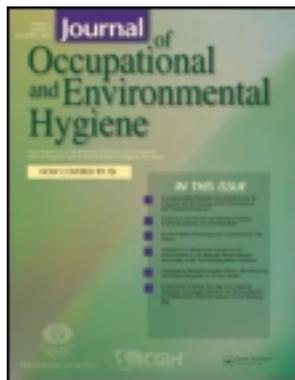


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# Use of and Occupational Exposure to Indium in the United States

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*Indium use has increased greatly in the past decade in parallel with the growth of flat-panel displays, touchscreens, optoelectronic devices, and photovoltaic cells. Much of this growth has been in the use of indium tin oxide (ITO). This increased use has resulted in more frequent and intense exposure of workers to indium. Starting with case reports and followed by epidemiological studies, exposure to ITO has been linked to serious and sometimes fatal lung disease in workers. Much of this research was conducted in facilities that process sintered ITO, including manufacture, grinding, and indium reclamation from waste material. Little has been known about indium exposure to workers in downstream applications. In 2009–2011, the National Institute for Occupational Safety and Health (NIOSH) contacted 89 potential indium-using companies; 65 (73%) responded, and 43 of the 65 responders used an indium material. Our objective was to identify current workplace applications of indium materials, tasks with potential indium exposure, and exposure controls being used. Air sampling for indium was either conducted by NIOSH or companies provided their data for a total of 63 air samples (41 personal, 22 area) across 10 companies. Indium exposure exceeded the NIOSH recommended exposure limit (REL) of 0.1 mg/m<sup>3</sup> for certain methods of resurfacing ITO sputter targets, cleaning sputter chamber interiors, and in manufacturing some inorganic indium compounds. Indium air concentrations were low in sputter target bonding with indium solder, backside thinning and polishing of fabricated indium phosphide-based semiconductor devices, metal alloy production, and in making indium-based solder pastes. Exposure controls such as containment, local exhaust ventilation (LEV), and tool-mounted LEV can be effective at reducing exposure. In conclusion, occupational hygienists should be aware that the manufacture and use of indium materials can result in indium air concentrations that exceed the NIOSH REL. Given recent findings of adverse health effects in workers, research is needed to determine if the current REL sufficiently protects workers against indium-related diseases.*

**Keywords** thin films, photovoltaics, semiconductor, indium tin oxide, copper indium gallium diselenide, indium phosphide

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## INTRODUCTION

The introduction of new technologies into the workplace can be accompanied by exposures to novel or relatively unknown materials. For such materials, animal and human toxicity data as well as exposure data may be limited. This lack of hazard information on emerging materials coupled with the rapid and often unpredictable translation of science into technology presents an ongoing challenge for occupational safety and health professionals.

Indium is a case in point. Historically, indium materials had limited commercial use. Consequently, few occupational hygienists are familiar with the material. With the introduction of flat-panel displays, and more recently, with the growth of the photovoltaic and optoelectronic industries, indium use worldwide has increased greatly. From 1991 to 2011, indium consumption in the U.S. rose 4-fold, from 30 metric tons to 120 metric tons.<sup>(1,2)</sup> Only as case reports have emerged in the past decade from Japan, China, and the U.S. of indium-related lung disease in workers did concern about the human toxicity of indium and its compounds gain increased attention.<sup>(3,4)</sup>

In 2009–2011, the National Institute for Occupational Safety and Health (NIOSH) contacted a broad spectrum of companies using indium materials. Our objective was to identify current workplace applications of indium materials, jobs and tasks with potential indium exposure, and exposure controls being used. We conducted air sampling for indium and obtained air sampling data from companies. In this article, we describe the results of this effort.

## BACKGROUND

### Physical and Chemical Characteristics

Indium (CAS 7440-74-6) atomic number 49, atomic weight 114.818, is a Group IIA post-transition metal.<sup>(5)</sup> Normally trivalent [+3], indium is also found in the +2 or +1 valence states.<sup>(6)</sup> Indium has a melting point of 156.60°C, a boiling point of 2072°C and a relative density of 7.31 at 20°C.<sup>(6)</sup> Indium is insoluble in hot or cold water but dissolves in mineral acids and amalgamates with mercury.<sup>(7)</sup>

### Source

Indium is a byproduct of smelting zinc ore (<1–100 ppm indium in zinc deposits).<sup>(1,7)</sup> From 2007–2010, major indium import sources into the U.S. were China (31%), Canada (25%), and Japan (16%).<sup>(1)</sup> Indium is not recovered from ores in the U.S. Dependence on the zinc market for primary production of indium, together with indium's relatively high cost (average U.S. producer price in 2011 of \$720/kg), has led to reliance on recycling and reclamation as important secondary sources of indium.<sup>(1)</sup>

### Commercial Applications

Indium is found in the workplace as the pure metal, alloyed with other metals, and as inorganic or organic compounds. Major commercial applications of indium materials include use as a transparent conductive oxide (TCO) coating in flat-panel displays, touchscreens, and photovoltaic (PV) cells, as a low melting point solder for bonding metal and ceramic sputter targets to backing plates, and as a semiconductor in PV cells and in certain electronic devices.

