VIII. APPENDIX II

METHOD FOR ANALYSIS OF ZINC OXIDE IN AIR

The procedure is based on Method No. 173 of the NIOSH Manual of Analytical Methods. [88]

Principle of the Method

The sample, collected on a cellulose membrane filter, is ashed using nitric acid to destroy the organic matrix. The zinc is solubilized in an acidic solution maintaining a pH of 1. Samples, blanks, and standards are aspirated into the atomic absorption flame. A hollow cathode lamp for zinc provides the characteristic line. The absorption of this line by the ground state atoms in the flame is proportional to the Zn in the aspirated sample.

Range and Sensitivity

The optimum working range is 0.025-2 μg Zn/ml. This value can be extended to higher concentrations by dilution of the sample. The sensitivity is 0.025 μg Zn/ml. This value will vary somewhat depending upon the instrument used.

Interferences

None have been reported.

Precision and Accuracy

In general, this analytical method will provide a coefficient of variation of approximately 2% depending upon the instrument used. Data on accuracy of the method are not yet available.

Advantages and Disadvantages

The method is rapid because there is little sample preparation. It does not require a high degree of technical skill. It is not affected by the presence of other common metallic elements. However, since it measures total zinc, it is not capable of distinguishing various zinc compounds from each other.

Apparatus

Hollow cathode lamp for zinc.

Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstroms/mm in the ultraviolet region, and equipped with a burner head for air-acetylene flame.

Oxidant: Air which has been filtered to remove water, oil, and other foreign substances.

Fuel: Acetylene, commercially available for atomic absorption use.

Pressure-reducing valves: A 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used.

Glassware, borosilicate:

125-ml Phillips beakers with watchglass covers

15-ml graduated centrifuge tubes

10-ml and 100-ml volumetric flasks

125-ml polyethylene bottles

Hotplates capable of reaching 400 C

Reagents

Doubly distilled or deionized water

Redistilled concentrated nitric acid

Distilled 1:1 hydrochloric acid

Aqueous stock standard containing 1000 μg zinc/ml (commercially available).

Procedure

(a) Cleaning of Equipment

Before use, glassware should be washed with a laboratory glassware detergent, rinsed with tap water, then 10% nitric acid, and finally rinsed with distilled water.

(b) Analysis of Samples

Samples are transferred to clean 125-ml Phillips beakers and several milliliters of concentrated nitric acid are added to each. Each beaker is covered with a watchglass and heated on a hotplate (140 C) in a fume hood until the sample chars or until a slightly yellow solution remains. Several additions of nitric acid may be needed to completely ash and

destroy the organic material.

Once the ashing is complete as indicated by a whitish residue in the beaker and following several minutes on the high temperature hotplate (400 C), the residue is converted to the chloride form by 3 successive evaporations with 1:1 hydrochloric acid. The ash is then dissolved with 1:1 hydrochloric acid and quantitatively transferred to a 15-ml graduated centrifuge tube and brought up to volume with deionized water. Aliquots of this can be diluted if necessary or the volume can be reduced by evaporation to get the zinc concentration within the working range of the method.

The sample is then aspirated into an oxidizing air-acetylene flame. The analytical wavelength is 2139 Angstroms. The other operating parameters are set according to the instrument instructions from the manufacturer. When very low zinc concentrations are found in the sample, scale expansion can be used to increase instrument response.

Calibration and Standards

From the 1000 μg zinc/ml stock standard solution, prepare working standards to cover the range between 0.025 and 2 μg/ml. The standard solutions are made 0.3 N in hydrochloric acid and are stored in polyethylene bottles. The low concentration standards may deteriorate and should be made on the day to be used.

Aspirate the series of standards and record the percentage of absorption.

Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in μg/ml. It is

advisable to run a set of standards both before and after a sample run to ensure that conditions have not changed.

Calculations

From the calibration curve, read the concentration in μg/ml in the analysis sample.

Blank values, if any, are subtracted from each sample.

The concentration of zinc in the original sample in μg/ml equals the μg/ml in the analysis sample times the dilution factor.

To obtain the concentration of zinc oxide in the original sample, multiply the concentration of zinc by 1.245.

IX. 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 in as large a type size 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 given 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 names 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, ie, "100 mg/kg LD50-oral-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. Flammable or reactive data

could be flash point, shock sensitivity, or other brief data indicating nature of the hazard.

(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 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 (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 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 effects 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 workers.

(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 workers 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 to comply with local, state, and federal anti-pollution 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 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 workers 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.

