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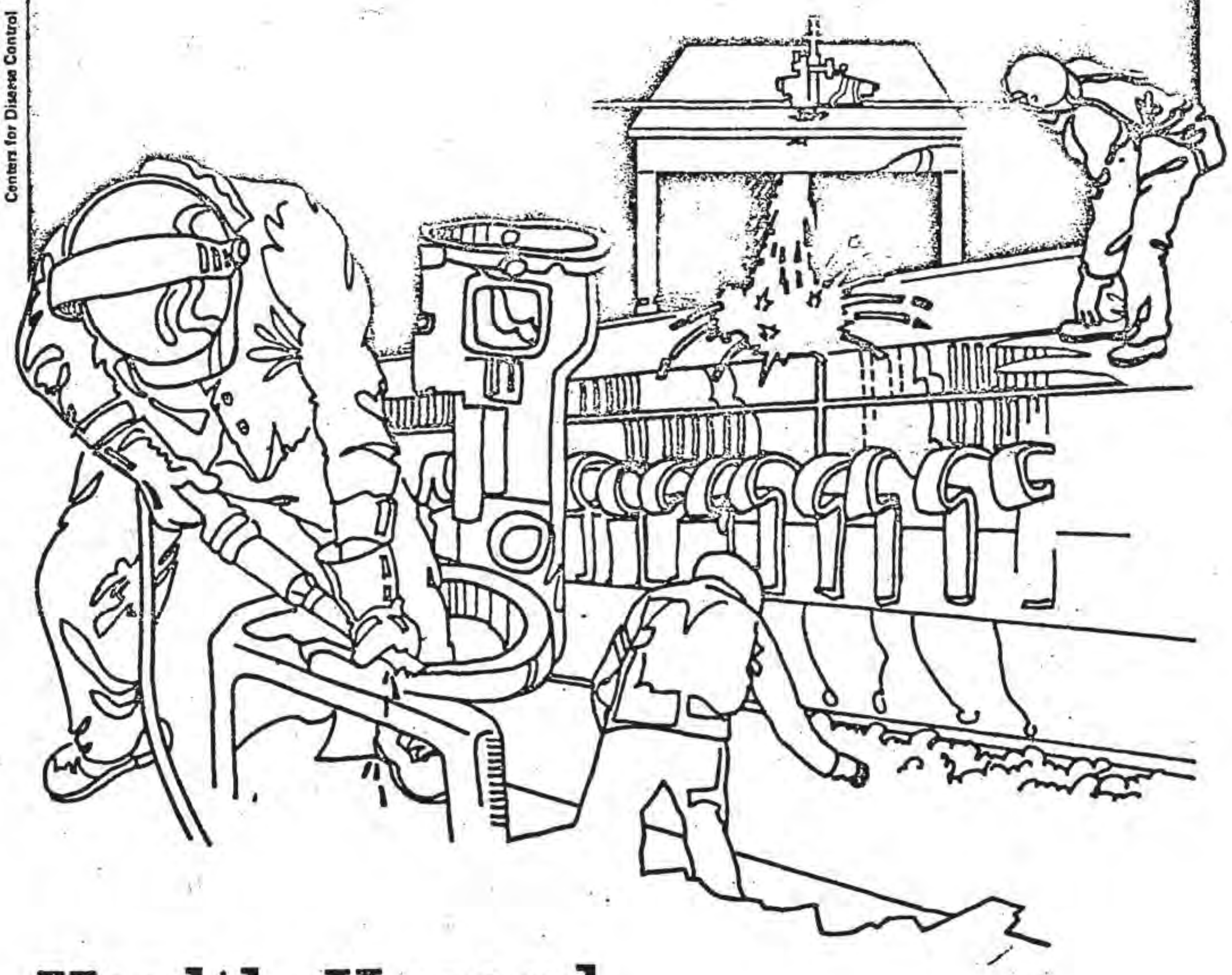

Health Hazard Evaluation Report

HETA 82-102-1464
UNIVERSITY OF CINCINNATI
CINCINNATI, OHIO

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

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UNIVERSITY OF CINCINNATI
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I. SUMMARY

On January 2, 1982, the National Institute for Occupational Safety and Health received a request to evaluate potential exposures of students and faculty to chemicals/gases used in the laboratories of the Department of Electrical and Computer Engineering, University of Cincinnati.

A NIOSH industrial hygienist made an initial site visit to the facility on February 3, 1982. Because a number of the processes to be evaluated were operated intermittently or were not to be operational for several months, three follow-up visits were made over the following 18 month period to determine airborne levels of substances used in the manufacturing of semi-conductors.

During the initial clean/oxide strip procedure, measurements of airborne levels of hydrochloric acid, and nitric acid were between 0.14 to 0.27 mg/m^3, with "trace" quantities of hydrofluoric acid detected. The NIOSH recommended and OSHA standards for nitric and hydrofluoric acids are 5.0 and 2.5 mg/m^3, respectively. One sample for acetone was collected, and reported below the analytical limit of detection.

During photolithography, measurements of airborne levels of substances used in the photo-resist operation and subsequent equipment cleaning included benzene, toluene, xylene, and acetone, plus nitric, phosphoric, sulfuric, and hydrochloric acids. Of 17 samples collected, six were above the detectable limit but well below applicable criteria; xylene at 2.3 to 19.2 mg/m^3 (NIOSH recommended and OSHA standards at 435 mg/m^3), acetone at 1.55 mg/m^3 (NIOSH - 590 mg/m^3, OSHA standard - 2400 mg/m^3), nitric acid at 0.12 mg/m^3, and sulfuric acid at 0.23 mg/m^3 (NIOSH recommended and OSHA standards at 1.0 mg/m^3).

