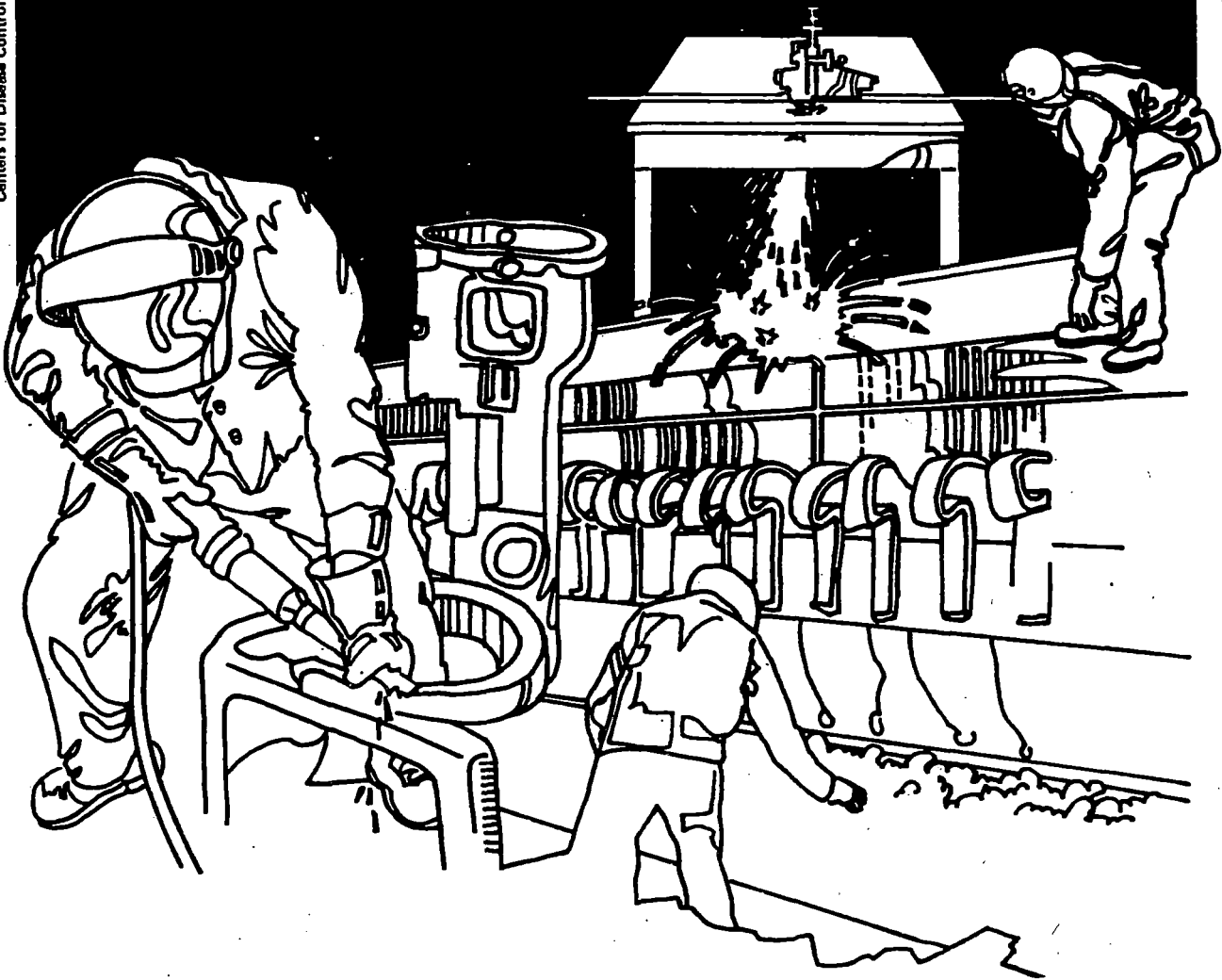


# NIOSH



## Health Hazard Evaluation Report

HETA 80-081-1173  
KEOKUK STEEL CASTINGS, INCORPORATED  
KEOKUK, IOWA

## 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.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 80-081-1173  
AUGUST 1982  
KEOKUK STEEL CASTINGS, INCORPORATED  
KEOKUK, IOWA

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## I. SUMMARY

On March 11, 1980 the National Institute for Occupational Safety and Health received a request from the United Steelworkers of America for an evaluation of possible health problems among workers at the Keokuk Steel Castings facility, Keokuk, Iowa. Due to legal delays, the initial survey was postponed until March, 1981.

