

Evaluation of a novel passive sampling technique for monitoring volcanogenic hydrogen sulfide

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Received 19th January 2004, Accepted 26th March 2004

First published as an Advance Article on the web 23rd April 2004

A novel, low-cost passive sampling procedure for monitoring of volcanogenic hydrogen sulfide is reported. The technique is based on absorption of H₂S onto treated sections of photographic paper, which are housed in plastic film canisters during exposure. The H₂S reacts with silver halide in the photographic paper, causing a colour-change reaction from white, through brown, to black, depending on concentration of atmospheric H₂S. The sampler is sensitive to << 30 ppb to ~1000 ppb of H₂S. Here we present results from a series of optimization and quantification experiments. An active sampling procedure for rapid H₂S measurement is also reported, based on absorption of H₂S onto Whatman No. 41 cellulose filters treated with silver nitrate, and was shown to be quantitative using a single filter at flow rates < 1.0 L min⁻¹ for collection of < 200 µg of sulfide (as H₂S). Determination of sulfide collected on the substrates was performed using a rapid flow-injection technique based on the fluorescence quenching of fluorescein mercuric acetate (FMA) by sulfide. This was optimized at a FMA concentration of 8 mg L⁻¹, at which 100% quenching was obtained at a solution sulfide concentration of 3 mg L⁻¹.

Introduction

Hydrogen sulfide (H₂S) is released from natural systems including the oceans, marshlands, soils and vegetation, and during volcanic activity. Although flux estimates remain poorly constrained, volcanism and the open oceans appear to constitute the largest individual source categories.^{1,2} Halmer *et al.*³ estimate the global annual volcanic flux of H₂S at 1.5–37.1 × 10¹² g y⁻¹. Once in the atmosphere, H₂S reacts with free radicals including the hydroxyl (OH) and nitrate (NO₃) radicals, ultimately forming sulfur dioxide,⁴ with an H₂S lifetime in the troposphere of several tens of hours.

Hydrothermal activity, where gases from cooling magmatic systems rise from depth through overlying layers of water-rich fractured rocks,^{5–8} is the major volcanic source of H₂S. In such emissions, H₂S is normally found alongside H₂O and CO₂ (major components), and H₂, N₂, CH₄ and CO (minor components),⁹ although magmatic gases (SO₂, HCl, HF) mix with hydrothermal vapours in more complex systems, as at Vulcano Island, Italy,¹⁰ Galeras volcano, Colombia,¹¹ Oldoinyo Lengai volcano, Tanzania¹² and Iturup island.¹³

In terms of human impact, H₂S is toxic at high concentrations, and of considerable nuisance at lower concentrations due to its characteristic smell, detectable between 0.025 and 100–150 ppm (in this paper H₂S concentrations in air are expressed as volume mixing ratios, either ppb or ppm). Human exposure is regulated *via* legislation such as the Control of Substances Hazardous to Health Regulations 1988 (COSHH) with long-term (8 hour) and short-term (15 minute) exposure limits for H₂S set at 5 ppm and 10 ppm respectively.¹⁴ In many regions human habitations exist close to strong sources of volcanogenic H₂S. For example, at the Colli Albani complex near Rome, high H₂S concentrations accumulate under conditions of low wind speed or at night (and are now continuously

monitored^{15,16}) and at Rotorua, New Zealand,¹⁷ where a large population (~60,000) lives on top of an active geothermal system. Plant growth rates are also reduced in the presence of H₂S,¹⁸ so that crop yields may be lowered where H₂S levels persistently exceed normal background concentrations.

As well as playing a role in mitigating impacts on the environment and human health, H₂S monitoring may assist in identification of changes in the nature of volcanic activity, where such changes are accompanied by altered ratios between the emitted gases.¹⁹ For example, changes were measured in SO₂/H₂S ratios during 2000 at El Chichon²⁰ and during 1997–2001 at Nisyros Island, Greece, where increasing ratios of H₂S/CO₂ were ascribed to an increased incorporation of magma within a hydrothermal system.²¹ Use of H₂S as a tracer for changes in activity is also useful where activity levels are low and where any magmatic SO₂ has been removed during passage through sub-surface aqueous systems.^{22,23}

