Method no.:	PV2075
Matrix:	Air
Target concentration:	0.5 ppm, 2 mg/m^3 (OSHA TWA PEL)
Procedure:	Samples are collected by drawing a known volume of air through a glass fiber filter impregnated with mercuric acetate. Phenyl mercaptan is regenerated from the mercuric phenyl mercaptide, formed during sampling, by treatment with hydrochloric acid. The phenyl mercaptan is extracted into toluene and analyzed by gas chromatography with a flame ionization detector. Samples should be protected from light after sampling.
Air volume and sampling rate:	20 L at 0.2 L/min
Status of method:	Stop gap method. This method has been only partially evaluated and is presented for information and trial use.

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1. General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA PEL for phenyl mercaptan is 0.5 ppm. Several solid sorbent sampling tubes were tried for the collection of phenyl mercaptan, but phenyl mercaptan either did not desorb well from them, or it was not stable on them. Phenyl mercaptan is readily oxidized by air. Derivatizing the phenyl mercaptan appeared to be necessary for stability considerations. OSHA Method 26 derivatizes methyl mercaptan with mercuric acetate (Ref. 5.1). This method of collection and analysis was tried. The collection, retention, extraction, and storage stability were all good using the mercuric acetate coated filters. The detection limit was the same using a flame ionization detector (FID) and a flame photometric detector in the sulfur mode (FPD), so a FID was used for this study.

1.1.2 Potential workplace exposure (Ref. 5.2)

Phenyl mercaptan is used as a chemical intermediate, solvent, and as an insect larvicide.

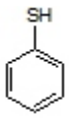
1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.)(Ref. 5.2)

Animal studies show phenyl mercaptan is metabolized to methylphenylsulfone. Exposure to phenyl mercaptan causes restlessness, then increased respiration, incoordination, muscular weakness, skeletal muscle paralysis of the hind limbs, cyanosis, lethargy and/or sedation, respiratory depression, followed by coma and death. Phenyl mercaptan is an eye and skin irritant. Prolonged exposure causes kidney changes along with hyaline casts in the tubules and hyperemia of the adrenal medulla. In mice, lung, liver and kidney changes were seen following high inhalation exposures.

1.1.4 Physical properties (Ref. 5.3):

Synonyms:	benzenethiol; thiophenol
Molecular weight:	110.17
Density:	1.0728
Freezing point:	-15˚C
Boiling point:	168˚C
Flash point:	56˚C (132˚F)
Odor:	offensive mercaptan and garlic-like odor
Color:	colorless liquid
Molecular formula:	C_6H_6S
CAS:	108-98-5
IMIS:	P105
RTECS:	14447 (DC0525000)
UDOT:	UN 2337

Compound:



1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 0.6 µg. This is the smallest amount that could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.004 ppm, based on a 2 mL extraction and a 20 liter air volume. (All ppm amounts in this study are based on a 20 liter air volume and a 2 mL extraction.)

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible.

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of column and GC parameters.

1.4 Disadvantages

1.4.1 The amount of sample that can be taken is limited by the amount of mercuric acetate on the filter.

1.4.2 Samples must be protected from light before analysis.

2. Sampling procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump, the flow of which can be determined within ±5% at the recommended flow.

2.1.2 Glass fiber filters impregnated with mercuric acetate. The filters are prepared by soaking 37 mm Gelman type A glass fiber filters (or equivalent) in a 5% (w/v) aqueous solution of mercuric acetate. The filters are allowed to dry, and then assembled in two piece filter cassettes without backup pads. The filters may be yellowish in color, which does not seem to affect their collection efficiency

2.2 Sampling technique

2.2.1 Immediately before sampling, remove the plugs from the filter cassette.

2.2.2 Connect the cassette to the sampling pump with flexible tubing.

2.2.3 Tubes should be placed in a vertical position to minimize channeling, with the smaller section towards the pump.

2.2.4 Air being sampled should not pass through any hose or tubing before entering the cassette.

2.2.5 Seal the cassette with the plugs immediately after sampling. Seal each sample with OSHA Form-21 sealing tape.

2.2.6 With each batch of samples, submit at least one blank, coated filter from the same lot used for samples.

2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.

2.2.8 Bulks submitted for analysis must be shipped in a separate mailing container from the samples.

2.3 Extraction Efficiency

Six mercuric acetate filters were liquid spiked at each loading of 2.2 µg (0.0488 ppm), 11 µg (0.244 ppm), and 2.2 µg (0.488 ppm). They were allowed to equilibrate overnight at room temperature, placed into separate 20 mL scintillation vials, extracted with 2 mL of toluene and 6 mL 25% HCl in water for 10 minutes with constant shaking, the toluene layer was removed, and analyzed by GC/FID. The overall average was 99.5% recovered (Table 1).

