

IX. APPENDIX I

METHOD FOR SAMPLING ORGANOTINS IN AIR

This sampling method is adapted from NIOSH Method No. P & CAM 173 [116] and No. 127 [121]. However, no report was found in the literature in which these sampling techniques were combined. Although this method of sampling is recommended, other methods shown to be at least equivalent may be used.

General Requirements

Collect personal samples in the breathing zone of individual employees, without interfering with the employees' freedom of movement. Enough samples should be collected to permit calculation of a TWA concentration to evaluate the exposure of each employee at every operation or location in which there is occupational exposure to organotins. Record the sampling locations and conditions, equipment used, time and rate of sampling, and any other pertinent information.

Equipment for Air Sampling

(a) Filter: Membrane filter with a pore size of 0.8 μm mounted with backup pad in a 2- or 3-piece closed-face cassette.

(b) Large charcoal tubes: Glass tubes with both ends flame-sealed, 11 cm long with an 8-mm outer diameter and a 6-mm internal diameter, containing two sections of 20/40-mesh activated coconut-shell

charcoal separated by a 2-mm portion of polyurethane foam. The adsorbing section contains 400 mg of charcoal, the backup section 200 mg. A 3-mm portion of polyurethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. Tubes meeting these specifications are designated commercially as "large."

(c) Battery-operated personal sampling pump: The pump should have a means for attachment, such as a clip, to the employee. All pumps and flowmeters must be calibrated using a calibrated test meter or other reference, as described in the Section on Calibration of Equipment.

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 recalibrated 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 membrane filter followed by a charcoal tube is shown in Figure XII-1. Since the flowrate given by a pump depends on the pressure drop across the sampling device, in this case a membrane filter followed by a charcoal tube, the pump must be calibrated while operating with a representative filter and charcoal tube 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) Break off the tips of a charcoal tube to produce openings at least 3 mm in diameter.

(c) Assemble the sampling train as shown in Figure XII-1.

(d) 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.

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

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

(g) Repeat the procedure in (f) at least 3 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.

(h) 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 of Samples

(a) Break both ends of the large charcoal tube to provide openings of at least 3 mm, which is half the internal diameter of the tube. A smaller opening may cause a limiting orifice effect which would reduce the flow through the tube.

(b) Assemble a sampling train consisting of a 0.8- μ m membrane filter followed by a large charcoal tube with a portable, battery-operated personal sampling pump. The smaller section of charcoal in the tube is used as a backup section and should therefore be placed nearest the sampling pump. Tubing may be used to connect the back of the tube to the pump. The front of the tube should be connected directly to the filter holder by a minimum length of tubing. The tube is supported in a vertical position for sampling to prevent channeling. When the environment to be sampled contains organotins only as vapor, the membrane filter may be eliminated. When only low-volatility particulate organotins are present,

the charcoal tube may be eliminated from the sampling train.

(c) The recommended sampling flowrate is 1 liter/minute. The calibrated flowrate should be established as accurately as possible, using the manufacturer's directions.

(d) Measure and record the temperature and pressure of the atmosphere being sampled.

(e) Record the initial and final counter readings. The sample volume is obtained by multiplying the number of counter strokes times the stroke factor.

(f) Immediately after sampling, seal the filter container and cap the charcoal tubes with the plastic caps provided with commercially available tubes. Do not use rubber caps.

(g) Treat at least one filter and one charcoal tube in the same manner as the sample tubes (break, seal, ship), but do not draw air through them. This filter and tube will serve as a blank.

X. APPENDIX II

ANALYTICAL METHOD FOR ORGANOTINS

This analytical method is adapted from a pyrocatechol violet method for the rapid and selective determination of tin [143].

Principle of the Method

(a) A known volume of air is drawn through a membrane filter followed by a charcoal tube to collect organotin particulate and vapor.

(b) The organic matter (filter and charcoal) is destroyed by treatment with sulfuric and nitric acids, leaving tin(IV) in solution in sulfuric acid.

(c) The tin is separated from the sulfuric acid, insoluble matter, and any elements that would interfere in the colorimetric measurement (molybdenum, titanium, high amounts of heavy metals or phosphate). This separation is carried out by extracting the tin as tin(IV) iodide with n-hexane from a strong sulfuric acid solution of potassium iodide. The tin is extracted from the hexane with a dilute solution of sulfuric and citric acids.