Passive samplers are useful for determination of longer-term averaged concentrations of volcanogenic gases, particularly where use of extensive networks of sites is desired, and have previously been used for ambient measurement of H₂S.^{24,25} In this paper we report a new passive sampling technique for the specific measurement of H₂S in volcanic or industrial environments. This technique uses inexpensive materials, readily available worldwide, so that samplers can be rapidly deployed wherever H₂S levels are of concern. The ease of mass-manufacturing the samplers allows deployment of tens or hundreds of samplers simultaneously so that a map of H₂S concentrations and zones can be assembled across a city or affected industrial area. This paper evaluates and quantifies the samplers. In a separate paper¹⁷ we describe a case study from Rotorua, New Zealand, a city which sits across an active geothermal system, and provide an example of the geological

implications of the ability to map H₂S concentrations across geothermal areas.

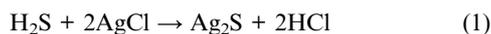
In this paper, we also assess a filter-based active sampling technique, designed to complement techniques used to measure concentrations and fluxes of volcanic species such as SO₂, HF, HCl, HNO₃ or aerosols.^{26,27} Such filters have been used previously in the volcanic context to make airborne measurements of H₂S in the dilute downwind plumes from the 1990 eruptions of Mt Redoubt.²⁸ However, this technique was based on that used by Saltzman and Cooper²⁹ to measure H₂S concentrations of 0–260 pptv in the Caribbean and the Gulf of Mexico. Concentrations of H₂S in near-source volcanic plumes or geothermal areas are likely to be much higher than these levels, necessitating adaptation of the technique for these more extreme volcanic environments. Analysis of sulfide extracted from both passive and active samplers was performed using a novel semi-automated flow-injection fluorescence technique.

Methodology

Passive samplers

Silver tarnishes when in contact with H₂S, forming silver sulfide (Ag₂S), hence a colour change reaction occurs. This effect was examined by Pope *et al.*,³⁰ who noted that the effect was specific to H₂S. Most passive samplers for H₂S employ silver nitrate impregnated filter paper. As an even distribution of silver nitrate is difficult to achieve, Pal *et al.*³¹ suggest the use of a silver-gelatine complex. Here, our passive sampling technique is based on the use of strips of black and white photographic paper (Ilford Multigrade IV RC deluxe MGD.1M), which contain silver halide retained in a thin surface layer (~0.005 mm) of gelatine.³² The silver acts as an effective sink for gaseous sulfide once the gelatine layer is disrupted by wetting (expanding it to a thickness of ~0.1 mm and allowing it to become gas permeable). The absorption of H₂S is accompanied by a characteristic colour change. The 3 inch × 1 inch photographic paper strips are activated by immersion in a mixture of 50/50 water and glycerol, with a small quantity (5 g) of salt (sodium chloride, optional) and 5 drops of surfactant (Kodak Photoflo 200) added to ensure an even coating. The samplers are then dried in sulfide-free air and positioned at the closed end of individual empty standard black plastic photographic film canisters. The sealed samplers remain completely inactive for long periods until opened and exposed to a sulfide-rich environment (photographic paper strips housed within sealed canisters showed no discernible colour change during storage over a period of six months). The samplers are inexpensive and easily mass-manufactured, thereby making them ideal for distribution across a city or industrial site, for simultaneous measurement.

The photographic paper undergoes a colour-change reaction through the formation of silver sulfide in the following reaction:



The colour change on exposure to H₂S proceeds from white, through yellow and brown, to black, depending on the degree of exposure. After sample collection the photographic paper strips are “fixed” using proprietary photographic reagent (*e.g.* Kodak Unifix) to prevent any further colour development. During sample collection, exposure to sunlight is minimised through the samplers being housed in black canisters and being mounted in dark places (*e.g.* inside American-style letter boxes or downward facing when outside). The fixing process also removes any colour change from the effect of sunlight on the samplers. A sample exposed in laboratory conditions for two years (without glycerol) turned a grey colour, which was

removed by the fixing process, indicating that short-term colour change from sunlight is not a problem.