Of four measurements of airborne hydrochloric acid collected during epitaxial growth, three were below the analytical limit of detection, and one was reported at 0.82 mg/m^3. During subsequent cleaning of glassware, one area sample for hydrochloric acid was measured at 4.4 mg/m^3. During preferential etching, airborne determinations of hydrazine in working areas were below the analytical limit of detection (0.02 mg/m^3). Airborne levels of isopropanol determined during polysilicon etching were also below detection levels in working areas (less than 2.6 mg/m^3). All samples collected for phosphine and diborane during chemical deposition were below detection limits, as were levels of arsenic and total fluorides collected during the gallium arsenide and the ion implantation process. No levels of ionizing radiation were above "background" levels during ion implantation. Asbestos was detected in the walls of the fumehoods at 20-50% chrysosile.

NIOSH determined that a health hazard did not exist for the students and faculty at the University of Cincinnati Semi-conductor laboratory during the time of the environmental evaluation. However, certain conditions exist such as the use of extremely hazardous substances, insufficient exhaust ventilation at certain fume hoods, and exhausting of toxic substances to the roof area, which may pose significant health hazards. Recommendations for reducing these potential health hazards are made in Section VII of this report.

KEYWORDS: SIC 8221 (Colleges and Universities) Semi-conductor, Acetone, Arsenic, Asbestos, Benzene, Diborane, Fluorides, Hydrazine, Hydrochloric acid, Hydrofluoric acid, Isopropanol, Nitric acid, Phosphoric acid, Sulfuric Acid, Toluene, Xylene, Ionizing radiation.

II. INTRODUCTION

NIOSH was requested to evaluate potential health hazards in the Department of Electrical and Computer Engineering, University of Cincinnati Semi-conductor Laboratory, Cincinnati, Ohio. Although no ill-health effects were reported, it was determined that the number and types of potentially hazardous chemicals used in the laboratories posed a significant potential for health hazards to the students and faculty.

An initial walk-through survey of the facility was conducted on February 3, 1982. At that time, the various laboratory operations were observed and a list of chemicals was obtained. Because a number of processes are operated intermittently, and some were not scheduled for operation for several months following the initial visit, follow-up surveys were conducted on April 12-16, 1982, June 22-24, 1983, and July 14, 1983. The purpose of the investigations was to document chemical exposures resulting from the routine laboratory procedures such as wafer cleaning and photolithography (which comprise approximately 90% of the laboratory activities) involving the more common solvents and acids. Also, environmental sampling was conducted during some of the non-routine laboratory procedures such as preferential etching and chemical deposition which involve relatively uncommon chemicals such as phosphine, diborane, and hydrazine. The surveys were designed to determine the extent of exposures to numerous process chemicals used within the semi-conductor laboratory, rather than investigating any causal relationships between exposures and ill-health effects. Letters were forwarded on February 8, 1982, and April 30, 1982, which provided interim information and recommendations for potential exposure reduction. Table I presents a listing of the laboratory processes and substances monitored during the evaluation.

III. BACKGROUND

The Solid State Electronics Laboratory in the Department of Electrical and Computer Engineering at the University of Cincinnati includes a 4100 square foot clean room complex consisting of 8 rooms for microelectronic processing and evaluation and over 5000 square feet of non-clean laboratory space devoted to research in solid state and optical electronics. Adjacent to these laboratory areas is a machine shop (1800 square feet), staffed by machinists, who support the laboratory activities. Laboratory operation is maintained by faculty-supervised technicians and graduate student assistants. Twenty-five to 30 senior students plus graduates and technicians use these facilities.

The pressurized clean room complex is built on an elevated floor with removable panels and contains over 170 linear feet of "clean" benches. Filtered air and filtered gases are available at fume hoods throughout the laboratory. The complex is separately heated and cooled in order to maintain the controlled environment. The complex allows for fabrication of silicon integrated circuits including computerized mask fabrication, photolithography, diffusion, ion implantation, metalization, bonding, plasma etching, vaccuum deposition, sputering, and epitaxial growth.

IV. EVALUATION DESIGN AND METHODS

Table II presents sampling and analytical methodologies for the various substances measured during the survey. Environmental monitoring was conducted while a student or instructor performed one or more of the laboratory tasks. For most tasks, breathing zone samples were obtained by attaching the personal sampling pump to the individual and obtaining the sample from their breathing zone for the duration of the process. General area samples were obtained by placing the monitors in the general vicinity of the process. In most instances, the device was attached to the sash on the appropriate fume hood and/or a central location to represent potential exposures to co-workers. The environmental evaluation was somewhat limited because most tasks were conducted by a single individual, and in some instances lasted for a very short period of time. Also, the nature of the work did not lend itself to repeated, extended sampling. Therefore, sampling results should be interpreted with caution; results may only approximate the actual exposure situations, reflecting only the conditions present at the time of the survey. Detector tubes, which gave instantaneous readings, were used in a number of locations. Following is a description of the processes included in the NIOSH evaluation.

Initial Clean/Oxide Strip

This procedure may be conducted several times during wafer processing, and is considered the most common of all the laboratory procedures. The purpose is to remove all foreign matter from the surface of the silicon wafer. Cleaning is conducted inside a fume hood. The primary chemicals used are hydrochloric acid, hydrofluoric acid, nitric acid, heated acetone, hydrogen peroxide, and ammonium hydroxide. "Q-Tips" dipped in trichloroethylene may also be used to remove heavy residues. The operation usually takes from 20 to 40 minutes to complete. Environmental air samples were collected for hydrochloric, nitric, and hydrofluoric acids, and for acetone.

Photolithography

The Photolithography process is conducted in the "Gold Room", named for the yellow lighting used due to photoresist sensitivity to ultraviolet light exposure. Photolithography involves pattern formation on silicon wafers. Instrumentation includes wafer spinners, wafer aligners, precision masks, and wafer developers. The commercial photoresist is applied while the wafer is spinning at high speed. Acetone and xylene are used as general cleaning solvents during this operation, and the photoresists are reported to contain mixtures of organic solvents (benzene, toluene, and xylene). After application, the wafers are baked at low temperature, then microscopically aligned to a mask pattern which is printed by exposing the unmasked photoresist with ultra-violet light. The unexposed photoresist is developed, dried, and baked. Personal and area environmental samples were collected for acetone, benzene, toluene, and xylene (substances contained in the photoresists), plus hydrochloric, phosphoric, and hydrofluoric acids (substances used for cleaning purposes).