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_2O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H_2O, % 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:

X. APPENDIX IV

TABLES AND FIGURE

TABLE X-1

CHEMICAL AND PHYSICAL PROPERTIES

Formula	ZnO
Formula weight	81.37
Specific gravity	5.606
Melting point	1975 C
Solubility	0.00016 g/100 ml water at 29 C; soluble in mineral acids, dilute acetic acid and ammonium chloride

Adapted from McMahon [1] and Weast [96]

TABLE X-2

POTENTIAL OCCUPATIONAL EXPOSURES TO ZINC AND ITS COMPOUNDS

Alloy makers	Metal cutters
Arc welders, electric	Metalizers
Brass foundry workers	Metal sprayers
Braziers	Paint manufacturers
Bronze foundry workers	Printing plate makers
Electric fuse makers	Roofing makers
Electroplaters	Shipyard workers
Galvanizers	Zinc founders
Gas welders	Zinc smelters
Junk metal refiners	Zinc workers

Derived from Gafafer [7]

TABLE X-3

SAMPLING IN AREAS OF POOR VENTILATION

Coating	Type Weld	Sampling Location	Concentration ZnO, mg/cu m
Zinc-silicate	Electric arc	2' directly above welding	159.9
"	"	2' above and 2 1/2' back	107.2
"	"	3' " " 2' "	68.9
"	"	3' " " 2' "	64.0
"	"	Welder's shoulder	199.44
			Mean 119.9
Zinc-silicate	Oxy-acetylene	1' above and 1' back	45.9
"	"	3' " " 2 1/2' "	22.8
"	"	3' " " 2 1/2' "	21.4
"	"	3' " " 2' "	18.0
"	"	3' " " 2' "	42.6
"	"	3' " " 2' "	19.9
"	"	3' " " 2' "	17.1
			Mean 26.81
Galv. Steel	Electric arc	2' above and 1' back	65.5
"	"	2' " welders' face	152.0
"	"	6' " floor and 5' in front of welder	31.5
"	"	Welder's shoulder	185.0
			Mean 108.5
Galv. Steel	Oxy-acetylene	2' above and 2' back	106.6
"	"	3' " " 2 1/2' "	33.0
"	"	2' " " 1' "	64.0
"	"	6' " " 5' "	30.0
"	"	3' " " 1' "	85.0
			Mean 63.72

From Pegues [58]

TABLE X-3 (continued)

SAMPLING IN AREAS OF POOR VENTILATION

Coating	Type Weld	Sampling Location	Concentration ZnO, mg/cu m
Clean Steel	Electric arc	2' above and 1' back (control sample)	14.9
"	"	20' from enclosure (Room air-control sample)	0
"	Oxy-acetylene	20' from enclosure (Room air-control sample)	1.3

From Pegues [58]

TABLE X-4

SAMPLING IN AREAS OF "GOOD" VENTILATION*

Coating	Type Weld	Sampling Location	Concentration ZnO, mg/cu m
Zinc silicate	Electric arc beading	Welder's hood	9.84
Zinc silicate	Electric arc welding	Welder's hood	19.81
Galv. steel	Electric arc welding	Near nose	6.63
Galv. steel	Oxyacetylene cutting	Welder's hood	12.28

*As qualified by Pegues

From Pegues [58]

TABLE X-5

ROOM AIR SAMPLES
ELECTRIC ARC WELDING ON ZINC-SILICATE COATING

Sampling Location		Concentration ZnO, mg/cu m	Average
3' downwind from welder	3' from floor	15.4	14.15
3' downwind from welder	3' from floor	12.9	
20' downwind from welder	3' from floor	4.9	5.86
20' downwind from welder	3' from floor	6.8	
20' downwind from welder	6' from floor	30.5	22.3
20' downwind from welder	6' from floor	14.1	

From Pegues [58]

TABLE X-6

OUTDOOR SAMPLES (10-MPH WIND)

Coating	Type Weld	Sampling Location	Concentration ZnO, mg/cu m
Zinc silicate	Electric Arc	Inserted in hood	4.22
Galv. steel	Electric Arc	Inserted in hood	13.24
Galv. steel	Oxyacetylene cutting	3" from welder's nose	2.40

From Pegues [58]

TABLE X-7

SAMPLES TAKEN IN TANKS VENTILATED BY FLEXIBLE EXHAUST TUBES TERMINATING NEAR CLOUD OF WELDING FUME

Sampling Conditions	Concentration ZnO, mg/cu m
Wing tank. Two welders. Bottom of tank near nose of welder	11
Blank determination in wing tank.* No welding	1
Ditto at height of 4m	3
Ditto at height of 9m	1
Ditto under deck head. Two welders. Near nose of welder	10
Duplicate of last condition	11

*Volume of wing tank was 1450 cu m

From Boekholt [59]

