Environmental Concentrations

In studying pneumoconiosis among smelter workers exposed to antimony trioxide, Cooper et al [9] found especially high concentrations at the bagging operations, where 138 mg antimony/cu m was measured. At ten other locations, concentrations ranged from 11 to 75 mg/cu m. At thirteen more locations, measurements ranged from 1.0 to 9.8 mg/cu m. A range of 0.081 to 0.95 was found at thirteen additional locations. No further specifications of these areas or the methods used in attaining the measurements were given.

McCallum [12] found the highest airborne antimony concentration in a smelter to occur during the tapping operation at the metal furnace. Duplicate samples of 1-2 cubic feet of air taken at breathing level on several days over 3 weeks revealed that the antimony concentration reached 36.70 mg/cu m during this brief operation. The workplace air concentrations of antimony at 19 other sample sites ranged from 0.53 to 5.34 mg/cu m. The analytical method and flowrate used were not given.

Renes [5] collected air samples in another smelter with an electrostatic precipitator except for the first 17 samples, which were obtained with the Greenberg-Smith impinger apparatus. Aliquots of each sample were analyzed chemically and spectroscopically. Results of these two methods did not vary by more than 2%. The average antimony concentration in the electric furnace zone was 10.1 mg/cu m before corrective measures had been instituted, and 4.7 mg/cu m after these improvements. The average antimony concentration in the cupel zone measured 11.8 mg/cu m before, and 8.2 mg/cu m after the changes. Before and after electric furnace zone average concentrations of arsenic were 1.10 mg/cu m and 0.8 mg/cu m, respectively. Cupel zone average arsenic levels were 0.4 mg/cu m both before and after changes. The zones had been established by what appeared to be a reasonable division after studying the smelting processes and the workers' medical situation. More of Renes's [5] sampling data are presented in Tables III-6, III-7, and III-8.

Okawa [118] evaluated health hazards due to lead and antimony exposure in a plant that rebuilt internal combustion engines of all types. Operations included all phases of rebuilding, from tearing down old engines to touchup painting of newly rebuilt engines. Worker exposures to lead and antimony were measured with personal air sampling equipment. All samples were taken with MSA Model G personal sampling pumps attached to Millipore cellulose membrane filters with 0.45-μm pores. The sampling rate was 1.8 liters/minute, and the sampling times ranged from 1.5 to 2.75 hours per sample.

A total of six samples were collected on five workers: the lead pot assembler, two engine assemblers, a crankshaft grinder, and a valve grinder. Only two samples showed detectable concentrations of lead (above 0.006 mg/cu m); 0.18 mg/cu m was found in one of two samples taken on the lead pot assembler, and 0.10 mg/cu m was found in the valve grinder's sample. Antimony levels in all six samples were below the limits of detection (0.02 mg/cu m) for the method used.

Two other health hazard evluations [119,120] demonstrated no detectable exposures to antimony. Gunter and Nelson [119] evaluated a plant that

prepared camouflage netting for use by the military. Before the netting was received at this plant, it was treated with antimildew agents containing lead, chromium, antimony, and tin. The process in question included unpacking the netting, cutting it to specification, sewing an edge on the netting, and folding, repacking, and shipping it out again. Eight-hour breathing zone samples taken on 25 workers were collected on AA filters using MSA Model G pumps operating at 1.5 liters/minute. Lead, chromium, antimony, and tin were analyzed by atomic absorption spectroscopy. All samples were below laboratory detection limits.

Moseley [120] evaluated the machinists' area/composing room of a large newspaper. The area was ventilated by a blower for air conditioning and heating with three ceiling exhaust vents. The source of antimony exposure was 8-9% antimony content of molten lead being cast into pigs used for spacing. Area samples were collected on 37-mm cellulose membrane filters with a Model G MSA vacuum pump operated at 2 liters/minute and analyzed by atomic absorption spectrometry. In all samples, antimony concentrations were below the limits of detection for the method used.

In an industry-wide study of the antimony industry, Donaldson and Cassady [121] monitored air levels of three major antimony producers. All three plants produced antimony oxide, but exposures were different in several respects. Two producers, Plants B and C, roasted antimony sulfide ore in rotary kiln-type furnaces to produce antimony oxide. Plant A oxidized antimony metal with air to form antimony oxide. Plant A was the only plant that produced antimony metal in addition to the oxide. Plant B manufactured several other chemicals besides antimony oxide. Plant B workers were exposed to soluble nickel, cadmium, and chromium as well as to antimony, arsenic, and sulfur dioxide, which were present in all the plants.

Personal samples were collected in the three plants [121]. The pumps worn by each worker during his shift (6-7 hours) operated at 2.0 liters/minute and collected dust on a 37-mm mixed cellulose ester membrane filters with 0.8-μm pores. General area sampling was also done. Analyses for both antimony and arsenic were performed by atomic absorption. Sulfur dioxide concentrations were estimated with detector tubes.

Results indicated that antimony concentrations in general area samples from all three plants ranged from 0.01 to 5.6 mg/cu m; breathing zone concentrations of antimony were 0.05-8.7 mg/cu m [121]. Arsenic concentrations found in the general area samples from the three plants ranged from nondetectable to 3.4 μg/cu m. Breathing zone concentrations of arsenic plants ranged from nondetectable to 87.0 μg/cu m. Sampling data from all plants are given in Tables IV-1 to IV-5. Essentially no sulfur dioxide was found in the plants except during upset furnace conditions at Plant A.

