

**Validation of Sulfur Dioxide Using
SKC UME^x 200 Passive Sampler Cat. No. 500-200**

Research Report

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Abstract

A partial validation was performed using the UME^x 200 Passive Sampler (SKC Inc., Eighty Four, PA, U.S.A., Cat. No. 500-200) to determine the accuracy of the sampler when sampling sulfur dioxide in workplace air. A desorption efficiency (DE) study was conducted at levels of 0.05, 0.10, 0.50, 1.0, and 2.0 times the PEL (2 ppm) for an 8-hour period. The average desorption efficiency was determined to be 97.8% with a relative standard deviation (RSD) of 4.41%. The uptake rate was determined for samplers exposed to sulfur dioxide levels ranging from 0.4 to 8.0 ppm and at 20 to 80% relative humidity (RH) at 25 C and sampling times ranging from 15 minutes to 24 hours. The mean sampling rate for 141 tests was 15.2 ml/min with an RSD of 16.5%. A reverse diffusion study conducted at 1.6 ppm indicated no losses of sulfur dioxide. A long term, 2 week, sampling and reverse diffusion study was conducted at 0.40 ppm exhibiting samplers can sample for up to 2 weeks with no significant losses. Samplers can be stored at both freezer and ambient temperatures with less than a 10% loss in recovery. This study demonstrates the sampler can be used for occupational exposures from 15 minutes to 8 hours and indoor and ambient air environments for up to 24 hours.

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Introduction

Sulfur dioxide (SO₂) is also known as sulfurous anhydride or sulfurous oxide. It is a colorless gas that is non-flammable and has a strong suffocating odor. From a global perspective, sulfur dioxide is produced by volcanoes and other various industrial processes. Sulfur dioxide can also be generated by the combustion of coal and petroleum. From an environmental perspective, when sulfur dioxide is further oxidized, it is normally in the presence of a catalyst such as nitrous oxide. From a health perspective, sulfur dioxide is sometimes used as a preservative for many dried fruits due to its antimicrobial properties. The preservative is used to maintain the appearance of the fruit and prevent rotting. The presence of sulfur dioxide in the fruit itself can yield a distinctive chemical taste. Sulfur dioxide is also a very important compound in winemaking and is designated in parts-per-million (ppm) in wine. It functions as an antibiotic and antioxidant by protecting the wine from spoilage by bacteria and oxidation. Some potential symptoms of overexposure are irritation of eyes, nose, and throat. It can also cause rhinorrhea, choking, coughing, reflex bronchoconstriction, and eye and skin burns. Sulfur dioxide can contribute to respiratory illness, particularly in children and the elderly.

Experimental

Reagents and Equipment

A 2-ppm and a 10-ppm sulfur dioxide cylinder (Scott Specialty Gases, Plumsteadville, PA, U.S.A.) were used to prepare concentrations in the test rig. Standard atmospheres were created at different concentration levels and at different relative humidities. The concentration within the atmospheric chamber was verified with a sorbent tube (SKC Inc., Eighty Four, PA, U.S.A, Cat. No. 226-80). The samplers, containing tape impregnated with triethanolamine (TEA), were exposed in the test rig. The diffusive sampler used was the UME^x 200 (SKC Inc., Eighty Four, PA, U.S.A., Cat. No. 500-200), which consists of a sampling compartment and a blank compartment. A square of coated chromatography paper cut to 2 x 2 cm (Whatman, Florham Park, NJ, U.S.A., PN #3001-614) was placed in each compartment. One square was used for sampling, the other as a blank for the sample. After exposure, the samplers were sealed until analysis. Each sampler was disassembled and the 2 pieces of tape placed in individual glass vials that were subsequently capped. The contents of each vial was desorbed with 2 ml of deionized ultra filtered (DIUF) water and shaken for 20 minutes on a sample vibrator. After the extraction period, 1 ml of the extract was transferred to another vial, where 1 ml of 0.15% hydrogen peroxide was added to convert the sulfur dioxide to sulfate ion. The samples were analyzed for sulfate by ion chromatography (IC) with a Dionex CD20 Conductivity Detector and a 4 x 250-mm AS14A column with Dionex ASRS 300 4-mm Suppressor. The Cat. No. 226-80 sorbent tubes were desorbed in 10 ml of 15 mM sodium hydroxide that contained 0.3 N hydrogen peroxide. The extracts were shaken for 1 hour on a sample vibrator and analyzed under the same IC conditions as the samplers.

