

IX. APPENDIX I

METHOD FOR SAMPLING DINITRO-ORTHO-CRESOL IN AIR

This sampling method is adapted from Method No. S166 of NIOSH Analytical Methods [50].

General Requirements

(a) Collect air samples in the breathing zones of workers to characterize the exposure from each job or specific operation in each work area.

(b) Collect samples representative of exposures of individual workers.

(c) Record the following:

- (1) Date and time of sample collection.
- (2) Sampling rate and duration and total sample volume.
- (3) Location of sampling.
- (4) Temperature, pressure, and relative humidity at time of sampling.
- (5) Other pertinent information.

Sampling

(a) Collect samples in the breathing zones of workers without interfering with their freedom of movement.

(b) Collect enough samples to permit calculation of TWA concentrations to evaluate the exposure of each worker at every operation or location in which there may be occupational exposure to DNOC.

(c) Use the following apparatus for sampling:

(1) Filter: Glass-fiber filter mounted in a filter holder and attachable to the inlet of a midget bubbler.

(2) Bubbler: Midget bubbler containing 10 ml of 0.1 M sodium hydroxide. Care should be taken to ensure that the bubbler is kept in a vertical position during sampling.

(3) Battery-operated personal sampling pump attachable to the workers' clothing, whose flowrate can be determined with an accuracy of at least 5%.

Calibration of Equipment

Since the accuracy of an analysis can be no greater than the accuracy with which the volume of air is measured, the accurate calibration of a sampling pump is essential. The frequency of calibration required depends upon the use, care, and handling to which the pump is subjected. Pumps should be calibrated if they have been abused or if they have just been repaired or received from the manufacturer. Maintenance and calibration should be performed on a routine schedule, and records of these should be maintained.

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 on the type

of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, a spirometer or soapbubble meter is recommended, although other calibration instruments, such as a wet test meter or dry gas meter, can be used. The actual setups will be similar for all instruments.

The calibration setup for a personal sampling pump with a glass-fiber filter and midget bubbler is shown in Figure XIII-2. Since the flowrate given by a pump depends on the pressure drop across the sampling device, in this case a glass-fiber filter and midget bubbler, the pump must be calibrated while operating with a representative glass-fiber filter and midget bubbler in line. Instructions for calibration with the soapbubble meter follow. If another calibration device is selected equivalent procedures should be used.

(a) Check the voltage of the pump battery with a voltmeter to ensure adequate voltage for calibration. Charge the battery if necessary.

(b) Assemble the sampling train as shown in Figure XIII-2.

(c) Turn on the pump and moisten the inside of the soapbubble meter by immersing the buret in the soap solution and drawing bubbles up the inside until they are able to travel the entire length of the buret without bursting.

(d) Adjust the pump flow controller to provide the desired flowrate.

(e) Start a soapbubble up the buret and measure with a stopwatch the time the bubble takes to move from one calibration mark to another.

(f) Repeat the procedure in (e) at least three times, average the results, and calculate the flowrate by dividing the volume between the

preselected marks by the time required for the soapbubble to traverse the distance. If, for the pump being calibrated, the volume of air sampled is the product obtained by multiplying the number of strokes times a stroke factor (given in units of volume/stroke), the stroke factor is the quotient obtained by dividing the volume between the two preselected marks by the number of strokes.

(g) Data for the calibration include volume measured, elapsed time or number of strokes, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and the name of the person performing the calibration.

Collection and Handling of Samples

(a) Place the filter and bubbler so that the sampled air passes first through the filter and then through the bubbler.

(b) Sample at a flowrate of 1.5 liters/minute. A sample size of 120 liters is recommended.

(c) Immediately after sampling, seal the filter container and remove and clean the bubbler stem. Wash the stem with 1-2 ml of the collecting medium. Include the wash solution in the bubbler and record the amount used. Seal the top of the bubbler tightly with a plastic stopper and place the bubbler upright in a carrying case. Care should be taken to minimize spillage or loss by evaporation at all times.

(d) Treat at least one filter and one bubbler in the same manner as those in the sample train, but do not draw air through them. These will serve as blanks.

X. APPENDIX II

ANALYTICAL METHOD FOR DINITRO-ORTHO-CRESOL

This analytical method is adapted from NIOSH Method No. S166 [50].