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TABLE IV-1

PLANT A
GENERAL AREA SAMPLE RESULTS, APRIL 1975

Location	Total Time (min)	Sb (mg/cu m)	As (mg/cu m)
Blast furnace	454	0.11	0.007
Slag tapping-blast furnace	454	0.26	0.0012
"	455	1.14	0.0024
Doubling furnace No. 2	451	1.13	0.0027
Starring furnace No. 1	458	1.12	0.0034
Starring furnace No. 2	457	0.52	0.0021
Casting area	453	2.02	0.0040
Warehouse	451	0.61	0.0018
Burner end of No. 1 starring furnace	437	1.24	0.0029
Oxide furnace	436	0.14	0.0011
Charge scale	417	0.36	0.0014
Change room	432	0.54	0.0006

Adapted from Donaldson and Cassady [121]

TABLE IV-2

PLANT A
SUMMARY OF RESULTS OF AREA SAMPLING FOR ANTIMONY AND ARSENIC
BY PLANT OPERATION, MARCH 1976

Operation	No. of Samples	Sb			As		
		Range mg/cu m	Mean mg/cu m	SD	Range mg/cu m	Mean mg/cu m	SD
Oxide manufacture	6	0.09-3.07	2.23	1.11	0.008-0.37*	0.022	0.011
Doubles furnace	4	0.89-2.10	1.45	0.50	0.002-0.010	0.006	0.004
Singles furnace	4	0.41-1.83	1.27	0.63	0.005-0.013	0.009	0.003
Maintenance	9	0.09-6.21	0.94	2.00	0.001-0.018	0.005	0.007
Laborers	22	0.09-4.91	1.26	1.08	0.001-0.041	0.009	0.010
Miscellaneous	6	0.05-3.74	1.11	1.35	0.001-0.047	0.010	0.020

*One arsenic value of 0.160 mg/cu m believed to be in error was dropped before calculating the mean.

Adapted from Donaldson and Cassady [121]

TABLE IV-3

PLANT A
PERSONAL AIR SAMPLE RESULTS, MARCH 1976

Operation/ Occupation	Total Time (min)	Sb (mg/cu m)	As (mg/cu m)
Oxide			
Furnace operator	455	0.090	0.008
"	464	2.980	0.022
"	460	3.070	0.037
"	471	2.010	0.017
Packer	457	2.590	0.160
"	470	2.610	0.024
Singles Furnace			
Tapper	505	1.62	0.005
"	480	1.22	0.008
"	466	0.41	0.010
Conveyor operator	460	1.83	0.013
Doubles Furnace			
Furnace operator	401	1.30	0.002
"	456	0.89	0.003
"	437	2.10	0.010
Furnace helper	455	1.52	0.007
Maintenance			
Blacksmith	431	0.15	0.001
Maint. man--shop	480	0.11	0.001
Mechanic	447	0.09	0.001
Mechanic shop	440	0.09	0.002
Maint. welder	447	0.09	0.002
Bricklayer	458	0.70	0.002
"	470	6.21	0.017
"	442	0.20	0.002
Laborer	440	0.09	0.001
"	448	1.63	0.013
"	451	1.92	0.009
"	477	0.94	0.002
"	485	1.34	0.041
"	482	0.38	0.004
"	457	1.61	0.013
"	466	0.67	0.005
"	487	1.07	0.005
"	454	1.600	0.009
"	456	0.230	0.003
"	468	0.980	0.007
"	461	0.120	0.001
"	427	0.140	0.001

TABLE IV-3 (CONTINUED)

PLANT A
PERSONAL AIR SAMPLE RESULTS, MARCH 1976

Operation/ Occupation	Total Time (min)	Sb (mg/cu m)	As (mg/cu m)
Laborer	453	1.240	0.008
"	454	1.880	0.010
"	458	2.100	0.029
"	443	0.470	0.002
"	439	1.640	0.011
"	441	4.910	0.025
"	459	1.530	0.009
"	450	1.230	0.004
Sweeper—yard	458	3.740	0.047
Fork lift operator	464	0.580	0.002
Gardener	443	0.050	0.001
Scale operator	459	1.210	0.009
Warehouse operator	455	0.460	0.003
"	452	0.500	0.003
Other	225	0.69	0.002
"	360	1.92	0.008
Oxide furnace operator	428	10.86	0.089
Laborer	456	10.24	0.044

Adapted from Donaldson and Cassady [121]

TABLE IV-4

PLANT B
AIR SAMPLING RESULTS, APRIL 1975

Job Description and Area	Type of Sample	Concentration		
		Antimony	Arsenic	Nickel
Furnace operator	Breathing zone	1.25	0.039	—
"	"	3.25	<0.035	—
"	"	0.21	<0.035	—
"	"	1.20	<0.035	—
"	"	0.78	<0.035	—
"	General air	0.28	<0.035	—
"	"	0.01	<0.035	0.018
"	"	0.43	<0.035	—
"	"	0.83	<0.035	—

Adapted from Donaldson and Cassady [121]

TABLE IV-5

PLANT C
GENERAL AIR AND PERSONAL SAMPLES, JUNE 1975

Location	Total Time (min)	Sb (mg/cu m)	As (mg/cu m)	Type of Sample
Operator--new system	420	2.7	0.0169	Personal
Operator--miscellaneous	420	5.0	0.0267	"
Bagging & No. 4 man	420	8.7	0.0560	"
Ore dumper (Wore air hood; Sampler not under hood)	420	4.5	0.0155	"
Top of coders	400	5.6	0.0061	General
At bagging station	405	2.3	0.0143	"
At ore hopper--operator wore air-supplied hood to dump ore	405	2.8	0.0092	"
Ore feed, second level outside	410	1.8	0.0017	"
On I-beam over bagging operation	390	2.6	0.0162	"
At control panel	390	1.9	0.0105	"
At operator's desk	400	2.9	0.0147	"
Feed oxide, out-of-doors, 2nd deck	405	5.3	0.0057	"

Adapted from Donaldson and Cassady [121]

Sampling and Analytical Methods for Antimony in Air

(a) Sampling Methods for Particulate Antimony

Although impinger and electrostatic precipitation methods have been used to sample antimony-containing aerosols [122,123], collection on filters is more appropriate for personal sampling [124]. Reasons for filter preference include ease and convenience of use, less interference with work operations, and less chance for spillage. The collection efficiency of Millipore Type AA 37-mm diameter filters for antimony potassium tartrate aerosol (1.08 mg Sb/ cu m), sampled at 1.5 liters/minute, was found to be 99.7% [125].

