The Stability of Sulfur Compounds, Low Molecular Weight Gases, and VOCs in Four Air Sample Bag Materials

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Introduction

Sampling bags have been used for many years to collect grab samples of gas and vapor contaminants in the air. Originally developed for the industrial hygiene market, sampling bags have also gained popularity in environmental applications including the following:
(1) investigating odor complaints at factories, refineries, and wastewater treatment plants, (2) sampling high vapor pressure materials where solid sorbents are unsuitable, (3) sampling in landfills, and (4) transporting and preparing calibration standards for direct-reading instruments and gas chromatographs.

In March 2009, DuPont® announced its plan to "phase out support" for Tedlar® film in the sample bag market. The elimination of Tedlar film, a mainstay in the industrial hygiene and environmental markets for many years, served as a catalyst for the study and adoption of other films as alternatives to Tedlar for bag sampling. In 2012, DuPont announced that due to market conditions, Tedlar film would again be available for the sample bag market. Therefore, this report includes data on Tedlar as well as on the performance of three other films. Each type of film features a unique blend of characteristics including background levels and the ability to contain certain groups of compounds. Film characteristics must be taken into account when selecting a sampling bag film for a specific application. To that end, SKC performed studies on different bag films to determine their suitability for different groups of compounds.

SKC Laboratories evaluated SamplePro® FlexFilm (proprietary material), FlexFoil® PLUS, FluoroFilm FEP, and Tedlar for effectiveness in holding 32 volatile organic compounds (VOCs). The VOCs covered a wide classification of chemicals including aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons, ketones, acetates, and alcohols. Some of the films were also evaluated for 2-day stability in holding 20 sulfur compounds, and low-molecular weight compounds such as ammonia (NH_3), carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), methane (CH_4), nitrogen dioxide (NO_2), sulfur hexafluoride (SF_6), and sulfur dioxide (SO_2).

Experimental/Methods

Throughout the study, tests were conducted using 1-liter bags of each type of film fitted with a single polypropylene fitting. SKC Laboratories tested VOCs by injecting known volumes of the test analyte into the bag filled with nitrogen. Concentrations ranged from 200 to 300 ppm, depending on the analytes. Bags were equilibrated for 20 to 30 minutes. Analysis was performed on day 0, day 1, and day 2 by extracting 100 µl of a gas sample from the bag and injecting it directly into a gas chromatograph (GC) equipped with a flame ionization detector (FID).

Sulfur compounds were tested at Air Toxics Inc. by using a certified cylinder containing 20 sulfur compounds in nitrogen. The test level of each compound was at the lower level of 90 ppb since this is primarily an environmental application. Bags were equilibrated for approximately 2 hours. Analysis was performed on day 1 and day 2. Samples were analyzed by ASTM Standard Test Method D-5504 using a gas chromatograph equipped with sulfur chemiluminescence detector (SCD). The method involved the direct injection of the air sample into the GC via a fixed 2.0-ml sampling loop.

Ammonia, carbon monoxide, carbon dioxide, methane, nitrogen dioxide, sulfur hexafluoride (SF_6), and sulfur dioxide were tested by SKC using certified Scotty 17 cylinders. The cylinder levels were 50 ppm, 50 ppm, 1000 ppm, 5000 ppm, 10 ppm, 1 ppm, and 20 ppm for these compounds, respectively. Hydrogen was tested at a concentration of 2% hydrogen in air. Bags were filled with the individual test gases and allowed to equilibrate for 20 to 30 minutes. Analysis was conducted on day 0, day 1, and day 2. Ammonia, carbon dioxide, carbon monoxide, sulfur dioxide, nitrogen dioxide, and hydrogen were analyzed using Dräger® color detector tubes. Methane was analyzed by extracting 100 µL of a gas sample from the bag and injecting it into a gas chromatograph equipped with a flame ionization detector. Sulfur hexafluoride was analyzed using GC with electron capture detector (ECD).

Results and Discussion

Bag evaluations must include both stability and background information, as both are critical factors when collecting samples of gases and vapors in air. The VOC stability data (percent recovery) for the 4 films tested is shown in Table 1. SamplePro FlexFilm, FlexFoil PLUS, and Tedlar bags had good VOC stability; the total VOC background for FlexFilm and FlexFoil PLUS was in the mid-ppb range or lower. FluoroFilm FEP had a negligible VOC background, but chemical stability was poor after 2 days of storage. Based on the results of this study, SamplePro FlexFilm, FlexFoil PLUS, and Tedlar would be the best choices for sampling VOCs.