The colour change from the reaction with H₂S may be measured qualitatively either by digitising (scanning) the paper strips and using a commercially available image analysis program (such as Photoshop *etc.*) to assign a greyscale value to the discolouration, or by using comparative colour charts. The relationship between sulfide content and paper discolouration then enables quantitative estimates of ambient H₂S concentrations to be made on the basis only of visual observation allowing, for example, a city to be assigned zones of different concentrations.¹⁷

Preparation of the samplers may be summarised as follows:

- In a darkened room, cut black and white resin-backed photographic paper into strips.
- Use plastic tweezers to place the strips face down in the glycerol solution (to reduce the effects of any light in the darkened room) for five minutes.
- Remove the strips from the solution and let them drain onto a paper towel. Leave strips to drain for five minutes before transferring to a dark place to allow drying to occur (at least 12 hours).
- Place strips in labelled black cylindrical photographic film containers. Replace container lids during storage. The samplers remain inactive until exposed to H₂S-laden air.
- Expose the samplers in the field for a set length of time. Collect the samplers.
- Fix the samplers using a photographic fixing solution (*e.g.* Kodak UNIFIX powder or solution and water) in subdued light. Leave in the solution for five minutes before thoroughly washing twice in cold water.
- Drain the samplers as before and leave to dry for at least 12 hours.

Laboratory experiments were conducted to establish whether concentrations measured using the passive samplers were influenced in any way by the use of fixing agent on the photographic papers, or by subsequent washing of the papers (which might also be needed during field sampling following particulate contamination during exposure). For this, replicate samplers were exposed to a relatively high (100 ppb) H₂S concentration, until significant visible colour change had occurred. The photographic paper was then either (a) extracted immediately (see Analysis section below) without fixing or washing; (b) washed and then extracted immediately; (c) fixed, then washed thoroughly prior to extraction (if fixing is carried out, one must then wash the fixer off the substrate).

Chemical analysis of the sulfide content of samplers provides a measurement of H₂S concentration. In order to quantify the response of the samplers to H₂S, and since linearity of response with H₂S concentration, as well as changes in absorption characteristics at the paper surface at different exposure times, could not be assumed, determination of sulfide accumulated by the samplers was conducted at three different H₂S volume mixing ratio levels (173, 926 and 3133 ppb), representative of different ambient H₂S concentrations found at volcanic sites worldwide. Samplers were exposed to H₂S in a perspex chamber measuring (cm) 30 × 30 × 30. The H₂S–air mixtures were prepared from certified cylinders containing either 10 ppm or 1000 ppm H₂S in air (BOC Special Gases, Guildford, UK), by mixing with purified (by passage through canisters of activated charcoal and Purafil) ambient air using mass flow controllers (Analysis Automation Model 1923). Incoming H₂S mixtures entered the chamber at the base, rising through a series of baffles to ensure thorough mixing, before arriving at the passive samplers positioned on an upper shelf within the chamber. Outlets to filter samplers exited the chamber adjacent to the passive samplers, and excess H₂S–air mixture was vented into a fume extraction hood. At each concentration, 18 passive samplers were placed in the chamber, with three samplers being removed after six different exposure times (*i.e.* removal in

triplicate), up to a maximum exposure time of ten days. A fourth experiment was carried out to test the effect of external turbulence on the samplers. Here, different conditions of turbulence were provided by using canisters whose openings were covered by either Teflon (PTFE) membrane filters (1 μm pore size) or cellulose filters (Whatman type 41), in addition to open-ended samplers and fully-exposed paper strips (*i.e.* without canister). The filters were secured in position using plastic ties. During all periods, the H_2S concentration within the chamber was monitored using the actively pumped filter procedure described in the following section. During the experiments laboratory temperatures ranged between 18–24 °C, and relative humidities between 40–60%.

The passive samplers were tested during field measurements across Rotorua city, within the Taupo Volcanic Zone, New Zealand, an area of extensive geothermal activity. The samplers were distributed in duplicate, in seventy locations across Rotorua during the winter (June, southern hemisphere) of 1997 during which time temperature varied between 1.0 and 13.7 °C and humidity between 72 and 100%. The experiment was repeated six months later during summer of 1997, to test for variations due to weather conditions (temperature was 12.0–20.8 °C and humidity was 60–92%, Rotorua Airport Automatic Weather Station). Canisters were placed horizontally with caps removed in American-style letterboxes or similar shelters, for periods of 7 days or 28 days. After sample collection the strips of photographic paper were fixed, and stored at room temperature without need for any further storage precautions. A full discussion of the results of this monitoring work is reported in Horwell *et al.*,¹⁷ however example results from a limited number of samplers are reported here. Samplers showing varying degrees of discoloration were selected as having been exposed to different ambient H_2S levels, and in each case the sulfide content was determined.