Calibration and Calculations

Certified sulfate stock solutions (AccuStandard, New Haven, CT, U.S.A., PN# IS-16073-10x) were used to prepare the calibration curve. The standards were prepared in distilled water. One milliliter extract of the solution was added to 1 ml of the 0.15% hydrogen peroxide solution to follow the same procedures as used with the UME^x 200 samplers. Sulfate standards were prepared to cover the expected target levels of sulfur dioxide.

To calculate from micrograms of sulfate anion to micrograms of sulfur dioxide, use the following formula:

$$\mu\text{g SO}_4 \times 0.667 = \mu\text{g SO}_2$$

where 0.667 is the ratio of molecular weights of sulfate and sulfur dioxide.

Testing Procedures

The desorption efficiency study was conducted by spiking at levels based on equivalent 8-hour exposures to 0.05, 0.10, 0.50, 1.0, and 2.0 times the TLV of 2 ppm. A desired concentration level of sulfur dioxide was pumped into the atmospheric chamber to allow samplers to be exposed to the necessary exposure level. Before the samplers were placed in the atmospheric chamber, the concentration level was tested with a sulfur dioxide detector tube (Dräger, Pittsburgh, PA, U.S.A., P/N 6728491) to ensure proximity to the target level. The Cat. No. 226-80 treated sorbent tubes were used to verify the concentration level during the atmospheric chamber run. The calculated uptake rate for the samples of sulfur dioxide was verified at the concentration range of 0.4 ppm to 8 ppm and at relative humidities ranging from 20 to 80%. Four samplers at each time period were exposed simultaneously to the test concentration. The sampling time periods consisted of 15, 30, 60, 120, 240, 360, 480, and 1440 minutes depending on the sulfur dioxide concentration level within the chamber. After the exposure, the samplers were taken out of the chamber, sealed, and stored in a freezer until analysis. Several of the Cat. No. 226-80 sorbent tubes were used to verify the test level. The flow through each tube was set at approximately 100 ml/min and the time varied depending on the concentration. A minimum of 6 tubes was used to characterize each test level. Each tube was capped and placed in a freezer until analysis.

The storage study consisted of injecting 28 pieces of TEA treated tape with 60 μg sulfur dioxide. Four pieces of tape were analyzed that day, 12 pieces were stored at ambient temperatures, and the remaining 12 were stored in a freezer (-22 C) for 3 weeks. Four pieces of the spiked, coated tape from each storage temperature were analyzed each week and the results were compared to the initial week to determine the analytical recovery.

The reverse diffusion study was conducted by exposing 8 samplers in the atmospheric chamber to 1.6 ppm of sulfur dioxide for 2 hours. Four samplers were placed back in the atmospheric chamber and exposed for 6 hours to 0 ppm SO_2 to evaluate the effects of reverse diffusion. The 2-week sampling and reverse diffusion study was performed by exposing 4 samplers to 0.40 ppm for 4 hours. Two samplers were analyzed while the other 2 samplers were hung with the slider open for 2 weeks. The samplers hung for 2 weeks were compared to the samplers initially analyzed.

Results and Discussion

The desorption efficiency results for sulfur dioxide with the diffusive samplers are shown in Table 1. The mean recovery of the samplers was 97.8% (4.41% RSD). The data in Table 2 shows that there was no reverse diffusion with the UME^x 200 samplers when exposed to sulfur dioxide. Tables 3 through 5 show the sampling rate results of all the tests at various concentrations, times, and relative humidities. The results of these 141 samples show that sulfur dioxide ranging from 0.4 to 8.0 ppm can be sampled with UME^x 200 diffusive samplers at an average sampling rate of 15.2 ml/min (16.5% RSD). The data indicates that the sampler can collect a 15-minute to 24-hour sample at 2.0 ppm of sulfur dioxide. The limits of quantitation for a 15-minute

and 8-hour sample for sulfur dioxide are 170 and 5.3 ppb, respectively. The 3-week storage study (Table 6) indicates that the samplers can be stored for 3 weeks at either ambient or freezer temperatures.

