Oil Mist in Workplace Atmospheres

Method no.:	ID-128
Control no.:	T-ID128-PV-01-0304-PM
Matrix:	Air
OSHA Standard:	5 mg/m^3
Validation Level:	
Collection Procedure:	37 mm PVC filters
Recommended Air Volume:	150 L at 1 to 2 L/min
Analytical Procedure:	Fluorescence
Detection Limit:	1 µg/mL
Determination Limit or Reliable Quantization Limit:	1 µg/mL
Precision:	Unknown
Method Classification:	PV

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1. Introduction

1.1 Scope

1.1.1 This method describes the sampling and analysis of oil mist by fluorescence spectrophotometry.

1.2 Advantages and Disadvantages

1.2.1 Sampling involves no liquids.

1.2.2 Desorption and preparation of samples for analysis involve simple procedures and instrumentation.

1.2.3 The analytical technique is not sophisticated.

1.2.4 The bulk oil must be identical to the oil in the samples.

1.2.5 This method is adequate for many oils, particularly many aromatic oils; however, not all oils fluoresce. Highly fluorescent compounds may interfere; however, these compounds are not ordinarily found with oils.

1.3 Principle

1.3.1 The sample is collected using a personal monitor and a 37 mm PVC filter with a flow rate of 1 to 2 L/min.

1.3.2 The oil from the filters is dissolved in chloroform and compared to standards prepared from bulk oil by means of fluorescence spectrophotometry.

1.3.3 Oils are mixtures which often contain compounds that fluoresce. Fluorescent compounds usually contain aromatic rings or extended conjugated double bonds. Because the fluorescent process is often very efficient, less than 1% of the oil need be a fluorescent compound for the oil to be analyzed.

Photochemical process:

absorbed excitation energy		emitted florescence energy
oil	-------> oil*	----------> oil

The analysis consists of two parts: choosing an appropriate excitation wavelength and analyzing the sample at the correct fluorescence wavelength.

2. Range and Detection Limit

2.1 Detection limit is 1 µg/mL. Range is 5-500 micrograms.

3. Precision and Accuracy

3.1 Unknown

4. Interferences

4.1 Highly fluorescent compounds may interfere if they are soluble in $CHCl_3$ - however, these compounds are not ordinarily found with Oils. Refer to appendix.

5. Sampling

5.1 Apparatus

5.1.1 Personal sampling pump

5.1.2 Tared 37 mm 5 µm PVC filters

5.2 Procedure

5.2.1 Sampling is done in accordance with current instructions contained in OSHA directives to the industrial hygienist.

5.2.2 A minimum sample size of 150 L is recommended.

5.2.3 The sample is collected on a tared 37 mm 5 µm pore PVC filter using a flow rate of 1-2 L/min. The net weight collected in milligrams is then divided by the air volume in cubic meters. If the result is less than 5 mg/m^3, the sample need not be submitted to the laboratory for analysis.

5.2.4 A bulk sample of the oil being used must be submitted for use in the preparation of standards. An unused filter should be sent in with the samples for use as a blank (do not ship bulk oil and samples in the same package).

6. Analytical Procedure

6.1 Apparatus

6.1.1 Perkin-Elmer Model 204-A Fluorescence Spectrophotometer.

6.1.2 Perkin-Elmer Model 56 Strip Chart Recorder.

6.1.3 Quartz cuvettes, 10-mm.

6.1.4 Screw-top test tubes, 50-mL.

6.1.5 Glass Volumetric pipettes.

6.1.6 Glass Separatory Funnel.

6.1.7 Glass wool.

6.1.8 Four place Mettler balance or equivalent.

6.2 Reagents: All chemicals should be ACS reagent grade or equivalent.

6.2.1 Spectrophotometric grade chloroform.

6.2.2 Sodium Chloride, NaCl

6.2.3 Sodium Sulfate, Na_2SO_4

6.3 Precautions

6.3.1 Do all work with chloroform in a hood, and afterwards discard all used chloroform into waste container.

6.3.2 Do not use plastic squirt bottles or plastic graduated cylinders in the analysis. The plasticizer used on plastic, bottles and cylinders will give a high blank.

6.4 Sample preparation

6.4.1 Divide the weight of oil on the filter by the, air volume. If the result is 5 mg/m^3 the filter need not be analyzed and the gravimetric result can be reported. Otherwise, place the filter from the cassette into a 50 mL screw-top test tube. Add 10.0 mL $CHCl_3$ and allow to stand for 30-60 minutes. Allow the spectrophotometer and exciter light to warm up for 30 minutes.