The antimony content of blank filters has been reported by several authors. Some glass fiber filters have been found to contain relatively large amounts of antimony, up to 0.23 μg Sb/sq cm, or approximately 2.3 μg Sb on a 37-mm filter [126]. Such high blank values indicate that these filters are not acceptable for personal sampling, where as little as 1 μg Sb may be collected. Cellulose-mixed ester membrane filters were found by neutron activation analysis to have only 0.00024 μg Sb/sq cm (about 0.0024 μg on a 37-mm filter) [127]. Cellulose acetate membrane filters were reported to contain 0.000013 μg Sb/sq cm, or about 0.0013 μg on a 37-mm filter [128]. Polystyrene

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filters used for area sampling were found to have blank values of 0.00018 μg Sb/sq cm, or about 0.0018 μg per filter [128], and less than 0.001 μg Sb/sq cm (0.01 μg per filter) [129,130].

(b) Sampling Methods for Vapors

Volatile antimony compounds include some of the halides, which either are soluble or decompose in water [131]. No reference to sampling methods for these compounds was found in the literature. The sampling method recommended for volatile antimony compounds uses a midget impinger containing 5% mercuric chloride in 6N hydrochloric acid. This will not distinguish individual volatile and particulate antimony compounds.

(c) Analytical Methods

Early analytical methods for antimony were based on reduction of antimony solutions by zinc, with evolution of stibine. The antimony deposited after pyrolysis of the stibine was determined gravimetrically [132] or colorimetrically [69]. The detection limits were 1-10 μg of antimony.

A number of wet chemical methods are available for the determination of milligram quantities of antimony in various alloys [133], but most are not sensitive enough for levels found in industrial hygiene work.

Fredrick described a sensitive colorimetric method for antimony based on rhodamine B in 1941 [99]. The detection limit demonstrated for standard solutions was 0.1-μg of antimony/5 ml of solution. Although Fredrick [99] realized the potential application of the method in industrial hygiene, sample handling procedures were not considered. In 1945, an improved method involving extraction of the metal-dye complex was described by Webster and Fairhall [134], and wet-ashing methods for determination of antimony in biologic samples were developed by Maren [101].

Results of a collaborative test on a rhodamine B method were reported in 1964 by the American Conference of Governmental Industrial Hygienists (ACGIH) [135]. Ten laboratories participated in the analysis of three sample solutions containing 3-8 μg antimony/ml. The overall coefficient of variation was 10.5%, and the average coefficient of variation within replicates for each analysis was 5%. Average recovery was 105.2%. As a result of this test, cooled reagents became required. The improved method was subsequently recommended by ACGIH for air and biological samples [122], by NIOSH for urine [136], and by Tabor et al for air samples [124]. The working range for a 50-liter air sample is 0.02-0.4 mg Sb/cu m.

Several other less thoroughly studied colorimetric methods have been published. These include procedures based on methyl fluorone [137], Brilliant Green [138-139], Malachite Green [140], iodine [141,142], and silver diethyldithiocarbamate [143]. A kinetic method with photometric end-point detection for microgram amounts of antimony was published in 1972 [144].

Spot tests have been used to detect traces of antimony compounds, including stibine. A ring-oven method for detection of particulate antimony compounds depends on conversion of the antimony to stibine, with detection by silver nitrate-impregnated paper [145,146]. Rapid detection of 10-20-μg amounts of antimony can be made with a modified Reinsch's test [147]. Feigl

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and Chan [148,149] described spot tests using mercuric cyanide that are useful for 100-μg quantities of elemental or bound antimony. Silver diethyldithiocarbamate can be used to detect as little as 60 pg of antimony in 60 nanoliters of solution [150]. To detect as little as 20 μg of antimony in 20 ml of body fluids, a copper reduction was described [151].

Chromatography is one of the few analytical techniques specific for individual antimony compounds including different oxidation states of antimony. Applications of gas-liquid chromatography have been described for determination of antimony trichloride [152], antimony triiodide [153], antimony pentafluoride [154], and triphenyl antimony [155].

Electrochemical methods also have application in trace determination of antimony. Dubois and Monkman [156] described the use of polarography for determination of antimony in air samples taken on glass fiber filters. Minimal sample manipulation is required. Tri- and pentavalent antimony can be determined separately, and the method is useful for microgram quantities [156]. Other polarographic procedures describe the determination of antimony using thiocyanate electrolyte [157] and in organic compounds [158]. An ion-selective electrode sensitive to as little as 10 nanomoles/liter of either tri- or pentavalent antimony was reported in 1975 [138].

Spark source mass spectrometry has been used for determination of many elements, including antimony, in biological samples [159,160]. Detection limits were on the order of 0.1 ppm, but accuracy was probably not better than $\pm 25\%$.

In clinical investigations of antimony process workers, McCallum [79] and others [161] made estimates of the antimony burden in intact lungs by X-ray spectrophotometry. The minimum detection limit was approximately 2 mg/sq cm. This method was described in Epidemiologic Studies.

Bloch [162], in 1970, described a gamma-ray spectrometric method similar to that of McCallum [79] for determining antimony concentrations in the lungs of antimony workers. This technique also was reported to have a minimum sensitivity of approximately 2 mg/sq cm. Recent information indicates that antimony concentrations in intact lungs may be assayed by this method at levels as low as 50 ppm (P Bloch, written communication, March 1978), but the method for calculating ppm was not described.

Neutron activation analysis (NAA) has been used by several investigators to determine elements in atmospheric particulates [127-129,163,164]. Good sensitivity for many elements, minimal sample manipulation, and the ability to determine twenty or more elements simultaneously have been cited as advantages of NAA, which requires expensive equipment and extensive data processing [165]. An absolute detection limit of approximately 0.3 ng of antimony/filter has been reported with 57-mm cellulose ester filters [128], and another group that used polystyrene filters found the detection limit to be 0.03 μg per 20 X 25-cm filter [163]. Photon activation analysis was also applied to determine antimony particulates in air but with much poorer sensitivity than NAA [130].

More than thirty elements, including antimony, have been determined in biologic materials by NAA [76,166-175]. Accuracy within 5% of the calculated value on samples containing 0.1-10 ng of antimony was reported in studies on

biologic materials [166]. Neutron activation anaylsis was also used for antimony in other matrices, including natural waters [176], pharmaceutical products [177], and laundry aids [178].