Conclusion

The UME^x 200 diffusive sampler has been validated for sampling sulfur dioxide over a concentration range of 0.4 to 8 ppm and at 20 to 80% RH. The mean sampling rate for the sampler was 15.2 ml/min (16.5% RSD). The samplers showed good stability when stored for 3 weeks at either ambient or freezer temperatures. The UME^x 200 diffusive sampler can be used for concentrations of sulfur dioxide ranging from 0.4 to 8 ppm for 15 minutes up to 24 hours.

References

- 1) *Sulfur Dioxide*, http://en.wikipedia.org/wiki/Sulfur_dioxide
- 2) Greenwood, N. N. and Earnshaw, A., *Chemistry of the Elements*, 2nd Edition, Oxford: Butterworth-Heinemann, 1997
- 3) U.S. Environmental Protection Agency, *National Trends in Sulfur Dioxide Levels*, Sept. 4, 2008, <http://www.epa.gov/airtrends/sulfur.html>

**Table 1. Analytical Recovery
Sulfur Dioxide**

| PEL | Spiked (µg) | Recovered (µg) | Recovery (%) |
|------------|--------------------|-----------------------|---------------------|
| 0.05 | 3.00 | 3.04 | 101 |
| | | 2.87 | 95.6 |
| | | 3.32 | 111 |
| | | 2.85 | 95.0 |
| 0.10 | 6.00 | 5.81 | 96.8 |
| | | 5.55 | 92.5 |
| | | 5.84 | 97.3 |
| | | 5.75 | 95.8 |
| | | 5.45 | 90.8 |
| 0.50 | 29.8 | 29.1 | 97.7 |
| | | 29.2 | 98.1 |
| | | 29.5 | 99.1 |
| | | 30.9 | 104 |
| | | 30.3 | 102 |
| 1.00 | 59.6 | 53.3 | 89.5 |
| | | 58.0 | 97.4 |
| | | 58.9 | 99.0 |
| | | 56.5 | 94.9 |
| | | 58.1 | 97.6 |
| 2.00 | 119 | 117 | 98.1 |
| | | 118 | 99.1 |
| | | 117 | 98.0 |
| | | 116 | 97.0 |
| | | 120 | 101 |
| | | Mean | 97.8% |
| | | Std. Dev. | 0.042 |
| | | RSD | 4.41% |

**Table 2. Reverse Diffusion
1.6 ppm Sulfur Dioxide at 20% RH, 25 C**

| Exposed for 2 hrs to 1.6 ppm SO₂ (µg) | | Exposed for 6 hrs to 0.0 ppm SO₂ (µg) | |
|--|----------------|---|----------------|
| 5.45 | | 5.05 | |
| 5.05 | | 5.25 | |
| 5.04 | | 4.96 | |
| 5.32 | | 5.27 | |
| Mean | 5.22 µg | Mean | 5.13 µg |
| Std. Dev. | 0.203 | Std. Dev. | 0.152 |
| RSD | 3.90% | RSD | 2.96% |
| Exposed for 4 hrs to 0.40 ppm SO₂ (µg) | | Exposed for 4 hrs to 0.40 ppm and 2 weeks to 0.0 ppm SO₂ (µg) | |
| 3.31 | | 3.67 | |
| 3.01 | | 3.47 | |
| Mean | 3.16 µg | Mean | 3.57 µg |
| Std. Dev. | 0.212 | Std. Dev. | 0.143 |
| RSD | 6.71% | RSD | 4.00% |

