Paraffin wax fumes

Method number:	PV2047
Target Concentration:	2 mg/m^3 ACGIH TWA TLV
Procedure:	Samples are collected by drawing a known volume of air through a glass fiber filter. Samples are desorbed with Carbon Disulfide and analyzed by gas chromatography using a Flame Ionization Detector.
Air volume studied:	100 minutes at 1 Lpm (100 L)
Status of method:	Partially Validated 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 Laboratory recently received samples collected on glass fiber filters requesting paraffin wax fume analysis. Although this collection method has been recommended for many years, the supporting documentation had not been collected. Since there is a TLV and samples were received, it was decided to perform the laboratory work needed to evaluate this sampling and analytical procedure.

1.1.2 Toxicity

Pure paraffin wax is widely regarded as non-toxic, but may possess some carcinogenic properties. (Ref 5.3) These properties are largely believed to be due to polycyclic aromatic hydrocarbons, but most processed waxes in use in America today do not possess any measurable levels of polycyclics. (Ref 5.1) Work around molten paraffin, especially if it is overheated is more uncomfortable and nauseating than dangerous. (Ref 5.4)

1.1.3 Potential workplace exposure

Workers are exposed to paraffin wax fumes in a variety of industries. Any time that paraffin solid is heated a fume may be produced. Paraffin is ideal for use as a sealer or waterproofing agent. Coating of paper for use as containers for milk is one of the largest uses of paraffin. (Ref 5.1) It is also used in the candle making industry and as an original mold in the casting industry.

1.1.4 Physical properties:

CAS:	8002-74-2
IMIS:	2000
RTECS:	RV0350000
Compound:	Paraffin Wax is macrocrystalline and is composed mostly, (40%-90%), of straight chain alkanes C_{18} – C_{36}. The remainder is composed of C_{18} – C_{36} isoalkanes and cycloalkanes. Paraffin wax contains very little oil. (Less than 0.1%)
Odor:	none
Color:	white

1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 6.8 ng per injection. This is the smallest mount of paraffin that will give a characteristic chromatographic pattern. (Figure 1)

1.2.2 The overall detection limit is 0.034 mg/m^3 based on a 100-liter air volume and a 2 mL desorption volume. Air concentrations given throughout this procedure are based on a 100-liter air volume and 2 mL desorption volume.

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.

1.4 Disadvantages

Paraffin produces a characteristic fingerprint pattern. Integration generally is done by using the total area of all peaks. An interfering peak counted as part of the total area would produce inaccurate results.

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 A three-piece plastic sampling cassette capable of holding a 37-mm glass fiber filter.

2.2 Sampling technique

2.2.1 The glass fiber filter is placed in the cassette and the inlet and outlet plugs are removed.

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

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

2.2.4 Seal the cassette with plastic plugs and then seal each sample, covering the plugs with a Form OSHA-21 seal.

2.2.6 With each batch of samples, submit at least one blank. This cassette should be subjected to exactly the same handling as the samples, except no air is drawn through it.

2.2.7 Send the samples and corresponding paperwork to the lab for analysis.

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

2.3 Extraction efficiency

Eighteen filters were spiked with a solution of Parowax in carbon disulfide. The solution was 6.26 mg/mL. Six filters were spiked with 6 uL (37-ug), six with 32 uL (200 ug) and the final six with 120 uL (751 ug). This corresponds to approximately 0.1, 0.5 and 2 times the target concentration. The tubes were refrigerated overnight, extracted the next day, and analyzed by gas chromatography using a flame ionization detector. The average extraction efficiency is 95.3%. (Table 1)

Table 1
Extraction Efficiency

sample #	0.1x (37 µg)	0.5x (200 µg)	2x (751 µg)
1	99	98	95
2	95	104	97
3	91	96	92
4	90	92	94
5	86	102	102
6	94	95	98
average	92	98	96
standard deviation -	±4.4	±4.1	±3.2

overall average = 95.3%

2.4 Retention efficiency

Six glass fiber filters were spiked with 60 uL of a 6.26 mg/mL solution of Parowax in carbon disulfide. This was equivalent to a loading of 372 ug of paraffin wax which is approximately the target concentration. They were stored overnight. Eighty, 100, and 125 liters of humid air (70%) were drawn through the filters the next day. The filters were extracted with carbon disulfide and analyzed. The average result including all air volumes is 101%. (Table 2)