6.5 Standard preparation

6.5.1 A pure bulk oil should be filtered through a 5 µm PVC filter before use to separate out any particulates. If the bulk is in an aqueous suspension no filtering is required. Instead place about half the bulk into a 60 mL separatory funnel which has a glass wool plug in the outlet tube. Extract two or three times with approximately ten mL of chloroform, each time pouring off the bottom chloroform layer into a single 100 mL beaker. If a suspension should occur add a small amount of NaCl to the funnel and swirl to break the suspension. After the last extraction add a little anhydrous Na_2SO_4 to the chloroform solution to remove any water. Decant the chloroform extract to another beaker and rinse the Na_2SO_4 with 5 mL of chloroform. Add the rinsings to the second beaker. Evaporate off this chloroform in a vacuum. Avoid heating the samples; this could cause the loss of the volatile fluorescent elements.

6.5.2 Prepare the bulk standard by, accurately weighing 0.1 gram of the purified bulk oil and dissolving it in chloroform.

Transfer the solution to a 100 mL volumetric flask and dilute to volume with chloroform. This stock solution is equivalent to 1000 µg/mL. Prepare the following working standards by diluting the indicated volumes of the stock solution to 50 mL with chloroform:

Volume of stock solution used (mL)	Final concn (µg/mL)
0.5	10
1.0	20
2.0	40
3.0	60
4.0	80
5.0	100
0.0	(solvent blank)

6.6 Analysis

6.6.1 Turn on the power to the spectrophotometer.

6.6.2 Turn on power to the xenon lamp power supply, wait 15 seconds, and then push momentarily the "Lamp Starter" button. If the lamp will not start, wait 15 seconds for the capacitors to recharge and repeat the procedure.

6.6.3 Turn on the recorder.

6.6.4 Wait 20 minutes and rotate the recorder "Zero" knob to adjust the recorder pan to coincide with the baseline when the spectrophotometer shutter is closed.

6.6.5 For manual rotation of either the "Excitation Wavelength" or “Emission Wavelength" control, make sure the "Wavelength Drive Selector" is in the Δ [image for up arrow] position. Forcible rotation of either dial when engaged for automatic drive will disturb the calibration or damage the gear train.

6.6.6 Insert the 100 µg/mL solution into the holder and rotate into position.

6.6.7 Set the "Excitation Wavelength" and "Emission Wavelength" controls at zero. Rotate the "Excitation Wavelength" control to 220 nm and scan. The "Output Selector Switch" on the rear panel should be in the upward position for recorder Output.

6.6.8 Set the "Wavelength Drive Selector" at "Excitation" and the Model 56 Recorder Selector switch at "Chart".

6.6.9 Turn the "Scan" switch to "On" and record the spectrum. Mark the wavelength positions on the chart paper for calibration purposes.

6.6.10 Set the "Wavelength Drive Selector" at Δ [image for up arrow], and the "Excitation Wavelength" control at the position of the shortest wavelength that gave a peak from step 6.6.9. The excitation wavelength is usually about 300 nm (do not use the peak at 370 nm).

6.6.11 With the proper excitation wavelength set, find the most sensitive emission wavelength. This is usually about 350 nm. Set the "Emission Wavelength" dial to 220 nm and the Wavelength Drive Selector to "Emission". Turn the "Scan" switch to "On", and record a preliminary spectrum. Turn the "Scan" switch "Off" when the scan is completed.

6.6.12 Set the "Wavelength Drive Selector" at Δ [image for up arrow] and rotate the "Emission Wavelength" control to the position of maximum emission as determined above. Adjust the "Sensitivity" control to bring the recorder pen to nearly a full scale setting.

6.6.13 Increase the "Sensitivity Range" as necessary up to 10 and also the "P. M. Gain" dial up to 5 if necessary. After a deflection is obtained, make fine adjustments with the "Excitation Wavelength" and "Emission Wavelength" dials until an optimum setting for each is found.

6.6.14 Rotate the "Emission Wavelength" control to a position 50 nm below the maximum emission band determined above. Turn on the "Scan" switch and scan over a 100 nm range.

6.6.15 Rotate the sample holder to put the cell containing the blank in the light beam, and scan the chloroform blank over the same range.

6.6.16 Scan the samples and standards over a 100 nm range of the emission wavelength. Run a standard calibration curve and the samples. A standard should be analyzed after every five or six samples.

6.6.17 Record the peak heights of the standards and samples. Use a least square regression to plot a calibration curve of peak height vs. concentration.

6.7 Calculations

6.7.1 Read the weight, in µg, corresponding to each response (mm), from the standard curve. No volume corrections are needed.