**Table 3. Sampling Rate and Capacity
Sulfur Dioxide, 20% RH**

| Level (ppm) | Time (min) | Collected (µg) | Sampling Rate (ml/min) |
|--------------------|-------------------|-----------------------|-------------------------------|
| 8 | 15 | 4.92 | 15.7 |
| | | 3.89 | 12.4 |
| | | 5.31 | 17.0 |
| | | 4.57 | 14.6 |
| 8 | 30 | 9.69 | 15.5 |
| | | 10.6 | 17.0 |
| | | 10.6 | 16.9 |
| 8 | 60 | 21.3 | 17.0 |
| | | 20.7 | 16.5 |
| | | 21.4 | 17.1 |
| 8 | 240 | 91.7 | 18.3 |
| | | 91.1 | 18.2 |
| | | 95.1 | 19.0 |
| 1.6 | 15 | 0.672 | 14.4 |
| | | 0.764 | 16.4 |
| | | 0.869 | 18.8 |
| | | 0.601 | 12.9 |
| | | 0.585 | 12.5 |
| | | 0.838 | 18.1 |
| 1.6 | 60 | 2.15 | 11.6 |
| | | 2.50 | 13.5 |
| | | 2.16 | 11.6 |
| | | 2.20 | 11.9 |
| | | 2.16 | 11.6 |
| | | 2.28 | 12.3 |
| | | 2.89 | 15.6 |
| | | 2.32 | 12.5 |
| 1.6 | 120 | 4.45 | 12.0 |
| | | 4.62 | 12.5 |
| | | 3.92 | 10.6 |
| | | 4.97 | 13.4 |
| | | 5.45 | 14.7 |
| | | 5.05 | 13.6 |
| | | 5.04 | 13.6 |
| | | 5.32 | 14.3 |
| 1.6 | 240 | 9.14 | 12.3 |
| | | 8.93 | 12.0 |
| | | 9.05 | 12.2 |
| | | 8.59 | 11.6 |

| Level (ppm) | Time (min) | Collected (µg) | Sampling Rate (ml/min) |
|--------------------|-------------------|-----------------------|-------------------------------|
| 1.6 | 360 | 13.4 | 12.1 |
| | | 13.7 | 12.3 |
| | | 13.6 | 12.3 |
| | | 12.5 | 11.2 |
| 1.6 | 480 | 17.0 | 11.5 |
| | | 20.5 | 13.8 |
| | | 20.2 | 13.6 |
| | | 20.2 | 13.6 |
| | | Mean | 14.1 µg |
| | | Std. Dev. | 2.36 |
| | | RSD | 16.8% |

**Table 4. Sampling Rate and Capacity
Sulfur Dioxide, 60% RH**

| Level (ppm) | Time (min) | Collected (µg) | Sampling Rate (ml/min) |
|--------------------|-------------------|-----------------------|-------------------------------|
| 4 | 15 | 2.43 | 17.7 |
| | | 2.38 | 17.4 |
| | | 2.92 | 15.0 |
| | | 2.84 | 14.5 |
| | | 2.44 | 12.5 |
| | | 2.73 | 14.0 |
| | | 2.47 | 18.0 |
| | | 2.32 | 11.9 |
| | | 2.40 | 12.3 |
| | | 2.41 | 12.3 |
| 4 | 30 | 5.07 | 13.0 |
| | | 5.07 | 13.0 |
| | | 6.84 | 17.5 |
| | | 5.90 | 15.1 |
| | | 4.45 | 16.2 |
| | | 4.31 | 15.7 |
| | | 3.60 | 13.1 |
| | | 4.37 | 15.9 |
| | | 5.79 | 14.8 |
| | | 7.01 | 17.9 |
| | | 6.74 | 17.3 |
| | | 7.49 | 19.2 |
| 4 | 120 | 21.2 | 19.3 |
| | | 21.0 | 19.1 |
| | | 19.6 | 17.9 |
| | | 20.3 | 18.5 |
| 4 | 360 | 66.0 | 20.1 |
| | | 66.3 | 20.2 |
| | | 65.3 | 19.8 |
| 0.8 | 120 | 2.06 | 11.7 |
| | | 2.20 | 12.5 |
| | | 2.02 | 11.5 |
| | | 2.16 | 12.3 |
| 0.8 | 240 | 4.31 | 12.2 |
| | | 4.15 | 11.8 |
| | | 4.11 | 11.7 |
| 0.8 | 360 | 8.35 | 15.8 |
| | | 7.09 | 13.4 |
| | | 6.82 | 12.9 |