Principle of the Method

(a) A known volume of air is drawn through a glass-fiber filter followed by a midget bubbler to collect DNOC particulate and vapor.

(b) The filter is extracted with 0.1 M sodium hydroxide, and the extract is analyzed with the sample collected in the midget bubbler.

(c) DNOC is measured directly in this solution with a spectrophotometer at 395 nm.

Range and Sensitivity

The method has been tested for a 120-liter sample of air over a range of 0.0821-0.295 mg/cu m.

Interferences

No information is available on the possible sources of interferences in the sampling and analytical methods discussed.

Precision and Accuracy

The mean coefficient of variation for the sampling and analytical method in the range of 0.0821-0.295 mg/cu m was 0.154. This value corresponds to a standard deviation of 0.03 mg/cu m at the 0.2 mg/cu m level.

Advantages of the Method

(a) The sampling device is small, portable, and suitable for determining DNOC in both the particulate and vapor forms.

(b) The analysis is accomplished by means of a quick instrumental method.

Disadvantages of the Method

The sampling device requires the use of liquid in bubblers that can pose problems in field measurements because breathing-zone samples are difficult to collect and to transport without spillage.

Apparatus

(a) Spectrophotometer, visible range.

(b) Volumetric flasks: convenient sizes for making dilutions and standard solutions.

(c) Cuvettes: 5-cm cells.

Reagents

- (a) DNOC, spectrograde (the specific isomer to use will depend on which one is used in the workplace).
- (b) Sodium hydroxide, 0.1 M.
- (c) Acetone.

Preparation of Calibration Curve

- (a) Prepare a standard solution containing 3.0 $\mu\text{g}/\mu\text{l}$ DNOC in acetone.
- (b) Place measured amounts, 2-40 μl , of this standard DNOC solution in 25 ml volumetric flasks containing 10 ml of 0.1 M sodium hydroxide.
- (c) Dilute to 25 ml with 0.1 M sodium hydroxide.
- (d) Prepare a blank consisting of 25 ml of 0.1 M sodium hydroxide with 8 μl of acetone.
- (e) Measure the absorbance of each standard solution at 395 nm in 5-cm cells against the blank.
- (f) Plot absorbance readings against μg of DNOC.

Analytical Procedure

- (a) Preparation of Sample

Analyze the samples from the glass-fiber filter and midget bubbler together. Extract the filter with 0.1 M sodium hydroxide and combine the extract with the contents of the midget bubbler.

(b) Measurement of DNOC

- (1) Dilute sample to 25 ml with 0.1 M sodium hydroxide.
- (2) Transfer sample to a 5-cm cell. Read absorbance at 395 nm against a blank.
- (3) Convert the corrected absorbance to micrograms of DNOC by means of the calibration curve.

Calculations

The concentration of DNOC in air can be expressed as milligrams of DNOC/cubic meter of air, which is numerically equal to micrograms of DNOC/liter of air:

$$\text{mg DNOC/cu m} = \mu\text{g DNOC/V}$$

,

where:

$\mu\text{g DNOC}$ = micrograms of DNOC from the calibration curve
 V = volume of air sampled (in liters) at 25 C and 760 mmHg

XI. APPENDIX III

ANALYTICAL METHOD FOR DINITRO-ORTHO-CRESOL IN THE BLOOD

This analytical method is based on methods described by Parker [52] and Fenwick and Parker [53].

Principle of the Method

Whole anticoagulated blood is extracted with methyl ethyl ketone (MEK) in the presence of sodium chloride and sodium carbonate. The absorbance of the yellow extract is measured before and after addition of acid at 430 nm against an MEK blank. Concentrations of DNOC in blood are calculated using a standard curve prepared with DNOC.

Range and Sensitivity

The range of the method is 5 to 50 $\mu\text{g/g}$ blood using the dilutions described below. The author reports a sensitivity of 0.5 $\mu\text{g/ml}$.

Interferences

This procedure measures MEK extractable yellow pigments. Interferences from yellow blood pigments such as beta-carotene and bilirubin are minimized by use of a blank. Possibilities for false positives exist only under marked abnormally high bilirubin or carotene blood concentrations.

Advantages and Disadvantages

The procedure is a simple, direct method for determining blood DNOC concentrations; however, it is not specific. It is known that 2,4-dinitrophenol reacts. The procedure is also subject to interference from abnormally high concentrations of beta-carotene and bilirubin in the blood.