Table 1
Extraction Efficiency

Filter#	% Recovered		
	2.2 µg	11 µg	22 µg
1	99.5	100	101
2	98.4	103	100
3	103	103	97.5
4	97.5	97.4	101
5	101	98.4	94.0
6	96.6	95.4	104
Average	99.3	99.6	99.6
Overall Average	99.5		
Standard Deviation	± 2.81		

2.4 Retention efficiency

2.4.1 Six mercuric acetate filters were liquid spiked with 22 µg (0.488 ppm) phenyl mercaptan, allowed to equilibrate overnight, and placed in a cassette with a backup filter coated with mercuric acetate. The cassettes had 20 liters of humid air (90% RH) pulled through them. They were opened, extracted and analyzed by GC/FID. There was no phenyl mercaptan found on the backup filters (Table 2). The retention efficiency averaged 97.8%.

Table 2
Retention Efficiency

Filter #	% Recovered 'A'	% Recovered 'B'	Total
1	95.3	0.0	95.3
2	98.1	0.0	98.1
3	98.2	0.0	98.2
4	101	0.0	101
5	98.8	0.0	98.8
6	95.1	0.0	95.1
		Average:	97.8

2.4.2 A collection study was performed using three cassettes, the first with a glass fiber filter followed by two with mercuric acetate coated filters. The glass fiber filter was spiked with phenyl mercaptan, then immediately afterwards 20 liters of humid air (85% RH) was pulled through the cassettes. The phenyl mercaptan vaporized off the glass fiber filter and collected onto the mercuric acetate coated filters. There was no residual phenyl mercaptan

found on the glass fiber filters. The amount of phenyl mercaptan recovered off the mercuric acetate filters averaged 100% (Table 3).

Table 3
Collection Efficiency

	% Recovered			
Filter	GFF	'A'	'B'	Total
1	0.0	100	0.0	
2	0.0	103	0.0	
3	0.0	98.3	0.0	
	Average			100

2.5 Storage

Mercuric acetate coated filters were spiked with 44 µg (0.976 ppm) phenyl mercaptan and stored at room temperature until opened and analyzed. After day three the storage samples were covered in foil for the remainder of the storage period. The recoveries averaged 99.0 % for the 17 days stored (Table 4).

Table 4
Storage Study

Day	% Recovered
3	102
3	99.0
10	97.9
10	96.8
10	97.0
17	99.6
17	101
17	98.9
Average	99.0

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 1.1, 5.5, 11, and 22 µg/mL phenyl mercaptan in toluene. The pooled coefficient of variation was 0.0105 (Table 5).

Table 5
Precision Study

Injection Number	1.1 µg/mL	5.5 µg/mL	11 µg/mL	22 µg/mL
1	21849	152180	325820	714720
2	21558	153360	322720	721980
3	21950	153540	322850	724130
4	21210	151170	323950	722910
5	21289	150720	329440	734120
6	21075	150590	329150	713360
Average	21489	151927	325655	721870
SD	± 357	± 1307	± 3032	± 7481
CV	0.0166	0.0086	0.00931	0.0104
Pooled CV	0.0105			

where:

$$\text{CV (Coefficient of Variation)} = \frac{\text{standard deviation}}{\text{average}}$$

$$\text{Pooled CV} = \sqrt{\frac{A_1CV_1^2 + A_2CV_2^2 + A_3CV_3^2 + A_4CV_4^2}{A_1 + A_2 + A_3 + A_4}}$$

A_1, A_2, A_3 , A_4 = # of injections at each level
CV_1, CV_2, CV_3 ,CV_4 = coefficients at each level

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied is 20 liters.

2.7.2 The sampling rate studied is 0.2 liters per minute.

2.8 Interferences

Suspected interferences should be listed on sample data sheets.

2.9 Safety precautions

2.9.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.9.2 Safety glasses should be worn at all times.

2.9.3 Follow all safety practices that apply to the workplace being sampled.

3. Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a flame ionization detector. A Hewlett-Packard 5890 was used for this study.

3.1.2 GC column capable of separating the analyte and an internal standard from any interferences. The column used in this study was a 60-meter RTx-1 1.5-µm df capillary column. The detection limit for the flame photometric detector was performed using a 60-meter DB-210 0.5-µm df capillary column.

3.1.3 An electronic integrator or some other suitable method of measuring peak areas.

3.1.4 Two milliliter vials with Teflon-lined caps.

3.1.5 A 10 µL syringe or other convenient size for sample injection.

3.1.6 Pipets for dispensing the toluene and hydrochloric acid solution.

3.1.7 Volumetric flasks - 5 mL and other convenient sizes for preparing standards.

3.1.8 20 mL scintillation vials for the extraction of the filters.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, and air.