Analysis of airborne particulates by emission spectroscopy was demonstrated for 15 elements, including antimony [179], but no working range of concentrations was given. Another publication indicated that the detection limit in biologic materials is on the order of 15 μg of antimony per sample by conventional methods [180]. However, other analytical methods based on emission spectra may be modified to be more sensitive. For example, Braman et al [181] converted antimony to stibine with sodium borohydride and obtained a detection limit close to 0.5 ng per sample. Inductively coupled plasma emission spectroscopy has a detection limit of 0.2 ppm for antimony, about the same sensitivity as flame atomic absorption [182]. An emission spectrographic method of analysis for microsamples (less than 400μg) was described by Svoboda and Kleinmann [183] in which the lower limit of detection for antimony was 4-10 ng.

Atomic absorption spectrophotometry (AAS) is one of the most widely used methods for the determination of antimony. Three major variations of the method have been developed: flame atomization, hydride generation, and flameless atomization.

A method evaluated and found acceptable by NIOSH [125] for determination of particulate antimony in air is based on flame AAS. The sensitivity of flame AAS is typically on the order of 0.3-0.5 ppm in the aspirated solution for 1% absorbance (5-10 μg total Sb in the sample), limiting the lower end of the working range to about 0.05-1.0 mg/cu m for a 360-liter air sample (approximately 18-36 μg/sample) [125,184,185]. Sensitivities about 50-100 times better than this may be obtained with either the hydride generation method or flameless atomization using a graphite furnace.

The graphite furnace (flameless) method has a sensitivity of about 120 pg/5-50-μm portion [186-189] or about 5-15 ng for an ashed air filter sample. A flameless method developed by NIOSH is presented in Appendix II. This method is recommended because a 50-liter air sample is adequate for analysis, as opposed to a 360-liter air sample required for equivalent sensitivity with flame AAS.

The first applications of hydride generation techniques to the determination of antimony used magnesium and titanium trichloride or zinc as reductants [190-192]. Subsequently, sodium borohydride showed advantages as a reductant because of its wide applicability and usefulness in both solid and solution forms [193-195]. Absolute sensitivity of 10 ng antimony was reported for an argon-hydrogen burner system [193]. With the use of a long path for the atomization of the hydride, a sensitivity of 0.6 ng was demonstrated [194]. Applications include the determination of antimony and other hydride-forming metals in steel [196], natural waters [197], and foods [198]. An automated procedure has been developed [199].

V. ENGINEERING CONTROLS, PERSONAL PROTECTION, AND WORK PRACTICES

General Control Principles

Occupational exposure to antimony and its compounds can be controlled by applying accepted industrial hygiene principles (1) at the point of generation, (2) in the general work environment, and (3) at the actual point of exposure to the worker. Although antimony and its compounds are associated with numerous processes, the control principles and methods can be applied to all.

Control methods applied at the point of generation include local exhaust ventilation, isolation, enclosure, process modification, and containment. These methods are generally the most effective means of control.

If control at the source cannot be made fully effective, methods must be used that minimize contamination of the work area. These include general dilution ventilation, good housekeeping, and good work practices.

In addition to control at the source and in the general work environment, personal protection must be afforded. Personal protective equipment (respirators, face shields, eyewear, hats) separates the worker from the contaminated environment. Individual protection involves some risks and problems, including the possibilities of equipment failure, improper fit or use, the discomfort of wearing the equipment, and increased risk of accidents due to restriction of vision or impairment of movement. Because of these drawbacks, the use of some personal protective equipment, such as respirators, should be relied upon only as a last resort, and not as an alternative to adequate engineering controls.

Appropriate application of source, work area, and personal protection control methods should provide effective worker protection under most conditions. A continuing health education program, environmental monitoring, and accurate and complete recordkeeping are also essential to a complete control system. Periodic inspection and quality checks of all aspects of the control system are necessary to ensure the system's continued effectiveness.

Engineering Controls

Guidance for specific design criteria for mechanical ventilation can be found in Industrial Ventilation--A Manual of Recommended Practice [200] and in Fundamentals Governing the Design and Operation of Local Exhaust Systems [201].

Complete enclosure or isolation of a process is a highly effective means of reducing worker exposure. The most effective method of control is a combination of local exhaust ventilation and enclosure. Because antimony ore is extremely brittle, certain operations (ie, reduction and screening) result in high workplace air concentrations of antimony dust. Local exhaust ventilation and enclosure should be used to control the dust. In addition, wetting the ore with a light water spray assists in reducing the amount of dust generated. Local exhaust ventilation and enclosure methods, as recommended by NIOSH for control of arsenic [89], are also recommended for the

control of antimony in smelting operations, where it is common for antimony trioxide fume to remain suspended in the air for an exceptionally long time [200].

In some operations, either local exhaust or enclosure may alone be sufficient. Local exhaust ventilation (exhaust hoods) can be located over pots containing molten metal for control of fumes, over crushing and packout operations for control of dust, and in areas where antimony trichloride or other halides may release irritating fumes. The toxic gas stibine can occur as a byproduct when storage batteries are overcharged [97]; therefore, appropriate ventilation controls should be used to control both hydrogen and stibine in battery charging areas.

A combination of isolation of the operation and process modification is another control possibility. In smelting, fettling, general furnace operation, and in battery charging, hazards can be minimized or eliminated through isolation and automation of processes.

Whenever mechanical ventilation is used to control antimony exposure, measurements that demonstrate the system's efficiency should be conducted frequently and recorded at least quarterly. Continous airflow indicators, such as water or or oil manometers, are recommended. Devices that measure air velocity (ie, anemometers) can also be used to determine the efficiency of the system. In addition to frequent checks, measurements should be conducted after any change in process, operation, or control method that might result in reduction of control efficiency. The employer should maintain a record of ventilation measurements, including the location of the test site, date, and results of tests. These records should be retained for 1 year.

Personal Protection

Working with antimony can lead to skin irritation and skin ulcers. To minimize or prevent skin contact, coveralls or long-sleeve shirts with trousers, gloves, and appropriate shoes and headwear should be worn.

Where antimony trichloride or other antimony halides may contact the skin, special care is necessary due to the very irritant properties of these compounds. Workers should wear gloves with gauntlets and aprons made of rubber or other material resistant to penetration by antimony halides, as well as chemical safety goggles or face shields (8-inch minimum) with goggles if spills or splashes are possible. Eye protection should follow the guidelines listed in 29 CFR 1910.133 to prevent damage to the eyes resulting from exposure to antimony.