On March 10-12, 1981, a NIOSH industrial hygienist and medical officer performed an environmental and medical survey at the Keokuk facility. A follow-up medical survey was conducted in March, 1982. Airborne concentrations of diphenylmethane diisocyanate (MDI), hydrogen cyanide, trace metals, and ammonia were found to be within their respective OSHA or NIOSH recommended standards. Aromatic amines in samples collected during metal pouring were below the analytical limit of detection. Two breathing zone samples collected from workers in the metal pouring area indicated exposures to carbon monoxide (CO) at 58 and 94 milligrams/cubic meter of air ( $\text{mg}/\text{M}^3$ ), as compared to the NIOSH recommended standard of  $39 \text{ mg}/\text{M}^3$ . Eight breathing zone samples for formaldehyde collected at the core and mold area indicated exposure levels ranging from 0.18 to  $0.50 \text{ mg}/\text{M}^3$ . NIOSH recently classified this substance as a potential occupational carcinogen and recommends that all exposures be kept to a minimum. Exposures to dimethylethylamine (DMEA) measured during core production ranged from 8.6 to  $26.5 \text{ mg}/\text{M}^3$ , averaging 13.1. No OSHA or NIOSH-recommended standard exists for this substance. Exposures to respirable free silica in the shakeout area were measured at 0.10 and  $0.12 \text{ mg}/\text{M}^3$ , in excess of the NIOSH recommended standard of  $0.05 \text{ mg}/\text{M}^3$ , and the OSHA calculated standard.

A medical questionnaire administered to 49 employees showed no large difference in symptom frequency between workers in different plant locations. However, interviews with employees who had worked in the core production area prior to the establishment of engineering controls for exposure reduction revealed the frequent occurrence of hazy vision and respiratory irritation at that time. Pre- and post-shift pulmonary function tests were performed on 22 core and molding workers and four skimmers. None revealed evidence of occupational asthma.

On the basis of the environmental data collected during this evaluation, NIOSH determined that a health hazard exists from overexposure to carbon monoxide and free silica. Further, exposures to formaldehyde should be minimized, since safe levels of exposure to carcinogens have not been demonstrated. Based on results of the medical survey, it appears that aliphatic amines were responsible for the previous hazy vision and shortness of breath experienced by workers in the core production area. Recommendations for control of exposures and medical monitoring are made on Section VIII of this report.

KEYWORDS: SIC 3321 (Foundries), Diphenylmethane diisocyanate (MDI), Dimethylethylamine, Carbon Monoxide, Formaldehyde, Trace Metals, Aromatic Amines, Free Silica, Ammonia, Hydrogen Cyanide, Pulmonary Function

## II. INTRODUCTION

On March 10, 1980, the national office of the United Steelworkers of America (USWA) requested a health hazard evaluation of the Keokuk Steel Casting facility located in Keokuk, Iowa, which employs members of USWA Local 3311. The official request stated that, "Workers have complained of extreme irritation, nausea, headaches, blurred vision, and other symptoms. In addition, we are concerned about potential long-term lung damage from the isocyanate systems used; permanent eye, heart, and other damage from aliphatic amines (as suggested by animal studies); and the possible formation of carcinogenic aromatic amines in the coremaking process and during pouring." The company contested in court NIOSH's authority to conduct this evaluation; delaying the investigation for one year. Hearings resulted in the U.S. Court of Appeals for the Eighth Circuit affirming the local U.S. District Court decision to authorize the NIOSH health hazard evaluation.

