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Performance of Sulfur Dioxide Passive Monitors*

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The following four commercial sulfur dioxide passive monitors were tested for performance and realiability: DuPont Pro-Tek® C-20 air monitoring badges; MSA Vaporgard™ Dosimeter tubes; REAL BioBadges; and 3M Sulfur Dioxide Nutshell monitors. The experiments conducted were designed to test factors critical to the operation of passive samplers: accuracy and precision; capacity; stability; analytical recovery; and the effects of exposure time, concentration, humidity, face velocity, orientation, chemical interference, and temperature. The DuPont Pro-Tek badges performed satisfactorily for all the factors tested, and the REAL BioBadges performed satisfactorily except for the instability of the SO_2/tetrachloromercurate complex when stored. An alternate monitoring system, REAL BioBadges containing deionized water absorbent had a limited capacity. Only the MSA dosimeters exhibited unsatisfactory performance. The 3M Nutshell monitor was withdrawn by the manufacturer after only partial evaluation.

Introduction

A set of experiments which were designed to examine factors critical to the operation of passive monitors was conducted to evaluate commercial passive monitors for sulfur dioxide (SO_2). The monitors tested were: DuPont Pro-Tek C-20 air monitoring badges [DuPont], Mine Safety Appliances Vaporgard Dosimeter tubes [MSA], and Reiszner Environmental and Analytical Laboratories BioBadges [REAL-TCM]. As an alternate monitoring system, deionized water was used in the REAL BioBadges [REAL-H_2O)] instead of the recommended absorbing solution. The 3M Sulfur Dioxide Nutshell monitor [3M] was partially evaluated in this study. The need to determine operating ranges and limitations of passive monitors has been illustrated by past studies.(1-4) In this study of SO_2 passive monitors, the factors were evaluated in the laboratory in the following order: sampling rate and capacity; stability during exposure; storage stability; performance parameters (effects of varying contaminant concentration, exposure time, face velocity, humidity, interferences, and monitor orientation); temperature effects; and accuracy and precision. In addition to laboratory evaluation, samples were taken to determine accuracy and precision under field conditions. This paper describes the procedure followed for each of the evaluation experiments and presents the results obtained for each monitor tested.

Experimental Section

Exposure Chamber

The exposure chamber used to maintain atmospheres of SO_2 in this study was a recirculating system with an internal volume of 520 liters (Figure 1). The chamber was constructed of 12-mm (½-inch) Plexiglas® and galvanized sheet metal ductwork incorporating a Dayton centrifugal blower powered by a ½-hp electric motor. All exposed metal surfaces inside the chamber were coated with acrylic. Face velocities were controlled by varying the pulley size on the blower and motor and by adjusting the throttle plates at the top of the chamber. Sleeve gloves on the face of the chamber and a double door access port on the side allowed for addition and removal of samplers during an exposure without disturbing the test atmosphere. The chamber had 18 sampling ports where passive monitors may be placed or active samplers may be attached via quick-connects to sampling pumps. Located at the bottom of the chamber, a 15-meter coil of stainless steel tubing (6.4-mm OD) was connected to a constant temperature bath (Forma Scientific Model 2095, Marietta, Ohio) to provide heating and cooling. Mass flow controllers (Tylan Model FC260, Torrence, CA) metered analyzed gases and air into the chamber through quick-connects located in a plate immediately above the blower. A septum was also located in this plate for syringe injection of water to increase and maintain a constant humidity. A dessicant, silica gel or Drierite™, was used to lower humidity. An Interscan SO_2 Meter, Model 1248 (Chatsworth, CA), was used to monitor the concentration of SO_2 continuously in the exposure chamber throughout the exposure time. A nitrogen dioxide continuous monitor (Columbia Scientific Industries, Model 1600, Oxides of Nitrogen Analyzer) was employed to determine the concentration of NO_2, a potential interfering gas for some samplers.

Field Sampling Chamber

During field sampling, the independent method samplers and the passive monitors were physically located such that both sampled the same air mass and were exposed to a face velocity sufficiently high to prevent passive monitor starvation. A field sampling chamber (Figure 2) was constructed from a 50-L carboy (38-cm diameter by 42 cm high) with the bottom cut off. The neck portion was inserted into a high volume blower mounted in a support stand. Sample holders were located 20 cm below the top of the chamber. To straighten the flow of air through the system, a removable

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*Mention of any manufacturer or product name does not constitute endorsement by the National Institute for Occupational Safety and Health.

Teflon® plate or polyproplyene screen was attached to the top of the chamber.

Sulfur Dioxide Passive Monitors

Commercial passive monitors for SO_2 available at the initiation of this study were used in the evaluation. Although the 3M SO_2 Nutshell monitor was available at the beginning of the study, the manufacturer withdrew the product before the evaluation was completed.