Twenty sulfur compounds were tested using 3 bag films. Table 2 displays the stability (percent recovery) of the compounds in each film, and Table 3 shows background data for the films. SamplePro FlexFilm showed high hydrogen sulfide and carbonyl sulfide backgrounds; this film should not be used to collect the tested compounds at ppb levels. FlexFoil PLUS had a low background and displayed the best overall stability for hydrogen sulfide and carbonyl sulfide. FluoroFilm FEP had the lowest background of the films evaluated but the poorest stability for all 20 compounds based on 2 days of storage. Proper choice of bag depends on the specific sulfur compound and the desired hold time. If a sample can be collected in a bag and analyzed within 24 hours, there may be several options for the user.

Stability data for ammonia, carbon monoxide, carbon dioxide, methane, nitrogen dioxide, sulfur hexafluoride, sulfur dioxide, and hydrogen are presented in Table 4. SamplePro FlexFilm, FlexFoil PLUS, and Tedlar showed good stability after 2 days of storage for 4 of the tested compounds; FluoroFilm FEP showed less stability after 2 days of storage. FlexFoil PLUS showed good stability for two days of hydrogen storage. SamplePro FlexFilm, FlexFoil PLUS, and Tedlar showed very poor stability for nitrogen dioxide. All films showed good stability for sulfur hexafluoride.

Summary

Based on the study data, the best film choices for VOC collection are SamplePro FlexFilm, FlexFoil PLUS, and Tedlar. FlexFoil PLUS is an optimal alternative for the collection of sulfur compounds. SamplePro FlexFilm, FlexFoil PLUS, and Tedlar are the best film alternatives for CO, CO_2, and methane. FlexFoil PLUS is the best choice for hydrogen. None of the films tested are recommended for nitrogen dioxide. All films tested may be used for sulfur hexafluoride with good results. Proper film choice depends upon matching the unique blend of bag film characteristics with the compound to be sampled, the concentration level, and the time between sample collection and analysis.

Table 1. Stability of 32 VOCs in Four Bag Films
% Recovery

Compound	SamplePro FlexFilm		FlexFoil PLUS		FluoroFilm (FEP)		Tedlar	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
Acetone	96.7	88.9	99.0	97.8	89.0	85.0	99.0	95.0
Acetonitrile	69.0	55.1	94.2	84.5	65.0	42.0	74.0	66.0
Acrylonitrile	76.1	62.2	98.2	99.5	77.0	59.0	90.0	80.0
Allyl chloride	95.6	91.9	98.5	95.6	92.0	89.0	102.0	94.0
Benzene	96.0	95.2	93.1	98.2	93.0	79.0	104.0	98.0
Bromoethane	95.2	90.9	95.2	98.0	88.0	86.0	99.0	100.0
1,3-Butadiene	80.0	86.0	89.0	92.0	84.0	73.0	99.0	95.0
Butane	91.0	96.0	86.0	88.0	94.0	94.0	98.0	94.0
Butyl acetate	85.1	91.8	88.1	88.7	72.0	66.0	104.0	102.0
Carbon tetrachloride	101.0	94.3	99.1	95.0	95.0	91.0	104.0	102.0
Chloroform	98.7	95.9	96.2	97.1	96.0	93.0	98.0	95.0
1,2-Dichloroethane	91.5	82.9	92.0	88.0	89.0	79.0	100.0	97.0
Dichloropropane	86.2	76.7	99.3	98.5	90.0	86.0	105.0	101.0
Ethyl acetate	94.9	95.4	100.0	97.3	94.0	94.0	98.0	96.0
Ethylene	104.0	100.0	108.0	94.0	99.0	94.0	100.0	102.0
Heptane	96.7	106.0	99.2	101.0	88.0	87.0	100.0	100.0
Hexane	99.0	98.9	95.8	99.4	98.0	95.0	101.0	101.0
Isooctane	100.0	97.9	87.5	86.1	97.0	96.0	100.0	97.0
Isopropyl alcohol	99.1	91.7	101.0	100.0	102.0	98.0	101.0	99.0
Methyl ethyl ketone (MEK)	96.2	95.8	96.5	101.0	90.0	83.0	99.0	98.0
Methylene chloride	93.2	87.2	98.7	101.0	84.0	77.0	102.0	97.0
Methyl-t-butyl ether	99.2	99.1	92.0	88.0	99.0	97.0	101.0	101.0
Octane	104.0	98.7	98.4	93.1	91.0	84.0	100.0	97.0
Perchloroethylene	94.8	84.9	85.3	82.4	81.0	69.0	105.0	94.0
Propylene	100.0	99.0	98.6	97.9	97.0	91.0	103.0	104.0
Propylene oxide	93.3	90.1	102.0	101.0	94.0	89.0	96.0	95.0
Tetrahydrofuran	96.7	93.6	101.0	99.3	90.0	88.0	103.0	100.0
Toluene	107.0	92.9	90.5	91.5	81.0	74.0	96.0	92.0
1,1,1-Trichloroethane	94.9	93.6	86.5	84.6	100.0	97.0	104.0	101.0
Trichloroethylene	92.4	82.9	93.7	94.6	80.0	69.0	104.0	103.0
Vinylidene chloride	95.6	91.8	98.3	99.5	96.0	92.0	102.0	100.0
p-Xylene	85.9	82.7	97.0	89.0	76.0	65.0	89.0	83.0