Table 2
Retention Study

sample #	air volume (L)	µg spiked	% retained
1	80	372	99
2	80	372	109
3	100	372	97
4	100	372	97
5	125	372	97
6	125	372	106

average retained = 101%

2.5 Storage

Five glass fiber filters were spiked with 60 uL of a 6.26 mg/mL solution of Parowax in carbon disulfide. This was equivalent to a loading of 372 ug of paraffin wax which is approximately the target concentration. They were stored in the refrigerator for five days, extracted with carbon disulfide, and analyzed. The average recovery after five-day storage is 95%. (Table 3)

Table 3
Storage Study

sample #	µg spiked	days stored	% recovered
1	372	5	94
2	372	5	91
3	372	5	101
4	372	5	95
5	372	5	93

average recovered = 95%

2.6 Air volume and sampling rate studied

2.6.1 The air volume studied is 100 liters.

2.6.2 The sampling rate studied is 1 liter per minute.

2.7 Interferences

Suspected interferences should be listed on sample data sheets.

2.8 Safety precautions

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

2.8.2 Safety glasses should be worn at all times.

2.8.3 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 (FID).

3.1.2 GC column capable of separating the analyte and an internal standard, if used, from any interference. The column used in this study was a fused silica capillary having the following dimensions: 6-m x 0.32-mm i.d., (1 µm d_f DB-1).

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

3.1.4 Four milliliter vials with PTFE-lined caps.

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

3.1.6 Pipettes for dispensing the desorbing solution. The Glenco 1-mL dispenser was used in this method.

3.1.7 Volumetric flasks, 10-mL, and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, and air.

3.2.2 Carbon disulfide, Reagent grade.

3.3.3 Parowax paraffin used as the analytical standard.

3.3 Sample preparation

3.3.1 Sample cassettes are opened and the filter is placed in a 4-mL vial.

3.3.2 Each filter is extracted with 2 mL carbon disulfide.

3.3.3 The vials are sealed immediately and extracted for 30 minutes with occasional shaking.

3.4 Standard preparation

3.4.1 Standards are prepared by diluting a known quantity of Parowax in carbon disulfide. One thousand ug of Parowax in 10 mL of carbon disulfide will give a standard equivalent to the TLV assuming 100-liter air volume and 2 mL extraction.

3.4.2 A range of separate standards should be made so that the sample results are bracketed.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

Flow rates	**(mL/min)**	**Temperature**	**(ºC)**
Hydrogen carrier:	1	Injector:	250
Hydrogen flame:	50	Detector:	300
Air:	300	Column:	250
Nitrogen makeup:	25		

Injection size: 4 uL
Elution time: 2 to 12 min.
Attenuation: 2

Chromatogram: Figure 2

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

3.5.3 Precision was measured by making 6 consecutive injections of 4 different standards containing Parowax concentrations of 37, 200, 372, and 751 µg/mL. The pooled coefficient of variation is 0.016. (Table 4)

Table 4
Precision

injection #	0.1x 37 µg/mL	0.5x 200 µg/mL	1.0x 372 µg/mL	2.0x 750 µg/mL
1	224100	1056200	1939300	3852800
2	219920	1082500	1866400	3831200
3	221010	1059100	1902900	4044400
4	227370	1065500	1906900	4065500
5	218380	1074300	----------	3686100
6	205610	1071900	----------	3694700
average -	219398	1068250	1903875	3862450
standard deviation –	±6952	±8963	±25855	±30425
CV -	0.032	0.0084	0.014	0.0079

pooled CV = 0.016

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

$$Pooled\ CV = \sqrt{\frac{A1(CV1)^2 + A2(CV2)^2 + A3(CV3)^2 + A4(CV4)^2}{A1 + A2 + A3 + A4}}$$

A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = Coefficients of variation at each level

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte or the internal standard used is 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

To calculate the mg/m^3 of analyte in samples, the following equation should be used:

$$mg/m^3 = \frac{(\mu g/mL,\ blank\ corrected)(2\ mL\ desorption\ volume)}{(100\ L\ air\ volume)(desorption\ efficiency,\ decimal)}$$

µg/mL = concentration of analyte in sample

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

The method seems adequate for both collection and analysis. The only thing that is left to look at is actual quantitative collection of fumes. Paraffin fumes have been produced by heating Parowax in a bubbler tube and collecting them on a filter attached to the exit port. The collection appeared to be good with no breakthrough to the backup pad. However, no quantitative check has been performed using an actual dynamic atmosphere of paraffin fumes.