Du Pont. The Du Pont Pro-Tek C-20 badge collected SO_2 by molecular diffusion and absorption into a solution specific for SO_2. The plastic holder housed a reagent blister pack, incorporating a proprietary diffuser element through which the contaminant gas (analyte) diffused to the blister containing the absorbing solution. Other blisters contained the reagents needed to produce a colorimetric reaction with the absorbed SO_2. The intensity of the color formed was proportional to the amount of SO_2 collected.(5)

MSA. A diffusion-controlled, direct-reading length of stain sampler, the MSA Vaporgard™ dosimeter for sulfur dioxide consisted of a glass tube containing a strip of phenolsulfonephthalein-impregnated paper.(6) The reaction of SO_2 with the phenolsulfonephthalein-impregnated paper produced a color change from red-purple to yellow, which was caused by a change in the structure of the pH indicator. The length of stain on the paper strip was read in millimeters from the scale printed on the tube, and the concentration of SO_2 was estimated from a family of calibration curves (stain length, mm *vs.* exposure time, hr) provided with each package of tubes.

REAL-TCM. The REAL BioBadge for SO_2 consisted of a silicone membrane cemented over a hollow plastic chamber.(7) When the device was exposed, SO_2 permeated through the membrane and was captured by the absorbing medium, a sodium tetrachloromercurate solution. Stabilized in a dichlorosulfitomercurate complex, the captured SO_2, was then determined by the colorimetric West-Gaeke procedure.(8) Because of the nature of the silicone membrane, the permeation constant for each badge must be calibrated individually. For each REAL BioBadge used in this study the permeation constant 'k' was determined in our laboratory.(9) Strong correlation was found between the determined k values and those provided by the manufacturer for the six BioBadges which were purchased precalibrated. REAL BioBadges are refillable, reuseable devices.

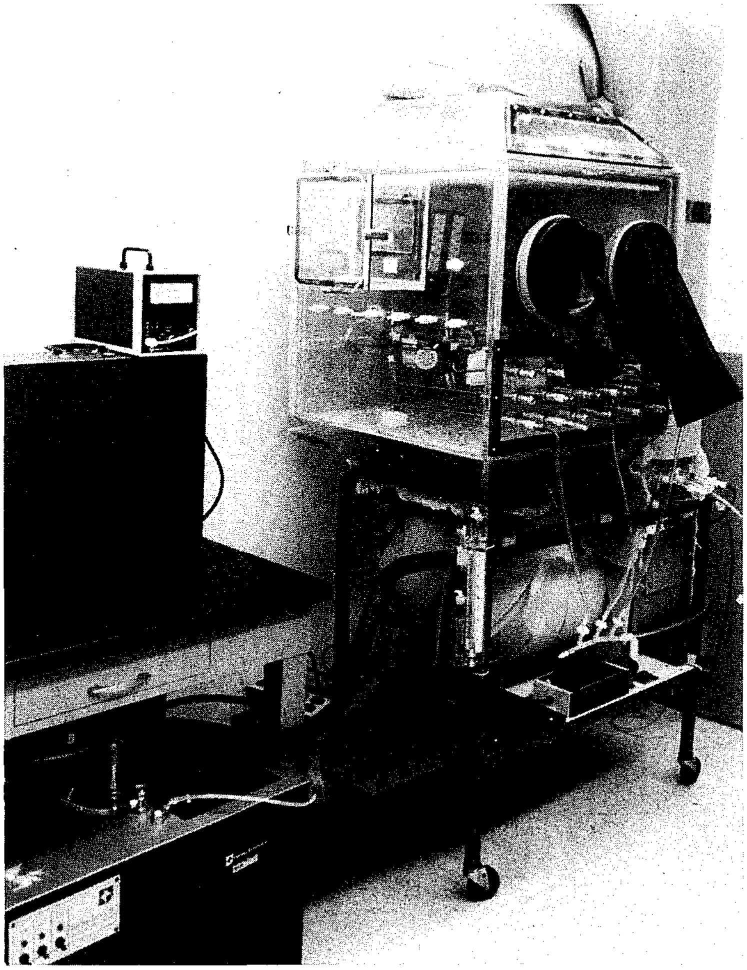

Figure 1—Laboratory exposure chamber.

