Cadmium(II)-Exchanged Zeolite as a Solid Sorbent for the Preconcentration and Determination of Hydrogen Sulfide in Air

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Hydrogen sulfide in air sorbs onto Zeolite AAA molecular sieves in the Cd(II) (white) form to give CdS (yellow) in the concentration range required for the determination of H_2S for personnel monitoring and excursion samples as well as high-level (ppb) air samples. The immobilized sulfide is determined by spectrophotometry after conversion to methylene blue with a spectrophotometric detection limit of 0.25 μg of sulfide. Linear calibration curves cover the range of 0.25–35 μg of H_2S. Factors affecting collection characteristics of the solid sorbent such as breakthrough, humidity, storage time, and interference by other atmospheric constituents were studied. Actual monitoring data are presented.

One of the most commonly accepted methods for the determination of H_2S in the air utilizes a liquid sorbent impinger containing a $Cd(OH)_2$ suspension (*1*, *2*) which immobilizes S^{2-} in the form of CdS. Other metal salt solutions as well as solutions of caustic soda have been used as liquid sorbents for the entrapment and determination of this pollutant (*3–9*). In terms of personnel monitoring, liquid sorbents are cumbersome and somewhat restrictive, hence the recent emphasis in pollutant monitoring has been toward the use of solid sorbents for the preconcentration of gaseous air pollutants. A small tube containing <1 g of a solid sorbent is easy to handle and convenient for storage. Sampling can be accomplished with a portable, battery-operated constant flow pump, and in cases where recovery is an equilibrium process, it is best to keep the quantity of the sorbent material minimal.

The use of Ag(I), Hg(II), and Pb(II) salts impregnated on paper tapes represents the first approaches of immobilization and determination of H_2S on solid sorbents (*10–16*). None of these methods are suitable for sub-parts-per-billion H_2S determinations. The Pb(II) method has fallen into disfavor because of reports that the brown stain decomposes in the presence of light, SO_2, or even air passing through the tape. Although the Hg(II) tapes give a more stable product, this method is still not very sensitive to low background levels. Furthermore, the Ag(I) method is reported to be very sensitive to ozone, and mercaptans are reported interferents.

Various other solid sorbents have been reported (*17–20*) for the preconcentration of H_2S. However, few of these solid sorbents are specific, leave the immobilized pollutant in an inert form, and meet the criteria (e.g., high recovery, lack of interferences, and suitable storage times) for successful validation of a solid sorbent preconcentration method (*21*, *22*). Various chromatographic materials have been evaluated for use as preconcentrators. One should bear in mind that low-temperature gas chromatography is functioning whereby pollutant molecules can migrate from one sorption site to the next and that the correct sorption–desorption properties for efficient collection and recovery are the two most self-conflicting properties of these systems. With this in view this research has developed a solid sorbent in the form of Cd-(II)-exchanged zeolite AAA molecular sieve which acts as a preconcentrator for H_2S and immobilizes the pollutant via direct covalent bonding to the surface (Cd(II)). The collected H_2S in the form of CdS is immobilized in a form which is chemically inert to all interferents tested except ozone.

Many analytical methods for the determination of H_2S involve gas chromatographic detection which requires a desorption of the collected sample (*19*, *20*, *23*, *24*). The Cd-(II)-exchanged surface has been selected with the future intention of eliminating recovery manipulations so that the collected sample is potentially suitable for direct, nondestructive spectroscopic surface analysis. In our laboratory we are restricted at this time to solution UV–visible spectrophotometry as the analytical technique for quantitation and the study and evaluation of the parameters necessary for characterization of the Cd(II) surface as an air sampling preconcentrator.

In this study CdS is converted to methylene blue (MB) for spectrophotometric analysis. Preliminary results are reported which show that photoacoustic spectroscopy may be feasible for direct nondestructive analysis. This method is selective for H_2S in the presence of other S-containing gases, and in addition, isolation of the sample surface from external sources of H_2S both prior to and after sample collection is the only storage requirement as the H_2S is bound very firmly.

EXPERIMENTAL SECTION

Instrumentation. Absorbance measurements were taken on a Cary 14 spectrophotometer. Calibration gas standards were prepared from a Metronics Dynacalibrator Model 230-50-Z equipped with certified Teflon permeation tubes (supplied by Metronics) for H_2S and other gases investigated. Known concentrations of the gases were obtained by passing known flow rates of air purified by the Dynacalibrator over the gravimetrically calibrated permeation tubes at constant temperature and then diluting to the correct concentration. Air samples were collected by means of a DuPont Model P-4000 constant-flow air sampler. Sorption tubes were constructed out of modified Pasteur pipets 8 cm in length with an inner diameter of 5 mm. Modification consisted of removing the tip and fire polishing the rough end while allowing it to constrict to 3 mm in diameter. Tubes were filled with a 200-mg portion of the Cd(II)-exchanged zeolite (primary sorption bed) followed by a 100-mg portion at the constricted end of the tube, and the beds were separated and held in place with silanized glass wool plugs. For the limited breakthrough studies a second 100-mg backup bed was added, and in the complete breakthrough study two 200-mg backup beds were used.

