BACKUP DATA REPORT
NIOSH Method No. 6012

Title: Sulfuryl fluoride
Analyte: Sulfuryl fluoride
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Date: May 12, 1993

Substance: Sulfuryl Fluoride
OSHA/NIOSH/ACGIH Standard: 20 mg/m^3
Compound used for validation: Vikane, tradename of the Dow Chemical Co. for sulfuryl fluoride, 99%; also calibrated standards of sulfuryl fluoride-in-air prepared by Scott-Marrin, Inc. , Riverside, CA 92507.

Storage Stability
Gas samples (0.275-L each) from a Tedlar® gas bag containing 417 mg/m^3 sulfuryl fluoride were collected on tubes of coconut shell charcoal, stored for various lengths of time at 0-5 °C, and analyzed by ion chromatography to check for storage stability.

Table 6012.1 Storage stability

Day	Recovered (mg/m^3)	Recovery (compared to day 1 mean)	Mean	Std dev	CV
1	409				
1	349				
1	377		378	30.02	0.0794
4	395				
4	383				
4	403	1.04	394	10.07	0.0257
12	382				
12	368				
12	372	1.01	382	17.52	0.0458

There were no significant differences in recovery due to storage time up to 12 days, compared to one-day old samples, $F(2,7)=0.47$ at $p=0.05$.

Breakthrough
Gas samples from Tedlar® gas bags containing 417 mg/m^3 SO_2F_2 in both 30°C "dry" air and 90% relative humidity (RH)/30 °C air were collected on charcoal at a flow rate of 0.1 L/min.

Two charcoal tubes, each containing only one section of charcoal (the front tube containing 800 mg, the rear tube 200 mg) were placed in series for sample collection. The rear charcoal tube was replaced, at timed intervals, until 10 liters total were collected (100 minutes time).

The charcoal tubes were analyzed for SO_2F_2 by ion chromatography. The calculated amount of sulfuryl fluoride collected on the front section was 3400µg for the 90% RH/30 °C air samples. Data for 90% RH/30 °C air samples is presented below.

Table 6012.2 Breakthrough (90% RH/30 °C air samples)

Volume (L)	Cumulative Volume (L)	µg SO_2F_2 found on rear section	Cumulative total on rear sections µg SO_2F_2	Cumulative % on rear sections
1	1	0	0	0
1	2	1.8	1.8	0.26
2	4	5.8	7.6	0.56
2	6	46	54	2.6
2	8	86	140	4.9
2	10	94	234	6.40

After collecting 10 liters of 417 mg/m^3 SO_2F_2, 6.4% of the total SO_2F_2 collected was found on the rear charcoal sections.

Data for “Dry" 30 °C air samples
After 10 liters total collection of dry 30 °C air, NO SO_2F_2 WAS FOUND ON ANY REAR SECTION. The calculated amount found on the front section was 3500 µg.

Desorption efficiency of Fluoride spikes on charcoal
Sulfuryl fluoride is converted to fluoride and sulfate on the charcoal sorbent by NaOH as shown by the equation:

$SO_2F_2 + 4NaOH \dashrightarrow 2NaF + Na_2SO_4 + 2H_2O$.

To measure the desorption efficiency, fluoride was spiked on charcoal and desorbed/extracted with NaOH. These samples represent 8.95 to 143 mg/m^3 SO_2F_2 for a 3-L sample.

Table 6012.3 Desorption Efficiency data

µg F spiked	µg F found	Desorption Efficiency (DE)	Mean DE	Std dev	CV
10	10.9	1.09			
10	9.45	0.945			
10	9.04	0.904			
10	9.13	0.913			
10	11.3	1.13	0.996	0.1058	0.106
20	20.8	1.04			
20	20.5	1.03			
20	19.0	0.950			
20	18.3	0.915			
20	21.2	1.06	0.999	0.06289	0.063
40	38.6	0.965			
40	37.9	0.948			
40	37.8	0.945			
40	38.8	0.970			
40	39.2	0.980	0.962	0.01484	0.0154
80	76.7	0.959			
80	76.5	0.956			
80	76.7	0.959			
80	77.7	0.971			
80	76.0	0.950	0.959	0.007648	0.00798
120	117	0.975			
120	116	0.967			
120	114	0.950			
120	113	0.942			
120	114	0.942	0.955	0.01506	0.0158
160	156	0.975			
160	157	0.981			
160	157	0.981			
160	151	0.944			
160	159	0.994	0.975	0.01867	0.0192

Pooled CV_1=0.0518

Sampling and Analysis
Calibrated gas standards were prepared in five-layer aluminized gas bags by injecting known amounts of pure Vikane into bags containing appropriate amounts of nitrogen gas. Two-liter samples were collected (0.1 L/min for 20 min.) on coconut shell charcoal, extracted, and analyzed for sulfuryl fluoride.

Table 6012.4 Recovery data

Level	Amount taken (mg/m^3)	Amount found (mg/m^3)	Recovery
1X	21	21.3	1.013
1X	21	21.3	1.015
1X	21	20.9	0.9948
4X	83	78.8	0.950
4X	83	78.8	0.950
4X	83	77.6	0.934
8X	167	174	1.041
8X	167	170	1.018
8X	167	173	1.034

1X mean=1.01; std dev=0.01113; CV=0.0110
4X mean=0.944; std dev=0.008718; CV=0.00923
8X mean=0.994; std dev=0.03984; CV=0.04007

Samples (0.2-L and 0.28-L) were collected on charcoal tubes from Tedlar® gas bags containing 417 mg/m^3 sulfuryl fluoride in dry air at room temperature.