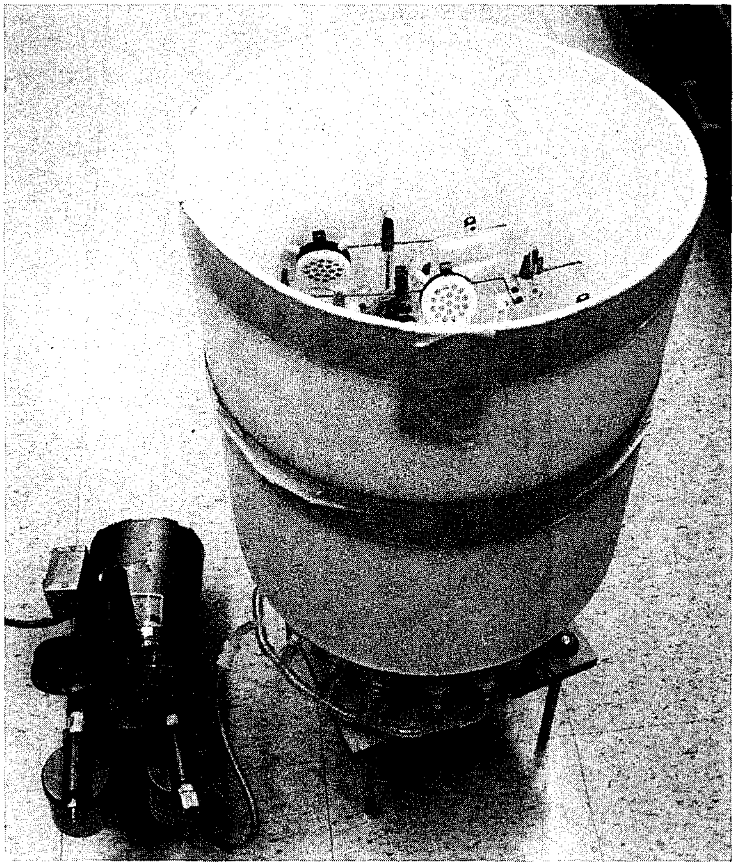

Figure 2—Field sampling chamber.

REAL-H_2O. As an alternate sampling and analysis system for SO_2, REAL BioBadges were filled with deionized water. After exposure to SO_2 and subsequent oxidation with hydrogen peroxide, the amount of sulfate present in the absorbing medium was determined by ion chromatography (IC).(10)

3M. A diffusion-controlled, direct-reading badge, the 3M SO_2 monitor was designed to measure eight individual levels of time-weighted average exposure. SO_2 diffused through a draft shield into the eight chambers of varying size and reacted with an indicator causing a color change from dark blue to gray. The exposure was determined from a conversion table listing the number of areas which completely changed color with the corresponding ppm-hours of exposure.

Reference Sampling Methods

In addition to the direct-reading Interscan SO_2 meter which monitored the concentration of SO_2 throughout the exposure time, samples of the chamber atmosphere were collected in bubbler sets (primary and back-up) at approximately 50 mL/min. Two bubbler sets contained 15 mL of 0.1 M sodium tetrachloromercurate (TCM) and were analyzed colorimetrically according to P&CAM 160.(11) Two sets contained 15 mL of 3 mM Na_2CO_3/2.4 mM $NaHCO_3$ buffer and were analyzed by ion chromatography (IC). The reference concentration of SO_2 in the test system was established from these independent samplers.

Analytical Methods

All chemicals used were ACS analytical grade or equivalent; deionized water was used throughout the study.

The DuPont monitors were analyzed according to the DuPont operating instructions.(5) The reagents from the blisters were released into the absorbing solution producing a color reaction. The SO_2 concentration was determined with a DuPont PT-3 Readout Unit. The 3M monitors and MSA dosimeters were direct-reading monitors requiring no chemical analysis.

Colorimetric Procedure

The REAL-TCM monitors and the bubblers from one of the independent methods employed 0.1 M sodium tetrachloromercurate (TCM) as the absorbing liquid for SO_2. After sampling, volumes were adjusted to 15 mL for the bubblers and to 10 mL for the monitors. If concentrations above 2 μg SO_2/mL were anticipated, the samples were diluted with absorbing solution prior to analysis. To a 10-mL sample aliquot, 1 mL each of pararosaniline reagent and 0.2%(v/v) formaldehyde solutions were added. Following a 30-minute color development period, the absorbance of the sample *vs.* a reagent blank (treated identically as the sample) was determined at 560 nm on a Beckman Model 26 spectrophotometer. Sample absorbances were compared to calibration curves to determine the quantity of SO_2 in the sample. Standards used for generating the calibration curves were prepared by dissolving dry sodium sulfite in the 0.1 M TCM solution.

Ion Chromatographic Procedure

Ion chromatography (IC) was utilized to determine the concentration of the SO_2 absorbed by: 1) the REAL-H_2O monitors containing deionized water, and 2) the independent method bubblers containing the carbonate/bicarbonate buffer. After the addition of 5 μL of 30% hydrogen peroxide to convert the SO_2 in the sample to a stable sulfate, the samples from the monitors were diluted to 10 mL with deionized water and the bubbler samples were diluted to 15 mL with buffer solution. The samples were analyzed on a Dionex Model 14 Ion Chromatograph equipped with a Waters WISP 710B autosampler and interfaced with a Hewlett-Packard 3356 Laboratory Automated Data System. The sulfate peak eluted in approximately 6.7 minutes with an eluent solution of 3 mM $NaHCO_3$/2.4 mM Na_2CO_3 at a flow rate of 3 mL/min (40% pump capacity); fast run anion separator (AS3) and guard (AG3) columns; a standard anion supressor; a conductivity detector set at 30 microSeimens (μS)/cm; and a 100μL injection volume. Samples were quantitated by comparison with a standard calibration curve (peak height *vs.* concentration). Working standards were prepared from a 1000 μg/mL sulfate stock solution.