#### *Indium Tin Oxide (ITO) Sputter Target Production*

ITO sputter targets can be produced by several methods.<sup>(8)</sup> One method involves acidifying indium metal, followed by neutralization and precipitation of indium hydroxide, and calcination of indium hydroxide to indium oxide.<sup>(9,10)</sup> Indium oxide is then blended with tin oxide powder (typically 90% indium oxide and 10% tin oxide by weight) and milled to specification. A water-based slurry of the indium oxide–tin oxide blend is cast into molds, and the molded “green” bodies are sanded, then fired (i.e., sintered) at high temperature to increase the material's density. The sintered body (called a “tile”) is cut and ground to specification. The finished sintered ITO tile is used as a sputter target.

#### *Sputter Target Bonding*

Sputter targets are bonded to copper backing plates, typically using pure indium solder. Bonding can be performed in-house or by specialty bonding service providers. Techniques for cleaning and wetting the backing plate and target surface include chemical fluxes, wetting in solder by hand with a wire brush or with an ultrasonic wand, or by sputtering on metal layers (e.g., when bonding to ceramic targets). Indium solder is heated slightly above its melting point, usually in a small pot on a warming plate, and flowed over the wetted and prepped

backing plate and target. The target is placed on the backing plate, and the bond is allowed to cool slowly. Solder protruding around the edges is removed, typically with a hand pick.

#### *Transparent Conductive Oxide (TCO) Coatings*

A TCO coating is transparent and electrically conductive when deposited at the correct thickness. TCO coatings of ITO are commonly deposited onto glass, polymers, or other substrates by sputtering, generally plasma-enhanced physical vapor deposition in a chamber operated under vacuum. The sputter target acts as the cathode; the substrate as the anode. The deposited film is extremely thin (a few microns or less). Sputter chambers range from bench top to room size units, with some larger units having roll-to-roll coating systems. ITO residues may deposit on interior walls and on shields. ITO targets may be lightly resurfaced between runs to remove nodules formed during sputtering (Falk 2012).<sup>(8)</sup> ITO targets eventually become “spent” and are returned to suppliers or recyclers for indium reclamation. Electron beam evaporation can also be used to deposit ITO thin films.<sup>(11)</sup>

#### *Photovoltaic (PV) Cells*

In PV cells, indium compounds can be used as a semiconducting (photoactive) absorber (e.g., copper indium gallium diselenide [CIGS]) or as a TCO “top contact” (e.g., ITO). In CIGS PV fabrication, the CIGS layer is deposited onto a molybdenum-coated glass, metal or polymer substrate (“back contact”). Vacuum-based technologies for depositing CIGS include co-evaporation from elemental sources of Cu, In, Ga, and Se, and co-evaporation or sputtering of Cu, In, and Ga followed by selenization in a hydrogen selenide atmosphere.<sup>(12,13)</sup> The CIGS layer can also be deposited by a screen printing process involving nanoparticles of the CIGS precursor materials dispersed in ink.<sup>(14,15)</sup> After CIGS deposition, cadmium sulfide is deposited by a chemical bath process, followed by thin film deposition of a TCO layer.<sup>(13)</sup>

#### *Compound Semiconductors*

Indium is found in certain compound semiconductors, most commonly as InP, but also as indium arsenide (InAs), indium antimonide, and indium gallium arsenide. InP is used in high-speed opto-electronic devices for telecommunication systems. Epitaxial layers of InP may be grown by metalorganic chemical vapor deposition (MOVCD) on InP substrates.<sup>(16)</sup> In MOVCD, an organic indium source (e.g., trimethylindium) is reacted with a phosphorus source (e.g. phosphine) in a heated reactor under vacuum. InP-based devices are fabricated using steps common to semiconductor processing, such as masking, patterning, etching, doping, thin film deposition, and backside preparation (thinning and polishing).

#### *Miscellaneous Applications*

Other applications include indium metal alloys as “lens blockers” in optical laboratories and in fusible links because of indium's low melting point, in cryogenic seals because of indium's ductility at low temperatures, in indium metal alloys

as neutron absorbers in nuclear control rods for pressurized water reactors, indium compounds in alkaline batteries to suppress hydrogen buildup, and indium sulfate as a hardener in gold electroplating baths.<sup>(7,17)</sup> Indium radioisotopes (e.g., <sup>111</sup>In) are used in medical imaging. Nano-scale applications of indium materials are also being developed.