Epitaxial Growth/Bell Jar Clean

The instrumentation for epitaxial growth includes an induction heater, quartz bell jar, wafer holder, and a gas dispensing apparatus; all part of the "system 800". The wafers are heated to approximately 800° C and exposed to hydrogen which cleans and etches the surface of the wafer. Gases which may be used in the subsequent deposition process include hydrogen chloride, silane, phosphine, dichlorosilane, diethyl telluride, tetrachlorosilane, arsine, ammonia and diborane. During the time of the environmental survey, hydrogen chloride and silane were used. Due to the non-availability of a sampling method for silane, environmental monitoring was limited to hydrogen chloride.

Following epitaxial growth, the bell jar is cleaned using hydrogen fluoride, hydrogen chloride, and nitric acid. Environmental monitoring was conducted for these substances for the duration of the process. Short-term detector tube samples were also obtained.

Preferential Etch

A portion of the preferential etch procedure involves submersion of the silicon wafer in a heated bath containing hydrazine. Approximately one liter of the solution is heated to 100° C on a hot plate located in a laboratory fume hood. The process varies in length of time depending on the extent of etch required (etch rate of 0.75 micrometer/min.). A cold water condensation unit is placed on the hydrazine container during the process to minimize vapors, but vapors are liberated when the wafers are immersed, examined, or inspected. Personal and area environmental monitoring plus detector tube sampling was conducted for hydrazine during the process. Personal protective equipment used by the operator during this procedure included a dual cartridge organic vapor respirator, rubber gloves and apron, goggles, and face shield.

Low-Temperature Chemical Deposition

Chemical vapor deposition is conducted in a small reactor located within a fume hood. This process imparts insulating, conducting, or semi-conducting layers on the silicon wafers. Air samples were collected for phosphine and diborane during this operation from the general area and from the operator. Also, detector tubes were used to check for phosphine leakage from the carrier lines and at the pressurized cylinder.

Polysilicon Etching

A solution of isopropanol, potassium hydroxide, and de-ionized water is heated to 75°C within a laboratory hood, and the polysilicon wafers are submerged in the solution for approximately 20 minutes. Personal and general area sampling was conducted for isopropanol during this procedure.

Gallium Arsenide Processing

Gallium arsenide is used under heat and negative pressure for the GaAs process. Specifically, the concern was for the thermal annealing of the wafers after ion implantation and the potential exposures to arsenic while conducting the operation. The negative pressure within the process and an exhaust hood "canopy" located overhead act to control exposures. Environmental air samples collected for arsenic were obtained from the process operator and in the vicinity of the process.

Ion Implantation

Wafers may be doped with selected impurities by using a high energy ion beam. The deposition pattern may be determined by masking, and the impurity depth may be determined by the ion energy. Common process materials include boron trifluoride, diborane, phosphine, arsine, arsenic, and hydrogen. A vapor source generates a beam of neutral atoms (depositant) that are bombarded with a beam of accelerated electrons. During the time of the environmental evaluation, the ion implantation process was utilizing boron trifluoride as the dopant, with the ion implanter operated at 100, 150, and 160 KeV. The concern was for leakage of the dopants, and the potential for "stray" ionizing radiation. Samples for total fluorides were obtained at several locations within the area of the ion implanter. A "Mini-Conrad" portable survey meter (model 3032) was used throughout the area of the ion implanter during its operation to determine the potential for stray ionizing radiation.

Ventilation

The ventilation system within the "clean area" of the laboratory is equipped with a "panic" switch which doubles the airflow out of the fume hoods and allows additional make up air into the rooms. Four separate systems comprise the exhaust ventilation network. A brief survey of the laboratory fume hoods was conducted to determine if performance was satisfactory, as compared to American Conference of Governmental Industrial Hygienists recommendations.[1] Face velocities were measured on most fume hoods in the clean room area. A Kurz® velometer was used to determine velocities at central points of pre-measured grids on each hood, and the mean of these readings was used as to determine the average face velocity. Face velocities on the hoods in the crystal growth room were measured while the booster exhaust ventilation was on.

Asbestos

The interior walls of three of the fume hoods in the clean room complex are showing signs of wear due to extensive exposures to corrosive fumes. Bulk samples of the materials were obtained and analyzed for percent and type asbestos.

V. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Criteria Documents and recommendations, 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV's), and 3) the U.S. Department of Labor (OSHA) occupational health standards. Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLV's usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended standards, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet only those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

Table III presents a listing of sampled substances along with brief summaries of their toxicities.

VI. RESULTS AND DISCUSSION

Tables IV through XI present results of the environmental survey by laboratory process. These results represent airborne concentrations of chemicals used for the various laboratory processes under the conditions of the survey. Because only one student or faculty member was involved in a particular process, sampling was usually limited to one personal sample collected over the duration of the process. When practical, multiple area samples were collected. As indicated in the tables, no exposure concentrations were measured above the NIOSH recommended or OSHA federal standards. In most instances, the concentrations were well below these criteria. Also, as noted earlier, most of these evaluation criteria are based upon a continuous 8-hr exposure, and because the processes were usually of relatively short duration the measured exposure concentrations, if averaged over a full work shift, would be considerably lower. Following is a discussion of the survey results by laboratory process.

Initial Clean/Oxide Strip

During the initial clean/oxide strip procedure air sampling was conducted for nitric, hydrochloric, and hydrofluoric acids, and acetone (Table IV). All airborne concentrations of the acids were less than (<) 10% of their respective evaluation criteria. Also, the cumulative calculation for multiple exposure (prescribed for substances which elicit similar toxicities) was 0.08. A cumulative calculation of 1.0 indicates an overexposure situation.[2] One personal sample collected for acetone was the analytical limit of detection, which was 0.008 mg/m^3, air volume adjusted.

