

IX. APPENDIX I
SAMPLING OF PHENOL IN AIR

Sampling

Air samples are collected in the breathing zone of employees by drawing air through an all-glass midget impinger containing 15 ml of 0.1 N sodium hydroxide solution. If the work operation allows the impinger to be maintained in a vertical position, it may be possible to attach the impinger to the employee's clothing. A personal sampling pump may also be attached to the employee's clothing. However, a significant amount of bending from the waist may make impinger sampling impractical. Samples should be collected as close to the breathing zone as possible. Air being sampled should not pass through any other tubing or equipment before entering the impinger. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm ID glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump. Sampling is performed for at least 15 minutes at a rate of 1 liter/minute. The flow rate, with the impinger on line, should be checked before and after the sample is taken.

After sampling, the impinger stem can be removed and cleaned, first tapping the stem gently against the inside wall of the sample flask to recover as much of the sampling solution as possible, then washing with a small amount (1-2 ml) of distilled water and adding the wash to the sample flask. The flask is then sealed tightly with a hard, nonreactive stopper, preferably Teflon, but never with rubber. Shipment of sample flasks should be with the stems in, the opening of the stem should be sealed with

Parafilm or equivalent nonrubber covers, and the standard taper joints should be sealed usually by means of plastic tape. Precautions should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analyses cannot be performed within a day in order to minimize chemical reactions which might otherwise occur. Whenever possible, hand delivery of samples is recommended, or special shipping cases should be used. A blank impinger should be handled in exactly the same manner as the other samples (fill, seal, and transport) except that no air is sampled through this impinger.

Calibration

Since the accuracy of an analysis is often limited by the accuracy of the volume of air which is measured, accurate calibration of a sampling device and flowmeters is essential. Frequency of calibration depends on the use, care, and handling to which the sampling system is subjected. Pumps should be calibrated if they have been subjected to abuse or if they have just been repaired or received from a manufacturer. When sampling highly polluted or dusty environments, frequent cleaning and calibration may be necessary because the orifices of flow meters and other equipment may become contaminated.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration depends highly on the type of instrument used as a reference, and choice of calibration procedure will depend largely upon where the calibration is to be performed. For laboratory testing, a 1-liter buret or a wet-test meter is recommended,

although other standard calibrating instruments, such as spirometer, Marriot bottle, or dry-gas meter, can be used. The actual set-up should be similar for all calibration systems used. The calibration instrument should be connected first in a series to the sampling train which will be followed by the sampler pump. In this way, the calibration instrument will be at atmospheric pressure. If a personal sampling pump is used, each pump must be calibrated separately. If a buret is used for calibration, it should be set up so that the flow is toward the narrow end of the unit.

Care in the assembly of the calibration set-up ensures that seals at the joints are airtight and that the length of connecting tubing is at a minimum. Calibration should be performed at essentially the same conditions of pressure and temperature as those under which it is anticipated that the sampling will occur. A calibrated pump rotameter should be used to establish flow rate in the field.

Apparatus

The sampling unit for the impinger collection method consists of the following components:

- (a) A standard glass midget impinger containing the collection medium.
- (b) A pump suitable for exhausting at least 1 liter/minute for 100 minutes.
- (c) Thermometer.
- (d) Manometer.
- (e) Stopwatch.

X. APPENDIX II
ANALYTICAL METHOD FOR PHENOL IN AIR

Principle of the Method

A known volume of air is drawn through a midget impinger containing 15 ml of 0.1 N sodium hydroxide as the collection medium. The resulting solution is acidified with sulfuric acid. An aliquot of the collected sample is injected into a gas chromatograph. The area of the resulting trace is determined and compared with similar areas obtained for standards. Use of an internal standard is highly recommended.

Range and Sensitivity

This method [313] was validated over the range of 9.46-37.8 mg/cu m at an atmospheric temperature of 22 C and atmospheric pressure of 760 mmHg, using a 100-liter sample. With a 100-liter sample, the probable useful range of this method is 5-60 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 6-mg sample.