### Recycling/Reclamation

Due to its high cost, recovery of indium from manufactured materials and waste is of great commercial interest. Metal scraps of indium are typically recycled to suppliers. Spent ITO sputter targets are especially targeted for reclamation.<sup>(18–21)</sup> Indium recovery from ITO targets can involve crushing and heating, processes that may expose workers to indium-containing aerosols.<sup>(22,23)</sup> Interest is also growing in recovering indium from etching waste,<sup>(24,25)</sup> sputter shield residues,<sup>(26)</sup> LCD glass,<sup>(27,28)</sup> and electronic scrap.<sup>(29)</sup>

### Toxicity/Health Effects/Disposition

Indium's toxicity and disposition in the body are related to its chemical form, water solubility, dose, and exposure route. Occupational exposure to indium is predominately by inhalation. Pulmonary clearance of both soluble and insoluble indium compounds is slow, with indium accumulating in the lungs and body after chronic exposure.<sup>(30–37)</sup> Some *in vivo* dissolution of indium particles occurs in the lungs.<sup>(33)</sup> Ionic (soluble) indium is transported in the blood bound to the protein transferrin, accumulates in the kidney, and is mainly excreted in the urine, whereas insoluble indium compounds are mainly excreted in the feces.<sup>(35,38,39)</sup> Indium is minimally absorbed after ingestion.<sup>(40,41)</sup> The clearance biological half-life of indium after inhalation varies by compound. During a 14-week inhalation study in rats, InP had a mean lung clearance half-life of 78 days, increasing to 202 days post-exposure.<sup>(32)</sup> The biological half-life of indium oxide particles in rats exposed by inhalation was 8–10 days.<sup>(42)</sup>

### Indium Tin Oxide (ITO) and Indium Oxide

Cases of interstitial lung disease and pulmonary alveolar proteinosis have been reported in ITO- and indium oxide-exposed workers in Japan, the United States, and China; two cases subsequently died from lung disease.<sup>(3,4)</sup> Cough and dyspnea were commonly reported at diagnosis. Animal studies as early as the 1960s<sup>(36)</sup> and more recently<sup>(31,43–46)</sup> have shown lung effects, including inflammation, alveolar proteinosis, and interstitial fibrotic changes, after inhalational or intratracheal exposure to indium oxide and indium tin oxide consistent with the human cases. Repeated inhalational exposure to ITO at or below 0.1 mg/m<sup>3</sup> produced a significant increase in malignant lung tumors in rats.<sup>(47)</sup> Epidemiology studies in Japan<sup>(23,48,49)</sup> and in Taiwan<sup>(50)</sup> of workers exposed to ITO and indium oxide have also shown associations between serum indium levels and biomarkers of interstitial lung disease.

### Indium Phosphide (InP)

The International Agency for Research on Cancer has classified InP as probably carcinogenic to humans (Group 2A).<sup>(51)</sup> In a 2-year InP inhalation study, rats and mice had increased incidences of benign and malignant lung tumors.<sup>(32)</sup> In another study, rats chronically exposed to InP by inhalation developed severe pulmonary inflammation as well as alveolar proteinosis, and an increased incidence of alveolar/bronchiolar adenomas.<sup>(52)</sup> Rats exposed to InP in a 14-week inhalation study accumulated indium in the testes as well as in the lungs.<sup>(32)</sup> Testicular damage has also been observed in hamsters after repeated intratracheal instillation of InP and InAs.<sup>(53)</sup>

### Copper Indium Gallium Diselenide (CIGS), Copper Indium Diselenide (CIS)

Only a few published studies describe the toxicity of CIGS and CIS. An inflammatory response in the lungs was observed after intratracheal instillation of CIGS<sup>(54)</sup> and CIS<sup>(55,56)</sup> in rats. Because occupational exposure is likely by inhalation, studies are needed in animals at inhalation doses consistent with occupational exposure.

### Indium Trichloride (InCl<sub>3</sub>) (Soluble Indium Salt)

Acute inhalation of InCl<sub>3</sub> in rats causes an inflammatory response and a partially reversible restrictive airway response.<sup>(34)</sup> InCl<sub>3</sub> also exerts a genotoxic effect (i.e., induces micronuclei) on mammalian cells both *in vivo* and *in vitro*, possibly due to oxidative stress,<sup>(57)</sup> similar to findings in rats for InP<sup>(52)</sup> and ITO.<sup>(43)</sup> Developmental toxicity has been observed in rats, mice, and rabbits administered InCl<sub>3</sub> orally or intravenously.<sup>(58–60)</sup>