Photolithography

During the photolithography operation, air sampling was conducted for benzene, toluene, xylene, and acetone, plus nitric, phosphoric, sulfuric, and hydrofluoric acids (Table V). As is the typical case in most of the operations, one worker was involved in the process, which limited the evaluation to one personal sample per substance. Two general area samples were collected per compound. For solvents, area samples were collected at the photoresist spinner, where solvents are applied to wafers in an enclosed process (not exhausted at the time of the survey), and at the photoresist ovens where wafers are baked following the photolithographic process. All solvent exposures were either below the analytical limit of detection (< 0.13 mg/m^3, air volume adjusted, for benzene and < 1.30 mg/m^3 for toluene) or well within their respective evaluation criteria. The highest solvent exposure measured was the xylene area sample collected at the spinner, at 19.2 mg/m^3. Two samples collected for acids were above the analytical limits of detection; one personal sample for sulfuric acid measured at 0.23 mg/m^3, and one area sample, collected for nitric acid above the fume hood at 0.12 mg/m^3.

Epitaxial Growth

During the epitaxial growth procedure, environmental sampling was conducted for hydrogen chloride (Table VI). Following this procedure, equipment cleaning is necessary using hydrogen chloride (HCl), and hydrogen fluoride (HF). Personal and area samples were collected for HF during the HCl etching phase of the process and during equipment clean-up, which used HCl and HF. Approximately 20 minutes into the process, a leak developed and detector tube readings indicated airborne levels of HCl at 50 to 100 ppm directly in front of the process (work area). The System 800 is an enclosed process, housing a bell jar under vacuum in which the actual etching procedure takes place. In the event of a leak, the system is locally exhausted. However, at the time of the HCl leak, which reportedly is very rare, it was discovered that the exhaust system was actually operating in reverse, thus forcing contaminated air into the work area. The system was shut down and repaired, and environmental sampling was then continued. Results for the initial HCl sample were below the analytical limit of detection (0.14 mg/m^3, air volume adjusted). The second sample which included the subsequent glassware cleaning procedure, indicated an average airborne level 0.82 mg/m^3; well below recommended exposure guidelines. The area sample obtained from the fume hood sash while glassware was being cleaned was reported at 4.41 mg/m^3. The sample for HFL was reported as a "trace" concentration (above the limit of detection, yet below the level of quantitation). Although the cleaning process is conducted inside a fume hood, the worker was observed placing his head inside the hood several times during the cleaning process, which undoubtedly contributed to his exposure.

Preferential Etching

One personal and three area samples were collected for hydrazine during the preferential etching operation (Table VII). Conducted in a fume hood, a solution containing hydrazine is heated and a silicon wafer is immersed in the solution. The personal and the area sample, collected on the outer sash of the hood, were below the analytical limit of detection (0.02 mg/m^3, air volume adjusted). The area sample collected inside the fume hood was reported at 4.4 mg/m^3. While the condensation unit placed over the container of hydrazine limits vapor escape, release is possible during placement or examination of the silicon wafer. One area sample was placed on the exhaust port on the roof. Although results were below the analytical limit of detection, a detector tube was used simultaneous to wafer removal and one stroke caused discoloration, indicating the presense of hydrazine.

Polysilicon Etching

One personal sample, and one area sample collected for isopropanol located on the fume hood sash, were below the analytical limit of detection (Table VIII). One "source" sample collected inside the fume hood during the operation was reported at 45.9 mg/m^3.

Low Temerature Chemical Deposition

All samples collected for phosphine and diborane during low temperature chemical deposition were below the analytical limit of detection (Table IX), including one collected inside the fume hood where the operation was conducted. Detector tube sampling gave no indication of leaks at any point near the process, nor within the fume hood.

Gallium Arsenide Processing

All personal and area samples collected for arsenic during gallium arsenide processing were below the analytical limit of detection (Table X).

Ion Implantation

To measure airborne concentrations of boron trifluoride, seven general area samples were collected for total fluorides. Although a number of other compounds may be used for the ion implant process (ie. diborane, phosphine, arsine, arsenic, and hydrogen phosphorus pentafluoride, silane), airborne levels of fluorides would indicate the potential and source of exposures to all substances used. Two samples were collected during the preliminary set-up of the process near the generation chamber, and five additional samples were collected while the process was being conducted. All results were below the analytical limit of detection, which was generally < 0.025 mg/m^3 (air volume adjusted).

The concern for exposure to ionizing radiation was investigated using a Mini-Conrad® radiation survey meter. All areas of the ion-implant instrument were monitored during the various phases of the procedure. No levels of ionizing radiation were above background levels, as determined in other areas of the semi-conductor laboratory.

Ventilation

Air flow measurements were made on several of the laboratory fume hoods and evaluated against the ACGIH guidelines. Obvious deficiencies were observed on two of the hoods (air flow from within the hoods to the outside, as demonstrated with smoke tubes). As a general rule for laboratory-type fume hoods, the ACGIH recommends an average hood entry face velocity of 125-200 feet/minute (fpm) and a minimum face velocity of 100 fpm to ensure that no contaminants escape into the work areas. Following is a discussion of each hood monitored during the survey.

Crystal Growth Room; Hood # "1 of 5"

This fume hood contained pressurized cylinders of ammonia, phosphine, germane, diborane, and silane. Airflow into the hood, with the sash completely open, ranged from -20 fpm to 40 fpm. The outward flow of air was verified with smoke tubes, and is a result of a cross draft (measured at 100 fpm) created by the "System 800". No outward flow was detected with the sash lowered to 4" from the bottom, and at this position, the face velocity averaged 60 fpm.

Crystal Growth Room; Hood # "2 of 5"

The "System 300" is located within this hood. With the sash completely open, the average face velocity was 36 fpm. However, with the sash in the working position (6" from the bottom) the face velocity averaged 150 fpm.

Crystal Growth Room; Hood # "3 of 5"

Solvents used in this hood for several purposes included methanol, trichloroethylene, isopropanol, and acetone. Face velocity averaged 126 fpm with the sash fully opened.