Active samplers

H_2S was collected as Ag_2S on AgNO_3 treated cellulose filters²⁹ according to the reaction



Whatman No. 41 filters (55 mm diameter) were pre-washed by rinsing several times with distilled, deionized water, and then saturated with 2% AgNO_3 solution in water in batches of four, in sealed 60 ml wideneck polypropylene bottles. After impregnation for 60 minutes the excess AgNO_3 solution was poured off, and the filters dried (within the 60 ml bottles with caps removed) over silica gel in an evacuated desiccator. After drying, the filters were removed from the bottles and stored, at 4 °C in the dark, in several layers of sealed “Ziplok” polyethylene bags. In use the filters were installed, using clean techniques, in 47 mm polycarbonate holders (Sartorius GmbH, Göttingen, type SM16598).

During the chamber experiments, filter samples were collected in duplicate using at least two filters in series to examine collection efficiencies and filter breakthrough effects (up to four filters in series were used for higher H_2S concentrations or higher flow rates where there was visible evidence of breakthrough from the second filter), at flow rates between 0.06 and 38 L min^{-1} . Filter sample flows were provided using diaphragm piston pumps (Charles Austen Ltd, Byleet, UK), with flow rates measured using gasmeters (Type E6, Charles Austen, Ltd, UK) calibrated using a Gilibrator-2 primary flow calibrator (Gilian Corp., USA).

H_2S concentrations obtained from filter analyses were used to determine chamber H_2S concentrations. The total H_2S on the filters was calculated by multiplying the concentration of S^{2-} in the extract solution by the total volume of extract. The concentration of H_2S in the gas mixture passing through the

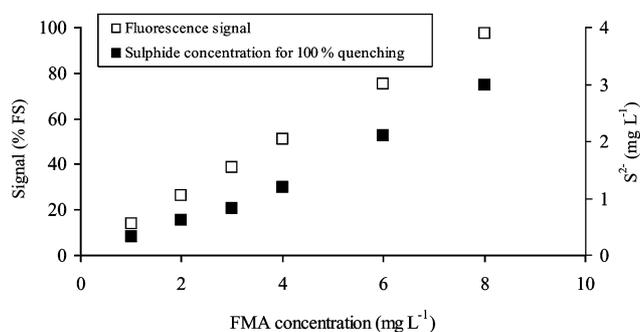


Fig. 1 Influence of FMA concentration on fluorescence signal and sulfide capacity.

filters was then calculated by dividing this mass by the total volume of gas that had been pumped through the filters.

Analysis

Determination of sulfide in exposed samplers was based on quenching of the fluorescence of fluorescein mercuric acetate (FMA) by sulfide.^{29,33} Samples collected on photographic paper were extracted in 30 ml polypropylene bottles by adding 5 ml of 0.1 M NaCN and shaking gently until all discoloration had been removed, followed by addition of a further 25 ml of 0.1 M NaCN–NaOH. Filters were extracted by adding 5 ml of 1.0 M NaCN, shaking until discoloration was complete, followed by further addition of 55 ml of 0.1 M NaCN–NaOH (it was found that use of 0.1 M NaCN–NaOH alone for extraction sometimes resulted in reprecipitation of black sulfide). Following addition of extractant solutions, all samples were agitated on a mechanical shaker for at least 60 minutes.

Known volumes of extract were then injected into a carrier eluent passing through a fluorescence analyser (JASCO Model 821-FP Intelligent Spectrofluorimeter) with emission and excitation wavelengths set to 525 nm and 500 nm, respectively. Two separate eluents were prepared, containing (a) 0.1 M NaOH–NaCN, and (b) 8 mg L^{-1} fluorescein mercuric acetate (FMA) in 0.1 M NaOH. The influence of FMA concentration on the unsuppressed fluorescence signal obtained, and the equivalent concentrations of sulfide required for 100% quenching of the signal, are illustrated in Fig. 1. The eluents were supplied from separate flasks using a dual channel peristaltic pump, and blended prior to arrival at a switching valve where sample solution was introduced *via* a 50 μL injection loop. A vacuum degasser was installed upstream of the valve to remove dissolved gases from the eluent and reduce the possibility of bubble formation. Peak heights were recorded on a strip chart recorder. Stock solutions of 1000 ppm sodium sulfide were prepared in 0.1 M NaOH–1.0 mM EDTA, with working standards prepared by further dilution into 0.1 M NaOH–NaCN, and calibration was achieved by direct injection of standards into the flow system. A typical calibration curve is illustrated in Fig. 2. In separate tests, quantitative recovery of sulfide was obtained from blank filters spiked with known quantities of Na_2S solution. Extract solution was used as a ‘blank’ in order to assess the effect of dilution on the FMA fluorescence, an effect ignored by Natusch *et al.*³³ Blanks were run periodically throughout sample runs and the mean value was subtracted from the sample signals.