The use of respirators should be limited to periods of installation and testing of engineering control equipment, nonroutine maintenance and repair, and during emergencies when concentrations of airborne antimony may exceed the recommended TWA. Requirements for a respiratory protection program are given in Chapter I, Section 4 of this document; the program should comply with the requirements of 29 CFR 1910.134. The selection of respiratory protective devices should comply with the provisions of 30 CFR 11.

Neither respiratory protective equipment nor personal protective clothing are to be regarded as substitutes for proper engineering controls.

Work Practices

Good work practices include recommended emergency procedures, proper use of facilities, careful sanitation practices and cleaning, and safe handling and storage. The importance of these practices should be continually emphasized.

(a) Emergency Procedures

For all work areas in which emergencies involving antimony may occur, employees should be properly trained to follow general specified procedures along with any others that may be appropriate for a specific operation or process.

Facilities for quick drenching of the body within the immediate work area should be provided whenever contact with antimony halides may occur. If halides contact the skin or mucous membranes, the involved area should be flushed with large quantities of water. The skin should then be washed with soap and water. Contaminated clothing should be removed promptly and not reworn until thoroughly washed.

If particulates or solutions of antimony halides have contacted the eyes, they should be washed out promptly with copious quantities of gently flowing water. The eyelids should be held open with the fingers during washing. The injured employee should receive medical attention at once.

Approved protective clothing and respirators should be ready for use by persons essential to emergency operations and should be stored in readily accessible locations. A worker who has received inhalation exposure to a halide should be moved immediately to fresh air and should receive medical attention.

Procedures should be prepared for maintenance or cleanup of areas where leaks or discharges of antimony have occurred. Employees not essential to emergency operations should be evacuated from the affected areas during emergencies, and perimeters of these areas should be delineated, posted, and secured.

Only personnel properly trained in emergency procedures and protected against the attendant hazards should clean up spills or control and repair leaks. After cleanup, protective clothing and equipment should be removed and decontaminated, and the cleanup personnel should shower.

Emergency telephone numbers should be prominently displayed.

(b) Handling and Storage

Procedures should be followed to avoid unintentional chemical reactions. Antimony and antimony compounds can generate highly toxic stibine gas under reducing conditions. Contact with various acids generates stibine; this potential must be recognized and avoided.

Three cases of accidental industrial poisoning by a mixture of arsine, stibine, and hydrogen sulfide have been documented [97]. Gases were liberated when water was added to a hot dross that contained metallic aluminum compounds

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(arsenic, antimony, and free sulfur) to speed up the operation. Arsine, stibine, and hydrogen sulfide were formed from the reaction of the metals with the liberated nascent hydrogen. Workers became extremely ill as a result, but recovered.

Stibine has been generated when storage batteries were overcharged [202]. The amounts of stibine in battery room atmospheres have been reported to be generally less than 1 ppm (about 5.1 mg/cu m), although 5 ppm (about 25 mg/cu m) has been determined directly over large open battery cells. Under various experimental conditions, maximum stibine concentrations of 45 ppm (about 225 mg/cu m) were detected in undiluted battery gases. Other potential sources of stibine generation are welding and cutting with blow torches, soldering, zinc etching, preparation of antimony trichloride, steel burnishing, purification of type metal with caustic soda, and procedures in laboratories and industry where nascent hydrogen comes in contact with metallic antimony or soluble antimony compounds [203]. Workers should be made aware of such possibilities at their workplace.

Antimony oxides, antimony sulfides, and antimony metal do not present storage problems, though the corrosive halides do. Drums and pails are adequate for some grades of antimony trichloride, but glass carboys are necessary for pharmaceutical-grade trichloride and for all other halides. Carboys should be protected by wooden frames. Liquid halides can be poured from the carboys, but the solid antimony trichloride must be removed by breaking the glass container. Procedures for breaking the glass have been outlined by the Manufacturing Chemists Association [204]. Storage containers should be kept tightly closed. Storage areas should be cool, dry, well-ventilated, protected from sunlight, and away from manufacturing areas.

Information on antimony and its compounds should be recorded on the "Material Safety Data Sheet" shown in Appendix III or on a similar form approved by the Occupational Safety and Health Administration, US Department of Labor. Workers should be made familiar with this information as part of the continuing education program outlined in Chapter 1.

(c) Sanitation Practices

Employers should provide rest areas, smoking areas, and facilities for food preparation, storage, dispensing, and eating that are physically separated from work areas to prevent ingestion of antimony.

Employees should not eat or smoke in areas where antimony is present. Signs should be posted that prohibit eating and smoking in work areas. Workers should wash their hands before putting anything in their mouths and before and after using toilet facilities.

A daily change of work clothing should be provided for workers. Separate lockers for work clothing and street clothing should be available. Workers should not wear their work clothing away from the workplace, but should shower and change into street clothing before leaving. Contaminated clothing should be put in closed containers until it is washed.

Washing and shower facilities, including eyewash fountains and quick-drench units for emergencies, should be provided by the employer and should be easily accessible to employees. The portions of 29 CFR 1910.141 pertaining to

facilities that are especially relevant to antimony are subsections (a) General, (c) Toilet Facilities, (d) Washing Facilities, (e) Change Rooms, and (g) Consumption of Food and Beverages on the Premises.

(d) Laundering

Used work clothing should be laundered frequently, preferably daily. Clothing should be washed with soap or other detergent and water. Precautions should be taken to protect personnel who handle and launder soiled clothing. These employees should be advised of the hazards of, and means of preventing, exposure to antimony. If an outside laundry facility is used, the launderers should be advised of the hazards and proper procedures involved in handling contaminated work clothing. Contaminated clothing that is to be transported to an outside laundry facility should be placed in containers and sealed.

(e) Decontamination

To reduce antimony dust exposures in the work area, cleaning by vacuuming, wet mopping, or hosing is advised. No dry sweeping or blowing should be permitted. Liquid spills should be copiously flushed with water and channeled to a treatment system or a holding tank for reclamation or proper disposal. Tanks that have contained antimony trichloride may be cleaned according to guidelines offered by the Manufacturing Chemists Association [204].