Crystal Growth Room; Hood # "4 of 5"

This hood contained phosphine and silane compressed gas cylinders, plus HCL. Face velocity averaged 115 fpm.

During face velocity testing of hoods within the Crystal Growth Room, variable flows were observed depending on the positioning of sashes of other hoods. If sashes were lowered on neighboring hoods, face velocities were significantly increased. This could be important for assuring adequate air flow when conducting processes involving toxic substances.

Gold Room; South Hood

Chemicals used in processes conducted in this fume hood included nitric, hydrofluoric, hydrochloric, sulfuric, and phosphoric acids, plus acetone, trichloroethylene, methanol, and isopropanol. Face velocities ranged from -20 to 130 fpm; averaging 68 fpm. A cross draft (right to left) caused the negative air flow, as demonstrated by smoke tubes. The draft was being generated from a nearby "clean table".

Gold Room; Northeast Hood

The average face velocity for this hood was 77 fpm. This hood receives only occasional use for processes utilizing various solvents.

Ion Implantation

With the sash completely open, face velocities averaged 62 fpm. Process chemicals used in this hood include nitric, sulfuric, and acetic acids, plus hydrazine, trichloroethylene, acetone, and potassium hydroxide.

Room 904B

Face velocities averaged 77 fpm with the sash completely open. Process chemicals used within this hood include phosphoric, hydrochloric, and nitric acids, plus acetone and trichloroethylene.

Room 904F

Acetone and trichloroethylene are used within this hood. With the sash opened, face velocities averaged 46 fpm.

Asbestos

Analysis of the three bulk samples collected from the internal walls of fume hoods showing signs of deterioration indicate an asbestos content of 20 to 50% crysotile. While it would be expected that any fibers liberated from this source would be exhausted through the hood, caution should be exersized if large portions of the walls become dislodged and fall to the bench area of the hood. If removal and replacement of these walls is considered practical, only an experienced contractor familiar with asbestos removal should be considered.

VII. CONCLUSIONS

As is apparent from the presented data, airborne concentrations of the sampled substances were within their respective evaluation criteria. However, there are areas of concern which should receive attention.

Detector tube sampling for hydrazine on the roof near the fume hood exhaust indicated the presence of this substance. While this probably presents little hazard potential for the students and faculty of the semi-conductor laboratory, University maintenance personnel were observed on the roof on several occasions. Furthermore, the extreme toxicity of hydrazine deserves special attention during its use within the laboratory, including personal protective equipment, and appropriately displayed warnings.

Deficient face velocities, in addition to cross drafts creating negative air flow patterns, create a significant potential for exposure to substances used in the laboratory.

VIII. RECOMMENDATIONS

The following recommendations are based on results of the environmental survey and observations made during the evaluation. Several of these recommendations were prescribed and subsequently implemented during the course of the site visits.

1. To lower the potential for solvent exposures during the photolithography operation, the photoresist spinner should be locally exhausted.
2. To eliminate cross drafts which reduce effectiveness of the fume hoods in the Gold Room, the ventilation for the "clean room" table should be turned off when not in use.
3. The waste recepticle in the Gold Room used to dispose of solvent soaked cloths should be covered and emptied daily, thus reducing solvent emissions from this source. Commercial solvent waste cans would be appropriate for this application.
4. Solvents should not be used or stored in the same fume hoods as acids, and solvents should be removed from fume hoods during acid cleaning of glassware.
5. A sign should be posted on the door leading to the roof displaying a warning as to the potential for exhausting toxic vapors from the fume hoods. A contact within the laboratory with telephone and room number should appear, preferably a person(s) knowledgable on the types of procedures and chemicals used in the fume hoods.

6. The local exhaust ventilation on the System 800 should be re-evaluated.

7. Due to the extreme toxicity of hydrazine and the conditions of its use within the laboratory, attempts should be made at substitution with a less toxic substance.

8. Students and faculty should be made aware of the asbestos content of the fume hood interior walls. If the walls are removed and replaced, a contractor knowledgable in asbestos removal procedures should be retained.

9. The laboratory fume hood exhaust ventilation system should be re-evaluated and designed to provide at least 125 fpm average face velocities at each hood. Also, sashes should be lowered when a hood is not being used.

IX. REFERENCES

1. American Conference of Governmental Industrial Hygienists. ACGIH industrial ventilation: a manual of recommended practice. ACGIH Committee on Industrial Ventilation: Lansing, Michigan, 1982.

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X. AUTHORSHIP AND ACKNOWLEDGEMENTS

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1. University of Cincinnati
2. NIOSH, Region 5
3. OSHA, Region 5

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

TABLE I

SAMPLED SUBSTANCES BY LABORATORY PROCESS

University of Cincinnati
Cincinnati, Ohio
HETA 82-102

July 1983

Process	Substances	(Personal)	(Area)
Initial Clean/Oxide Strip	Nitric Acid	1	1
	Hydrogen Chloride	1	1
	Hydrogen Fluoride	1	1
	Acetone	1	0
Photolithography	Benzene	1	2
	Toluene	1	2
	Xylene	1	2
	Acetone	0	1
	Nitric Acid	0	1
	Phosphoric Acid	1	1
	Hydrogen Fluoride	0	1
Epitaxial Growth	Hydrogen Chloride	2	4
Bell Jar Clean (following epitaxial growth)	Hydrogen Fluoride	1	0
	Hydrogen Chloride	1	0
	Nitric Acid	1	1
Preferential Etch	Hydrazine	1	3
Polysilicon Etching	Isopropanol	1	2
Chemical Deposition	Diborane	1	2
	Phosphine	1	3
Ion Implantation	Fluorides	0	7
Gallium Arsenide Processing	Arsenic	1	3