Interference

Any compound which has the same retention time and detector response as phenol under the GC operating conditions described in this method may interfere in the analysis. Retention time data on a single column cannot be considered proof of chemical identity. If there is possible interference, separation conditions (column packing, temperature, flow rate, etc) must be changed to circumvent the problem.

Precision and Accuracy

The coefficient of variation for the total analytical and sampling method in the range of 9.46-37.8 mg/cu m was 0.068. This value corresponds to a 1.3 mg/cu m standard deviation at 19 mg/cu m. A collection efficiency of 1.00 ± 0.01 was determined for the collecting medium.

In general, the analytical results obtained for phenol at concentrations of 5 ppm (19 mg/cu m) using the recommended overall sampling and analytical method averaged 2.6% less than the "true" concentrations for a limited number of laboratory experiments. Since the coefficient of variation is greater than 0.026, any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally prepared "true" concentration. Therefore, it should not be necessary to apply a recovery correction to the final result.

Advantages and Disadvantages of the Method

Samples collected in impingers are analyzed by means of a quick, instrumental method. However, under certain work conditions, impingers attached to an employee's clothing and containing sodium hydroxide may not be suitable for breathing zone samples. The GC instrumental method is precise and accurate, but it does require that samples be returned to the laboratory for analysis.

Apparatus

- (a) Gas chromatograph (GC) equipped with a flame ionization detector (FID)
- (b) Column (4-ft long x 1/4-in OD stainless steel) packed with 35/60 mesh Tenax. [325]
- (c) An electronic integrator or some other suitable means for measuring peak areas.
- (d) Microl syringes - 10 μ l and other convenient sizes for making standards and injecting samples into the GC.
- (e) Volumetric flasks - convenient sizes for making solutions.
- (f) Pipets - 15 ml and other convenient sizes.

Reagents

- (a) Distilled water.
- (b) Phenol - reagent grade.
- (c) Sulfuric acid - reagent grade.
- (d) Sodium hydroxide - 0.1 N solution.

Dissolve 4.0 g of sodium hydroxide in distilled water (carbon dioxide free) and dilute to a final volume of 1 liter.

- (e) Purified nitrogen.
- (f) Purified hydrogen.
- (g) Filtered compressed air.
- (h) Standard solutions.

Six standard solutions at each of the three concentrations (0.5x, 1x, and 2x the recommended TWA concentration limit) are prepared by adding 1 mg, 2 mg, or 4 mg of phenol to 15-ml aliquots of 0.1 N sodium hydroxide

contained in 25-ml volumetric flasks. The amounts introduced are equivalent to that present in a 100-liter air sample at multiples of the recommended limit. The solutions are acidified with 0.1 ml of concentrated sulfuric acid and made up to volume with distilled water. The solution should be checked to confirm that the pH is less than 4. A reagent blank is prepared in the same manner, except that no phenol is added. The standards and blank are analyzed in the manner indicated below.

Procedure

(a) Cleaning of equipment

All glassware used for the laboratory analysis should be washed with detergent and thoroughly rinsed with tap water and distilled water.

(b) Analysis of samples

Transfer the solution to a 25-ml volumetric flask. Rinse the impinger twice with 1 ml of distilled water and add the rinses to the flask. Add 0.1 ml of concentrated sulfuric acid to the flask and mix. Check to ensure that the pH is less than 4. Dilute to mark with distilled water and mix. Typical operating conditions for the gas chromatograph are:

- (1) 50 ml/min (60 psig) nitrogen carrier gas flow.
- (2) 65 ml/min (24 psig) hydrogen gas flow to detector.
- (3) 500 ml/min (50 psig) air flow to detector.
- (4) 215 C injector temperature.
- (5) 225 C manifold temperature (detector).
- (6) 200 C column temperature.