Errors in the experimental procedures were assessed by consideration of the variability obtained between concentrations from replicate samplers placed in the exposure chamber. This could arise from non-uniform H_2S concentrations within the chamber, differences in the AgCl content of the photographic paper strips, or depth of gelatine layer, and includes any non-systematic errors in the analysis. This quantity was

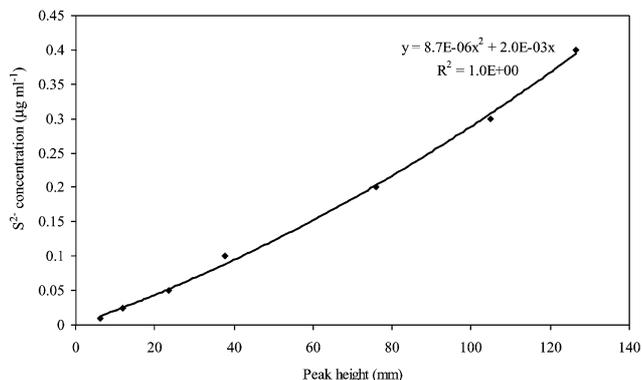


Fig. 2 Typical sulfide calibration curve.

determined from 4 simultaneous samplers exposed for 6 different time intervals between 20 hours and 196 hours. The average difference between the samplers giving the highest and lowest concentrations at each time interval was 22%, with a range of 10–28%. A further possible source of error lies in recovery of sulfide from the sampler substrates. 100% recovery was obtained for filters spiked with known quantities of Na₂S solution. In this application routine recovery checks were simplified by the colour change (brown/black to clear) observed as insoluble silver sulfide converts to highly soluble silver cyanide during the extraction process. From this it was clear that the conversion was always quantitative, however we allow a further estimated 5% maximum error in the recovery of sulfide. Errors arising from inaccurate flow rate measurements were considered to be negligible. The estimated overall error (27%) is illustrated using error bars in Fig. 3.

Results and discussion

Passive samplers

No significant difference in measured sulfide was obtained between the different fixing/washing procedures tested, giving confidence that field samples can be quite robustly handled, and washed, in cold water, to remove any particulate surface contaminants. It is likely that the physical and chemical composition of photographic paper may vary slightly between batches. It is, therefore, advisable that a sampling run should always be carried out from a single batch of samplers manufactured under identical and controlled conditions.

In our tests there was no significant influence (confirmed

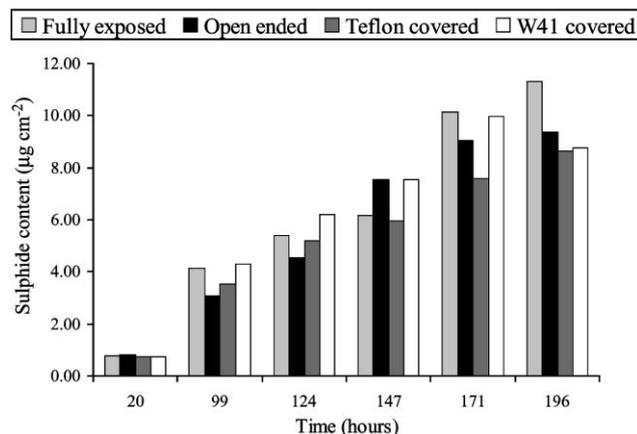


Fig. 4 Rate of sulfide uptake by passive samplers under different exposure conditions.

