency of H_2S, the amount of sulfide collected per unit time and concentration was determined over a range 20–80% relative humidity at 500 μg m^{-3} for about 10 h at room temperature. The collection rates were unaffected by the relative humidity (r.h.) and averaged to 7.6±0.9 cm^3 min^{-1} at 20% r.h. and 7.7±0.5 cm^3 min^{-1} at 80% r.h.

Interference

The effect of O_3 as such on the determination of H_2S was investigated in a series of experiments on the H_2S passive samplers. O_3 at a concentration of about 1,800 μg m^{-3} in clear air was admitted for 27 h in the exposure chamber containing 6 H_2S samplers which were previously loaded by exposing them to a stream of H_2S of 200 μg m^{-3} for 7 h. The experiment was repeated at 20%, 50% ,and 80% relative humidity. At the end of each experiment the analysis of absorbing pad showed that O_3 as such is able to

Table 1 Characteristics of the diffusive sampler

Uptake rate (ml min^{-3})	Precision (%)	LOD (µg m^{-3} h)	Storage condition
7.5±1.2*	3.8–6.2**	400***	Room temperature

*Average value±S.D. on six samplers; **set of six samplers; ***blank value plus 3×S.D., see text

cause a 5±1% (average±standard deviation on six trials) interference for the determination of H$_2$S. To test the interference of SO$_2$ and NO$_2$, six samplers for each pollutant were loaded with H$_2$S in the exposure vessel. Three samplers were analyzed immediately, whereas the other three were exposed to 700 μg m^{-3} of SO$_2$ for 17 h and to 970 μg m^{-3} of NO$_2$ for 24 h at different relative humidities of 20%, 50%, and 80% and then analyzed. Even at these extreme conditions SO$_2$ and NO$_2$ did not have any measurable interference effect.

Conclusions

Diffusive samplers are an ideal tool for determining the pollutant distribution over a large area and to assess integrated concentration levels over a long period of time. The main advantage of these sampling devices is that they are inexpensive and easy to use. In addition, the passive device is not constrained to sites where electrical power is available. This work shows that the developed diffusive method offers a favorable alternative to other sensing systems employed to date for the detection of H$_2$S. The proposed system is very simple and does not require pretreatment or absorption in any liquid. Uptake rate, precision, LOD and storage conditions are presented in Table 1.

The method was successfully applied for the determination of low levels of H$_2$S in ambient air and can be presented as an alternative to other commercially available systems for monitoring H$_2$S. The characteristics of the method here developed are:

– The method is inexpensive and does not involve a time-consuming procedure.
– The response is not affected by other commonly encountered pollutants such as O$_3$, SO$_2$, NO$_2$, and COS.
– The method has adequate sensitivity to detect the low concentrations normally encountered in the urban and rural atmospheres when one-month-long exposure time is used.
– The sampler can be stored at room temperature prior as well as after sampling and can therefore be used even in remote areas.

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