(d) The tin is measured directly in this solution at 660 nm after adding a mixed reagent of pyrocatechol violet and cetyl trimethyl ammonium bromide, a quaternary salt catalyst.

Range and Sensitivity

(a) The detection limit is in the range of 0.04-0.08 μg of tin at a concentration of 0.004-0.01 ppm in organic materials, which must be digested with strong mineral acids.

(b) The optimal amount of tin is up to 10 μg in the sample.

(c) Relative standard deviations of 0.55-1.4% have been obtained in the range of 1-10 μg of tin in various types of organic samples.

Interferences

(a) Metals which have shown positive interference are: Ge(IV), Mo(VI), Ti(IV), Ga(III), Sb(III), Sb(V), Bi(III), Cr(III), Cr(VI), Cu(II), Ni(II), Hg(II), Zr(IV), Fe(II), and Fe(III). These interferences are removed during the separation procedure.

(b) Elements and radicals which have shown no interference (error less than $\pm 0.001 \mu\text{g}$ of tin) at the maximum indicated level are: NO_3 (200 mg); K, Li, Mg, Na, NH_4 (100 mg); Al (50 mg); B₄O₇, Br, ClO₃, IO₃, IO₄, PO₂ (20 mg); CNS, I (10 mg); NO₂, S₂O₈ (4 mg); Ag, As, Cd, Ce, Co, In, La, Mn, Th, U, V, Zn, Zr (2 mg); Se, Tl (1 mg); Sr, Te (0.1 mg).

Advantages of the Method

(a) It provides one basic method suitable for determining many different organotins.

(b) The sampling device is small and portable, and involves no liquids.

(c) The analysis is readily accomplished.

- (d) No elaborate equipment is required.

Disadvantages of the Method

- (a) Sampling rate is limited by the decreased adsorption efficiency of charcoal at higher flowrates.
- (b) Pressure drop becomes excessive at higher flowrates.
- (c) Organic compounds in high concentrations in the environment sampled may displace organotins from the charcoal.

Apparatus

- (a) Spectrophotometer.
- (b) Digestion vessels: narrow-mouth flasks of various capacities.
- (c) Separatory funnels: pear-shaped type with Teflon stopcock and capacities of 125 and 250 ml.
- (d) Cuvettes: 5-cm or 10-cm cells.

Reagents

- (a) Acids: reagent-grade concentrated hydrochloric, nitric, and sulfuric acids; citric acid; and L-ascorbic acid.
- (b) Pyrocatechol violet: both catechol violet, B.D.H. Chems., Ltd., Prod. No. 20022, and pyrocatechol sulfone phthalein, Eastman 7589, have been found to be satisfactory.
- (c) Cetyl tri-methyl ammonium bromide (CTAB).
- (d) Potassium iodide.
- (e) Tin.

Reagent Solutions

(a) Standard tin solutions:

(1) 500 $\mu\text{g/ml}$: Dissolve 0.2500 g of pure tin in 150 ml of concentrated hydrochloric acid. Dilute to 500 ml with water.

(2) 10 $\mu\text{g/ml}$ in 20% w/v sulfuric acid and 10% citric acid: Place exactly 10 ml of standard tin solution, 500 $\mu\text{g/ml}$, in a flask or beaker of resistant glass, and add 50 ml of concentrated sulfuric acid and 5 ml of concentrated nitric acid. Heat to evolution of strong fumes of sulfuric acid and cool. Add concentrated sulfuric acid to bring to a total of 100 g. Place in a cooling bath and cautiously dilute with 150-200 ml of water. Cool to room temperature and add a water solution of 50 g of citric acid. Transfer to a 500-ml volumetric flask, dilute to volume, and mix well.

(3) 0.5 $\mu\text{g/ml}$: Prepare fresh in 5% w/v sulfuric acid and 2.5% w/v citric acid.

(4) 0.025 $\mu\text{g/ml}$: Prepare fresh in 5% w/v sulfuric acid and 2.5% w/v citric acid.

(b) Sulfuric-citric acid solution: 5 g of sulfuric acid and 2.5 g of citric acid/100 ml in water. This mixed solution is used in preparing the calibration curve.

(c) CTAB solution: 5.5 mg/ml CTAB in water.