Reagents. The amine–sulfuric acid reagent was prepared by diluting 50 mL of concentrated sulfuric acid (J. T. Baker A.R. grade) with 30 mL of distilled deionized water. The resulting solution was cooled and 12 g of Baker Grade *N,N*-dimethyl-*p*-phenylenediamine monohydrochloride (J. T. Baker) was dissolved in it. This stock solution was stored under refrigeration. The chromophore forming test reagent (DPA reagent) was prepared by diluting 25 mL of stock solution to 1 L with 1:1 sulfuric acid. Ferric chloride reagent was prepared by dissolving 100 g of reagent grade $FeCl_3 \cdot 6H_2O$ (J. T. Baker) in water and then diluting to 100 mL. A standard S^{2-} stock solution was prepared by dissolving 0.71 g of analyzed reagent grade $Na_2S \cdot 9H_2O$ (J. T. Baker) in water then diluting to 1 L. The S^{2-} stock solution was standardized by

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Table I. Recovery of S^{2-} from Cd(II)-Exchanged Zeolite

	amt of H_2S determined, μg						
	primary sorbent bed extractions				backup bed		
sample, μg	ext 1	ext 2	ext 3	ext 4	extraction	total	% recovered
10.0 (aq S^{2-} std)	3.57	2.45	0.55	0.33		6.9	69[a]
3.73 (aq S^{2-} std)						2.80	73 ± 1.6[b]
2.86 (aq S^{2-} std)						2.09	75 ± 1.0[b]
32 (gas std)	20.3	8.0	1.0		0.1	29.4	92[a]
18 (gas std)	12.9	3.6	0.2		0.0	16.7	93[a]
9.7 (gas std)	6.9	2.0				8.9	92[a]
6.4 (gas std)	5.8	1.0				6.8	106[a]
3.2 (gas std)	3.4	0.2				3.6	113[a]
3.0 (gas std)						2.37	79 ± 3.4[b]
1.00 (gas std)						0.81	81 ± 3.6[b]

[a] Preliminary data included only to demonstrate the need for successive chromophore forming reactions. [b] Typical data averaged for five determinations.

the iodine and thiosulfate method (*25*). The "H_2S" standard, 1 mL = 1 μg of H_2S, was prepared by dilution of 10 mL of the S^{2-} stock solution to 1 L. Cadmium(II)-exchanged zeolite sorbent was prepared by stirring 100 g of 18/35 mesh zeolite AAA sieves in 500 mL of 0.5 or 1.0% solution of reagent grade $CdCl_2 \cdot 2.5H_2O$ (J. T. Baker) for 24 h. The zeolite AAA molecular sieve, $Na(AlO_2)(SiO_2)_{3.0}(H_2O)_{3.9}$, was provided by Amco, Arizona Minerals. The sorbent was washed three to four times with distilled water followed by a methanol wash and then dried at 120 °C for 4 h.

Experimental Procedures. Laboratory investigations of the various sorbent parameters, breakthrough volume, recovery of H_2S from air and from sorption tubes, storage time, and effect of humidity and other possible interferents, were performed on gaseous standards collected at a sampling rate of 2.0 L/min. The sorbent capacity study for S^{2-} uptake was conducted by equilibrating known amounts of S^{2-} from the Na_2S stock solution with 1.0-g portions of the sorbent and determining the unsorbed excess of S^{2-} spectrophotometrically after conversion to methylene blue. The process was repeated until less than 10% of the amount of added S^{2-} was sorbed. Triplicate samples of sorbent (200 mg) were equilibrated twice with 25-mL portions of 0.025 M Na_2S solution. The samples were washed with water and methanol and dried overnight over anhydrous P_2O_5. These samples were Wig-l-Bugged for 2 min and sent out for combustion analysis followed by nondispersive IR analysis (a Leco IR-32 automatic sulfur determinator system).

