Non-Dietary Exposure Review

Subject:	**RE-VALIDATION OF AIR MONITORING METHOD FOR SULFURYL FLUORIDE**
Guidelines:	
Other:	**Special Review**
DP Barcode:	**D227297**
MRIDs:	
Chemical Codes:	**078003 Sulfuryl fluoride**
Formulation Type:	
Exposed Individual:	
Application Method:	
Outdoor Use Sites:	
Indoor Use Sites:	
Greenhouse Use Sites:	
Other Use Sites:	
Airborne Techniques:	
Dermal Techniques:	
Hand Techniques:	
Foliar Techniques:	
Indoor Surf. Techniques:	
Reviewers:	**David Jaquith**
Review Approvers:	**Jeff Evans, Ed Zager Approved on: May 23, 1997**

Sulfuryl.O

MEMORANDUM

SUBJECT: RE-VALIDATION OF AIR MONITORING METHOD FOR SULFURYL FLUORIDE

FROM: David Jaquith
Special Review and Registration Section I
Occupational and Residential Exposure Branch
Health Effects Division (7509C)

TO: John Redden
Risk Characterization and Analysis Branch
Health Effects Division (7509C)

THRU: Jeff Evans, Acting Section Head
Special Review and Registration Section I
Occupational and Residential Exposure Branch
Health Effects Division (7509C)

Ed Zager, Acting Chief
Occupational and Residential Exposure Branch
Health Effects Division (7509C)

Please find below the OREB review of ....

DP Barcode: D227297 Pesticide Chemical Code: 078003

EPA Reg. No.: _____

Deferral to:

PHED: N/A

1.0 INTRODUCTION

OREB has been requested to review a re-validation of an analytical method for the fumigant sulfuryl fluoride (Vikane) in air. The submission presents the results of an updated method originally developed in 1979 and revised in 1994. The original method utilized trapping on charcoal tubes, followed by desorption with 0.04 N NaOH and quantification by ion chromatography. It was subsequently determined that there was a negative bias associated with this method and the study contained in this submission was conducted to address these concerns.

2.0 CONCLUSIONS

The registrant has conducted a re-validation study for measuring air concentrations of the fumigant sulfuryl fluoride. Previous methods had problems with a negative bias. The study consisted of spiking charcoal tubes and drawing air through them at a rate of 0.1 liters per minute. The samples were desorbed with 0.04 N NaOH and quantified using an ion specific electrode. Samples were spiked at levels of ~10, ~400, and ~1000 μg. Recoveries during this study averaged 66.1 percent with a standard deviation of 7.14 percent (CV = 11%). On set of spikes at the 10 μg level had higher recoveries (77.6-84.7 %). The reason for this is not known. All other samples showed consistent recovery values. Use of the overall average should yield a conservative measurement of sulfuryl fluoride air concentrations. A breakthrough, perhaps related to the level of loading of the charcoal tubes, was observed at the 400 and 1000 μg levels.

3.0 DETAILED CONSIDERATIONS

3.1 Materials and Methods

The revised method uses 1-g coconut-based charcoal tubes (800 mg front section/200 mg back section). Injections of sulfuryl fluoride were made directly onto the charcoal tubes, located on a spiking manifold system, using gas-tight syringes (except for 10 μL spikes which uses a two-sided water plug technique). The spikes were placed on a spike box attached to a vacuum pump with a flow rate of 100 mL per minute.

The front and back sections were separated into two pre-washed glass vials, each section desorbed with 20 mL of 0.04 N NaOH, and the vials shaken on a flatbed shaker for approximately one hour. Ten mL of the extract was transferred to another vial and the aqueous portion boiled off on a hot plate to digest the sulfuryl fluoride down to fluoride. The residue was redissolved in 10 mL of Milli-Q water. An aliquot (~3 mL) was combined with an equal volume of total ionic strength

adjustment buffer (TISAB) and the fluoride content quantified by ion specific electrode (ISE) analysis.