Apparatus

- (a) Spectrophotometer, 20 nm band pass, equipped for round cuvettes.
- (b) Tabletop centrifuge culture tubes, 12 x 125 mm, with Teflon-lined caps (for extraction).
- (c) Matched set of round cuvettes.
- (d) Trip balance.
- (e) Analytical balance.
- (f) Hot plate.
- (g) Round bottom flask, 250 ml, attached to a condenser.
- (h) Beaker, 1 liter.
- (i) Volumetric pipets, assorted sizes.
- (j) Volumetric flasks for standards.
- (k) Rubber suction bulb.
- (l) Disposable transfer pipets.
- (m) Fume hood.
- (n) Test tubes, 13 x 100 mm.

Reagents

All reagents shall be ACS reagent grade or equivalent.

- (a) Methyl ethyl ketone (2-butanone).
- (b) Sodium chloride-sodium carbonate: Mix 1 part anhydrous sodium chloride with 9 parts anhydrous sodium carbonate.
- (c) Concentrated hydrochloric acid.
- (d) DNOC: 4,6-dinitro-o-cresol (IUPAC); 3,5-dinitro-o-cresol (common name).

Procedure

(a) Cleaning of Equipment

Glassware should be cleaned with detergent and rinsed with distilled water.

(b) Collection and Shipment of Samples

Venous blood should be collected without stasis in a 5-7 ml vacuum blood collecting tube containing EDTA anticoagulant. Blood tubes shall be inverted 10-20 times immediately after collection to insure mixing of blood and EDTA. Blood samples should be maintained at 4 C until analysis. Avoid freezing. Blood samples can be conveniently shipped in styrofoam cartons containing bagged "camp ice." Blood samples should be stable up to 7 days at 4 C.

(c) Analysis of Samples

(1) Weigh out 1.0 g of well-mixed whole blood in each of two extraction tubes. Label the tubes "test" and "blank." Five ml of MEK is added to each tube, and the tubes are capped and gently shaken to

disperse the blood. (Caution: Use a fume hood and avoid breathing MEK vapors.)

(2) One to two (1-2) grams of the sodium chloride-sodium carbonate mixture is added to each tube, and the tubes are capped and vigorously shaken for 30 seconds. The tubes are centrifuged briefly (1 minute), and the upper MEK layer is transferred to marked test tubes. To the tube marked "blank," add one drop of concentrated hydrochloric acid and centrifuge for 1 minute to remove cloudiness. Transfer the contents of both tubes to match cuvettes and read the absorbance at 430 nm, setting the spectrophotometer to zero with an MEK blank. Subtract the "blank" reading from the "test" reading, and determine the concentration of DNOC in blood by reference to a standard curve. If the absorbance of the "blank" exceeds 0.15, interference from blood pigments can be suspected.

Preparation of the Standard Curve

One hundred (100) milligrams of free DNOC and 100 ml of a 0.5% (w/v) sodium carbonate solution are placed in a 250-ml round-bottom flask equipped with a condenser. Heat the mixture on a boiling water bath (hot plate and 1 liter beaker with water) until the DNOC is dissolved. (Note that the boiling point of DNOC is 85-86 C and that a condenser is needed to avoid loss of DNOC.) Cool, rinse the condenser with 0.5% sodium carbonate solution, transfer the DNOC solution and the rinse to a 250-ml volumetric flask, and make up to volume with distilled water. This is the stock standard at 400 μg DNOC/ml. Prepare working dilutions with distilled water from 5-50 μg /ml. The standard curve is prepared by extracting 1.0-ml

portions of the diluted standards exactly as described above for blood.
Plot the absorbance vs the concentration of DNOC in μg .

Calculations

The absorbance of the blood ("test" - "blank") is compared with the standard curve. The μg DNOC then is a direct measure of DNOC in $\mu\text{g/g}$ blood if 1.0 g blood was used.

XII. APPENDIX IV
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 trade 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, eg, "100 ppm LC50-rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," 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 hazardous 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 (mmHg); 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 (indicated 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 flashpoint 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 for DNOC might be:

Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possible irritation, skin staining and local and systemic effects.