The sorbent with collected H_2S in the form of yellow CdS was transferred to a closed 25-mL volumetric flask and cooled for about 5–10 min in cold water. The chromophore forming reagent (0.6 mL of DPA reagent and 1 drop of $FeCl_3$ reagent) and 5 mL of distilled water were rapidly added to the flask. The contents of the flask were vigorously swirled for a few seconds and the solution immediately decanted into another 25-mL volumetric flask. The sorbent was then quickly washed twice with 1–2-mL portions of water followed by 5.0 mL of reagent grade methanol decanting all washings into the same volumetric flask. The solution was diluted to volume with water and allowed to stand for 0.5 h prior to measuring the absorbance of the MB chromophore at 665 nm in 5.0-cm cells. In the event that greater than 2 μg of H_2S was collected (empirically determined by inspection of the collection tube for relative amounts of yellow CdS) a second chromophore-forming reaction was carried out prior to washing the sorbent with methanol but after the aqueous washings. The first and subsequent extractions were recovered in separate 25-mL volumetric flasks. For large amounts of H_2S many extractions were required to completely recover the S^{2-}. Table I should be used as a guide to the number of extractions required. The samples absorbance readings should be compared to a calibration curve prepared by an identical extraction procedure on gaseous standards collected on the Cd(II)-exchanged zeolite sorbent. A detection limit of 0.25 μg of H_2S (based on spectrophotometric reading of 0.05 A above the blank) was obtained when samples were scanned from 720 to 640 nm in 5.0-cm cells to make the peak at 665 nm more apparent.

The wavelength of maximum absorption was shifted several nanometers toward the UV from the reported methylene blue method (*25*) due to the presence of 20% methanol in the solvent matrix. In addition to the wavelength shift an increase of 17% in the *molar absorptivity* from 3.8×10^4 to 4.6×10^4 was noted. Although both molar absorptivity and wavelength of peak maximum change with solvent composition, both remained relatively constant if the methanol concentration varied only slightly (±1.0 mL). Addition of as much as 80% methanol caused precipitation problems when the samples were allowed to stand for over 1 h prior to the measurement step. The detection limit for the air analysis is therefore dependent on sample collection time and on subsequent sample treatment. For example, an analysis which yields 0.25 μg of H_2S for a collection time of 2.0 min (under specified collection conditions) yields an air value of 45 ppb. For this same sample of 0.25 μg collected over a 3-h period, the air concentration would correspond to 0.28 ppb which demonstrates the collection time dependency on detection limits. A more serious dependency arises from the subsequent sample treatment. A pure water matrix measurement of MB would yield an absolute lower level detection as 0.28 μg of H_2S whereas in a methanol–water matrix approaching 80% alcohol content the absolute detection would be ca. 0.20 μg.

Field Sampling. Ambient air samples were collected on sorbent tubes at different locations in Cincinnati, OH, for subsequent H_2S determination. The DuPont constant-flow sampler was used to pull air through the sorbent tube containing a 200-mg primary sorbent bed and an additional 100-mg backup bed of cadmium-exchanged zeolite separated by a glass wool plug. A flow rate of 2.0 L/min for sampling periods of 12–24 h was used. Indoor air was sampled in the freshman laboratory when the qualitative analysis course was in progress. The sampling period was for one laboratory period (about 2–3 h).

Interference Studies. Evaluation of the interference caused by the presence of other gases found in actual sampling environments was peformed by placing the appropriate permeation tube for the potential interferent in the permeation chamber of the Dynacalibrator along with the H_2S permeation tube for simultaneous sampling. The H_2S wafer permeation device was selected as the permeation standard of choice as it gave the lowest permeation rate (in the order of 20 ng/min at 30 °C). In addition to giving the H_2S concentrations closest to those encountered in actual air monitoring, it also yielded the highest possible interferent to H_2S concentration ratio. The samples were collected for 3 h on 200-mg portions of the Cd(II)-exchanged zeolite at a flow rate of 2 L/min using purified air of ambient humidity as diluent. All interferent compounds containing S as well as NO_2 were evaluated in this manner in triplicate and were compared to standards collected and treated in a similar manner.

For the interference studies involving ozone, a different procedure had to be employed as we were only able to generate the standard H_2S samples in our laboratory. The permeation tube giving an intermediate permeation rate (0.3 μg/min at 30 °C) was chosen for preparation of these samples as it facilitated the manufacturing of samples. The final diluted concentration of the H_2S gas sampled was 0.07 μg/L. The samples were collected from between 600 and 1400 s noting the collection time for each. The H_2S samples were prepared by collecting several concentrations

of H_2S (1–4 μg) in the usual manner and then transferring the samples to another facility for exposure to ozone.