| Level (ppm) | Time (min) | Collected (µg) | Sampling Rate (ml/min) |
|--------------------|-------------------|-----------------------|-------------------------------|
| | | 6.67 | 12.6 |
| 0.8 | 418 | 6.92 | 11.29 |
| | | 8.15 | 13.3 |
| | | 8.65 | 14.1 |
| | | 8.36 | 13.6 |
| 0.2 | 1440 | 8.66 | 16.0 |
| | | 8.20 | 15.1 |
| | | 8.54 | 15.8 |
| | | 8.58 | 15.8 |
| 0.5 | 1440 | 15.1 | 18.3 |
| | | 15.3 | 18.4 |
| | | 14.7 | 17.7 |
| | | 14.9 | 18.0 |
| | | Mean | 15.3 µg |
| | | Std. Dev. | 2.70 |
| | | RSD | 17.7% |

**Table 5. Sampling Rate and Capacity
Sulfur Dioxide, 80% RH**

| Level (ppm) | Time (min) | Collected (µg) | Sampling Rate (ml/min) |
|--------------------|-------------------|-----------------------|-------------------------------|
| 2 | 30 | 3.70 | 14.9 |
| | | 3.13 | 12.6 |
| | | 3.04 | 12.2 |
| | | 3.05 | 14.2 |
| | | 3.49 | 16.2 |
| | | 3.06 | 14.2 |
| | | 4.05 | 18.8 |
| | | 3.57 | 16.6 |
| | | 2.99 | 13.9 |
| | | 3.25 | 15.1 |
| 2 | 60 | 6.52 | 18.6 |
| | | 6.11 | 17.4 |
| | | 5.25 | 15.0 |
| | | 5.50 | 15.7 |
| 2 | 120 | 11.3 | 16.2 |
| | | 11.5 | 16.4 |
| | | 13.4 | 19.1 |
| | | 10.5 | 14.9 |
| 2 | 240 | 26.6 | 19.0 |
| | | 22.2 | 15.9 |
| | | 22.5 | 16.0 |
| | | 21.7 | 15.5 |
| 2 | 360 | 33.5 | 15.9 |
| | | 35.8 | 17.0 |
| | | 32.8 | 15.6 |
| | | 35.3 | 16.8 |
| 2 | 480 | 47.5 | 16.9 |
| | | 46.4 | 16.6 |
| | | 49.2 | 17.6 |
| | | 46.4 | 16.5 |
| 0.4 | 240 | 2.40 | 17.4 |
| | | 1.92 | 13.9 |
| | | 2.15 | 15.5 |
| | | 2.16 | 15.6 |
| | | 1.88 | 13.6 |
| 0.4 | 360 | 4.13 | 19.9 |
| | | 3.29 | 15.9 |
| | | 3.26 | 15.7 |

| Level (ppm) | Time (min) | Collected (μg) | Sampling Rate (ml/min) |
|--------------------|-------------------|---|--------------------------------------|
| 0.4 | 480 | 5.51 | 19.9 |
| | | 4.73 | 17.1 |
| | | 5.61 | 20.3 |
| | | 4.62 | 16.7 |
| | | Mean | 16.7 μg |
| | | Std. Dev. | 1.64 |
| | | RSD | 9.90% |

**Table 6. Storage Study
Sulfur Dioxide, 60 μg spike**

| Week | Recovery (%) | |
|-------------|---------------------|-------------|
| | < 4 C | 25 C |
| 0 | 100 | 100 |
| 1 | 97.5 | 95.8 |
| 3 | 96.4 | 97.3 |

Appendix A

Sulfur Dioxide IC/HPLC Conditions

IC Conditions:

Waters HPLC

Column: Dionex IonPAC Analytical
4 x 250 mm, AS14A

Run Time: 10.55 minutes

Detector: Dionex CD20 Conductivity Detector

Suppressor: Dionex ASRS 300

Injection Volume: 20 μ l