(f) Disposal

Waste materials contaminated with antimony should be disposed of in a manner not hazardous to employees. The disposal method should conform to applicable local, state, and Federal regulations.

VI. DEVELOPMENT OF STANDARD

Basis for Previous Standards

The first maximum allowable concentration (MAC) for antimony dusts, fumes, and mists was recommended in 1947 by the American Conference of Governmental Industrial Hygienists (ACGIH) [205]. The recommended value was 0.1 mg/cu m of air. No basis for the recommendation was given.

In 1948, the ACGIH adopted the term "Threshold Limit Value" (TLV) to replace maximum allowable concentration. Both terms were imprecise, implying to some a ceiling, and to others a time-weighted average (TWA). Antimony was one of five substances that had values raised from 1947 values. The TLV for antimony became 0.5 mg/cu m [206].

In his 1950 text on industrial toxicology, Elkins [207] proposed a MAC of 1 mg/cu m, citing the animal experiments by Dernehl et al [102]. However, Elkins [207] wrote that his MAC proposal of 1 mg/cu m was based on insufficient information. That same year, the ACGIH [208] continued to recommend a TLV of 0.5 mg/cu m for antimony dusts, fumes, and mists.

TLV's adopted in 1953 by the ACGIH were, for the first time, defined as maximum average concentrations over an 8-hour workshift that should not be exceeded rather than as ceilings not to be exceeded even momentarily [209]. The recommended value for antimony, however, remained at 0.5 mg/cu m.

In his 1956 review of TLV's, Smyth [210] cited the studies by Bradley and Fredrick [17] and Dernehl et al [102] and suggested that the TLV of 0.5 mg/cu m was low enough to prevent injury.

The ACGIH published documentation for the TLV of 0.5 mg/cu m in 1962 [211]. The value was based on the industrial studies of Brieger et al [15] in 1954 and Renes [5] in 1953. A later ACGIH documentation, published in 1966, stated that the recommended level of 0.5 mg/cu m would prevent accumulation of antimony in the body [212]. The 1971 documentation [213] cited industrial studies by Klucik et al [11,214,215] and continued to recommend 0.5 mg/cu m.

Notices of intent to change the TLV for antimony and its compounds were published by ACGIH in 1975 and 1976 [216,217]. The changes proposed separate TLV's for the handling and use of antimony trioxide, and for the production of antimony trioxide. A TLV of 0.5 mg/cu m was proposed for handling and use, and a TLV of 0.05 mg/cu m was proposed for production. The 0.05 mg/cu m value for antimony trioxide production was most likely based on the epidemiologic report of Davies [14] that suggested an increased incidence of lung cancer among antimony production workers.

In 1976, the term "Short-Term Exposure Limit" (STEL) was instituted by the ACGIH. It was defined as the maximal concentration to which workers could be exposed for up to 15 minutes continuously without suffering from intolerable irritation, chronic or irreversible tissue change, or narcosis of sufficient degree to increase accident proneness, impair self-rescue, or materially reduce work efficiency, provided that no more than four excursions per day were permitted, with at least 60 minutes between exposure periods, and

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provided that the daily TLV-TWA was also not exceeded [217]. The STEL for antimony and compounds was tentatively set at 0.75 mg/cu m but did not appear in the 1976 documentation [218].

In 1977, the ACGIH [219] again listed the TLV for antimony as 0.5 mg/cu m with notice of intended changes. The tentative STEL value of 0.75 mg/cu m proposed the year before was not adopted and did not appear in the 1977 list.

The most recent intended change, appearing in 1977, was a TLV of 2 mg/cu m proposed for soluble salts of antimony. This value was based on the reports of Taylor [96] and Cordasco [95], who studied accidental poisoning by antimony trichloride and pentachloride, respectively. The proposed TLV's of 0.5 mg/cu m for handling and use of antimony trioxide, and 0.05 mg/cu m for antimony trioxide production remained in the notice of intended changes.

Tables in Occupational Exposure Limits for Airborne Toxic Substances—A Tabular Compilation of Values from Selected Countries were published by the International Labour Office in 1977 [220]. The environmental limits for antimony in other countries are presented in Table VI-1.

The Occupational Safety and Health Administration, US Department of Labor, has adopted the 1968 ACGIH TLV for antimony of 0.5 mg/cu m determined as a TWA concentration limit [221] as the Federal standard (29 CFR 1910.1000).

TABLE VI-I

HYGIENIC STANDARDS OF SEVERAL COUNTRIES
FOR ANTIMONY AND COMPOUNDS IN THE WORKING ENVIRONMENT

Country	Standard (mg/cu m)	Qualifications
Finland	0.5	Not stated
Federal Republic of Germany	0.5	8-hour TWA
Democratic Republic of Germany	0.5	Not stated
Rumania	0.5	"
USSR	0.5	For antimony dust
	0.3	For flourides and chlorides (tri- and pentavalent); obligatory control of HF and HCl
	1.0	For trivalent oxides and sulfides
	1.0	For pentavalent oxides and sulfides
Sweden	0.5	Not stated
USA	0.5	8-hour TWA
Yugoslavia	0.5	Not stated

Modified from references 220 and 222

Basis for the Recommended Standard

(a) Permissible Exposure Limit

Adverse health effects reported for antimony and its compounds in occupational settings include effects on the heart, respiratory system, skin and mucous membranes, and a suggestion of reproductive problems.

Many nonoccupational reports have implicated antimony in adverse heart effects manifested by ECG alterations, primarily a flattening or inversion of the T wave. These effects have followed iv or im administration of antimony salts in high multiple doses (about 0.5-6.0 mg/kg per dose) for the treatment of parasitic infections [36-50].