A NIOSH industrial hygienist and medical officer visited the Keokuk facility on March 10 through 12, 1981. Environmental sampling was conducted during the second shift of March 10 and during the first shifts of the 11th and 12th. A medical questionnaire was administered during the first shifts of March 11 and 12, 1981. A follow-up medical evaluation, including pulmonary function tests, was performed March 29-30, 1982. An interim report containing results of the initial survey was issued in December, 1981.

The purpose of the investigations was to document the extent of employee exposures to the various airborne substances liberated during the foundry operation and to evaluate any health effects suffered by employees. The evaluation centered around the core production area, with emphasis on exposures to the isocyanate and catalyst.

## III. BACKGROUND

Keokuk Steel Casting, a subsidiary of Kast Metals, Inc. produces medium-sized ferrous products used primarily for the subsequent manufacture of excavation equipment. "No-bake" type cores and molds are used in the production process. Cores are produced by means of an automated "Isocure" system, in which the core sets, or hardens, instantaneously. Ashland Chemical's Isocure I-308 (phenol-formaldehyde resin with solvents) and Isocure II-612 (diphenylmethane diisocyanate with solvents) are mixed with sand immediately prior to entering the metallic core mold. As a curing system, Ashland Chemical's Catalyst 702 (dimethylethylamine) is then blown into the mixture, the mold separates, and the core is manually removed and stacked onto skids. (The use of triethylamine as a catalyst was discontinued in 1980.)

Engineering controls for reduction of chemical exposures include general dilution ventilation, local exhaust ventilation, and the use of seals around closure points on the metal molds. Union officials and workers in this area said that these controls, installed and improved

within the year prior to the survey, substantially reduced chemical exposures. Eight workers are employed in the core production area. Three operators, two on the smaller core system (small blower) and one on the larger, are involved in actual core production. The remaining workers are involved in painting cores with an alcohol-based substance, trimming, and transporting the cores to temporary storage.

Molds are produced in two areas, one for small molds and one for larger molds. Pepset 2590, consisting primarily of diphenylmethane diisocyanate (MDI) and hydrocarbons, or Pepset 1590, a phenol-formaldehyde and hydrocarbon mixture, are mixed with sand and fed into molds, manually tamped down, then allowed to air set. Seven workers are employed in these two areas. Three operators, two on the large mold system and one on the small, fill the mold shells with the chemically treated sand. The remaining four workers strike off, transport, and "finish" the molds. The remainder of the process prior to metal pouring deals with combining cores and molds, which takes place in an assembly line fashion downstream of the core/mold production area.

The metal pouring area is partially enclosed and ventilated via dilution ventilation. Approximately once per hour a "heat" is poured. The primary job categories in this area are the Pourer (the worker who pours molten metal into the molds) and the Skimmer (involved with skimming contaminants from the top of the molten metal during pouring operations). Half-face respirators are required for entry into this area.

Subsequent to metal pouring, the casts are allowed to set and harden. Once the casts are sufficiently cool, they are transported to the shakeout area where the casts are separated from the molds (Georgia Iron Works or "GIW" process). The primary job in this area involves the manual separation of the casts from the broken sand molds at a position downstream, yet adjacent to the mold destruction process. Two workers are normally stationed at this position and manually remove the casts. The broken molds are crushed, treated, and the sand is returned to the mold production process for reuse.

#### IV. METHODS AND MATERIALS

##### A. Environmental

Environmental sampling began during the second shift on March 10, and continued on the first shift of March 11 and 12. Breathing zone and general area environmental air samples were collected at the core production station for determination of exposures to MDI, formaldehyde, DMEA, and ammonia. Samples were collected from the mold production workers and their work area for MDI and formaldehyde. At the metal pouring station, samples were collected for MDI, carbon monoxide, trace metals, aromatic amines, and hydrogen cyanide. At the shakeout area (separation of sand molds from casts), two personal samples were obtained for respirable free silica and dust exposures, and one sample was collected from the blast worker, who also worked in the shakeout area.