For both the colorimetric and IC procedures, the total mass (μg) of SO_2 in the sample was determined from a calibration curve. Time-weighted average air concentrations of SO_2 were determined for the REAL BioBadge samples following equation:[9,12]

$$C = \frac{wk}{t}$$

C = air concentration of SO_2 (ppm)
w = mass of SO_2 found (μg)
k = permeation constant $\left(\frac{\text{ppm-h}}{\mu g}\right)$
t = exposure time (h)

The performance of the SO_2 passive monitors was evaluated using the set of experiments described below.

Evaluation Experiments

Sampling Rate and Capacity

Twenty passive monitors from each manufacturer were exposed to a constant SO_2 concentration of 10 ppm, relative humidities of 74±6%, and face velocities of 0.5±0.05 meters per second (100±10 fpm) for time periods of 0.125, 0.25, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 hours. Two monitors were removed and analyzed for each time interval.

Figure 3 presents the data in a concentration *vs.* time plot with error bars shown at ±25% of the SO_2 concentration. In general, the initial response for all the monitors, with the exception of 3M, was 2 to 2.5 times the actual concentration as determined by the reference methods. Within 0.5 to 2 hours, the curve reached a linear horizontal line at the actual air concentration. This linear horizontal portion of the curve indicates a constant sampling rate. The curve remains horizontal until the sampler begins to approach its capacity. At this point, the curve drops off, indicating an apparent decrease in sampling rate. In this study, the capacity was defined as the point where the curve deviated from the horizontal, indicating a decrease in uptake rate. To compensate for any reduction in capacity caused by sorption of interfering gases at the sampling site, a maximum recom-

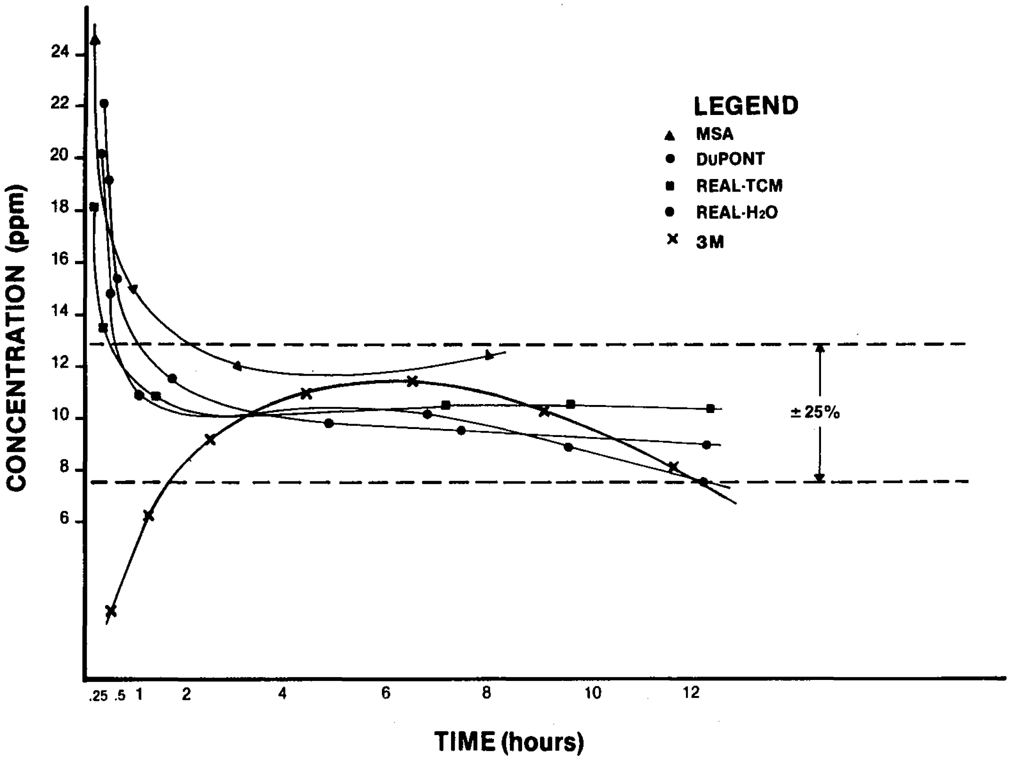

Figure 3—Sulfur dioxide badge responses.