Brieger et al [15] noted seven deaths of antimony workers attributed to cardiac disease. Of 75 workers in the department where the deaths occurred, 37 had altered ECG's, primarily of the T wave. Concentrations of antimony trisulfide in the department ranged from 0.58 to 5.5 mg/cu m, with most samples over 3.0 mg/cu m, according to Brieger et al. According to Bradley and Fredrick [17], rats had myocardial damage after LD50 administration of antimony. T wave alterations were also found in rats and rabbits given inhalation exposures of 3.07 and 5.6 mg antimony/cu m, respectively, for 6 hours/day, 5 days/week for 6 weeks [15]. Similar abnormal ECG's in workers exposed to antimony trisulfide and trioxide were described by Klucik and Ulrich [11] at concentrations that were reported to range from 1.3 to 237 g Sb/cu m (sic); however, these stated concentrations may be in error, since they are inordinately high. It may be questioned whether arsenic, present as a contaminant in industrial antimony compounds, caused the observed ECG changes because arsenic has produced the same effects [89-93]. Although some reports have failed to note ECG changes in antimony workers [9,10], ECG alterations in animals [15,17], in patients receiving arsenic-free antimony drugs [36-50], and in workers exposed at concentrations generally above 3 mg/cu m are judged to be due to antimony.

Simple pneumoconiosis, manifested as moderate, dense reticulo-nodular formations scattered throughout pulmonary fields on X-rays [7], is a frequent finding among antimony workers [6,7,9,12,79]. Fibrosis appears to be absent [6,79]. According to some reports, workers seem to be free of symptoms [12,79], but decrements in pulmonary function have been reported occasionally [6,7,9]. Quantitative information was lacking in these reports, as were specifics on the procedures used. Environmental levels were reported to exceed 0.5 mg/cu m for antimony trioxide and antimony metal dust [12,79], to be mostly less than 10 mg/cu m (range, 0.08-138 mg/cu m) for antimony ore and trioxide [9], to measure 16-248 mg/cu m for a mixed dust that included antimony oxides and silica [6], and to be 0.3-14.7 mg/cu m for antimony metal and trioxide [7]. Airborne exposures to antimony workers generally involved materials other than antimony. Contaminants have included silica and arsenic as well as other particulates and gases characteristic of smelter operations.

Reported environmental concentrations frequently lack detail, such as whether they constituted breathing zone or area measurements and what specific operations were evaluated; however, most environmental levels appear to be greater than 0.5 mg/cu m and less than 10 mg/cu m. The bulk of the dust loads consisted of antimony or antimony compounds in these cases and it is reasonable to conclude that simple pneumoconiosis was attributable to the

antimony dusts. It is unknown whether the effects were due to worker exposures at 10 mg/cu m or less or whether they were the result of higher concentrations.

A question was raised in 1973 concerning increased mortality due to lung cancer in a group of antimony smelter workers in England that originally numbered 1,081 people [14]. Of 56 deaths recorded from 1961 to the end of 1971, 10 were due to lung cancer; 68 individuals in the cohort remained untraced. Eight deaths from lung cancer occurred among individuals 45-64 years old who were engaged in antimony smelting or related activities. The eight deaths represented a two-fold excess over the number expected from a comparison with local death rates. Because of the small group, the excess deaths were not necessarily considered by the author [14] to be due to antimony. In the factory and office as a whole, the number of deaths from all causes was less than expected. Because of the lack of knowledge of smoking habits and the small size of the study group, the findings were considered by the author [14] to be equivocal. The study was to be continued to include a detailed investigation of smoking habits.

A recent update of the figures reflected essentially the same two-fold ratio, 13 deaths observed vs 7.2 deaths expected (KP Duncan, written communication, July 1978). With the exception of observed vs expected figures, further data have not been forthcoming. Many questions remain such as smoking habits of the workers, the makeup of the local (control) group used to generate the expected estimate, work locations and worker histories, other smelter contaminants, environmental levels of antimony and contaminants, and changes that have taken place in processes or procedures. Therefore, the question raised in 1973 on lung cancer in antimony workers in England remains equivocal. Because of the lack of definitive data, lung cancer is not judged to be a factor at this time in consideration of a recommended occupational exposure limit for antimony and its compounds.

Dermatitis and mucous membrane irritation are common complaints of antimony workers [5,6,77,78]. Renes [5] correlated most incidents of dermatitis with a 1-week period of heavy exposure when concentrations reached 70.7 mg/cu m, but some cases of dermatitis and mucous membrane irritation occurred at exposures in the range of 0.4-70.7 mg/cu m. The occurrence of dermatitis seems to be related at least as much to conditions of heat, perspiration, and friction, as to actual exposure level.

Of concern is the single report of Belyaeva [13] in which 318 antimony-exposed female workers were stated to have higher incidences than controls of late-occurring spontaneous abortions (12.5% vs 4.1%), premature births (3.4% vs 1.2%), and gynecologic problems (77.5% vs 56%). Although subsequent animal findings in female rats by the same author [13] were reported to support the findings of human reproductive effects due to antimony, the dose (50 mg/kg ip) and the concentration (250 mg/cu m) given to rats were high and of questionable relevance to the occupational setting. Many procedural points were not discussed and a definitive interpretation of the work is not possible without further evidence. The percentage of gynecologic problems reported in the control group (56%) seems abnormally high. It is unclear whether the overall working conditions in this smelter were representative of smelter conditions in the US.

Blood and urine levels of antimony were reported to be about the same in dusty operations as in less dusty operations, such as the chemical laboratory or in quality control [13]. Average urine levels of antimony for exposed workers ranged from 2.1 to 2.9 mg/100 ml. The highest value found was 18.2 mg/100 ml and the lowest was 0.5 mg/100 ml. These levels would appear to be reasonable when compared with the statement by Renes [5] that one heavily exposed worker had a urinary antimony level of 60 mg/100 ml. Clearly, further work is needed on the effects of antimony on reproduction. At this time, the available information on reproductive effects is insufficient to make recommendations pertaining to an occupational exposure limit for antimony.

The present Federal limit for occupational exposure to antimony and its compounds is 0.5 mg/cu m (as Sb) as a time-weighted average concentration limit. Stibine is excluded from this recommended standard because it is a transitory byproduct of operations involving other sources of antimony, and decomposes rapidly in the air. From a review of the data and all available information, it is believed that a TWA limit of 0.5 mg/cu m will afford worker protection from the health effects associated with exposure to antimony including dermatitis, mucous membrane irritation, pneumoconiosis, and ECG alterations. Therefore, NIOSH recommends that the current Federal limit of 0.5 mg/cu m as a TWA concentration limit be retained.