using the Students *t*-test) of sampler configuration (fully exposed without canister, open-ended canister, or canister openings covered by PTFE or Whatman 41 cellulose filters) on the quantity of absorbed sulfide (Fig. 4). This can be explained by the dominance of diffusion through the expanded gelatinous surface layer of the paper strips in controlling the H₂S uptake rate, demonstrated by consideration of the diffusion coefficients for H₂S in either aqueous medium (D_{aq}) or air (D_{air}). At 293 K, D_{aq} has been reported as $1.41 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Arnold³⁴) $1.34 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Tavares de Silva and Danckwerts³⁵), and more recently as $1.75 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Tamimi *et al.*;³⁶ Haimour and Sandall³⁷). Diffusion through air is much faster, by a factor of 10^4 , with a D_{air} of $0.17 \text{ cm}^2 \text{ s}^{-1}$ (since the coefficient for diffusion in air was not readily available, it was determined graphically from the relationship obtained between diffusion coefficients of several other gases³⁸ and molecular weights of the compounds). The approximate distances through which molecules of H₂S must diffuse through the air and aqueous medium, once entering the mouth of the sampler housing, are 60 mm in air (the length of the canister housing the photographic paper) and 0.05 mm in the gelatinous layer (*i.e.* half of the depth of the expanded gelatine layer, which takes into account more rapid collection early on while AgCl is available near the surface, and slower collection later as H₂S needs to penetrate to greater depths). The ratio of the travel distances in the air and gelatine layers is around 10^3 , which is an order of magnitude less than the difference in diffusivity between the two media. Any turbulent air transport

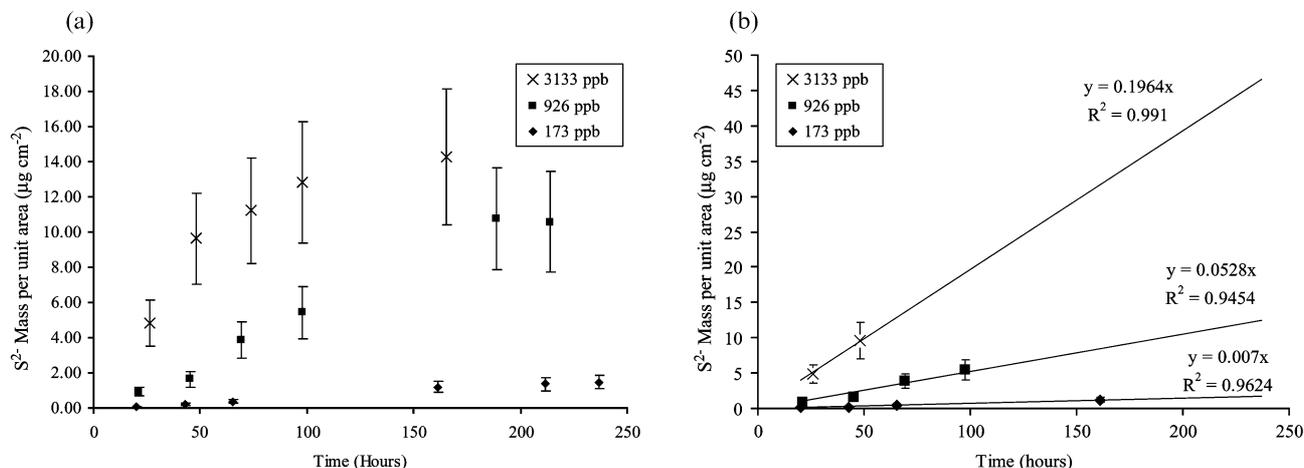


Fig. 3 (a) Rate of sulfide uptake by passive samplers according to H₂S concentration. (b) Rate of sulfide uptake by passive samplers for linear portion of graph.

within the tube would effectively increase even further the dominance of diffusion within the gelatinous layer as the controlling mechanism.

The principle of operation of the technique is distinct from that of commercially-available passive diffusion tubes, which rely on the presence of a perfect "sink" (absorbent) for the gas of interest, and require compliance with Fick's Law of gaseous diffusion. In our case, the existence of an absorbent layer through which uptake of H₂S is rate-limited offers an alternate, and inherently simpler, methodology for determination of atmospheric H₂S concentrations (in the future, the procedure could be adapted for measurements of other trace gases, by changing the chemical composition of the absorbent layer).

