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. 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), SamplePro PVDF (*also sold as Kynar®, Solef®, and Hylar®*) FlexFoil® PLUS, and FluoroFilm FEP for effectiveness in holding 30 volatile organic compounds (VOCs), 20 sulfur compounds, carbon monoxide (CO), carbon dioxide (CO_2), methane, and sulfur hexafluoride (SF_6) over a 2-day period. The VOCs covered a wide classification of chemicals including aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons, ketones, acetates, and alcohols.

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 because 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 (GC) 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.

Carbon dioxide, carbon monoxide, methane, and sulfur hexafluoride (SF_6) were tested by SKC using certified Scotty 17 cylinders. The cylinder levels were 50 ppm, 1000 ppm, 5000 ppm, and 1 ppm for CO, CO_2, methane, and SF_6 respectively. 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. Carbon dioxide and carbon monoxide 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 (GC) equipped with a flame ionization detector (FID). 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 four films tested is shown in Table 1. SamplePro FlexFilm, FlexFoil PLUS, and SamplePro PVDF bags had good VOC stability; the total VOC background for these films 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 SamplePro PVDF would be the best choice for sampling VOCs.

Twenty sulfur compounds were tested using 4 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. While the carbonyl sulfide background in SamplePro PVDF film was low enough to be used for ppb-level detection of hydrogen sulfide and carbonyl sulfide, the hydrogen sulfide stability was approximately 73 percent after 1 day of storage. 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 carbon monoxide (CO), carbon dioxide (CO_2), methane, and sulfur hexafluoride are presented in Table 4. SamplePro FlexFilm, SamplePro PVDF, and FlexFoil PLUS showed good stability after 2 days of storage for 3 of the tested compounds; FluoroFilm FEP showed less stability after 2 days of storage. All films showed good stability for sulfur hexafluoride.

Summary

Based on the study data, the best film alternatives to Tedlar for VOC collection are SamplePro FlexFilm, FlexFoil PLUS, and SamplePro PVDF. FlexFoil PLUS and SamplePro PVDF are the optimal alternatives for the collection of sulfur compounds. SamplePro FlexFilm, FlexFoil PLUS and SamplePro PVDF are the best film alternatives for CO, CO_2, and methane. 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 Thirty VOCs in Four Bag Films
% Recovery

Compound	SamplePro FlexFilm		SamplePro PVDF		FlexFoil PLUS		FluoroFilm (FEP)	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
Acetone	96.7	88.9	81.6	69.8	99.0	97.8	89.0	85.0
Acetonitrile	69.0	55.1	55.0	36.3	94.2	84.5	65.0	42.0
Acrylonitrile	76.1	62.2	59.0	54.1	98.2	99.5	77.0	59.0
Allyl chloride	95.6	91.9	95.7	90.8	98.5	95.6	92.0	89.0
Benzene	96.0	95.2	94.9	93.9	93.1	98.2	93.0	79.0
Bromoethane	95.2	90.9	94.5	95.4	95.2	98.0	88.0	86.0
1,3-Butadiene	80.0	86.0	90.0	92.0	89.0	92.0	84.0	73.0
Butane	91.0	96.0	93.0	100.0	86.0	88.0	94.0	94.0
Butyl acetate	85.1	91.8	71.6	59.6	88.1	88.7	72.0	66.0
Carbon tetrachloride	101.0	94.3	99.0	95.3	99.1	95.0	95.0	91.0
Chloroform	98.7	95.9	97.5	95.4	96.2	97.1	96.0	93.0
1,2-dichloroethane	91.5	82.9	84.0	80.0	92.0	88.0	89.0	79.0
Dichloropropane	86.2	76.7	101.0	99.9	99.3	98.5	90.0	86.0
Ethyl acetate	94.9	95.4	83.5	74.5	100.0	97.3	94.0	94.0
Ethylene	104.0	100.0	101.0	104.0	108.0	94.0	99.0	94.0
Heptane	96.7	106.0	93.0	86.9	99.2	101.0	88.0	87.0
Hexane	99.0	98.9	97.3	101.0	95.8	99.4	98.0	95.0
Isooctane	100.0	97.9	99.1	96.9	87.5	86.1	97.0	96.0
Isopropyl alcohol	99.1	91.7	97.4	90.5	101.0	100.0	102.0	98.0
Methyl ethyl ketone	96.2	95.8	70.4	63.3	96.5	101.0	90.0	83.0
Methylene chloride	93.2	87.2	101.0	94.5	98.7	101.0	84.0	77.0
Methyl-t-butyl ether	99.2	99.1	96.0	98.0	92.0	88.0	99.0	97.0
Octane	104.0	98.7	105.0	91.0	98.4	93.1	91.0	84.0
Perchloroethylene	94.8	84.9	93.0	87.3	85.3	82.4	81.0	69.0
Propylene	100.0	99.0	100.8	97.1	98.6	97.9	97.0	91.0
Propylene oxide	93.3	90.1	91.8	84.4	102.0	101.0	94.0	89.0
p-xylene	85.9	82.7	69.0	49.0	97.0	89.0	76.0	65.0
Tetrahydrofuran	96.7	93.6	91.8	84.8	101.0	99.3	90.0	88.0
Toluene	107.0	92.9	77.8	76.2	90.5	91.5	81.0	74.0
1,1,1-trichloroethane	94.9	93.6	96.7	94.6	86.5	84.6	100.0	97.0
Trichloroethylene	92.4	82.9	95.1	89.1	93.7	94.6	80.0	69.0
Vinylidene chloride	95.6	91.8	98.8	96.2	98.3	99.5	96.0	92.0