TABLE II

SAMPLING AND ANALYTICAL METHODOLOGY

University of Cincinnati
Cincinnati, Ohio
HETA 82-102

July 1983

Substance	Collection Device	Flow Rate (lpm)	Analysis	Detection Limit mg./Sample	Reference[3]
Acetone	charcoal	0.2	GC FID	0.01	NIOSH P&CAM 339
Arsenic	AA filter	2.0	AA Spectroscopy	0.0003	NIOSH S-341
Asbestos	Bulk	---	PL Microscopy	---	NIOSH Labs
Benzene	Charcoal	0.2	GC FID	0.001	NIOSH P&CAM 127
Diborane (Boron)	Charcoal	1.0	Emission spectroscopy	0.026	NIOSH P&CAM 341
Fluorides	AA filter	2.5	Specific Ion Electrode	0.010	NIOSH P&CAM 212
Hydrazine	Silica gel	0.2	GC FID	0.001	NIOSH P&CAM 248
Hydrochloric Acid	Silica gel	0.2	Ion Chromatography	0.004	NIOSH P&CAM 310
Hydrofluoric Acid	AA filter	2.5	Ion Electrode	0.01	NIOSH P&CAM 212
Isopropanol	Charcoal	0.2	GC FID	0.01	NIOSH S-65
Nitric Acid	Silica gel	0.2	Ion Chromatography	0.004	NIOSH P&CAM 339
Phosphine	Silica gel	0.2	Spectrophotometry	0.001	NIOSH S-332
Sulfuric Acid	Silica gel	0.2	Ion Chromatography	0.004	NIOSH P&CAM 339
Toluene	Charcoal	0.2	GC FID	0.01	NIOSH P&CAM 127
Xylene	Charcoal	0.2	GC FID	0.01	NIOSH P&CAM 127

TABLE III

EVALUATION CRITERIA

University of Cincinnati
Cincinnati, Ohio
HETA 82-102

July 1983

Substance	Evaluation Criteria (mg/m³) NIOSH[4]	OSHA[5]	ACGIH[2]	Primary Health Effects[6]
Acetone	590	2400	1780	May produce a dry, scaly, and fissured dermatitis after repeated exposure. High vapor concentrations may irritate the conjunctiva and mucous membranes of the nose and throat, producing eye and throat symptoms. In high concentrations, narcosis is produced, with symptoms of headache, nausea, light headedness, vomiting, dizziness, incoordination, and unconsciousness.
Arsenic	0.002	0.01	0.2	The NIOSH recommended standard was designed to protect workers from the possible development of lymphatic and respiratory arsenic-related cancer. This relationship has been suggested by numerous studies of working populations.

Continued

Table III continued

Substance	Evaluation Criteria (mg/m³) NIOSH[4]	OSHA[5]	ACGIH[2]	Primary Health Effects[6]
Benzene	LFL**	30	30	Exposure to the liquid and vapor may produce primary irritation to skin, eyes, and upper respiratory tract. Acute exposure to benzene results in central nervous system depression. Headache, dizziness, nausea, convulsions, coma, and death may result. Death has occurred from large acute exosure as a result of ventricualr fibrillation, probably caused by myocardial sensitization to endogenous epinephrine. Chronic exposure to benzene is well documented to cause blood changes. Benzene is basically a myelotoxic agent. Erythrocyte, leukocyte, and thrombocyte counts may first increase, and then aplastic anemia may develop with anemia, leukopenia, and thrombocytopenia. The bone marrow may become hypo- or hyper-active and may not always correlate with peripheral blood. Recent epidemiologic studies along with case reports of benzene related blood dyscrasias and chromosomal aberrations have led NIOSH to conclude that benzene is leukemogneic.
Diborane	--	0.1	0.1	Although irritating to skin, Diborane is the least toxic of the boron hydrides. In acute poisoning, the symptoms are similar to metal fume fever. Chronic exposure results in CNS symptoms such as headache, dizziness, vertigo, chills, fatigue, muscular weakness, and possibly tremors.

Continued

Table III continued

Substance	NIOSH[4]	OSHA[5]	ACGIH[2]	Primary Health Effects[6]
	Evaluation Criteria (mg/m^3)			
Hydrazine	LFL	1.3	0.1	The vapor is highly irritating to the eyes, upper respiratory tract, and skin, and causes delayed eye irritation. A sensitization dermatitis may be produced. Inhalation and skin contact are important routes of exposure, and evidence from animal experiments suggest that hydrazines are carcinogenic.
Hydrogen Chloride	--	7	5	When hydrogen chloride is inhaled, it may cause irritations of the respiratory tract with burning, choking, and coughing. Ulceration of the nose and throat may occur. May cause eye irritation, severe burns, and permanent damage with loss of sight. Repeated or prolonged exposure to hydrogen chloride may cause errosion of the teeth. Repeated skin exposure may cause skin rash.
Hydrogen Fluoride	2.5/5C*	2.5/5C	2.5	One of the most corrosive of the inorganic acids, the fluoride ion readily penetrates the skin and travels to deep tissue layers causing liquifaction necrosis of the soft tissues and decalcification and corrosion of bone. The tissue destruction is accompanied by severe pain. While there are no accounts of loss of vision from direct exposure, mild eye irritation was experienced in five human subjects exposed to HF at concentrations averaging 2.59-4.74 ppm. No irritation was noticed at 1.42 ppm.

continued

Table III continued

Substance	Evaluation Criteria (mg/m³) NIOSH[4]	OSHA[5]	ACGIH[2]	Primary Health Effects[6]
Isopropanol	980	980	980	High concentrations may cause mild irritation of the eyes, nose, and throat. Drowsiness, headache, and incoordinaton may also occur. Drying and cracking of the skin may result from prolonged skin exposure. Epidemiological investigations have established that a carcinogenic substance is present in isopropyl alcohol manufacturing areas, but have not confirmed isopropyl alcohol as a causative agent of cancer.
Nitric Acid	5	5	5	Exposures are mostly to oxides of nitrogen; resulting from using NA with metals or with oxidizable substances, as well as when nitric acid is exposed to air, nitorgen oxides are released. Literature reports include varying degrees of upper respiratory irritation, which may or may not be manifested immediately. Epidemiological studies are concerned with dental errosion.
Phosphine	--	0.4	0.4	Ignites at very low temps. The strong odor may be nausiating. Acute effects are secondary to central nervous system depression, irritation of the lungs, and damage to the liver and other organs. Common effects include weakness, fatigue, headache, vertigo, anorexia, nausea, vomiting, abdomnal pain, diarrhea, tenesmus, thirst, dryness of the throat, difficulty in swallowing, and sensation of chest pressure.