TABLE I
Stability of SO_2 Passive Monitors

	DuPont	MSA	REAL-TCM	REAL-H_2O	3M
Stability during exposure					
4-h SO_2	12.1±0.3	10.5±1.1	8.2±0.4	8.6±1.1	11.9±1.0
4-h SO_2 + 4-h clean air	11.7±0.3	12.8±1.3	8.4±0.5	7.4±1.8	12.8±1.5
Difference (%)	- 3	+22*	+ 2	-14	+8
n	10	10	9	11	7
Storage stability					
Day 1 conc. (ppm±s)	6.5±0.4	6.1±0.8	4.7±0.2	3.9±0.3	N/A
n	10	10	8	8	
14-day ambient (ppm±s)	4.5±0.4	N/A	3.9±0.2	4.2±0.2	--
Difference (%)	-31*		-17*	+ 8	
n	10		7	7	
15-day refrig. (ppm±s)	5.9±0.4	N/A	3.6±0.5	4.5±0.2	--
Difference (%)	- 9		-23*	+15	
n	10		7	6	

s = standard deviation
N/A = not applicable
* Failed application criterion at 95% confidence level

TABLE II
SO_2 Passive Monitor Summary

Evaluation Experiment	DuPont	MSA	REAL-TCM	REAL-H_2O	3M
Sampling rate and capacity					
Uniform rate (h)	1-12	2-8	0.5-12	0.5-8	2-8
MRST (h)	8	5	8	5	5
Mfg. recommendation	10-100ppm-h	2.5-25ppm	None	N/A	None
Minimum	1h				10 ppm-h
Stability during exposure					
Difference (%)	- 3	+22*	+ 2	- 14	+8
Storage stability					
14-day ambient recovery (%)	69*	N/A	83*	108	N/A
15-day refrigerated recovery (%)	91		77*	115	
Mfg. recommendation	7 d refrig. 1 d ambient		None	N/A	
Performance parameters					
Significant parameter	None	None	None	Time	--
Experimental error(%)	15	60	7	10	
Temperature Effects					
(Theor. ratio=0.95)					
M_L/M_H	0.96	0.89	1.34	0.94	--
Mfg. literature	$\frac{273+t}{298} \times \frac{760}{P}$	4-32°C	+0.5%/°C	N/A	
Accuracy and precision					
Mean recovery (%)	98.7	144	90.5	97	--
Pooled s_r	0.05	0.179	0.098	0.09	
Range (ppm)	2.5–10	1-10	2.5-10	1-10	
Mfg. literature	±12.6%	±25%	None	N/A	

N/A=Not applicable
*Failed application criterion at 95% confidence level.

mended sampling time (MRST) was set at two-thirds of the time required to reach the capacity of the monitor. Specific monitor responses, their MRST values and manufacturers' sampling recommendations are discussed below:

- DuPont monitors required approximately 1 hour to fall within the ±25% error range. After 2 hours they were very close to the true value, and the curve was still linear at 12 hours exposure. The MRST was determined to be 8 hours. DuPont recommended a 1-hour minimum sampling time.
- MSA dosimeter tubes required more than 2 hours to fall within the ±25% range. After 8 hours, the impregnated paper strip had completely changed color. The calibration information provided in the MSA literature indicated that the sampling time was valid only to 8 hours. No minimum exposure time was recommended by the manufacturer. The MRST was found to be 5 hours.
- REAL-TCM BioBadges came within ±25% after only 0.5 hour. The curve was linear and accurate from 2 to 12 hours. The manufacturer's literature made no sampling recommendations. The data indicated that the MRST was 8 hours.
- REAL-H_2O monitors also came within the ±25% range after only 0.5 hour. However, after about 6 hours, it appeared that the concentration of free SO_2 molecules in the water was having an effect on the amount of SO_2 passing from the air into the liquid, with the results having shown an apparent decrease in sampling rate. The MRST for this sampling system was 5 hours.
- 3M monitors had very low initial responses up until 2 hours of exposure. The response curve peaked at approximately 6.5 hours and then began dropping off, indicating an apparent decrease in sampling rate. The plastic draft shield on this monitor probably inhibited the diffusion of SO_2 either by adsorption or by slowing the diffusion rate—in effect, acting as a permeation membrane. The manufacturer recommended a minimum loading of 10 ppm-hours.

Figure 3 illustrates that all the SO_2 monitors tested, except 3M, exhibit very high uptake rates for exposure times of less than 30 minutes. This phenomenon held true for both diffusion-controlled monitors (DuPont and MSA) and permeation-controlled monitors (REAL). The reason was not clear: it may be caused by one or a combination of several mechanisms. Two possibilities are offered. One is the theory which proposes that, until a constant concentration gradient is achieved between the monitor and the surrounding air, there is an initial high flux of contaminant into the quiescent zone or the permeation membrane of the monitor. Although this quantity is quite small, it may be an important consideration in the quantities of contaminant collected for short time periods. Another possibility is that SO_2 adheres to the outside surface of the badge during sampling and is later collected by the sorbent as it off-gasses from the badge surface while in the shipping pouch. The effect is an apparent high sampling rate for short time intervals. The latter explanation would not necessarily hold true for the direct-reading MSA monitors. Because of the variability in the initial response of passive monitors, a minimum sampling time should be given for all monitors.