The instrumentation used to generate the O_3 standard was a Bendix dynamic calibration system, Model 8850-2 permeation system. The samples containing collected H_2S were then exposed to the O_3-containing atmosphere in the following manner: The flow rate through the samples from a multiport glass manifold was limited to 1.5 L/min by the output capacity of the Bendix and the sampling requirements of the ozone analyzer. The Bendix instrument generated O_3-containing air by exposing purified air to UV radiation at a constant temperature and flow rate of 1.8 L/min. The O_3 atmosphere was sampled simultaneously from the manifold by a Monitor Labs, Inc., ozone analyzer, Model 8410, at a rate of 300 mL/min and by our H_2S-containing samples. The flow rate of 1.5 L/min was maintained in the samples by using suction from a Gast Manufacturing $^1/_8$-hp pump, and the flow rate was monitored with a 0–2 L/min Matson rotameter connected between the samples and the Gast pump. Each sample was exposed to the 0.38 ppm O_3 standard for a period of 1 h which corresponds to an integrated exposure of 67 μg of O_3.

RESULTS AND DISCUSSION

Best results were achieved when samples were compared to linear calibration curves constructed from gaseous standards collected on the Cd(II) zeolite surface and treated in a manner similar to the samples in order to avoid losses due to decomposition or possible desorption of the S^{2-} during chromophore formation. Direct comparison of samples collected on Cd(II)-exchanged zeolite to aqueous standards gives 20% lower values due to loss of gaseous H_2S in combination with incomplete recovery of MB from the zeolite surface. Although comparison to aqueous standards equilibrated with 200-mg portions of Cd(II)-exchanged zeolite gives recoveries similar to gaseous standards collected on 200-mg portions of this sorbent, their use is not recommended as some of the solution S^{2-} may be lost during equilibration in the form of H_2S. Calibration curves in the 0–5 μg H_2S range for 5-cm absorption cells have a slope of 0.18 ± 0.02 which are linear and usually intercept 0 μg of H_2S at slightly negative absorbance values. The average deviation for absorbance values at each concentration is about +10%, but when several standards of similar concentration are averaged and a calibration curve is constructed from the averages, all points fall on the curve. Calibration curves constructed in this manner are linear in the 0–40 μg H_2S concentration range with 80% recovery of the collected S^{2-} in the form of MB when compared directly to aqueous standards.

Characterization of Sorbent Material. Several lots of the Cd(II)-exchanged zeolite were prepared, and the surface capacity for S^{2-} uptake was evaluated by exhaustive uptake of aqueous S^{2-}. Excess S^{2-} was determined after each successive equlibration of stock S^{2-} solution with 1.0 g of Cd(II)-exchanged zeolite. Lots prepared with similar mesh size gave similar capacities (0.143 ± 0.015 mequiv/g for lots 1–3) while lots prepared from smaller particles gave high values. Samples of equilibrated sorbent material sent out for sulfur determination by combustion analysis followed by nondispersive IR gave lower results (0.077 ± 0.019 mequiv/g) but similar capacities between lots. No attempt was made to correlate nondispersive IR results with methylene blue results. The S^{2-} capacities of the sorbent were taken as an indication of gas-phase breakthrough capacity. However, sampling tubes prepared with smaller particles gave too much of a pressure drop for the DuPont pump and, because of this, were not suitable for sample collection at 2.0 L/min.

Table I demonstrates the necessity for multiple extractions of samples containing >2 μg of collected S^{2-}. Data in Table I should be used as a guide to the number of extractions necessary for each sample by comparing the color of the samples to the color of standard amounts of H_2S collected on Cd(II)-exchanged zeolite. For samples requiring multiple extractions there is no relationship between amounts recovered during each extraction, but the total recovered was found to be a constant (ca. 80%) for four-point calibration curves constructed on each day of sampling at these high levels. Linear calibration curves were obtained during every experiment. This will not be necessary in H_2S analysis of most ambient air samples since it is normally present in <ppb concentrations. Nevertheless, more than one extraction may be necessary in the analysis of industrial-type air samples containing higher concentrations of H_2S. Alternatively, lower sampling flow rates may be more desirable to limit the quantitites of collected H_2S to amounts which require only a single extraction. Samples used in other experiments which were collected at much slower flow rates and at higher H_2S concentration indicate complete sorption of H_2S. Visual inspection of the beds indicate that the slower flow rates improve collection efficiency; i.e., the canary yellow CdS appears localized at the front portion of the sorbent bed as opposed to color intensity trailing off toward the end of the primary sorbent bed. Evaluation of backup sections indicate quantitative removal of H_2S in the primary bed. Additionally, finer particles can be used at reduced flow rates. Other studies not reported here indicate that under 0.1 L/min sampling flow rates 35/45 mesh sorbent is suitable. The properties of this smaller particle material are such that in addition to being a much more efficient sorbent, the collection capacity for H_2S is greatly enhanced with respect to breakthrough.