The absorption characteristics of the samplers at different H₂S concentrations are illustrated in Fig. 3a & b. From this it is evident that, at least at the two lower concentrations, absorption was linear (an unchanging relationship was obtained between the quantity of sulfide absorbed and exposure time) for < ~10 µg cm⁻² S²⁻ absorbed. With continuing exposure to H₂S the rate of absorption becomes non-linear, as availability of AgCl declines. The results suggest that full saturation (complete loss of AgCl) occurs at ~15 µg cm⁻² S²⁻. These features were in agreement with observed colour changes, with the fully saturated strips being dark brown-black in colour.

Further confidence in the linearity of response for < ~10 µg cm⁻² S²⁻, irrespective of H₂S concentration, is obtained by consideration of the degree of correlation between the slope of the lines describing the linear regions of the sulfide concentration-time curves (Fig. 3b), and the H₂S concentrations. A correlation coefficient (*R*²) of 0.997 was obtained, and the relationship between sulfide uptake rate (*U*, having units µg cm⁻² h⁻¹) and H₂S concentration (*C*, having units ppb) was

$$U = 6.218 \times 10^{-5} C$$

This relationship could be used directly to obtain ambient H₂S concentrations for the samples exposed in Rotorua. Six Rotorua samplers, ranging from almost white to dark brown were extracted. Of these, five had < ~10 µg cm⁻² S²⁻, with mean calculated H₂S concentrations over a seven day period ranging from 0–800 ppb. The lowest of these (0, 30 and 40 ppb) were representative of H₂S concentrations experienced in the west of the city (*i.e.* little or no H₂S). These results were in good agreement with the values (0–30 ppb) obtained from a co-located continuous H₂S analyser (TLD-1, MDA Scientific) operated during the winter experiment by the National Institute of Water and Atmospheric Research (NIWA, New Zealand). The Rotorua samplers giving highest concentrations (320 ppb and 800 ppb) were representative of the samplers found near the centre of the city where there is a permanent, acrid smell of H₂S. The sixth sampler, located in an emissions hotspot, was almost black, and contained 25 µg cm⁻² S²⁻, giving an estimated H₂S concentration of 2.5 ppm. Visual observations indicated that the relationships between colour change and mean H₂S exposure concentration were in agreement with the colour changes observed during the chamber experiments. In the field, the best way to achieve linearity is to vary exposure duration with location, based on estimated H₂S concentrations. Where the sampler operating conditions should exceed the linear response condition (for example where extremely high levels of H₂S are encountered, or when excessively long exposure periods are used), mean atmospheric H₂S concentrations can be estimated from the exposure time-dependent relationships between amount of sulfide collected at the different levels of H₂S shown in Fig. 3a. The difference in temperature and humidity during the winter and summer experiments did not appear to significantly affect

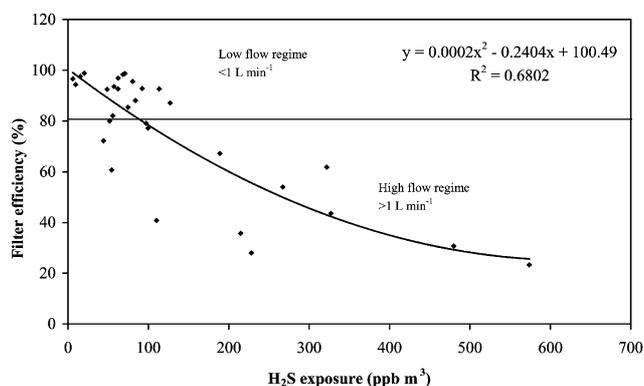


Fig. 5 Relationship between filter efficiency and accumulated H₂S exposure.

the extent of the colour change reaction observed on the samplers. The greatest variation between the two experiments was due to wind direction, as is discussed in Horwell *et al.*¹⁷