Table 1 presents a summary of sampling and analytical methodology for sampled substances. The following discussions pertain to methods used which may be considered non-routine.

MDI samples were collected with 13-mm glass fiber filters impregnated with a reagent, N-p-nitrobenzyl-N-propylamine, at a sample collection rate of one liter/minute (lpm). Appendix A describes the analytical method. To measure time-weighted average (TWA) exposures, samples were collected for approximately 6 hrs. Three ceiling concentration determinations were made by collecting samples for 10-minute periods.

Five samples were collected for determination of trace metal exposures. One sample was submitted for inductively coupled argon plasma analysis (ICP), which analyzes for a broad range of metals. Once results of this analysis were obtained, the remaining metal samples were analyzed via the less involved "AA" method for predominant metals as identified through ICP analysis.

#### B. Medical

On the first survey in March 1981, a questionnaire was distributed to 49 employees during the day shifts of March 10 and 11, 1981. The questionnaire elicited information on smoking history, allergic history, history of heart problems, and the occurrence of the following symptoms: headache, cough, phlegm, stuffy nose, wheezing, shortness of breath, chest pain, skin irritation, eye irritation, blurry vision, sore throat, nausea, dizziness, and drowsiness.

All employees working in the Isocure process were interviewed, as well as a systematic sample of employees in other areas. Of the 49 interviewed six worked in Isocure, 24 in other core and molding work, and 19 in other areas of the foundry (six in skimming and pouring, three in utility, two in the crane, two on forklifts, two in shakeout, two in finishing, and one in machining).

Pulmonary function tests were performed during the second survey in March 1982. Twenty-six workers with current and significant past exposure to the core and molding process received pulmonary function tests both before their shift and after working for at least five hours, and after having been off work for at least two days. Four persons employed as skimmers also received their tests after a weekend off. An attempt was made to test those who had worked as head operators or had worked in core and molding over a long period. Fourteen employees in other jobs (shakeout, 5; lift truck, 3; burning, 3; GIW yard and foundry repairs, 1 each) received these tests after one day on the job. Those participating in each job category, as a percentage of total employment in that category on the day of the survey were as follows:

Isocure	7/7	100%
Other core and molding	19/41	46%
Pouring and Skimming	5/14	36%
Other	14/22	64%

The pulmonary function tests were performed using an 8-liter, dry-rolling seal spirometer equipped with an air temperature probe (Model 822, Ohio Medical Products). The predicted normal forced vital capacity (FVC) and forced expiratory volume (FEV-1) for each person were calculated, using the person's age, height, sex, and race, according to the method of Knudson et al.(1) The ratio FEV1/FVC was also calculated. Each person was tested at least three times at each session; the values used were the best achieved by the individual. A test was considered technically adequate if the two best values for either FEV1 or FVC differed by less than 10% or if the FVC changed by less than 10% between the first and second test.

A respiratory questionnaire was administered to each participant which this elicited information on cough, phlegm, wheezing, shortness of breath, and chest tightness, as well as past medical history, occupational history, and smoking history.

## V. EVALUATION CRITERIA

### A. Environmental

The environmental evaluation criteria used in this report as related to airborne exposures to toxic substances are 1) NIOSH recommended standards, 2) Federal Occupational Health Standards (as promulgated and enforced by the Occupational Safety and Health Administration (OSHA), U.S. Department of Labor (29 CFR 1910.1000)), and 3) American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV's).

Table 2 presents a summary of the evaluation criteria for all sampled substances along with brief descriptions of their primary health effects. The following discussions pertain to substances that are of special concern.