Stability During Exposure

Two sets of 10 monitors from each manufacturer were exposed to 80% relative humidity and 0.5 m/sec face velocity for 4 hours. The concentration of SO_2 was 12.0±0.2 ppm for the exposure of DuPont and MSA monitors and 8.4±0.2 ppm for the BioBadges, REAL-TCM and REAL-H_2O. After the 4 hour period, Set 1 samples were removed and analyzed; Set 2 samples were exposed for an additional 4 hours in an atmosphere with detectable levels of SO_2.

This experiment was designed to determine if any off-gassing of SO_2 occurs during periods of low analyte concentration following a period of high concentration. The data are shown in Table I. (The stability results are also noted in Table II, a summary of the passive monitor evaluation). To determine whether the differences between the two sets of monitors were within 10% at the 95% confidence level (C.L.), the data were calculated according to a statistical equation for the comparison of means and variances for a stated difference between two sets of data.(13) Each of the monitor types, except MSA, successfully met this criterion. Although the difference in mean concentration for the REAL-H_2O monitor sets was greater than 10%, when the standard deviation was considered, the difference was not significant.

Storage Stability

Three sets of 10 monitors each were exposed to approximately 5 ppm SO_2, 70±5% relative humidity, and 0.5 m/sec face velocity for 5 hours: Set 1 samples were analyzed on the first day; Set 2 samples were stored at ambient temperature (26° C) for 14 days; and Set 3 samples were refrigerated (6° C) for 15 days.

The data for the stored monitors are found in Table I. The statistical equation(13) was again used to determine whether the difference between the stored sets and the set analyzed on the first day was within 10% at the 95% C.L.

- DuPont monitor samples were unstable when stored for 14 days at ambient temperature but met the criterion for refrigerated storage. DuPont literature stated that exposed monitor samples are stable for 7 days when refrigerated. Recently published data indicated that DuPont field samples stored for 5 days at ambient temperatures showed no loss of SO_2.(14)
- MSA. Diffusion of the dye on the impregnated strip in the MSA dosimeter tube caused very high erroneous readings when stored. Since these monitors were direct-reading, the storage stability criterion did not apply.
- REAL-TCM monitor samples showed a significant loss

TABLE III
Sulfur Dioxide Field Data

	Mean(ppm)	s	s_r	N
Chamber A				
REAL BioBadge	1.2	0.14	0.117	10
MSA	3.5	0.85	0.243	15
Filters	0.66	0.023	0.035	11
Bubblers	0.42	0	0	3
Reference mean	0.61			14
Chamber B				
DuPont	0.54	0.058	0.107	14
Filters	0.42	0.015	0.035	12
Bubblers	0.44	0.150	0.340	4
Reference mean	0.42			16

Levels shown are below the manufacturers' recommended ranges for MSA and DuPont.

of SO_2 and therefore failed the 10% criterion for both refrigerated and ambient storage. The manufacturer supplied no stability data.

- REAL-H_2O monitor samples met the 10% criterion at the 95% C.L. for both ambient and refrigerated storage. The apparent gain during storage was possibly owing to more complete oxidation of the SO_2 in the water to sulfate.

- 3M monitors are direct-reading monitors; therefore, the storage stability criterion does not apply. Because additional 3M monitors were unavailable, no further testing was done.

Performance Parameters

A 16-run fractional factorial screening design[(15)] was used to test the performance parameters of concentration (2.5 and 10 ppm SO_2); exposure time (1 and 8 hours); face velocity (0.1 and 1.5 m/sec); humidity (30 and 80%); interference (0 and 5 ppm NO_2); and orientation (parallel and perpendicular to airflow). A scheme which tests extremes of variables, this experimental design reveals parameters and interactions of parameters which have a significant effect on the performance of the passive monitor; the design also gives an estimate of experimental error. Interactions are combinations of factors which, when working together, may affect the performance of the monitor, *e.g.*, time and concentration. A computer spreadsheet program for the 16-run fractional factorial was used in calculating the SO_2 data.[(16)] A detailed discussion of these data is covered in a separate publication.[(17)]

Four monitors of each type were exposed per run with the test concentrations 0.5 and 2 times the permissible exposure limit (PEL)(2.5 and 10 ppm). Exposure times were 1 and 8 hours; the only exception was for the MSA monitors where 6 hours was used as the long exposure time. The ability of the experimental design to determine interaction effects out caused by a reduced. uptake rate was tested utilizing an 8-hour exposure time for the REAL-H_2O monitors. The ranges for face velocity and relative humidity were those achievable in the exposure chamber. Since it is often found in conjunction with SO_2 and interferes in some chemical reactions, nitrogen dioxide (NO_2) was tested for interference at 0 and 5 ppm. Orientation of the passive monitor with respect to airflow may change the length of the quiescent diffusion zone or may otherwise affect the collection of the analyte (*e.g.,* liquid absorbers may not be in complete contact with the diffuser or the permeation membrane). Monitors were tested parallel and perpendicular to the airflow.