(d) Sensitized pyrocatechol violet solution: For each 100 ml of solution, dissolve 12 mg of pyrocatechol violet in water, add 2 ml of CTAB solution, and dilute to volume. Prepare fresh daily as needed.

(e) Acid-iodide wash solution: Mix one volume of sulfuric acid with two volumes of water and cool. Add one volume of potassium iodide,

20% w/v. Prepare fresh as needed.

(f) Ascorbic acid: 5% w/v in water. Prepare fresh daily as needed.

Preparation of Calibration Curve

(a) Place a measured amount, 1-20 ml, of standard tin solution, 0.5 $\mu\text{g/ml}$, in a 50-ml volumetric flask.

(b) Dilute to 20 ml with a measured amount of sulfuric-citric acid solution, 5% and 2.5% w/v, respectively.

(c) Add 2 ml of ascorbic acid, 5% w/v, and dilute to 40 ml.

(d) Add 5 ml of sensitized pyrocatechol violet solution and dilute to 50 ml.

(e) After 30 minutes, measure the absorbance at 660 nm in a 10-cm cell.

(f) Repeat with the next dilution. After each reading, rinse the cell twice with water, once with 2M hydrochloric acid, twice with water, and three times with the next solution to be read.

(g) Plot absorbance readings against amount of tin.

Analytical Procedure

A blank is carried through the entire procedure along with the samples.

(a) Preparation of Sample

Details of sample preparation vary with the nature of the organotins present. Appropriate pretreatment or separation procedures may be required

if more than one organotin is present and if quantitative determination of each organotin is required. In general, the membrane filter and first section of charcoal from the charcoal tube are analyzed together. The backup section of the charcoal tube is analyzed separately to verify that breakthrough of the first section has not occurred. The filter and charcoal are digested by treatment with nitric and sulfuric acids. After elimination of organic matter and volatile acids (including traces of nitric acid), the tin is present as tin(IV) in a known amount of concentrated sulfuric acid.

(b) Separation of Tin

(1) Dilute the known volume of sulfuric acid digest (one volume) with two volumes of water, mix, and cool to room temperature.

(2) Add one volume of potassium iodide solution, 20% w/v, and mix.

(3) Transfer to a 250-ml separatory funnel. Rinse the digestion vessel with 2-3 volumes of n-hexane and add rinsings to the funnel.

(4) Extract for 1 minute and allow to settle for 5-10 minutes.

(5) Draw off the aqueous solution and transfer the hexane containing the tin(IV) to a second (125-ml) separatory funnel by pouring from the neck of the first funnel. Rinse the extraction funnel with a few milliliters of hexane and add to the main portion.

(6) Add to the 125-ml funnel, including the funnel containing the reagent blank, exactly 20 ml of standard tin solution, 0.025 $\mu\text{g}/\text{ml}$, freshly prepared in 5% w/v sulfuric acid and 2.5% w/v citric acid.

(7) Shake the hexane and acid wash for 30 seconds to 1 minute and allow to separate.

(8) Draw the aqueous phase into a 50-ml volumetric flask.

(9) Wash the hexane with two 10-ml portions of water, allowing the phases to separate for 5 minutes each time, and combine in the volumetric flask. Make to volume. Let stand overnight.

(c) Measurement of Tin

(1) Add 2 ml of a 5% w/v ascorbic acid solution to each aqueous extract to be read. Prepare a mixed reagent as follows: For each 100 ml (sufficient for 20 readings), place 12 mg of pyrocatechol violet in a container and dissolve in water. Add 2 ml of CTAB solution (0.55% w/v), swirl gently, and dilute to 100 ml. Mix well.

(2) Add exactly 5 ml of the mixed reagent to the sample flask, dilute to volume, and mix.

(3) Do the same to each of the other samples at about 4-minute intervals.

(4) Measure each solution after 30 minutes by filling a 5-cm or 10-cm cell and reading the absorbance at 660 nm.

(5) Deduct the absorbance of the blank from that of the samples.

(6) Convert the corrected absorbances to tin by means of the calibration curve.

Calculations

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

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

where:

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

XII. 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 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 might be:

Skin Contact--single short contact, possible adverse effects;
prolonged or repeated contact, mild to severe dermatitis.

Eye Contact--highly irritating with possibility of severe
corneal damage.

"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 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 _____