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 must 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," 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 and 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 exposed to the hazardous substance. 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 in 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 ODOOR		

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 _____

XIII. TABLE AND FIGURES

TABLE XIII-1

PHYSICAL AND CHEMICAL PROPERTIES OF 4,6-DINITRO-o-CRESOL

Molecular formula	C ₆ H ₂ (CH ₃)OH(NO ₂) ₂
Formula weight	198.13
Appearance	Yellow solid
Melting point	85.8 C
Vapor pressure	0.000052 mmHg at 20 C
Saturated concentration (at 20 C)	0.56 mg/cu m (0.068 ppm)
Specific gravity	-
Solubility	0.01 % by weight in water at 20 C 1.82 in alcohol at 15 C
Minimum cloud ignition temperature	340 C
Minimum explosive dust concentration	0.03 g/liter (30 g/cu m)
Vapor density (air = 1)	6.8
Conversion factors (760 mmHg and 20 C)	1 mg/cu m=0.12 ppm 1 ppm=8.2 mg/cu m

Adapted from references 2-4

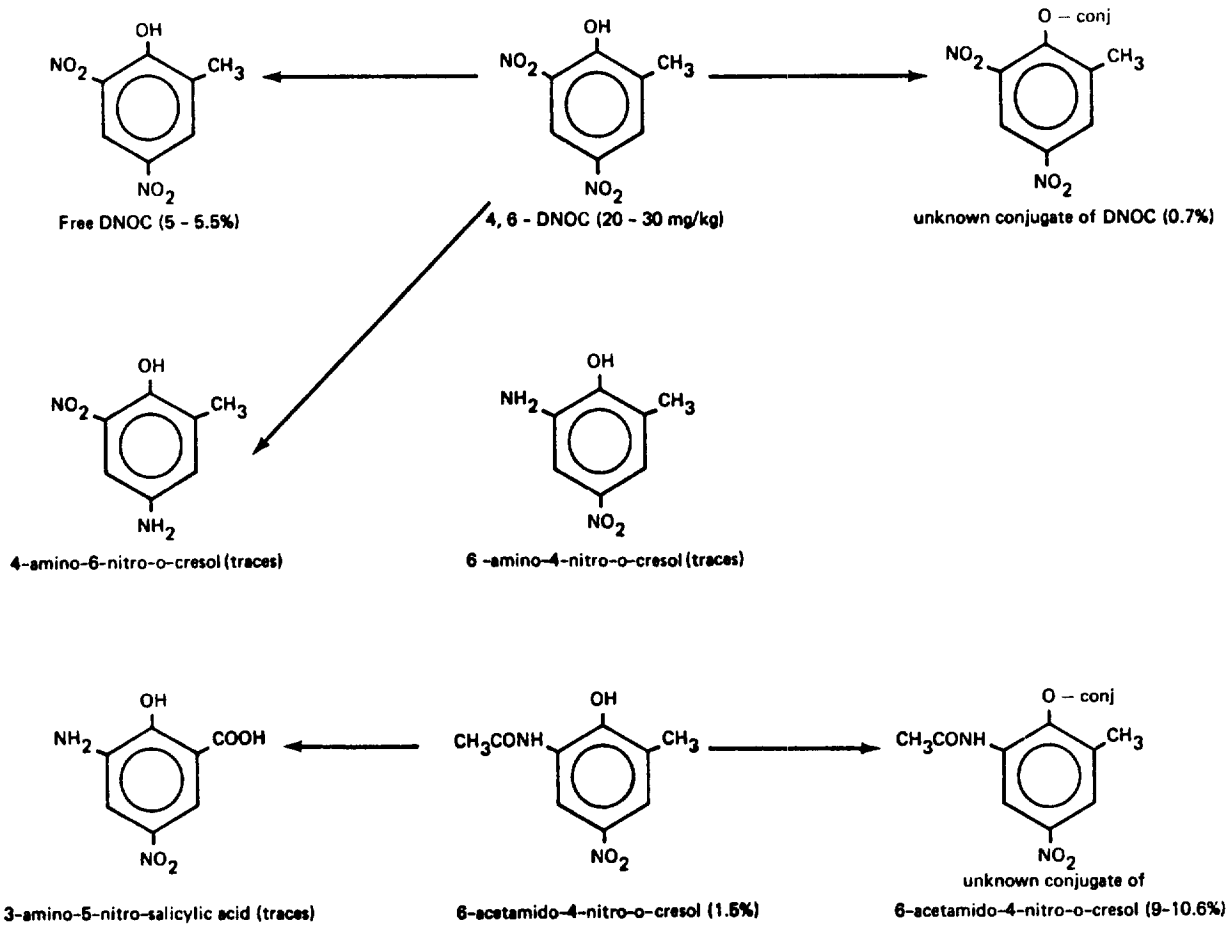


FIGURE XIII-1

METABOLIC PATHWAYS OF 4,6-DINITRO-o-CRESOL
ADMINISTERED BY STOMACH TUBE TO RABBITS

Adapted from Smith et al [46]