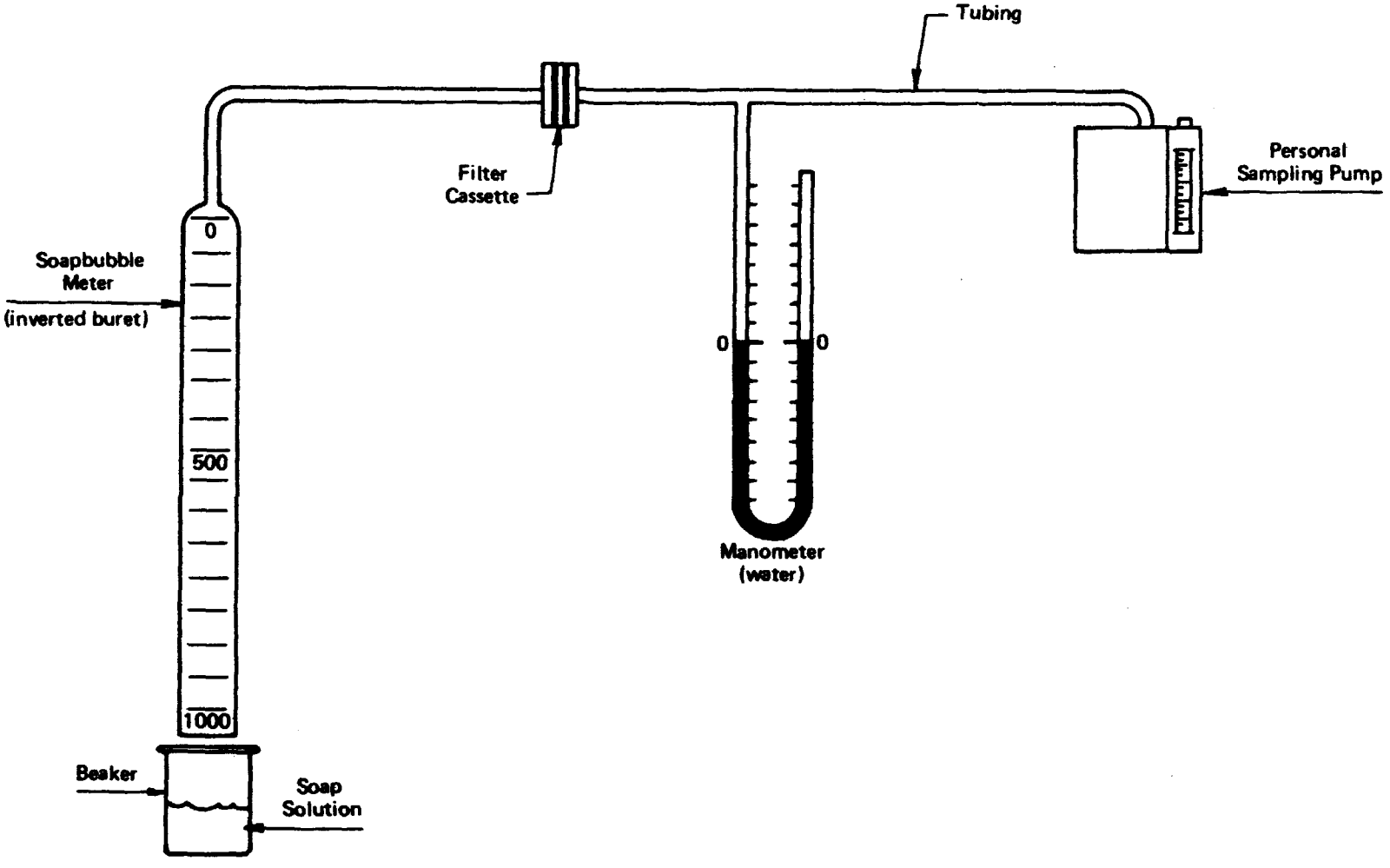
TABLE X-8

SAMPLES TAKEN FROM STEEL PLATES AND SECTION SHOPS WITH ZINC DUST PAINT 20 μm THICK

Sampling Conditions		Concentration ZnO, mg/cu m
Near welder's nose during manual welding		11
In cloud of welding fume		13
Near worker's nose during gas cutting		
at various locations,		
	automatic	5-10
	by hand	13
In workshop between units at man's height,		
blue smoke visible		2-4

From Boekholt [59]

FIGURE X - 1. CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH FILTER CASSETTE



☆ U.S. GOVERNMENT PRINTING OFFICE: 1975— 657-645/207

DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
RM. 532, U. S. POST OFFICE, CINCINNATI, OHIO 45202

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF H.E.W.
HEW 399

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service
Center for Disease Control
National Institute for Occupational
Safety and Health

HEW Publication No. (NIOSH) 76–104