Table 2. Stability of Twenty Sulfur Compounds in Four Bag Films
% Recovery

Compound	SamplePro FlexFilm		SamplePro PVDF		FlexFoil PLUS		FluoroFilm FEP	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
n-Butyl mercaptan	69.5	50.0	62.5	39.8	47.8	50.0	74.5	60.2
tert-Butyl mercaptan	92.5	92.5	96.8	85.0	91.4	98.8	86.0	78.0
Carbon disulfide	80.0	74.1	88.3	77.7	58.9	54.4	58.3*	35.6*
Carbonyl sulfide	126*	135*	93.3*	80.0*	98.9*	108*	82.9*	71.2*
Diethyl disulfide	68.2	54.1	53.3	36.7	11.1	12.2	62.9	49.5
Diethyl sulfide	88.2	83.9	84.2	71.6	25.6	13.3	78.0	66.0
Dimethyl disulfide	77.3	69.3	77.3	59.1	42.2	44.4	74.0	62.0
Dimethyl sulfide	90.9	89.8	89.1	78.3	81.4	74.4	77.0	69.0
2,5-Dimethylthiophene	68.6	54.7	48.9	33.3	14.4	15.6	60.0	45.3
Ethyl mercaptan	81.3	76.9	88.0	75.0	92.1	97.8	78.0	65.0
Ethyl methyl Sulfide	88.2	83.9	93.3	78.9	52.2	40.0	77.0	68.0
2-Ethylthiophene	72.2	60.0	65.1	45.8	17.8	17.8	65.0	53.0
Hydrogen sulfide	7.8*	2.2*	73.1	46.2	104.4	102.0	72.2	47.8
Isobutyl mercaptan	81.3	69.2	81.5	62.0	62.2	64.4	83.0	67.0
Isopropyl mercaptan	89.2	86.0	90.4	77.7	92.9	98.8	84.0	74.0
Methyl mercaptan	78.9*	67.8*	87.0	73.9	93.4	102	74.0	57.0
3-Methylthiophene	75.9	65.5	67.5	50.6	32.2	32.2	67.0	53.0
n-Propyl mercaptan	80.0	70.0	84.6	64.8	77.8	82.2	79.0	66.0
Tetrahydrothiophene	79.6	70.45	71.6	53.4	0.00	0.00	71.0	56.0
Thiophene	81.6	75.9	80.7	64.8	61.1	62.2	76.0	64.0

** Blank corrected.*

Table 3. Sulfur Background (ppb) for Four Films

Compound	SamplePro FlexFilm		FlexFoil PLUS		SamplePro PVDF		FluoroFilm FEP	
	Day 1	Day 2	Day1	Day 2	Day1	Day 2	Day 1	Day 2
n-Butyl mercaptan	ND	ND	ND	ND	ND	ND	ND	ND
tert-Butyl mercaptan	ND	ND	ND	ND	ND	ND	ND	ND
Carbon disulfide	ND	ND	ND	ND	ND	ND	6.5	9
Carbonyl sulfide	46	68	11	13	5.7	10	4.4	5.9
Diethyl disulfide	ND	ND	ND	ND	ND	ND	ND	ND
Diethyl sulfide	ND	ND	ND	ND	ND	ND	ND	ND
Dimethyl disulfide	ND	ND	ND	ND	ND	ND	ND	ND
Dimethyl sulfide	ND	ND	ND	ND	ND	ND	ND	ND
2,5-Dimethylthiophene	ND	ND	ND	ND	ND	ND	ND	ND
Ethyl mercaptan	ND	ND	ND	ND	ND	ND	ND	ND
Ethyl methyl Sulfide	ND	ND	ND	ND	ND	ND	ND	ND
2-Ethylthiophene	ND	ND	ND	ND	ND	ND	ND	ND
Hydrogen sulfide	20	22	ND	ND	ND	ND	ND	ND
Isobutyl mercaptan	ND	ND	ND	ND	ND	ND	ND	ND
Isopropyl mercaptan	ND	ND	ND	ND	ND	ND	ND	ND
Methyl mercaptan	9	14	ND	ND	ND	ND	ND	ND
3-Methylthiophene	ND	ND	ND	ND	ND	ND	ND	ND
n-Propyl mercaptan	ND	ND	ND	ND	ND	ND	ND	ND
Tetrahydrothiophene	ND	ND	ND	ND	ND	ND	ND	ND
Thiophene	ND	ND	ND	ND	ND	ND	ND	ND

Table 4. Storage Stability of CO, CO_2, Methane, and Sulfur Hexafluoride on Four Bag Films
% Recovery

Compound	SamplePro FlexFilm		SamplePro PVDF		FlexFoil PLUS		FluoroFilm FEP	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
Carbon monoxide	100	100	100	90	100	100	90	50
Carbon dioxide	100	90	100	100	99	100	90	50
Methane	96	92	100	101	99	100	84	72
Sulfur hexafluoride	104	99.8	96.8	92	98.1	93.2	96.4	92.8