Evaluation of Breakthrough. For the evaluation of breakthrough capacity, specially designed sorbent tubes were prepared as described previously. Sample collection was performed in the normal manner at 0.29, 1.2, and 1.7 μg H_2S/min of sampling time at a flow rate of 2.0 L/min. The collected H_2S was then determined in both backup sections, and the amount collected on the primary bed was calculated by difference. Extrapolation of this breakthrough curve (not shown) for the primary bed with sampling at 0.29 μg of H_2S/min to where 50% is recovered and 50% loss occurs is at approximately 350 μg of H_2S (36% saturation of the primary sorbent bed). As a general rule, if greater than 90% of the total determined H_2S is recovered from the primary sorbent bed, then no breakthrough has occurred (22). For this surface 90% recovery in the primary sorbent bed is obtained when approximately 155 μg of H_2S has been collected. Another general rule is that when less than 75% of the total H_2S determined is from the primary sorbent bed, then significant breakthrough has occurred, and it is recommended that the results be reported as minimum concentration rather than the actual concentration (22). A 75% recovery in the primary sorbent bed for the Cd(II) surface is obtained when 255 μg of H_2S has been sorbed. For the method this corresponds to a net loss of less than 5% H_2S through both primary and first backup sections, with 100% sorption of H_2S at lower concentrations normally encountered in air sampling. The breakthrough curve for collection at 1.2 μg H_2S/min is similar with the following exceptions: (1) The 90% collection in the primary sorbent bed occurred after collection of only 73 μg of H_2S. (2) The 75% collection occurred at 150 μg of H_2S. For the breakthrough curve shown in Figure 1 samples were collected at 1.7 μg/min, and both of the backup sections were 200 mg portions. Sections containing <10 μg of S^{2-} were analyzed in our laboratory by the MB procedure while other sections were sent out for analysis using the LECO system. For the curve shown in Figure 1 the 90% recovery in the primary bed occurred after collection of 95 μg and the 75% recovery in the primary bed occurred after collection of 182 μg. This indicates that collection from the gas phase is efficient at our sample concentrations of H_2S, although no exact correlation exists between sample concentration and break-

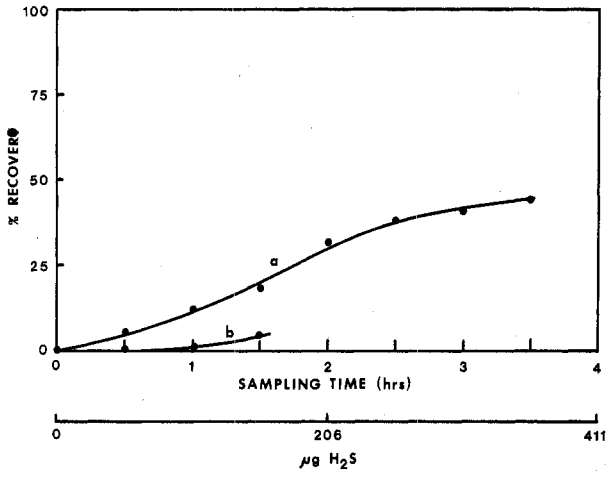

Figure 1. Concentration distribution in Cd(II)-exchanged zeolite sorbent tube and vapor breakthrough with sampling rate at 2.0 L/min. Key: (a) H_2S breakthrough for primary sorbent bed. (b) H_2S breakthrough for primary sorbent bed and backup section.

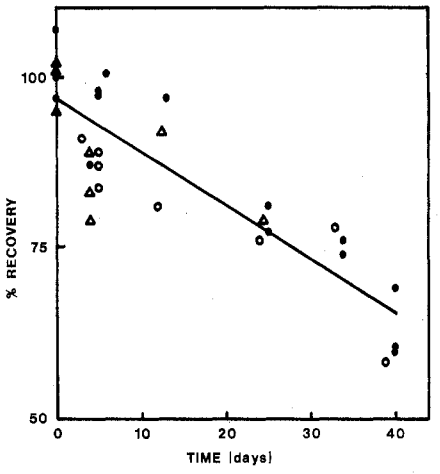

Figure 2. Recovery of H_2S as a function of storage time based on 100% recovery at time = 0 for 0.82 and 2.45 μg of H_2S. Key: (a) ●, 0.82 μg of H_2S; (b) △, 2.45 μg of H_2S; (c) O, other (1.9–4.4 μg of H_2S).

through for this sorbent. For collection at slower flow rates this sorbent material appears to be more efficient although no actual breakthrough data were collected.