continued

Table III continued

Substance	Evaluation Criteria (mg/m³) NIOSH[4]	OSHA[5]	ACGIH[2]	Primary Health Effects[6]
Phosphoric Acid	--	1.0	1.0	May cause skin burns; contact with the eyes may produce irritation and eye burns. Mist may cause irritation of the eyes, nose, and throat. Repeated or prolonged exposure may cause irritation of the skin.
Toluene	375/750C	375	375	May cause irritation of the eyes, respiratory tract, and skin. May also cause fatigue, weakness, confusion, headache, dizziness, and drowsiness. Peculiar skin sensation may be produced such as a "pins and needles feeling" or numbness. Liquid in eyes may cause irritation and temporary damage. Inhalation may also cause difficulty in seeing in bright light. Repeated or prolonged exposure may cause drying and cracking of the skin.
Xylene	435/870C	435	435	May cause irritation of the eyes, nose, and throat. At high concentrations, may cause severe breathing difficulties which may be delayed in onset and may also cause dizziness, staggering, drowsiness, and unconsciousness. Also may cause loss of appetite, nausea, vomiting, and abdominal pain. May cause reversible damage to the kidneys and liver. Repeated or prolonged exposure may cause skin rash and reversible eye damage. In animals, causes blood changes reflecting mild toxicity to the hematopoetic system.

*C = Ceiling concentration
**LFL = Lowest Feasible Limit

TABLE IV

ANALYTICAL RESULTS; INITIAL CLEAN/OXIDE STRIP

University of Cincinnati
Cincinnati, Ohio
HETA 82-102

July1 1983

Substance	Type Sample	Duration	Exposure (mg/m^3)
Nitric Acid	Personal	13:18-14:30	0.14
Nitric Acid	Area	13:31-14:36	0.27
Hydrochloric Acid	Personal	13:18-14:30	0.21
Hydrochloric Acid	Area	13:31-14:36	0.18
Hydrofluoric Acid	Personal	13:17-14:29	TRACE*
Hydrofluoric Acid	Area	13:27-14:36	TRACE*
Acetone	Personal	13:20-14:28	< 0.008**

EVALUATION CRITERIA (mg/m^3):***	NIOSH	OSHA	ACGIH
ACETONE	590	2400	1780
HYDROGEN CHLORIDE	---	7.0	7.0 ceil.
HHDROGEN FLUORIDE	2.5/5.0 ceil.	2.5	2.5
NITRIC ACID	5.0	5.0	5.0

* Trace quantity detected; above analytical limit of detection, yet non-quantifiable

**"<" indicates "less than" which is not indicative of an airborne concentration, but rather the lowest detectable value considering the sampled air volume.

***Expressed as Time Weighted Averages unless otherwise specified

TABLE V

ANALYTICAL RESULTS; PHOTOLITHOGRAPHY

University of Cincinnati
Cincinnati, Ohio
HETA 82-102

July 1983

Substance	Type Sample	Duration	Location	Concentration (mg/m^3)
Benzene	Personal	14:31-15:15	Gold Room	< 0.10*
Benzene	Area	14:42-15:15	Photo-Resist Spinner	< 0.13
Benzene	Area	15:03-16:55	Photo-Resist Ovens	< 0.05
Toluene	Personal	14:31-15:15	Gold Room	< 1.03
Toluene	Area	14:31-15:15	Photo-Resist Spinner	< 1.28
Toluene	Area	14:31-15:15	Photo-Resist Ovens	< 0.47
Xylene	Personal	14:31-15:15	Gold Room	11.3
Xylene	Area	14:42-15:15	Photo-Resist Spinner	19.2
Xylene	Area	15:03-16:55	Photo-Resist Ovens	2.36
Acetone	Area	14:48-15:15	Gold Room-Central Area	1.55
Nitric Acid	Personal	14:32-16:55	Gold Room	< 0.16
Nitric Acid	Area	14:48-16:55	Above Fume Hood	0.12

continued

Table V continued

Substance	Type Sample	Duration	Location	Concentration (mg/m^3)
Phosphoric Acid	Personal	14:32-16:55	Gold Room	< 0.16
Phosphoric Acid	Area	14:48-16:55	Above Fume Hood	< 0.16
Sulfuric Acid	Personal	14:32-16:55	Gold Room	0.23
Sulfuric Acid	Area	14:48-16:55	Above Fume Hood	< 0.16
Hydrogen Fluoride	Area	13:27-14:36	Above Fume Hood	Trace**

EVALUATION CRITERIA (mg/m^3):***	NIOSH	OSHA	ACGIH
BENZENE	LFL****	3.1	30.0
TOLUENE	375/750 ceil.	750/1125 ceil.	375
XYLENE	435/870 ceil.	435	435
ACETONE	590	2400	1780
NITRIC ACID	5	5	5
PHOSPHORIC ACID	---	1	1
SULFURIC ACID	1	1	1
HYDROFLUORIC ACID	2.5/5.0 ceil	2.5	2.5

*< indicates "less than" which is not indicative of an airborne concentration, but rather the lowest detectable value considering the sampled air volume.
** Trace quantity detected; above analytical limit of detection, yet non-quantifiable
***Expressed as Time Weighted Averages unless otherwise specified
****LFL = Lowest Feasible Limit; Potential occupational carcinogen.