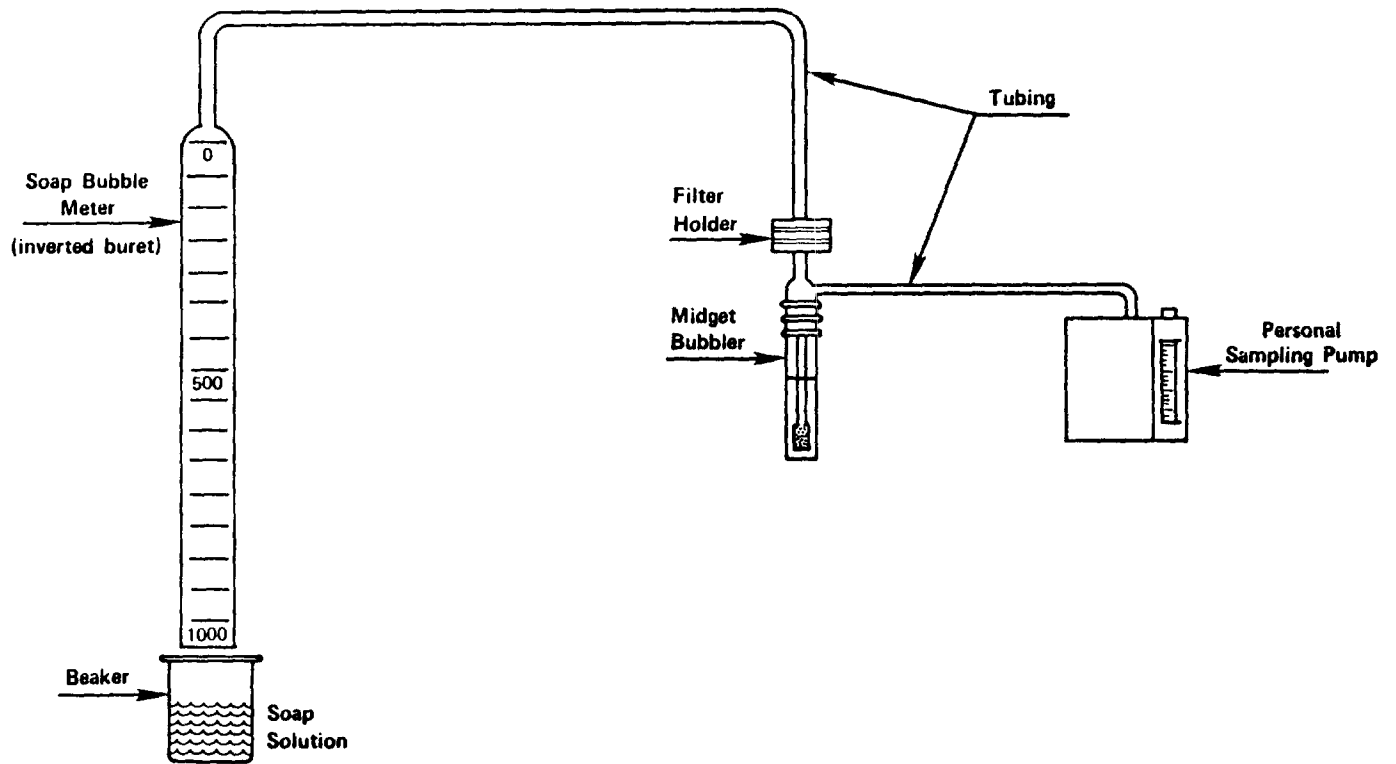


FIGURE XIII-2

CALIBRATION SETUP FOR PERSONAL SAMPLING
PUMP WITH FILTER HOLDER AND MIDGET BUBBLER

DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
ROBERT A. TAFT LABORATORIES
4676 COLUMBIA PARKWAY, CINCINNATI, OHIO 45226

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