Standard solutions were prepared by injecting varying volumes of standard fluoride solution into solutions of 1:1 TISAB/millipore water. The log of concentration was plotted against millivolt readings to obtain a log/linear standard curve. Full sets of standards were analyzed before any blanks, spikes or references were analyzed and again after completion of all sample analyses. Since the standards and samples were diluted 1:1 with TISAB a dilution factor of 2 was used in the calculations. Mass of fluoride was converted to sulfuryl fluoride using the following factor:

Total Sulfuryl fluoride (SF) = MW of SF/(2 x At. Wt. of Fluoride)

= 102.07/(2 x 19) = 2.686

3.2 Results

The ISE analysis system was found to have a dynamic range equivalent approximately 2 to 1060 μg per sample (0.7 to 395 μg of fluoride per sample). A background level of ~0.4 - 0.6 μg fluoride/samples was associated with the use of the charcoal tubes. The lowest standard prepared that gave a discernable reading from the TISAB/water matrix was ~0.8 μg/sample (~2 μg SF/sample). Therefore 2 μg SF/sample was used as the limit of quantitation for this method.

Reference solutions were prepared by spiking 20 mL of 0.04 N NaOH with the same volumes of SF as those loaded on the charcoal tubes. Recoveries from these solutions were comparable to those obtained from the charcoal tubes. This supports the conclusion that hydrolysis of SF to fluoride is incomplete with this method. The recoveries from the charcoal tubes are presented in Table 1. The average recovery for this method was 66 percent (S.D. = 7.14). Recoveries were fairly consistent over a range of ~10 μg to 1000 μg, with the exception of one set of spikes (10 μg) that ranged from 77.6 to 84.7 percent.

Breakthrough of SF was observed during this validation study. This may be due to spiking technique or loading of the tubes. Spikes at the 10 μg level did not exhibit this problem but it was observed at the higher (~400 μg and ~1000 μg) levels. There appeared to be no appreciable difference in the amount of breakthrough between samples where air was passed through the tubes for 15 minutes or 8 hours, indicating that the loading of the tube may be the most important factor.

Table 1. Summary of the Recovery Data for the Analysis of Sulfuryl Fluoride Validation Spikes on Charcoal Tubes (μg levels listed are for sulfuryl fluoride).

NOMINAL TARGET (μg)	μg FOUND	% RECOVERY	% RELATIVE HUMIDITY	AIR VOLUME (L)	FLOW RATE (mL/min)	TIME INTERVAL (hrs)
418	263	62.9	80	12	100	2
418	268	64.1	80	12	100	2
418	279	66.7	80	12	100	2
418	264	63.2	80	12	100	2
418	260	62.2	80	12	100	2
418	249	59.6	80	12	100	2
418	251	60.0	80	12	100	2
418	257	61.5	80	12	100	2
418	258	61.7	80	12	100	2
418	255	61.0	80	12	100	2
10.4	8.69	83.6	80	1.5	100	0.25
10.4	8.07	77.6	80	1.5	100	0.25
10.4	8.55	82.2	80	1.5	100	0.25
10.4	8.48	81.5	80	1.5	100	0.25
10.4	8.81	84.7	80	1.5	100	0.25
10.4	6.55	63.0	80	24	100	4
10.4	6.80	65.4	80	24	100	4
10.4	6.94	66.7	80	24	100	4
10.4	6.74	64.8	80	24	100	4
10.4	6.65	63.9	80	24	100	4
1040	718	69.0	80	1.5	100	0.25
1040	712	68.5	80	1.5	100	0.25
1040	672	64.6	80	1.5	100	0.25
1040	647	62.2	80	1.5	100	0.25
1040	677	65.1	80	1.5	100	0.25
1040	640	61.5	80	24	100	4
1040	690	66.3	80	24	100	4
1040	691	66.4	80	24	100	4
1040	682	65.6	80	24	100	4
1040	719	69.1	80	24	100	4
418	254	60.8	80	12	100	2
418	253	60.5	80	12	100	2
418	251	60.0	80	12	100	2
418	247	59.1	80	12	100	2
418	249	59.6	80	12	100	2

AVERAGE % RECOVERY **66.1**
STANDARD DEVIATION **7.14**

Regression analysis of the registrant's Biostatistics Group indicated significant loading, air volume, and volume/loading interaction.

cc: Correspondence file
Sulfuryl fluoride file/078003
L. Schnaubelt (SRRD/7508W)
D. Jaquith (OREB/7509C)