#### 1. Carbon Monoxide (CO)

NIOSH has recommended that occupational exposures to CO be kept below  $39 \text{ mg/M}^3$ , as averaged over up to a 10-hour work shift, and below  $220 \text{ mg/M}^3$  as a ceiling concentration. The current OSHA standard for CO is  $55 \text{ mg/M}^3$  (TWA). Exposure to CO decreases the ability of the blood to carry oxygen to the tissues. Inhalation of CO may cause headache, nausea, dizziness, weakness, rapid breathing, unconsciousness, and death. High concentrations may be rapidly fatal without producing significant warning symptoms. Exposure to this gas may aggravate heart disease and artery disease and may cause chest pain in those with pre-existing heart disease.

#### 2. Formaldehyde

As of April 5, 1981, NIOSH recommends that formaldehyde be considered a potential occupational carcinogen, and that

exposures be reduced to the lowest feasible limit. (Recent evidence for the carcinogenicity of formaldehyde prompted NIOSH to issue a Current Intelligence Bulletin warning of the carcinogenic potential.(2)) Previously, NIOSH recommended that formaldehyde exposures be limited to 1.2 mg/M<sup>3</sup> for any 30-minute sampling period, based on the irritating effects of exposure including burning of the eyes, tearing (lacrimation), and general irritation to the upper respiratory passages.

The current OSHA standard for formaldehyde is 3.6 mg/M<sup>3</sup> for an 8-hour TWA, with a ceiling concentration of 6 mg/M<sup>3</sup> and an acceptable maximum peak above the ceiling concentration of 12 mg/M<sup>3</sup> for no more than a total of 30 minutes during an 8-hour shift. The TLV for formaldehyde was set at a 3.0 mg/M<sup>3</sup> as a ceiling limit.

### 3. Dimethylethylamine (DMEA)

While no OSHA or NIOSH-recommended standard exists for DMEA, this class of compounds (aliphatic amines) has been shown to be a local irritant, affecting the eyes, mucous membranes, and skin. They are also known to cause hazy or blurry vision and to produce headache, nausea, and faintness. Corneal opacity has been observed in animal studies using triethylamine (TEA). Some animal studies have noted degeneration of the heart muscle on exposure to high levels of TEA. The lack of any recommended standard for DMEA is due largely to the small amount of health research conducted on this particular compound.(3,4)

### 4. Diphenylmethane diisocyanate (MDI)

MDI is an irritant of the eyes and mucous membranes and a sensitizer of the respiratory tract, and can cause a chronic decrease in pulmonary function. In individuals who are sensitized to diisocyanates, exposure to extremely low concentrations can cause symptoms of asthma. The effect on lung function is most noticeable on the first day of the work week and the worker may be asymptomatic. A person sensitized to an isocyanate who continues exposure to it may experience chronic loss of pulmonary function.(5) NIOSH has recommended that exposure to MDI be controlled to concentrations below 50 micrograms (ug)/M<sup>3</sup> averaged over up to a 10-hour work shift, and 200 ug/M<sup>3</sup> as a 10-minute ceiling concentration. The OSHA standard and ACGIH TLV for MDI is 200 ug/M<sup>3</sup> as a ceiling concentration.(6)

### 5. Silica

Crystalline silica, usually referred to as free silica, is defined as silicon dioxide (SiO<sub>2</sub>) molecules arranged in a fixed pattern as opposed to a nonperiodic, random molecular arrangement defined as amorphous silica. The three most common



crystalline forms of free silica encountered in industry are quartz, tridymite, and cristobalite, with quartz being by far the most common of these. NIOSH, in its recommendations for a free silica standard, has proposed that exposures to all forms of free silica be controlled so that no worker is exposed to respirable airborne concentrations greater than 0.05 mg/M<sup>3</sup>, as averaged over a 10-hour working day, 40-hour work week. This recommendation was designed to protect workers from silicosis, a lung disease caused by the inhalation of silicon dioxide containing dust. The silica causes nodules and fibrosis to occur in the lung. The onset of symptoms may be a few months after exposure but, more typically, is several years, depending on the extent of exposure.(7) A worker with silicosis generally first notes the onset of shortness of breath on exertion. This becomes gradually worse and is accompanied by cough. The current federal, or OSHA standard for respirable free silica exposure is an 8-hour TWA based upon the 1968 ACGIH TLV formula (10mg/M<sup>3</sup>/%SiO<sub>2</sub> + 2) for respirable quartz. One-half this amount was established as the limit for cristobalite and tridymite. The OSHA regulation is thus based on the percentage of free silica contained in the respirable particulate exposure, whereas the NIOSH recommended standard applies directly to the airborne concentrations of respirable free silica.