6.7.2 Corrections for the blank must be made for each sample. The mg/m^3 of oil mist is determined as follows:

$$mg/m^3 = \frac{\mu g\ oil\ mist \times sample\ vol\ (mL)}{air\ vol\ (L)}$$

sample vol (mL) = volume of chloroform used to extract the filter.

air vol (L) = volume of air sampled in liters

7. References

7.1 Roy, E. M., *American Industrial Hygiene Journal*, 31, 472 (1970).

7.2 Tippmann, M., at al. *Arch. Environ. Health*, 21, 591 (1970).

7.3 Schenk, G. H., Absorption of Light and Ultraviolet Radiation, Fluorescence and Phosphorescence Emission (1973).

7.4 The Condensed Chemical Dictionary. 8th Ed., Van Nostrand Reinhold Co.

7.5 NIOSH Manual of Analytical Methods, HEW (1974).

Appendix

Fluorescence is a type of luminescence in which molecules emit visible radiation in passing from a higher to a lower electronic state. The time interval between absorption and emission of energy is extremely short (10^{-8} to 10^{-3} seconds). This distinguishes fluorescence from phosphorescence, in which the time interval may extend to several hours. Of the following list of oils, only the aromatic oils respond well to fluorescence analysis:

1. Mineral

1.1 Petroleum

1.1.1 Aliphatic or wax-base (Pennsylvania)

1.1.2 Aromatic or asphalt-base (California)

1.1.3 Mixed-base (Midcontinent)

1.2 Petroleum-derived

1.2.1 Lubricants: engine oil, machine oil, cutting oil

1.2.2 Medicinal: refined paraffin oil

2. Vegetable (chiefly from seeds or nuts)

   2.1 Drying (linseed, tung, oiticica)

   2.2 Semidrying (safflower, soybean)

   2.3 Nondrying (castor, cottonseed, coconut)

   2.4 Inedible soap stocks (palm. coconut)

3. Animal

   These usually occur as fats (tallow, lard, stearic acid). The liquid types include fish oils, oliec acid, sperm oil, etc. They usually have a high fatty acid content.

4. Essential

   Complex volatile liquids derived from flowers, stems, and leaves, and often the entire plant. They contain terpenes (pinene, dipentene, etc.) and are used chiefly for perfumery and flavorings. Usually resinous products are mixed with them. Turpentine is a highly resinous essential oil.

5. Edible

   Edible oils include some vegetable oils, such as olive, cottonseed, corn and peanut, as well as some special fish oils (cod-liver, haliver, shark liver, etc.), used largely as medicines for their high vitamin content. Many edible oils are hydrogenated for use in cooking and for industrial purposes.

   The following classes of molecules are generally fluorescent to some degree:

   1. Some Conjugated Aryl-substituted Olefins. Examples are trans-stilbene (not cis-stilbens), diphenyistilbene (DPS), and diphenyihexatriene.

   2. Most Unsubstituted Aromatic Hydrocarbons. Examples are benzene (weak), naphthalene, anthracene, and pyrene. Aromatics such as triphenylene and biphenyl fluoresce so weakly that they are measured by, phosphorimetry. Alkyl substitution increases the fluorescence of benzene but not necessarily other hydrocarbons.

   3. Some Fluoro- and Chloro- substituted Aromatic Hydrocarbons. The substitution of fluorine and chlorine does not increase the rate of inter-system crossing to such an extent that useful fluorescence cannot be observed. Both 1-fluoro- and 1-chloronaphthalene fluoresce measurably.

   4. Most Phenols (Hydroxy- substituted Aromatics) and Aryl Ethers. Most phenols, naphthols, and so forth, are more intensely fluorescent than the parent hydrocarbon. The pH of the solution is important, but its effect is not always the same. Phenol itself is fluorescent in neutral solution but when the basicity of the solution is increased so that the phenoxide ion is the principal equilibrium form, no fluorescence is observed. In contrast, both 2-naphthol and its anion (basic solution) are fluorescent. The same is true for salicylic acid, an intensely fluorescent molecule. (It appears that the hydroxyl group dominates the excited state properties of this acid.) Phenols such as *p*-nitrophenol, dinitrophenols, and trinitrophenol do not fluoresce.

      Aryl ethers such as anisole and 1-methoxynaphthatene are also intensely fluorescent.

   5. Protonated Forms of Some Aromatic Carboxylic Acids. The neutral and anionic forms of acids like benzoic acid and naphthoic acid do not fluoresce at useful intensities. However,

both of these acids fluoresce in aqueous sulfuric acid; it appears that the protonated form ($C_6H_5CO_2H_2^+$ in the case of benzoic acid) emits. Benzoic acid and acetylsalicylic acid also fluoresce in 1% acetic acid-chloroform.

6. Most Aromatic Amines. Examples are 1-naphthylamine, 2-naphthylamine, anthranilic acid, and anilines. The pH of the solution is as important for aniline as it is for phenol. In neutral solution, aniline is fluorescent, but when the acidity is increased so that the anilunim ion is the principal species, no fluorescence is observed. In contrast, both the unprotonated and protonated naphthylamines are fluorescent. Amines such as *p*-nitroaniline, the dinitroanilines, and trinitroaniline are not fluorescent.