Recovery of H_2S. Evaluation of the efficiency of recovery of H_2S from the sorbent in the form of MB was critical. Gas standards as well as aqueous standards were used to determine recoveries from the sorbent. Five separate determinations were made at several concentrations; reproducible recoveries were obtained. Recovery of 80 ± 4% was obtained from the surface when gas standards were used and absorbance values compared to calibration curves constructed from aqueous standards that were not equilibrated with Cd(II)-exchanged zeolite (Table I). It is essential that the MB layer be separated from the solid sorbent as soon as it is formed (actually as soon as the chromophore-forming intermediate is formed) or the MB chromophore adsorbs irreversibly to the sorbent material. Furthermore the reagents should be added rapidly to prevent loss of gaseous H_2S formed as the strongly acid DPA reagent comes in contact with the sorbent. Addition of reagents by use of calibrated eye droppers is recommended since the reagent delivery rate is faster with eye droppers than by pipetting. Data are included in Table I to demonstrate the need for repetitive extractions at high concentrations of H_2S.

Storage of Samples. Storage experiments were conducted with cadmium exchanged zeolite to test the feasibility of collecting air samples in the field and returning them to the laboratory for analysis. Collected samples of 0.8–4.4 μg of hydrogen sulfide on 200-mg portions of the sorbent were stored in unsealed tubes in a clean desiccator at room temperature over a 40-day period. A least-squares evaluation of the data in Figure 2 gives a curve intercepting time = 0 at 97 ± 3.5% recovery with a net loss of 0.78% H_2S/day of storage.

Interferences. Interference studies were conducted to determine the effect of other possibly interfering pollutants on the collection and determination of H_2S. Results are reported in Table II. Methyl mercaptan and carbonyl sulfide were found not to interfere, whereas the presence of large amounts of dimethyl sulfide and dimethyl disulfide relative to ambient H_2S concentration gave higher values. Neither dimethyl sulfide or dimethyl disulfide react in the MB method. It is anticipated that either these two compounds decompose on the surface of the sorbent to form CdS or the permeation tubes are contaminated with H_2S. Sampling in the presence of nitrogen dioxide and sulfur dioxide lowers results by oxidation of H_2S as described in the literature. We assumed that the interference at these artificially large ratios for NO_2 (or SO_2) to H_2S may not be a significant problem in ambient

Table II. Effects of Other Atmospheric Constituents on Collection and Determination of H_2S

interferent		amt of H_2S, μg		%
type	amt, μg	taken	determined	recovery[a]
SO_2	1190	1.96 ± 0.00	2.04 ± 0.16[b]	104 ± 8
	79.0	2.57 ± 0.03	2.48 ± 0.20[b]	96 ± 8
	1.3[c]	2.70	2.81	104[d]
NO_2	198[c]	2.57 ± 0.03	2.45 ± 0.11[b]	95 ± 4
	9.6-12.0[e]	4.35-5.26[e]		101[f]
COS	99[c]	1.77 ± 0.11	1.58 ± 0.05[b]	89 ± 3
CH_3SH	28.8[c]	1.77 ± 0.11	1.77 ± 0.21[b]	100 ± 12
C_2H_5SH	<10.8[g]	2.70	2.81	104[d]
$(CH_3)_2S$	14.4	2.70	3.35	124[d]
$(CH_3S)_2$	3.6	2.70	3.02	112[d]

[a] Based on 100% recovery for H_2S collected in the absence of potential interferents. [b] Standard deviation on triplicate determination. [c] Values based on information provided with permeation devices. [d] Single determination. [e] Range for three samples. [f] Average recovery for three samples. [g] Based on permeation rate given at 50 °C but with sampling at 30 °C.

samples. Our assumption received support from experiments with lower ratios of sulfur dioxide and nitrogen dioxide to H_2S where no interference was found (Table II).

In addition to data indicating SO_2 and NO_2 oxidize collected H_2S, ozone was found to be another even more serious oxidant occurring in actual sampling environments. Due to the lack of equipment at our laboratory we were unable to sample H_2S and O_3 simultaneously or under the same sampling conditions. However, if we assume that any H_2S coming in contact with O_3 prior to collection would destroy H_2S, then collection of H_2S under these conditions would not be indicative of the original H_2S concentration but would be a measure of the combined effects of O_3 degradation of the sample prior to collection as well as after isolation. The more serious problem would be the effect of O_3 oxidation on collected, immobilized pollutant during sampling. As a means of evaluating how O_3 affects the immobilized pollutant, samples were collected in the normal manner from O_3-free atmosphere and then "recollected" using H_2S-free, O_3-containing atmosphere and in a manner as closely approximating the original sampling procedure as instrumental constraints would allow. At high O_3 concentrations (0.38 ppm) the O_3 appeared to lower the total recovered H_2S by a constant nonstoichiometric amount as shown in Figure 3. The total exposure of samples to O_3 was 1.4 μmol, resulting in a constant loss of 0.037 μmol of