TABLE VI

ANALYTICAL RESULTS; EPITAXIAL GROWTH

University of Cincinnati
Cincinnati, Ohio
HETA 82-102

July 1983

Substance	Type Sample	Duration	Location	Concentration (mg/m^3)
Hydrochloric Acid	Personal	12:43-15:08	Crystal Growth Room	< 0.14
Hydrochloric Acid	Personal	15:10-17:36	Crystal Growth Room	0.82
Hydrochloric Acid	Area	13:01-15:12	Front of Grower	< 0.15*
Hydrochloric Acid	Area	15:14-16:58	Front of Grower	< 0.20
Hydrochloric Acid	Area	17:06-17:36	#6 Fume Hood	4.41
Hydrofluoric Acid	Area	17:06-17:37	#6 Fume Hood	Trace**

EVALUATION CRITERIA (mg/m^3):***	NIOSH	OSHA	ACGIH
HYDROFLUORIC ACID	2.5/5.0 ceil.	2.5	2.5
HYDROGEN CHLORIDE	---	7.0	7.0 ceil.

*"<" indicates "less than" which is not indicative of an airborne concentration, but rather the lowest detectable value considering the sampled air volume.
** Trace quantity detected; above analytical limit of detection, yet non-quantifiable
***Expressed as Time Weighted Averages unless otherwise specified

TABLE VII

ANALYTICAL RESULTS; PREFERENTIAL ETCHING
University of Cincinnati
Cincinnati, Ohio

HETA 82-102

July 1983

Substance	Type Sample	Duration	Location	Concentration (mg/m^3)
Hydrazine	Personal	09:46-11:11	Ion Implantation Room	< 0.02*
Hydrazine	Area	09:49-11:11	Fume Hood Sash	< 0.02
Hydrazine	Area	09:55-11:11	Inside Fume Hood	4.41
Hydrazine	Area	10:05-11:16	Roof-Near Exhaust	< 0.02

EVALUATION CRITERIA (mg/m^3):**	NIOSH	OSHA	ACGIH
HYDRAZINE	LFL	1.3	0.13

*"<" indicates "less than" which is not indicative of an airborne concentration, but rather the lowest detectable value considering the sampled air volume.
**Expressed as Time Weighted Averages unless otherwise specified

TABLE VIII

ANALYTICAL RESULTS; POLYSILICON ETCHING
University of Cincinnatiy
Cincinnati, Ohio
HETA 82-102

July 1983

Substance	Type Sample	Duration	Location	Concentration (mg/m^3)
Isopropanol	Personal	13:05-13:28	Ion Implantation Room	< 2.13*
Isopropanol	Area	13:08-13:29	Fume Hood Sash	< 2.61
Isopropanol	Area	13:08-13:30	Inside Fume Hood	45.8

EVALUATION CRITERIA (mg/m^3):**	NIOSH	OSHA	ACGIH
ISOPROPANOL	980/2000 ceil.	980	980

*"<" indicates "less than" which is not indicative of an airborne concentration, but rather the lowest detectable value considering the sampled air volume.
**Expressed as Time Weighted Averages unless otherwise specified

TABLE IX

ANALYTICAL REULSTS; LOW-TEMPERATURE CHEMICAL DEPOSITION
University of Cincinnati
Cincinnati, Ohio
HETA 82-102

July 1983

bstance	Type Sample	Duration	Location	Concentration (mg/m^3)
osphine	Personal	09:26-11:05	Crystal Growth Room	< 0.06*
osphine	Area	09:30-11:05	Fume Hood Sash	< 0.06
osphine	Area	09:31-11:05	Inside Fume Hood	< 0.06
osphine	Area	09:44-11:08	Roof	< 0.07
borane	Personal	09:27-11:05	Crystal Growth Room	< 0.27**
borane	Area	09:32-11:05	Fume Hood Sash	< 0.28**
borane	Area	09:44-11:08	Roof	< 0.31**

ALUATION CRITERIA (mg/m^3):***	NIOSH	OSHA	ACGIH
PHOSPHINE	---	0.4	0.4

<" indicates "less than" which is not indicative of an airborne concentration, but ther the lowest detectable value considering the sampled air volume.
Expressed as approximate "less than" values. Although diborane was detected on e smapling media, quantities were below blank levels.
*Expressed as Time Weighted Averages

TABLE X

ANALYTICAL RESULTS; GALLIUM ARSENIDE PROCESSING
University of Cincinnati
Cincinnati, Ohio
HETA 82-102

July 1983

Substance	Type Sample	Duration	Location	Concentration (mg/m^3)
Arsenic	Personal	13:00-13:33	903C GaAs Processing	< 0.045*
Arsenic	Area	13:01-13:35	Over Furnace	< 0.044
Arsenic	Area	13:01-13:33	End of Furnace	< 0.044
Arsenic	Area	13:01-11:08	Center of Room	< 0.004

EVALUATION CRITERIA (mg/m^3):**	NIOSH	OSHA	ACGIH
PHOSPHINE	---	0.4	0.4

*"<" indicates "less than" which is not indicative of an airborne concentration, but rather the lowest detectable value considering the sampled air volume.
**Expressed as Time Weighted Averages

TABLE XI

ANALYTICAL RESULTS; TOTAL FLUORIDES DURING ION IMPLANTATION
University of Cincinnati
Cincinnati, Ohio
HETA 82-102

July 1983

Substance	Type Sample	Duration	Location	Concentration (mg/m^3)
Fluorides	Area	10:47-14:04	Near Chamber Door	< 0.025*
Fluorides	Area	10:47-14:04	Above Gas Cylinders	< 0.025
Fluorides	Area	13:11-16:41	Gas Manifold	< 0.024
Fluorides	Area	13:23-16:38	Main Console	< 0.026
Fluorides	Area	13:18-16:40	Outside Chamber	< 0.025
Fluorides	Area	13:16-16:39	Top of Chamber	< 0.025
Fluorides	Area	13:25-16:42	Implanter Controls	< 0.025

*"<" indicates "less than" which is not indicative of an airborne concentration, but rather the lowest detectable value considering the sampled air volume.

DEPARTMENT OF HEALTH AND HUMAN SERVICES
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