### Occupational Exposure Limits (OELs)

The NIOSH recommended exposure limit (REL) and the American Conference of Governmental Industrial Hygienists' Threshold Limit Value (TLV<sup>®</sup>) for airborne indium and compounds as elemental indium is 0.1 mg/m<sup>3</sup>.<sup>(61–62)</sup> The TLV was based primarily on lung effects observed in animals.<sup>(36,63)</sup> No permissible exposure limit for indium has been established by the U.S. Occupational Safety and Health Administration. Most countries have adopted 0.1 mg/m<sup>3</sup> as an OEL.<sup>(64)</sup> The Japan Society for Occupational Health has proposed a biological exposure limit of 3 μg/L of indium in serum<sup>(65)</sup>; the Japan Ministry of Health, Labor and Welfare has a limit of 0.0003 mg/m<sup>3</sup> for respirable indium.<sup>(66)</sup>

## METHODS

### Company Recruitment

No pre-existing list of indium-using companies was available. Hence, we identified candidate companies from Internet searches (n = 50), referrals from industry experts (n = 20), United States Geological Survey contacts (n = 9), trade association listings (n = 9), and the ThomasNet of American manufacturers (n = 1). Our search included companies in major indium application areas (e.g., soldering, thin films,

photovoltaics, semiconductor), as well as in miscellaneous applications. We initially contacted companies by letter, with follow-up by telephone or electronic mail. We queried companies to confirm indium use, and if used, obtained a general description of the indium materials used, processes, jobs, tasks, and exposure controls related to working with indium materials. Depending on the description of indium use, NIOSH conducted a site visit to assess potential for indium occupational exposure and to conduct exposure monitoring.

### Exposure Monitoring

NIOSH conducted personal breathing zone and area air sampling and analysis for indium according to NIOSH Method 7303.<sup>(67)</sup> Air samples were collected on 37-mm (diameter), 0.8- $\mu$ m (pore size) mixed cellulose ester (MCE) filters in closed-face cassettes at a nominal flow rate of 3 L/min using a SKC Model 224-PCXR4 pump (Eighty Four, Pa.) pre- and post-calibrated with a DryCal DC-Lite calibrator (Bios Int., Butler, N.J.). Samples were analyzed by Bureau Veritas North America, Novi, Mich. Filters were digested with 2.5 mL of 12.1 M hydrochloric acid at 95°C for 15 min and cooled. After the addition of 2.5 mL of 15.6 M nitric acid, the sample was heated at 95°C for another 15 min. After cooling, samples were diluted to a final volume of 25 mL. Elemental indium was determined by inductively coupled plasma, atomic emission spectroscopy (ICP-AES). Samples included at least 10% field blanks. Each analytical run included media blanks, analyst and blind spikes, and replicate analyses to ensure analytical accuracy and precision. Results were corrected for media blanks; indium was not detected in field blanks. The limit of detection (LOD) across analytical runs was 0.2–0.6  $\mu$ g/sample.

We also asked companies to provide their indium air sampling data. Although full details of air sampling and analytical methods were not always provided, typical reported conditions were 37-mm, 0.8- $\mu$ m MCE filters, a flow rate of 2 L/min and analysis by ICP-AES—conditions similar to NIOSH. Reporting limits, where provided, were 0.06–1.8  $\mu$ g/sample.

## RESULTS

We contacted 89 companies regarding indium use; 65 (73%) responded (Table I). Of the 65 responding companies, 23 did not use or process indium materials. The most frequent use of indium among the 42 remaining responding companies was sputter target bonding with indium solders ( $n = 13$  companies), followed by ITO thin film deposition ( $n = 7$ ), semiconductor fabrication of materials containing InP ( $n = 6$ ), and PV cell manufacturing ( $n = 6$ ). The 24 nonresponding companies included 11 PV companies, 2 semiconductor companies, 1 thin film coating company, and 10 companies that could not be categorized without additional information.

Data for 63 air samples (personal,  $n = 41$ ; area,  $n = 22$ ) were obtained from 10 respondent companies that used indium. These data include samples collected by NIOSH at five companies (2010–2011) and sampling data provided by

**TABLE I. Indium Applications at Contacted Companies**

	Number
Companies contacted	89
Companies not providing information	24
Companies providing some information <sup>A</sup>	65
Do not process/use indium materials	23
Perform sputter target bonding with indium solder	13
Thin film deposition of ITO onto glass, polymer, or metal substrate	7
Semiconductor fabrication with InP substrates or thin films	6
Photovoltaic cell manufacturing	6
Sputter target manufacturing (metal alloys or ITO)	4
Indium chemical manufacturing	2
Alkaline battery manufacturing	2
Other bonding with indium solder	2
Scribe, cut, deburr glass pre-coated with ITO	1

<sup>A</sup>One company had more than one indium application. ITO = indium tin oxide; InP = indium phosphide.

seven companies (2004–2011) (two companies overlapped). The 63 air samples were distributed by facility type as follows: sputter indium-containing thin films onto polymer substrates ( $n = 10$  samples, Table II), manufacture PV cells ( $n = 23$ , Table III), manufacture inorganic indium compounds ( $n = 18$ , Table IV), bond sputter targets ( $n = 3$ , Table V), manufacture compound semiconductors ( $n = 3$ , Table V), and manufacture alkaline batteries ( $n = 6$ , Table V).