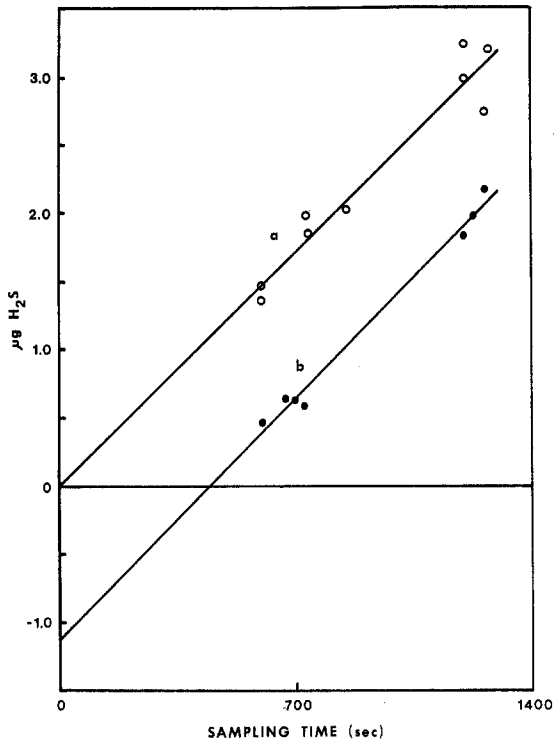

Figure 3. Effect of ozone exposure on recovery of sulfide from Cd-(II)-exchanged zeolite. Key: (a) no ozone exposure; (b) after exposure to 67 μg of ozone.

pollutant (corresponding to 1.2 μg of H_2S) from samples initially containing between 1.5 and 3.8 μg of H_2S.

We suspect two possible pathways or some combination thereof contributed to the lower recoveries of H_2S after O_3 exposure. Firstly, some of the immobilized S^{2-} may be buried too deeply within the zeolite structure for the O_3 to come into contact with it and react. Secondly, as more of the H_2S is collected, more of the surface sites at the front of the sorbent bed become saturated and subsequent collection occurs at a greater distance from the front of the sorbent bed. This leads to greater concentrations of H_2S being immobilized on a greater portion of the sorbent bed. If the O_3 is also destroyed by contacting the zeolite surface, then the O_3 would be destroyed before coming in contact with the S^{2-} immobilized further down the sorbent bed. Hence for increasing amounts of H_2S and loss of a constant amount of H_2S, the net effect is an increasing recovery as shown in Figure 3. No attempts were made to distinguish which of the two pathways is the one contributing to the low recoveries most predominantly or to selectively remove or destroy the O_3, prior to contacting the sorbent bed.

Effect of Humidity. Two independent studies were conducted in order to evaluate the effect of humidity on the collection of H_2S and subsequent determination thereof. Calibration curves were established in the 0–5 μg of collected H_2S concentration range where the gaseous standard matrix consisted of dry N_2, dry air, ambient air (relative humidity = 58% at 23 °C) and ambient air after bubbling through saturated aqueous solutions of $CuSO_4$ (98% relative humidity), $(NH_4)_2SO_4$ (80% relative humidity), and $Ca(NO_3)_2$ (50% relative humidity) (*26*) prior to passing the air through the Dynacalibrator rotameters. For the saturated solution experiments, the air stream was split into two channels, each passing through two 500-mL bubblers in series each containing 300 mL of saturated salt solution to handle the high flow rate. Two humidity gauges (one wet and dry bulb thermometer type and one "aneroid" type) were used to monitor the humidity of the effluent gas. Humidity values for the air samples

Table III. Time Weighted Average Exposure in Freshman Qualitative Analysis Laboratory

sample	collection time[a] (h, min)	amt of H_2S determined, μg	TWA H_2S concn, ppb
anion analysis	2, 30	1.00	2.4
acid metal sulfide	2, 30	16.1	38.0
precipitation	2, 44	31.0	74.0
basic metal sulfide	2, 57	9.16	18.6
precipitation			

[a] Sample collection at a flow rate of 2.0 L/min.

prepared by bubbling air through saturated salt solutions did not compare well to specified values, the $CuSO_4$ solution deviating the most from published values giving only about 70% humidity indicating inefficiency in our bubbler system. All calibration curves constructed in the 0–5 μg of H_2S range collected under the previously specified conditions were linear with similar slope and intercept except for that of $CuSO_4$. It appears that traces of $CuSO_4$ may have come through the filter (a 7-cm glass wool plug) following the bubbler system which accumulated on the sample tube as evidenced by a pale blue coloration on the front section of the sampling tube. The Cu(II) may have interfered with the subsequent chromophore-forming step giving a lower sloping calibration curve.