In general, the results of the experimental design showed:

1. There were no significant effects from SO_2 concentration, humidity, NO_2 interference, face velocity or orientation for any of the monitors tested.
2. Exposure time was a significant parameter with the REAL-H_2O monitoring system.
3. There were no significant interactions.
4. A large error was found for the MSA dosimeter.

Specific Results for individual passive monitors showed:

- **DuPont.** There were no significant effects or interactions observed with this monitor from any of the six parameters. Some interaction, although not significant, was indicated between time and orientation with SO_2 concentration and NO_2 interference. DuPont badges had an experimental error of approximately 15% as calculated from the significant factor effect.[(15)]

- **MSA.** An experimental error of about 60% was found for the MSA monitors. This extremely large experimental error—4 to 6 times greater than that of the other monitors—masked the effect of any factor that may have been significant. As indicated in the sampling rate and capacity experiment, time is a consideration with these monitors.

- **REAL-TCM.** The data indicated that none of the factors had a significant effect on the performance of the REAL BioBadges containing TCM as recommended by the manufacturer. Although not significant, a slight interaction was indicated between SO_2 concentration and NO_2 interference. This monitor had the smallest experimental error of approximately 7%.

- **REAL-H_2O.** The fractional factorial experimental design showed that, as expected, exposure time had a significant effect on the performance of this monitor. The results confirmed the earlier findings by indicating that the effect from exposure time was almost twice that of the experimental error for this monitor (10%). A small interaction between time and concentration was indicated.

Temperature Effects

Two sets of 10 monitors of each type were exposed to 8.0±0.4 ppm SO_2, 65±5% relative humidity and 0.5 m/sec face velocity for 4 hours. One set of 10 monitors was exposed at 14°C; the other set was exposed at 44.5°C.

Since the quantity of material sampled by a diffusional sampler is proportional to the square root of the absolute temperature,[(18,19)] the ratio of the mass collected at low temperature, M_L, to the mass collected at high temperature, M_H, is equal to the ratio of the square roots of the corresponding absolute temperatures:

$$\frac{M_L}{M_H} = \frac{(T_{low})^{0.5}}{(T_{high})^{0.5}} = \frac{(287° K)^{0.5}}{(317.5° K)^{0.5}} = 0.95$$

The data were normalized to 10 ppm prior to calculating the mass ratios. The summary table (Table II) lists the M_L/M_H ratios of the quantities of SO_2 found for each monitor type, also noting whether or not the manufacturer provided a temperature correction factor. Since DuPont and MSA are diffusional monitors utilizing a quiescent zone, they should compare favorably with the theoretical ratio. In permeation-controlled monitors, the temperature variation is dependent on the nature of the permeation membrane.

- **DuPont.** The mass ratio of 0.96 for the DuPont monitors compared very favorably with the theoretical ratio of 0.95. The manufacturer's literature provided a formula to convert SO_2 values to 25° C and standard pressure.
- **MSA.** The mass ratio for the MSA dosimeters was somewhat low at 0.89 but was well within the ±25% accuracy stated by the manufacturer. The high temperature used in this study was approximately 12° C higher than the upper limit of the temperature range recommended in the manufacturer's instruction; consequently, a variation could be expected.
- **REAL-TCM.** REAL BioBadges are permeation-controlled monitors where temperature variation depends on the properties of the membrane. In addition to the temperature effect on the permeability of the membrane, the high experimentally determined M_L/M_H ratio of 1.34 found for these badges may be caused by an instability of the dichlorosulfitomercurate complex at higher temperatures. Application of the 0.5%/° C correction factor provided by the manufacturer to the data improved the percent recovery at 14° C, but only slightly improved the recovery at the high temperature (44.5° C).
- **REAL-H_2O.** The M_L/M_H ratio for the REAL BioBadges containing deionized water was 0.94 and compared very favorably with the theoretical, indicating that temperature has a negligible effect on the permeation rate of the membrane.

Accuracy and Precision

Sets of 10 of each type of monitor were exposed to concentrations of SO_2, corresponding to 0.1, 0.5, 1, and 2 times the PEL (1 to 10 ppm) at 80% humidity, and 0.5 m/sec face velocity for 4 hours. In this study, the accuracy of each monitor was defined as the mean percent recovery of SO_2 based on the independent methods over the concentration range in which the data showed homogeneous variance. As determined by Bartlett's Test at the 1% significance level, this range is referred to as the homogeneous range. The precision was defined as the pooled relative standard deviation over the range of homogeneous variance. The data are presented in Table II.