### Indium Tin Oxide (ITO)

Among sampled companies, ITO was used as a TCO in one company coating polymer substrates (Table II) and in two PV companies (Table III). Worker exposure does not occur during sputter deposition of ITO as the process is fully enclosed and under vacuum; however, worker exposure can occur when ITO targets are resurfaced between runs and when chamber interiors and shields are cleaned. Light target resurfacing can be performed manually with sandpaper or Scotch-Brite pads, whereas heavier resurfacing may require a mechanical sander. NIOSH results (Company 1, Table II) indicate that pneumatic sanding of ITO targets resulted in an approximately 100-fold higher worker exposure to indium (3.1 mg/m<sup>3</sup>) than manual sanding (0.030 mg/m<sup>3</sup> and 0.018 mg/m<sup>3</sup>). A similar finding was also observed in the company-provided data (Company 1, Table II), although the difference was less pronounced. Factors likely to influence indium air concentrations during resurfacing include number of ITO targets resurfaced, use of local exhaust ventilation (LEV), and dust removal methods.

Cleaning sputter or evaporation chambers used to deposit ITO resulted in personal indium air concentrations ranging

**TABLE II. Indium Air Concentrations at Companies That Sputter Indium-containing Thin Films onto Polymer Materials**

Type	Job/Task or Area	Reported Controls	Data Source	Year	Indium Source	Dur. (min)	Air Vol. (L)	Mass ( $\mu\text{g}$ )	Air Conc. ( $\text{mg}/\text{m}^3$ )	RL ( $\mu\text{g}$ )
<b>COMPANY 1</b>										
<u>Resurface ITO Target(s)</u>										
P	Use sandpaper—manual	Non-HEPA vacuum	NIOSH	2010	ITO	7	21.2	0.64	0.030	0.6
P	Use sandpaper—manual, clean chamber interior	Non-HEPA vacuum	NIOSH	2010	ITO	86	261.3	4.7	0.018	0.6
P	Use 6" pneumatic disc sander, compressed air blow-off		NIOSH	2010	ITO	6	15.4	48	3.1	0.6
P	Use pneumatic grinder, clean sputtering equipment		Comp.	2004	ITO	42	NP	NP	9.8	NP
P	Use sandpaper and Scotch-Brite pads		Comp.	2004	ITO	30	NP	NP	0.61	NP
P	Use sandpaper and Scotch-Brite pads		Comp.	2004	ITO	15	NP	NP	2.9	NP
<u>Target Reflow</u>										
P	Set up and tend reflow		NIOSH	2010	In metal	6	18.2	<0.6	<0.03	0.6
A	Reflow room		NIOSH	2010	In metal	81	244.1	<0.6	<0.002	0.6
A	Reflow room		NIOSH	2010	In metal	120	363.8	0.88	0.002	0.6
<b>COMPANY 2</b>										
P	Clean parts, abrasive blasting of sputtered material		Comp.	2010	ITO	63	NP	NP	<0.0048	NP

A = area sample; Comp. = Company; Conc. = concentration; Dur. = duration; ITO = indium tin oxide; NP = information not provided; P = personal sample; RL = reporting limit; Vol. = volume.

from 0.072  $\text{mg}/\text{m}^3$  to 5.4  $\text{mg}/\text{m}^3$  (Companies 3 and 5, Table III). In one company, personal exposure to airborne indium while cleaning an ITO evaporation chamber was reduced 19-fold after a HEPA vacuum was attached to the scraping tool (Company 5, Table III). Two companies provided personal air samples taken during abrasive blasting of parts with sputtered residues; one sample had an indium air concentration of <0.0048  $\text{mg}/\text{m}^3$  (Company 2, Table II), the other 0.24  $\text{mg}/\text{m}^3$  (Company 5, Table III). Based on the company's description, the latter sample appears to have been taken in an inadequately ventilated room.

### Copper Indium Gallium Diselenide (CIGS)

In 2008, indium was not detected (i.e., <~0.01  $\text{mg}/\text{m}^3$ ) in personal air samples collected on two manufacturing and two maintenance technicians at a PV facility with CIG as the indium source (Company 4, Table III). In 2010, however, indium air concentrations at this facility for two maintenance technicians were 0.049  $\text{mg}/\text{m}^3$  and 0.061  $\text{mg}/\text{m}^3$ . Two area samples in 2008 were <0.013  $\text{mg}/\text{m}^3$  and <0.021  $\text{mg}/\text{m}^3$ ; eight area samples in 2010 were all <0.01  $\text{mg}/\text{m}^3$ .