Much of the analytical work could possibly be avoided by the use of pre- and post-weightings'. It is unusual to have other contaminates in areas where paraffin wax fumes are being emitted. By using weighings to determine the total mass present on the filter it may be possible to eliminate the chromatographic determination of samples with little or no contamination. Most samples received at the laboratory fall into this category. This is an area that may warrant further study.

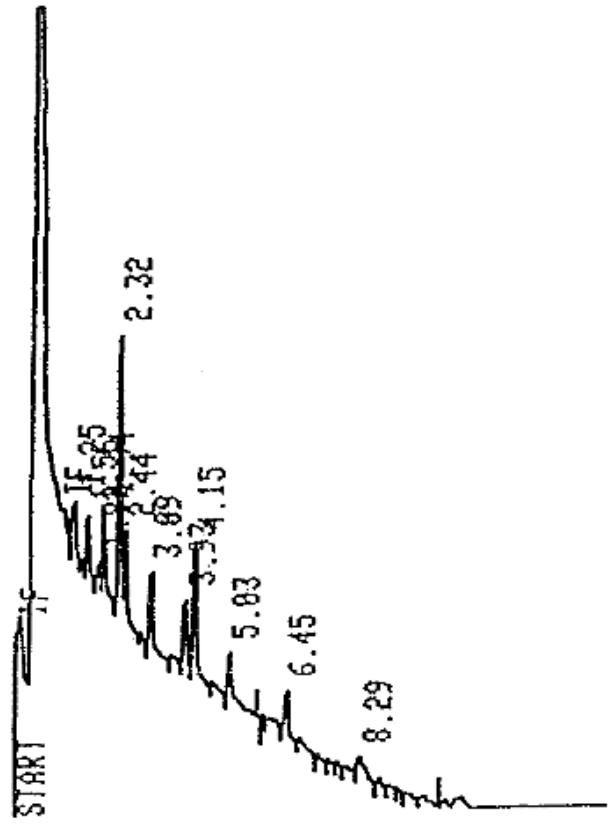

Figure I. Parowax detection limit (1.708 µg/mL)

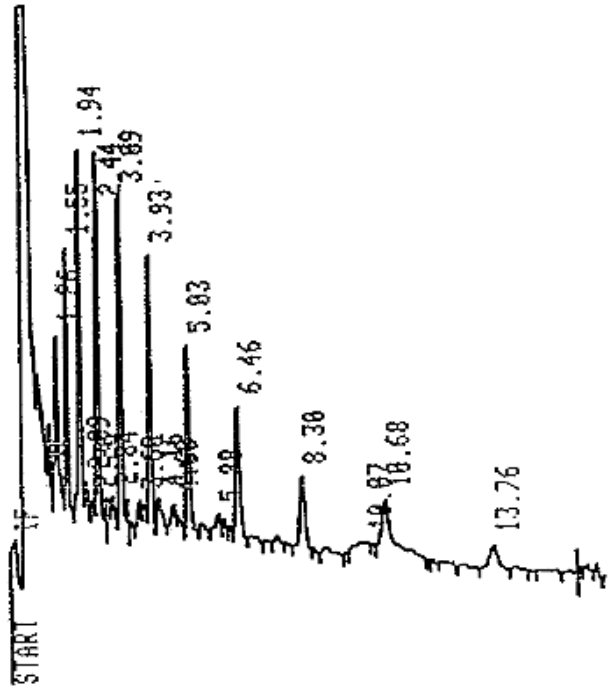

Figure 2. Parowax standards in Carbon Disulfide (I5.8 µg/mL)

5 References

5.1 P. Shubik et al; "Studies on the Toxicity of Petroleum Waxes," Toxicology and Applied Pharmacology; Aug. 2 1962.

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5.3 R. Prosser White "The Dermatergoses or Occupational Affections of the Skin" London H.K. Lewis & Co. 1934.

5.4 "Queries and Minor Notes" Journal of American Medical Assoc. 110:2102 1938.