3.2.2 Phenyl mercaptan, Reagent grade

3.2.3 Toluene

3.2.4 Deionized water

3.2.5 Hydrochloric acid, a 25% v/v solution is made with deionized water

3.3 Sample preparation

3.3.1 Place into a scintillation vial 2 mL toluene and 6 mL 25% hydrochloric acid in water solution.

3.3.2 Remove the filter from the cassette. Fold the filter and push it into the vial with the cap as the vial is sealed.

3.3.3 Extract the filter for 10 minutes with continuous shaking. It is allowed to sit for 1 minute for the layers to separate. The upper toluene layer is removed and placed into a separate 2-mL vial for analysis.

3.4 Standard preparation

3.4.1 Standards are prepared by diluting a known quantity of phenyl mercaptan with toluene.

3.4.2 At least two separate stock standards should be made. Dilutions of the stock standards are made to cover the range of the samples so that all samples are bracketed with standards. The range used in this study was from 0.2 µg/mL to 44 µg/mL phenyl mercaptan in toluene.

3.5 Analysis

3.5.1 Gas chromatograph conditions

Flow rates (mL/min)		Temperature (°C)	
Nitrogen(make-up):	30	Injector:	200
Hydrogen(carrier):	1	Detector:	220
Hydrogen(detector):	30	Column:	90
Air:	240		
Injection size:	3 µL		
Chromatogram:	(See Figures 1 and 2)		

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte is an interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted if necessary so these interferences will pose no problems.

3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

3.7.1 A curve with area counts versus concentration is calculated from the calibration standards.

3.7.2 The area counts for the samples are plotted with the calibration curve to obtain the concentration of phenyl mercaptan in solution.

3.7.3 To calculate the concentration of analyte in the air sample the following formulas are used:

$$\text{mass of analyte per sample} = \frac{(\mu g/mL)(\text{desorption volume})}{\text{desorption efficiency}}$$

$$\text{number of moles of analyte} = \frac{\text{mass of analyte per sample}}{\text{molecular weight}}$$

(number of moles of analyte)(molar volume at 25°C and 760 mmHg) = volume the analyte will occupy at ~25°C and 760 mmHg

$$\text{ppm} = \frac{(\text{volume analyte occupies})(10^6)}{\text{air volume}}$$

* All units must cancel.

3.7.4 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 20 liter air sample:

$$\text{ppm} = \frac{(\mu g/mL)(EV)(24.26)(10^6)(g)(mg)}{(20\ L)(DE)(MW)(1000\ mg)(1000\ \mu g)}$$

µg/mL	=	Concentration of analyte in sample or standard
24.46	=	Molar volume (liters/mole) at 25 °C and 760 mmHg.
MW	=	Molecular weight (g/mole)

EV = Extraction volume of 2 mL
20 L = 20 liter air sample
DE = Desorption efficiency

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4. Recommendations for further study

A vapor generated collection study should be performed.

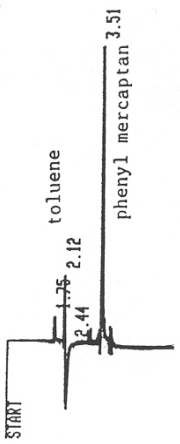


Figure 1. A standard of 11 µg/mL phenyl mercaptan in toluene analyzed by GC/FPD on a DB-210 capillary column at 100 °C.

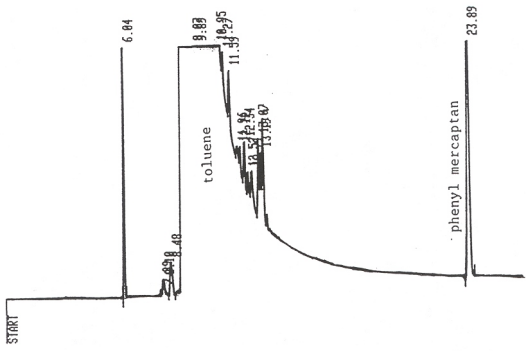


Figure 2. A standard of 11 µg/mL phenyl mercaptan in toluene analyzed by GC/FID on a RTx-1 capillary column at 90 °C.

5. References

5.1 Elskamp, C., Method 26, "Ethylenediamine, diethylenetriamine, and triethylenetetramine", Organic Methods Evaluation Branch, OSHA Analytical Laboratory, 1981.

5.2 "Documentation of the Threshold Limit Values and Biological Exposure Indices", Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986, p. 478.

5.3 Windholz, M., "The Merck Index", Tenth Edition, Merck & Co., Rahway N.J., 1983, p. 1340.