### Indium Metal

Personal exposure to indium during the reflow of an indium metal target was <0.03  $\text{mg}/\text{m}^3$ ; two area samples for this

operation were <0.002  $\text{mg}/\text{m}^3$  and 0.002  $\text{mg}/\text{m}^3$  (Table II). Personal indium air concentrations in sputter target bonding with indium metal solder averaged 0.011  $\text{mg}/\text{m}^3$  (n = 3), with a maximum concentration of 0.016  $\text{mg}/\text{m}^3$  (Table V).

### Inorganic Indium Compounds

The manufacture of inorganic indium compounds involves several proprietary processes where indium materials are handled. Personal airborne exposure to indium in metal alloy production averaged 0.05  $\text{mg}/\text{m}^3$  (n = 3) (Table IV). In inorganic salts production, personal indium exposures averaged 0.08  $\text{mg}/\text{m}^3$  (n = 3) with a maximum of 0.2  $\text{mg}/\text{m}^3$  (Table IV). Two area samples in inorganic salts production averaged 0.003  $\text{mg}/\text{m}^2$ . The single worker exposure sample in paste production had a relatively low indium air concentration, 0.0038  $\text{mg}/\text{m}^3$ , with no indium detected in an area sample taken at the paste preparation work bench. Personal indium air concentrations in sputter target production (composition proprietary) ranged from 0.017  $\text{mg}/\text{m}^3$  to 0.39  $\text{mg}/\text{m}^3$ , with an average of approximately 0.1  $\text{mg}/\text{m}^3$  (n = 6).

### Indium Phosphide (InP)

Indium was not detected in a personal air sample collected on a worker running the backside thinning and polishing operations in an InP semiconductor facility, likely because

**TABLE III. Indium Air Concentrations for Two Copper Indium Gallium Diselenide (CIGS) and One Amorphous Silicon (a-Si) Photovoltaic Companies**

Type	Job/Task or Area	Reported Controls	Data Source	Year	Indium Source	Dur. (min)	Air Vol. (L)	Mass (µg)	Air Conc. (mg/m <sup>3</sup> )	RL (µg)
<b>COMPANY 3 (CIGS)</b>										
P	Clean sputter chamber, grinding	LEV hood for parts cleaning	NIOSH	2010	ITO	122	374.4	260	0.69	0.3
P	Clean sputter chamber, grinding	HEPA vacuum	NIOSH	2010	ITO	291	859.6	62	0.072	0.3
<b>COMPANY 4 (CIGS)</b>										
P	Operate roll coater		Comp.	2008	CIG	420	858	NP	<0.012	NP
P	Operate roll coater		Comp.	2008	CIG	384	753	NP	<0.013	NP
P	Clean chamber, scraping, Scotch-Brite pads		Comp.	2008	CIG	430	867	NP	<0.012	NP
P	Clean chamber, scraping, Scotch-Brite pads		Comp.	2008	CIG	435	948	NP	<0.011	NP
A	Near chamber		Comp.	2008	CIG	455	946	NP	<0.013 <sup>A</sup>	NP
A	Computer work station		Comp.	2008	CIG	472	927	NP	<0.021	NP
P	Clean chamber, scraping, chiseling	Tent enclosure, HEPA vacuum	Comp.	2010	CIG	270	447	22	0.049	0.06
P	Clean chamber, scraping, chiseling	Tent enclosure, HEPA vacuum	Comp.	2010	CIG	270	432	26	0.061	0.06
A	Inside chamber tent enclosure during cleaning		Comp.	2010	CIG	380	652	3.9	0.006	0.06
A	Perimeter walkway		Comp.	2010	CIG	375	619	0.16	0.00026	0.06
A	Entrance to tent enclosure		Comp.	2010	CIG	315	538	0.12	0.00022	0.06
A	Behind chamber		Comp.	2010	CIG	375	608	0.073	0.00012	0.06
A	Near slitter and conveyor		Comp.	2010	CIG	487	931	0.74	0.0008	0.06
A	Between conveyors		Comp.	2010	CIG	487	980	0.43	0.0004	0.06
A	Below slitter tool		Comp.	2010	CIG	487	969	0.62	0.0006	0.06
A	Workstation		Comp.	2010	CIG	466	936	0.28	0.0003	0.06
<b>COMPANY 5 (a-Si)</b>										
P	Clean sputter chamber, hand sanded target with abrasive screen, hand scraper on shields	Non-HEPA vacuum	Comp.	2011	ITO	31	62.3	9.8	0.16	0.1
P	“Sandblast” 3 shields	Canopy hood, dust collection system vented into blasting room	Comp.	2011	ITO	231	464.5	110	0.24	0.1
P	Clean sputter chamber, hand scraper on inside surfaces, wire brush to clean target	Non-HEPA vacuum	Comp.	2011	ITO	23	47.3	15	0.32	0.1
P	Clean evaporation chamber, hand scraper on inside surfaces and on a screen	Non-HEPA vacuum	Comp.	2011	ITO	97	178	970	5.4	0.1
P	Clean same evaporation chamber as above	Hand scraper attached to HEPA vacuum	Comp.	2011	ITO	53	108.8	31	0.28	0.1

<sup>A</sup>Computational error in company data corrected.