Samples collected from dry air did not appear to give the pale yellow CdS color at the front portion of the sampling tube for the calibration curve studies although quantitative collection was achieved. The presence of humidity in the sampling air may cause more efficient collection of H_2S in this concentration range at the very front of the sorbent bed. Although the samples from dry air have comparable collection efficiencies, the beds had no perceptible coloration in the front portion of the sorbent bed indicating that collection occurred throughout the sorbent bed in a more diffuse manner. Samples sent out for photoacoustic analysis gave the same spectral characteristics regardless of the humidity of the sampling atmosphere. As a consequence of the alteration of collection efficiency, breakthrough curves were also determined at a collection rate of 1.2 μg of H_2S/min for dry and ambient air (50% relative humidity at 22 °C). Both curves were similar although for collection of small amounts of H_2S as in a calibration curve dry air gave colorless samples when compared with similar quantities of H_2S collected from ambient air. Collection and determination of gross amounts of H_2S (0–250 μg) did not appear to be affected by a lack of humidity. This peculiar collection effect (lack of observable coloration in the primary bed) was also observed for sampling of H_2S in the presence of virtually all of the potential interferent compounds examined under interference studies.

Field Sampling. Indoor and ambient air samples were collected on sorbent tubes for subsequent analysis of H_2S (Table III). For indoor sampling, air samples were collected in the freshman qualitative analysis laboratory. Sampling time was approximately 2–3 h, one laboratory period.

Ambient air sampling was performed in Cincinnati, OH, at different locations. For a 24-h collection period under our specified conditions, the minimum atmospheric concentration detectable was ca. 0.06 ppb H_2S. The four samples collected near the University of Cincinnati campus (three for 24 h and one for 30 h) contained less H_2S than our detection limit which is probably a consequence of long-term low-concentration ozone exposure. One sorbent section turned pale blue indicating collection of a very small amount of H_2S.

Surface Investigations. In addition to the foregoing spectrophotometric method, we are trying to devise a method where we can use the sorbent with sulfide on it directly for the analysis of H_2S, thus eliminating the intermediate steps

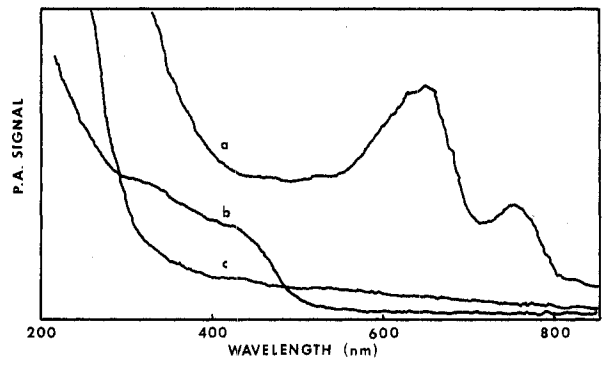

Figure 4. Photoacoustic spectra of species involved in collection and determination of H_2S on Cd(II)-exchanged zeolite. Key: (a) methylene blue sorbed on Cd(II)-exchanged zeolite; (b) immobilized H_2S on Cd-(II)-exchanged zeolite in the form of yellow CdS; (c) Cd(II)-exchanged zeolite blank.

of conversion of CdS to MB and its elution, etc. Alternative methods for surface determination of the collected H_2S which extend the quantitation range are in progress and are the topic of a future article. In these attempts we are using photoacoustic spectroscopy (PAS) and combustion analysis followed by nondispersive IR. Figure 4 is the PAS record of the species involved in the sample collection and subsequent analysis of H_2S with respect to the Cd(II)-exchanged zeolite as blank. The canary yellow (14.2 μg of sulfide/500 mg of zeolite) CdS spectrum is partially obscured by the zeolite UV cutoff, but a distinct peak at 300 nm and a shoulder in the 450-nm region were identifiable. The MB spectrum contains an equivalent amount of reacted sulfide to that of the CdS spectrum and demonstrates that the absorptivity of the CdS is considerably less than that of MB. The peaks in the MB spectrum correlate well with those of visible internal reflectance spectroscopy on glass (27). The peaks at 630 and 750 nm correspond to dimer or aggregates adsorbed on glass and the one at 660 nm to the monomer. Attempts at obtaining quantitative results by surface techniques such as PAS directly on the CdS or the MB on zeolite have yielded preliminary results indicating that an order of magnitude lower detection limit for MB on the Cd(II)-exchanged zeolite can be expected from PAS. The anticipated sensitivity of PAS will allow us to lower the sampling time for ambient air samples to where the effect of ozone will be negligible.

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