(b) Medical Surveillance and Recordkeeping

Medical surveillance should include preplacement and periodic examinations with attention directed to the skin, lungs, and heart. Chest X-rays should be taken annually to screen for possible pulmonary problems including pneumoconiosis that may be attributed to antimony exposure. Several authors [6,7,9] have suggested that pulmonary functional impairment may be a feature of antimony pneumoconiosis; therefore, tests of ventilatory function should also be required on an annual basis. Because of the findings of ECG alterations in workers exposed to antimony trisulfide [15] and also in rats and rabbits [15], annual ECG's of antimony-exposed workers should also be mandatory.

The uncertain nature of the evidence of liver dysfunction makes a requirement for liver function tests difficult to justify. However, liver function tests are encouraged because of their possible relationship to antimony exposure as well as their relevance to an evaluation of general health.

The research is inconclusive with regard to possible adverse effects of antimony exposure on reproduction. Belyaeva [13] reported that women working with antimony experienced more late spontaneous abortions, premature births, and gynecologic problems than did women not exposed to antimony. Animal experiments [13] suggested that antimony may interfere with the normal development of ova. No investigation of the fertility of male antimony workers or further animal experiments involving either sex has been reported. Until Belyaeva's findings are confirmed or refuted, NIOSH recommends workers be advised that a single report indicates that there may be an increased risk of reproductive disorders resulting from occupational exposure to antimony.

Because of the possibility of chronic lung changes and cardiac alterations as a result of antimony exposure, medical records of antimony workers should be kept for 30 years after termination of employment.

(c) Sampling and Analysis

Personal sampling with a membrane filter is the primary recommended technique, since most antimony compounds in the industrial environment exist as particulates. A Millipore type AA or equivalent cellulose ester membrane filter with 0.8-μm pores provides optimum sampling efficiency. The residue obtained from digesting the collected particulate matter in a mixture of nitric, perchloric, and sulfuric acids is diluted with distilled water; aliquots are analyzed for antimony at 217.6 nm by flameless atomic absorption. If lead is present in the sample, the 231.2-nm resonance line should be used.

The recommended sampling method for volatile antimony compounds uses a midget impinger containing 5% mercuric chloride in 6N hydrochloric acid. The sample solutions are diluted with distilled water and analyzed directly by flameless atomic absorption.

Analysis by atomic absorption spectrophotometry has been successfully used to monitor air for antimony and antimony compounds. The flameless method is relatively simple and quick, and is highly sensitive. Recommended procedures for sampling and analysis are discussed in Chapter IV and are presented in greater detail in Appendices I and II.

(d) Personal Protective Equipment and Clothing

The irritant properties of antimony make it necessary to protect the skin and eyes from contact with antimony materials. Coveralls with long sleeves, head and neck protection, and gloves should be worn during exposure to antimony dusts. When antimony halides may contact the skin, gloves with gauntlets and aprons made of rubber or other material resistant to antimony halides should also be worn to prevent burns. Because of the occurrence of conjunctivitis following antimony exposure [5,6], it is important to protect the eyes from antimony by wearing chemical safety goggles in work situations where antimony could contact the eyes. Respirators should be worn when airborne concentrations of antimony exceed 0.5 mg/cu m, but this should occur only during unusual circumstances, ie, during installation and testing of engineering controls, during nonroutine maintenance or repair, or during emergencies. For initial selection of a respirator to be assigned to an individual worker, a quantitative fit test of facepiece to face seal is recommended for negative pressure respirators. This method provides a numerical index of respirator fit, does not rely solely on the subjective response of the wearer, and therefore provides more reliable protection than qualitative fit testing. Procedures and allowable leakages as specified in A Guide to Industrial Respiratory Protection [223] should be followed. All protective clothing and equipment should be provided by the employer and be cleaned, maintained in good condition, and replaced as necessary by the employer.

(e) Informing Employees of Hazards

Continuing education is important in a preventive hygiene program for employees exposed to hazardous materials such as antimony. Workers should be periodically informed by properly trained persons of the possible sources of antimony exposure, the adverse health effects associated with excessive exposure to antimony, the engineering and work practice controls in use and being planned to limit exposure to acceptable concentrations, and good

personal hygiene and housekeeping practices. The procedures used in environmental and medical monitoring should also be explained, and the benefits to workers of participating in these environmental and medical monitoring procedures should be stressed.

(f) Work Practices

To prevent the intake of antimony, NIOSH recommends that storage, handling, dispensing, and eating of food be prohibited in antimony exposure areas. While antimony does not pose a fire hazard, its deposition on smoking materials may result in inhalation or ingestion of antimony during smoking; therefore, smoking as well as carrying uncovered smoking materials in the workplace should be prohibited. Workers should shower and change clothes before leaving work so as to minimize their exposure to antimony and to prevent contamination outside the workplace.

(g) Monitoring and Recordkeeping Requirements

In workplaces where antimony is present, an annual industrial hygiene survey is recommended to determine if exposure exceeds the action level. If there is occupational exposure to antimony, ie, if the action level is exceeded, personal sampling representative of the worker's exposure should be instituted on at least a semiannual basis. Records of sampling and analysis should be preserved for at least 30 years after the last work-related exposure to antimony to enable correlations between air levels of antimony in the workplace and any health effects on workers. Medical records should be kept for the same period. The Toxic Substances Control Act of 1976 requires that "Records of...adverse reactions to the health of employees shall be retained for thirty years from the date such reactions were first reported to or known by the person maintaining such records."

(h) Action Level

Many workers handle small amounts of antimony or work in situations in which, regardless of the amount used, there is only negligible contact with the substance. Under these conditions, it should not be necessary to comply with some provisions of this recommended standard that were prepared primarily to protect workers' health under more hazardous conditions. Concern for worker health requires that protective measures and emergency procedures be instituted below the enforceable limit to ensure that exposures stay below that limit. For these reasons, the action level has been defined as one-half the recommended TWA environmental limit, thereby delineating those work situations that do not require the expenditure of health resources for environmental and medical monitoring and for associated recordkeeping. However, because of nonrespiratory hazards such as those resulting from eye contact or skin contact, NIOSH recommends that the appropriate work practices and protective measures be required regardless of airborne concentration.