A = area sample; a-Si = amorphous silicon; CIG = copper indium gallium; Comp. = Company; Conc. = concentration; Dur. = duration; ITO = indium tin oxide; LEV = local exhaust ventilation; NP = information not provided; P = personal sample; RL = reporting Limit; Vol. = volume.

**TABLE IV. Indium Air Concentrations at a Company Manufacturing Inorganic Indium Compounds**

Type	Job/Task or Area	Data Source	Year	Indium Source	Dur. (min)	Air Vol. (L)	Mass ( $\mu\text{g}$ )	Air Conc. ( $\text{mg}/\text{m}^3$ )	RL ( $\mu\text{g}$ )
<b>COMPANY 6</b>									
<u>Metal Alloy Production</u>									
P	Technician	NIOSH	2011	In metal alloys	382	1146	3.8	0.0033	0.2
P	Technician	NIOSH	2011	In metal alloys	422	1277	110	0.086	0.2
P	Technician	NIOSH	2011	In metal alloys	369	1114	83	0.074	0.2
A	Production area	NIOSH		In metal alloys	472	1439	2.9	0.0020	0.2
<u>Inorganic Salts Production</u>									
P	Technician	NIOSH	2011	Proprietary	478	1442	6.9	0.0048	0.2
P	Technician	NIOSH	2011	Proprietary	433	1295	260	0.20	0.2
P	Technician	NIOSH	2011	Proprietary	423	1277	56	0.044	0.2
A	Production area	NIOSH	2011	Proprietary	558	1674	0.64	0.0004	0.2
A	Production area	NIOSH	2011	Proprietary	355	1074	6.2	0.0058	0.2
<u>Paste Preparation</u>									
P	Technician	NIOSH	2011	Proprietary	44	133	0.5	0.0038	0.2
A	Paste preparation bench	NIOSH	2011	Proprietary	44	132	<0.2	<0.0015	0.2
<u>Sputter Target Production</u>									
P	Technician	Comp.	2011	Proprietary	435	870	190	0.22	0.2
P	Technician	Comp.	2011	Proprietary	450	900	350	0.39	0.2
P	Technician	Comp.	2011	Proprietary	373	756	24	0.032	0.2
P	Technician	Comp.	2011	Proprietary	433	866	15	0.017	0.2
P	Technician	Comp.	2011	Proprietary	504	1008	51	0.051	0.2
P	Technician	Comp.	2011	Proprietary	500	1000	20	0.020	0.2
A	Production area	Comp.	2011	Proprietary	502	1004	3.7	0.004	0.2

A = area sample; Comp. = Company; Conc. = concentration; Dur. = duration; P = personal sample; RL = reporting limit; Vol. = volume.

**TABLE V. Indium Air Concentrations in Miscellaneous Industries**

Type	Job/Task or Area	Data Source	Year	Indium Source	Dur. (min)	Air Vol. (L)	Mass ( $\mu\text{g}$ )	Air Conc. ( $\text{mg}/\text{m}^3$ )	RL ( $\mu\text{g}$ )
<u>Sputter Target Bonding Services</u>									
<b>COMPANY 7</b>									
P	Technician	Comp.	2009	In metal (solder)	540	NP	NP	0.016	NP
<b>COMPANY 8</b>									
P	Technician	NIOSH	2010	In metal (solder)	416	1265	9.5	0.0075	0.6
P	Technician	NIOSH	2010	In metal (solder)	467	1387	13	0.0094	0.6
<u>Compound Semiconductor Manufacturing</u>									
<b>COMPANY 9</b>									
P	Technician, thinning and polishing	NIOSH	2011	InP	471	1439	<0.3	<0.0002	0.3
A	At back grinder, LEV, enclosure	NIOSH	2011	InP	464	1410	0.45	0.0003	0.3
A	At polisher (in laboratory hood)	NIOSH	2011	InP	467	1422	<0.3	<0.0002	0.3
<u>Alkaline Battery Manufacturing</u>									
<b>COMPANY 10</b>									
P	Process Operator	Comp.	2011	Proprietary	300	753.4	<1.8	<0.0024	1.8
P	Process Operator	Comp.	2011	Proprietary	17	42.59	<1.8	<0.042	1.8
P	Process Operator	Comp.	2011	Proprietary	300	756	<1.8	<0.0024	1.8
A	Production Area	Comp.	2011	Proprietary	180	448.7	<1.8	<0.0040	1.8
A	Production Area	Comp.	2011	Proprietary	180	450.5	<1.8	<0.0040	1.8
A	Production Area	Comp.	2011	Proprietary	180	451.6	<1.8	<0.0040	1.8

A = area sample; Comp. = Company; Conc. = concentration; Dur. = duration; LEV = local exhaust ventilation; NP = information not provided; P = personal sample; RL = reporting limit; Vol. = volume.

the process was enclosed and under LEV (Table V). Indium was detected in an area sample at the back grinder enclosure ( $0.0003 \text{ mg/m}^3$ ), but not in an area sample at the polishing station (Table V).