The first step in the analysis is injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, employ the solvent flush injection

technique. The 10- μ l syringe is first flushed with solvent several times to wet the barrel and plunger. To increase the accuracy and reproducibility of the injected sample volume, 3 μ l of solvent are drawn into the syringe. The needle is removed from the solvent, and the plunger is pulled back about 0.2 μ l to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5- μ l aliquot is withdrawn taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 μ l to minimize evaporation of the sample from the tip of the needle. Note that the sample occupies 4.9-5.0 μ l in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

The area of the sample peak is measured by an electronic integrator or some other suitable means of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml of collection medium because samples are collected in this amount of collection medium. Solutions varying in concentration over the range of interest are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/15 ml versus peak area. Note that since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

Calculations

Read the weight in mg corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/15 ml collection medium and the volume of sample injected is identical to the volume of the standards injected. Corrections for the blank must be made for each sample.

$$\text{corrected mg} = \text{mg sample} - \text{mg blank}$$

where:

$$\text{mg sample} = \text{mg found in sample impinger}$$

$$\text{mg blank} = \text{mg found in blank impinger}$$

The concentrations of phenol in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg} \times 1000 \text{ (liter/cu m)}}{\text{air volume sampled (liter)}}$$

Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{\text{T} + 273}{298}$$

where:

P = pressure (mmHg) of air sampled

T = temperature (degrees C) of air sampled

24.45 = molar volume (liter/mole) at 25 C and 760 mmHg

MW = molecular weight (g/mole) of phenol = 94.11

760 = standard pressure (mmHg)

298 = standard temperature (degrees K)

XI. APPENDIX III
MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or

competitor's name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, ie, "100 ppm LC50-oral-rat," "25 mg/cu m LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.93," or, if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flashpoint, shock sensitivity,

or similar descriptive data may be used to indicate flammability, reactivity, or similar properties of the material.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mm Hg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicate if by weight or volume) at 70 degrees Fahrenheit (21.1 degrees Celsius); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flash point and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50, if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement, if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

Skin Contact--single short contact, no adverse effect likely;
prolonged or repeated contact, mild irritation and possibly
some blistering.

Eye Contact--some pain and mild transient irritation; no
corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first-aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed employees.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It shall also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect employees assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill," or "incineration." Warnings such as "comply with local, state, and federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," "Suitable for dusts not more toxic than lead," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling or storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to employees potentially exposed to the hazardous material. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

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MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION		
MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.	
ADDRESS		
TRADE NAME		
SYNONYMS		
II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA
III PHYSICAL DATA		
BOILING POINT, 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H ₂ O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H ₂ O, % BY WT
% VOLATILES BY VOL		EVAPORATION RATE (BUTYL ACETATE=1)
APPEARANCE AND ODOR		

IV FIRE AND EXPLOSION DATA				
FLASH POINT (TEST METHOD)		AUTOIGNITION TEMPERATURE		
FLAMMABLE LIMITS IN AIR, % BY VOL.		LOWER		UPPER
EXTINGUISHING MEDIA				
SPECIAL FIRE FIGHTING PROCEDURES				
UNUSUAL FIRE AND EXPLOSION HAZARD				
V HEALTH HAZARD INFORMATION				
HEALTH HAZARD DATA				
ROUTES OF EXPOSURE				
INHALATION				
SKIN CONTACT				
SKIN ABSORPTION				
EYE CONTACT				
INGESTION				
EFFECTS OF OVEREXPOSURE				
ACUTE OVEREXPOSURE				
CHRONIC OVEREXPOSURE				
EMERGENCY AND FIRST AID PROCEDURES				
EYES				
SKIN				
INHALATION				
INGESTION				
NOTES TO PHYSICIAN				

VI REACTIVITY DATA	
CONDITIONS CONTRIBUTING TO INSTABILITY	
INCOMPATIBILITY	
HAZARDOUS DECOMPOSITION PRODUCTS	
CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION	
VII SPILL OR LEAK PROCEDURES	
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED	
NEUTRALIZING CHEMICALS	
WASTE DISPOSAL METHOD	
VIII SPECIAL PROTECTION INFORMATION	
VENTILATION REQUIREMENTS	
SPECIFIC PERSONAL PROTECTIVE EQUIPMENT	
RESPIRATORY (SPECIFY IN DETAIL)	
EYE	
GLOVES	
OTHER CLOTHING AND EQUIPMENT	

IX SPECIAL PRECAUTIONS

PRECAUTIONARY
STATEMENTS

OTHER HANDLING AND
STORAGE REQUIREMENTS

PREPARED BY _____

ADDRESS: _____

DATE: _____