Active samplers

The filter samplers showed a progressive colour change during collection of sulfide, similar to the passive samplers and varying from pale yellow to dark brown. Breakthrough of H₂S from the filters was indicated by the appearance of discolouration on the downstream side of the filters, followed shortly afterwards by progressive discolouration of the downstream filter (this readily visible colour change provides a convenient method of avoiding excessive sample collection duration in the field). Visual observation of the filters during exposure indicated that at flow rates of up to ~1 L min⁻¹ no breakthrough occurred until high filter loadings had been achieved, while at higher flows breakthrough occurred at progressively faster rates as the collection proceeded. The relationship between filter efficiency and the integrated amount of H₂S collected (expressed as ppb m³ of H₂S) is illustrated in Fig. 5. At low flow rates collection efficiencies, corresponding to integrated amounts of < 130 ppb m³ of H₂S, were in the range 80–100%, however at flow rates of 17 L min⁻¹ or above (a single experiment was conducted at 38 L min⁻¹) filter efficiencies rarely exceeded 50%. Since samples collected at the higher flow rates inevitably showed visible evidence of breakthrough from the single filter used, a second experiment was conducted using several filters installed in series and a flow rate of 17 L min⁻¹ (Fig. 6). At the highest exposure (34 ppm min) a single filter was only 23% efficient, while the inclusion of an additional one or two filters raised the efficiency to 65% and 91%, respectively. While Hobbs *et al.*²⁸ used this technique to measure H₂S in a dilute downwind volcanic plume, data compiled in Delmelle and Stix³⁹ suggest that upon emission, volcanic H₂S mixing ratios

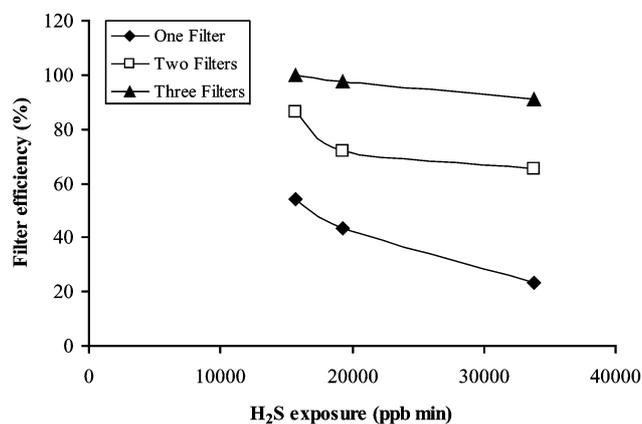


Fig. 6 Filter efficiency at high flow rate (17 L min⁻¹).

could be as high as ~10400 ppm. The number of AgNO₃ filter stages used must be adjusted according to the volcanic setting of the measurement.

Conclusions

Monitoring of volcanic gases is frequently undertaken at remote or difficult locations where use of sophisticated instrumentation may be impractical. Moreover, financial constraints in many developing countries which experience active volcanism often require use of inexpensive technology. The passive sampler described here can readily provide information on H₂S levels. This simple technique, based on the use of activated photographic paper and film canisters (which are easily available everywhere) provides an accessible option for emergency planners and health professionals and could be used not only in geothermal areas but also downwind of industrial sites which release H₂S (e.g. oil refineries, pulp mills, waste water treatment plants etc.). With appropriate selection of exposure duration they can be applied under a wide range of ambient H₂S concentrations and, in use, only require provision of a simple protective shelter such as a letter box or the roof eaves of a house. Separate, independent calibration of the samplers is required where the materials or techniques used differ from those employed in the present study, however such calibration can conveniently be undertaken subsequent to field measurements. Comparative H₂S levels can then be obtained quickly and easily by visual observation of the photographic strips throughout the rest of the sampling network without the need for recalibration or further chemical analysis. These samplers can be cheaply and usefully deployed over a very wide area in order to identify localities showing particularly high H₂S concentrations warranting more detailed study.

Active filter sampling is useful for short term measurements of various volcanic plume components, both particulate and gas phase. For hydrogen sulfide collection, a silver nitrate treated filter can be conveniently incorporated into a filter train designed for simultaneous measurements of several different species, and may be especially useful in the context of volcanic flux measurements. We have shown that, when used in series in triplicate, these filters provide efficient collection up to at least 35 ppm min.

Acknowledgements

C. J. H. acknowledges a Leverhulme Trust Research Interchange Grant, which allowed the collaboration with A. G. A. and T. A. M. to take place under the auspices of the International Volcanic Health Hazard Network (IVHHN). T. A. M. acknowledges financial support from the Natural Environment Research Council UK, Shell and The Aerosol Society. The authors would like to thank Dr Ed Llewellyn, University of Bristol, for significant and helpful advice on diffusive processes and insightful reviews of the manuscript.

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