Table 2. Stability of 20 Sulfur Compounds in Three Bag Films
% Recovery

Compound	SamplePro FlexFilm		FlexFoil PLUS		FluoroFilm FEP	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
n-Butyl mercaptan	69.5	50.0	47.8	50.0	74.5	60.2
tert-Butyl mercaptan	92.5	92.5	91.4	98.8	86.0	78.0
Carbon disulfide	80.0	74.1	58.9	54.4	58.3*	35.6*
Carbonyl sulfide	126.0*	135.0*	98.9*	108.0*	82.9*	71.2*
Diethyl disulfide	68.2	54.1	11.1	12.2	62.9	49.5
Diethyl sulfide	88.2	83.9	25.6	13.3	78.0	66.0
Dimethyl disulfide	77.3	69.3	42.2	44.4	74.0	62.0
Dimethyl sulfide	90.9	89.8	81.4	74.4	77.0	69.0
2,5-Dimethylthiophene	68.6	54.7	14.0	15.5	60.0	45.3
Ethyl mercaptan	81.3	76.9	92.1	97.8	78.0	65.0
Ethyl methyl Sulfide	88.2	83.9	52.2	40.0	77.0	68.0
2-Ethylthiophene	72.2	60.0	17.8	17.8	65.0	53.0
Hydrogen sulfide	7.8*	2.2*	104.4	102.0	72.2	47.8
Isobutyl mercaptan	81.3	69.2	62.2	64.4	83.0	67.0
Isopropyl mercaptan	89.2	86.0	92.9	98.8	84.0	74.0
Methyl mercaptan	78.9*	67.8*	93.4	102.0	74.0	57.0
3-Methylthiophene	75.9	65.5	32.0	32.0	67.0	53.0
n-Propyl mercaptan	80.0	70.0	77.8	82.2	79.0	66.0
Tetrahydrothiophene	79.6	70.45	0.0	0.0	71.0	56.0
Thiophene	81.6	75.9	61.1	62.2	76.0	64.0

** Blank corrected*

Table 3. Sulfur Background (ppb) for Three Films

Compound	SamplePro FlexFilm		FlexFoil PLUS		FluoroFilm FEP	
	Day 1	Day 2	Day1	Day 2	Day 1	Day 2
n-Butyl mercaptan	ND	ND	ND	ND	ND	ND
tert-Butyl mercaptan	ND	ND	ND	ND	ND	ND
Carbon disulfide	ND	ND	ND	ND	6.5	9
Carbonyl sulfide	46	68	11	13	4.4	5.9
Diethyl disulfide	ND	ND	ND	ND	ND	ND
Diethyl sulfide	ND	ND	ND	ND	ND	ND
Dimethyl disulfide	ND	ND	ND	ND	ND	ND
Dimethyl sulfide	ND	ND	ND	ND	ND	ND
2,5-Dimethylthiophene	ND	ND	ND	ND	ND	ND
Ethyl mercaptan	ND	ND	ND	ND	ND	ND
Ethyl methyl sulfide	ND	ND	ND	ND	ND	ND
2-Ethylthiophene	ND	ND	ND	ND	ND	ND
Hydrogen sulfide	20	22	ND	ND	ND	ND
Isobutyl mercaptan	ND	ND	ND	ND	ND	ND
Isopropyl mercaptan	ND	ND	ND	ND	ND	ND
Methyl mercaptan	9	14	ND	ND	ND	ND
3-Methylthiophene	ND	ND	ND	ND	ND	ND
n-Propyl mercaptan	ND	ND	ND	ND	ND	ND
Tetrahydrothiophene	ND	ND	ND	ND	ND	ND
Thiophene	ND	ND	ND	ND	ND	ND

Table 4. Stability of Low Molecular Weight Gases in Four Bag Films
% Recovery

Compound	SamplePro FlexFilm		FlexFoil PLUS		FluoroFilm FEP		Tedlar	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
Ammonia	18.0	10.0	16.0	8.0	59.0	28.0	62.0	37.0
Carbon monoxide	100.0	100.0	100.0	100.0	90.0	50.0	90.0	90.0
Carbon dioxide	100.0	90.0	99.0	100.0	90.0	50.0	100.0	100.0
Hydrogen	---	---	100.0	100.0	---	---	---	---
Methane	96.0	92.0	99.0	100.0	84.0	72.0	101.0	99.0
Nitrogen dioxide	9.75	0.0	0.0	0.0	---	---	54.5	36.4
Sulfur hexafluoride	104.0	99.8	98.1	93.2	96.4	92.8	94.7	93.2
Sulfur dioxide	80.0	67.0	0.0	0.0	33.0	0.0	80.0	67.0