- **DuPont.** The replicate data for DuPont monitors exhitited homogeneous variance over the range of 2.5 to 10 ppm SO_2 (0.5 to 2×PEL) with a mean recovery of 98.7% and with a pooled relative standard deviation ($\bar{s}_r$) of 5%. Some of the monitors that were used very close to their expiration date gave high results. This is consistent with absorbent loss from the badge by evaporation. If the volume of the absorbing solution is determined after exposure, this bias may be corrected.
- **MSA.** Although the experimental data for the MSA dosimeters had homogeneous variances over the entire range (1 to 10 ppm SO_2), the accuracy and precision were not acceptable. Recovery was 143.8% with a precision of 17.9%. This error was much greater than the ±25% accuracy claimed by the manufacturer.[6]
- **REAL-TCM.** For REAL BioBadges containing TCM, variances of the data were homogeneous over the range of 2.5-10 ppm SO_2. The mean recovery for the three concentration levels was 90.5%; the pooled $\bar{s}_r$ was 9.8%. Both precision and accuracy were acceptable in accordance with NIOSH validation tests.[20]
- **REAL-H_2O.** The REAL monitors containing deionized water and analyzed by IC had a mean recovery of 97% over the range of 1 to 10 ppm with a pooled s_r of 9%. This sampler system exhibited a wider concentration range of acceptable accuracy and precision than the monitor/absorbing solution combination recommended by the manufacturer.

Laboratory testing in controlled atmospheres indicated that with the exception of MSA dosimeters all the monitors had recoveries and precision within the targeted 10%. In field use, the "true" concentration of SO_2 is unknown and may fluctuate. Conditions will vary from industry to industry. For these reasons accuracy and precision must be determined under field conditions.

Field Sampling

Field samples were collected at a heavy industry where low levels of SO_2 were present. Two field sampling chambers (Figure 2) were used, each containing the passive monitors and two independent sampling systems: 1) TCM-filled bubblers (P&CAM 160); and 2) alkali-impregnated filters (P&CAM 268).[21] The data are tabulated in Table III. In each case the passive monitors indicated higher SO_2 concentrations than were found by the independent methods. Several factors may be responsible; chief among them was the low concentration level of SO_2 present during sampling, which was well below the manufacturers' recommended ranges. The laboratory evaluation data indicated that the sampling rates of passive monitors appeared to be high for short sampling periods or low loadings. For the average 4-hour exposure time, the respective loadings of 2.2 and 1.6 ppm-hours found in the field chambers were less than the recommended ranges of 10 to 100 ppm-hour for DuPont and 2.5 to 25 ppm-hour for MSA. No operating range information was given for the REAL BioBadges. Another consideration is the fact that some of the SO_2 collected in the bubblers and on the filters may have reacted with the metal dust present in rather high concentrations in the area producing lower results. Such an occurrence would be more apparent at very low SO_2 concentrations. The trends shown in the data were consistent with those found in the laboratory.

Summary and Conclusion

NIOSH developed the passive monitor evaluation experiments to provide a uniform basis for comparing passive monitors and to aid in the selection of the proper monitor for each sampling situation. The evaluation data for the four SO_2 passive monitors are summarized below and in Table II:

- DuPont Pro-Tek C-20 badges were acceptable both in performance and in the information provided by the manufacturer; *e.g.,* operating range, minimum exposure time, correction factors and stability data. Accuracy (98.7%) and precision (0.05) were excellent over the range of 0.5 to 2×PEL.
- MSA Vaporgard dosimeter tubes for SO_2 were unacceptable for accurate monitoring. They exhibited a consistently positive bias with respect to reference methods. Recovery data at 144% were much greater than the ±25% claimed by the manufacturer. Recalibration of the length of stain *vs.* concentration curves would improve the accuracy of the monitor, but the precision probably would remain unacceptable. The manufacturer's literature did provide concentration and temperature range information.
- REAL BioBadges, containing tetrachloromercurate absorbing solution (REAL-TCM), performed very well, but were unstable for both refrigerated and ambient 14-day storage. A constant sampling rate was reached after only 0.5 hour, and experimental error was small. The manufacturer had provided a temperature correction factor but no accuracy, precision, operating range or stability data.
- The alternate sampling system used in this study, REAL BioBadges containing deionized water (REAL-H_2O) exhibited excellent accuracy (97%) and precision (0.09) over the range of 0.1 to 2×PEL, and were stable for at least 14 days at ambient temperatures. However, after about 6 hours, the monitor exhibited an apparent decrease in sampling rate. The MRST for this system was 5 hours. A carbonate/bicarbonate absorbing solution, as is used in one of the reference methods, would eliminate this apparent decrease, since a reaction would take place between the SO_2 and the buffer.

The evaluation experiments have exhibited the flexibility to evaluate both diffusion and permeation controlled monitors, both liquid and impregnated solid sorbents, as well as providing an estimate of the experimental error. The DuPont Pro-Tek badges performed well for all the factors tested. The MSA dosimeter tubes did not perform satisfactorily for most of the factors tested. In general, the REAL BioBadges performed well except for the instability of the dichlorosulfitomercurate complex in the REAL-TCM monitors, and for the limited capacity of the deionized water absorbent in the REAL-H_2O samplers.

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