Table 6012.5 Recovery data

Level	Amount taken (mg/m^3)	Amount found (mg/m^3)	Recovery
20X (0.2L)	417	412	0.9890
20X (0.2L)	417	370	0.8880
20X (0.2L)	417	340	0.8161
20X (0.2L)	417	212*	0.5088*
20X (0.2L)	417	726*	1.740*
20X (0.28L)	417	324	0.7779
20X (0.28L)	417	352	0.8451
20X (0.28L)	417	315	0.7549

0.2L mean=0.898; std dev=0.08686; CV=0.0968
0.28L mean=0.793; std dev=0.04685; CV=0.0591
*results lie beyond the mean±3sd

Two- to six-liter samples were taken on charcoal tubes from Tedlar® gas bags containing 21 mg/m^3 and 167 mg/m^3 SO_2F_2 in both dry air and in 90% relative humidity air, at room temperature (RT) and 30 °C.

Table 6012.6 Recovery data

Level	Amount taken (mg/m^3)	Amount found (mg/m^3)	Recovery
1X (dry air, RT)	21	15.0	0.7128
1X (dry air, RT)	21	14.6	0.6928
1X (dry air, RT)	21	15.2	0.7228
1X (90% RH, RT)	21	14.8	0.7028
1X (90% RH, RT)	21	13.7	0.6514
1X (90% RH, RT)	21	13.6	0.6471
4X (dry air, 30°C)	83	60.1	0.7235
4X (dry air, 30°C)	83	59.2	0.7134
4X (dry air, 30°C)	83	59.6	0.7184
4X (dry air, 30°C)	83	59.2	0.7134
4X (90% RH, 29°C)	83	59.6	0.7184
4X (90% RH, 29°C)	83	59.2	0.7134
4X (90% RH, 29°C)	83	58.4	0.7034
4X (90% RH, 29°C)	83	56.7	0.6832
8X (dry air, RT)	167	169	1.011
8X (dry air, RT)	167	166	0.9964
8X (dry air, RT)	167	174	1.044
8X (90% RH, RT)	190	190	1.139
8X (90% RH, RT)	170	170	1.018
8X (90% RH, RT)	165	165	0.9862
8X (90% RH, RT)	184	184	1.101
8X (90% RH, RT)	169	169	1.014

Note 1: In December 1989 DPSE/MRSB was requested by DSHEFS/IWSB to evaluate the method of Bouyoucos et al.[1] for sampling at fumigation sites for low and high levels of SO_2F_2 under conditions of high relative humidity.
Note 2: The 5-layer aluminized gas bags were consistently better for SO_2F_2 recovery in this study. Recovery from 5-layer bags was 0.994 ± 0.03984 sd, n=9, (21-167 mg/m^3). Recovery from Tedlar® bags was 0.828 ± 0.1547 sd, n=28, (21-417 mg/m^3).
Note 3: During the analyses of charcoal tubes for SO_2F_2 the Dionex AS4A anion separator column showed signs of loss of resolution. Fluoride was not being successfully separated from a closely eluting peak (thought to be formate or acetate). This problem is possibly due to the binding of polyvalent anions from the charcoal sampling media to active sites on the column. None of the clean-up procedures restored the column to a satisfactory level of performance. Another AS4A column was used to complete the analyses. A regularly scheduled testing of the guard column (Dionex AG4A) for contamination may allow for the timely cleaning of the separator column. Even though sulfate theoretically could be used to measure levels of sulfuryl fluoride, fluoride results were more reliable and so were used exclusively.

Precision and Accuracy[2]

$$\overline{CV}_1 = [4(0.106)^2+4(0.063)^2+4(0.0154)^2+4(0.00798)^2+4(0.0158)^2+4(0.0192)^2]^{1/2} / [4+4+4+4+4+4]^{1/2}$$

$$\overline{CV}_1 = 0.0518$$

Sampling and Analysis[2]

$$\overline{CV}_2=[2(0.0110)^2+2(0.00923)^2+2(0.0114)^2+2(0.0968)^2+2(0.0591)^2+2(0.0215)^2+2(0.0465)^2+3(0.00674)^2+3(0.0221)^2+2(0.0238)^2+4(0.0618)^2]^{1/2}/[2+2+2+2+2+2+2+3+3+2+4]^{1/2}$$

$$\overline{CV}_2=0.0437$$

$$\begin{aligned}\overline{CV}_T &= [(CV_2)^2+ 0.1667(CV_1)^2+ (0.05)^2]^{1/2} \\ &= ((0.0437)^2+ 0.1667(0.0518)^2+ (0.05)^2]^{1/2}\end{aligned}$$

$$\overline{CV}_T = 0.0697$$

References

[1] Bouyoucos SA, Melcher RG, Vaccaro JR [1983]. Collection and determination of sulfuryl fluoride in air by ion chromatography. Am Ind Hyg J *44*:57-61.

[2] NIOSH [1977]. Documentation of NIOSH Validation Tests. Cincinnati, OH: U.S. Department of Health, Education and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health. DHEW (NIOSH) Publication No. 77-185.