### Alkaline Battery Manufacturing

Personal and area indium air concentrations in alkaline battery manufacturing were all nondetectable (Table V).

## DISCUSSION

Occupational exposure to indium can occur at levels that exceed current recommended occupational exposure limits for certain processing and maintenance activities in industries that manufacture or use indium-containing materials. The physical state and composition of the indium material, methods of handling, and use of controls are key factors that affect exposure.

Published air sampling data for occupational indium exposure is limited, and except for one U.S. facility,<sup>(10,68)</sup> has been collected largely in Asia.<sup>(48,69,70)</sup> The published data clearly indicate that, if not well controlled, indium exposure can exceed recommended exposure limits in the manufacturing of ITO sputter targets, in the handling of indium oxide and indium hydroxide, and in reclaiming indium from recycled materials.<sup>(10,68,69)</sup> Little has been known about indium exposure to workers in downstream applications of ITO and other indium materials. The results presented here begin to address this data gap by identifying other activities that are likely (if not well controlled) and unlikely to result in worker exposure to indium. This information may also be useful for generating exposure scenarios under REACH.<sup>(71)</sup>

Activities with an increased potential for indium exposure include the manufacturing of inorganic indium compounds, ITO sputter target resurfacing between deposition runs, cleaning sputter chamber interior walls and shields, and abrasive blasting to remove residues on sputter chamber parts. Indium materials in these processes are either powders or ceramics with the potential to release aerosols during handling or mechanical disturbance. NIOSH data suggest that it may take only 15 min of pneumatically sanding on an ITO target to reach  $0.1 \text{ mg/m}^3$  as an 8-hr TWA (Company 1, Table II). The sampling data also indicate that measures such as hand-tool mounted LEV systems, portable LEV systems, and containment effectively reduce exposure. The sampling data presented here represent potential indium exposure without regard to respirator use, a control measure frequently used by workers at these companies in lieu of or in addition to engineering controls.

A limitation of this work is that for company-provided data we were not always provided with complete information on tasks performed, exposure controls, and sampling and/or analytical conditions. We checked concentration computations for the 72% of company air samples where analyte mass and air volume were provided.

Activities with low indium exposure included the use of indium metal solders, reflow of indium metal targets, alloying of indium metal with other metals, fabrication of InP-based semiconductor devices, and preparation of solder pastes. If mechanical sanding is performed on indium metal or its alloys, thereby increasing the potential for aerosol generation, air sampling should be performed. The control of indium exposure in InP-based semiconductor facilities is linked to the need to strictly control exposure to phosphine, which can be released when InP hydrolyzes upon exposure to moisture in the air.<sup>(72)</sup> While InP is a crystalline material that can produce aerosols when machined, the imperative to prevent phosphine exposure has led to the use of strict containment, LEV, wet processing, and supplied air respirators in the compound semiconductor industry.

Exposure assessment for clinical evaluations and epidemiological studies has relied primarily on indium in serum, plasma, and/or urine.<sup>(10,29,30,48–50,70,73–80)</sup> Hoet et al.<sup>(30)</sup> found no correlation between indium in air and indium in plasma or urine in workers at an indium ingot production plant. Nakano et al.<sup>(49)</sup> found that workers who had been away from indium exposure for approximately five years on average had serum indium levels comparable to currently exposed workers and significantly higher than unexposed workers. The lengthy clearance of indium compounds in the lungs in animals and the apparent persistence of indium in formerly exposed workers are indicators that serum indium levels may better reflect chronic rather than recent exposure. For substances with long half-lives in the body (i.e., several weeks or more), fluctuations in air concentrations, such as those related to short-term high exposure tasks, are physiologically dampened (have less variability) in the body.<sup>(81,82)</sup> Serum indium, while useful for assessing body burden, is unlikely to capture the timing and intensity of highly variable short-term exposures and, therefore, may not be as useful as air sampling for identifying high exposure tasks.

## CONCLUSION

Occupational hygienists should be aware that the manufacture and use of indium materials can result in indium air concentrations that exceed the NIOSH REL. Air sampling for indium exposure should be conducted whenever indium-containing aerosols are generated in order to establish appropriate levels of engineering controls and respiratory protection. Research is needed to evaluate the adequacy of the current REL for protecting workers from indium-related disease and whether indium exposure limits, including biological exposure limits, should apply to all indium compounds or be compound-specific.

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