B. Medical

Forced vital capacity (FVC) is the amount of air that one can blow out of the lungs after taking a deep breath. One-second forced expiratory volume (FEV-1) is the amount of that air that is blown out in the first second of expiration. A condition causing a decrease in the FVC is termed restrictive, examples of such illnesses being silicosis, tuberculosis, and heart failure. A condition causing a decrease in FEV-1 is termed obstructive, examples of these being asthma, chronic bronchitis, and emphysema.

Knudson's criteria for predicted FEV-1 and FVC were used in this study.(1) They are, for males, as follows:

	16-35 years % predicted	>36 years % predicted
FEV1	>81.75%	>72.92%
FVC	>81.50%	>74.46%

These represent "normal" ranges derived from the testing done by Knudson on a healthy, non-smoking population (Knudson has similar criteria for females). The ratio FEV-1/FVC was considered normal if greater than 70%.

An FEV-1 decrease of greater than 10% between the pre- and post-shift testing sessions was considered evidence of occupational asthma.

## VI. RESULTS

### A. Environmental

#### 1. Diphenylmethane diisocyanate (MDI)

Table 3 presents environmental sampling results for MDI. All measured concentrations were well within the NIOSH recommended standard for both TWA exposure concentrations (50 ug/M<sup>3</sup>) and ceiling concentrations (200 ug/M<sup>3</sup>). Results of TWA samples ranged from below the analytical limit of detection (0.43 to 0.66 ug/M<sup>3</sup>, air volume adjusted) to 1.77 ug/M<sup>3</sup>, with an overall average of 0.84 ug/M<sup>3</sup>. All samples collected for ceiling determinations were below the analytical limit of detection (20.0 ug/M<sup>3</sup>, air volume adjusted). The highest exposure concentration was measured during metal pouring from the Skimmer, at 1.77 ug/M<sup>3</sup>. The average of three measurements made during this operation was 1.19 ug/M<sup>3</sup>. Only two of seven breathing zone samples obtained from workers at the core production station were above the limit of detection. These samples were reported at 0.79 ug/M<sup>3</sup> for the Head Operator and 0.67 ug/M<sup>3</sup> for the Small Blower Operator. Three samples each were collected from the large and small mold operations, indicating average exposure concentrations of approximately 0.65 and 0.68 ug/M<sup>3</sup>, respectively.

#### 2. Formaldehyde

Table 4 presents results of environmental monitoring for formaldehyde. Three breathing zone samples collected from workers in the core production area and three from the mold production area indicate an overall average of approximately 0.36 mg/M<sup>3</sup> for both locations. The highest measured exposure, 0.50 mg/M<sup>3</sup>, was obtained from the Stripper at the core production location.

#### 3. Dimethylethylamine

One general area sample and eight breathing zone samples were obtained for determination of worker exposures to DMEA during core production (Table 5). Of three samples obtained from Head Operators, concentrations ranged from 5.3 to 26.5 mg/M<sup>3</sup>, averaging 15.5. Five breathing zone samples were obtained from Small Blower Operators, with concentrations ranging from 4.2 to 18.8 mg/M<sup>3</sup>, averaging 11.6. The area sample, collected near the Head Operator's work station, was reported at 8.8 mg/M<sup>3</sup>.

4. Trace Metals

One area and two breathing zone samples were obtained for determination of worker exposures to trace metals during metal pouring operations. Also, one sample was collected from the crane cab, located over the electric arc furnace, and one sample was collected near the pre-mix operation located at the small mold production station. No significant exposures were measured (Table 6).

5. Carbon Monoxide

One general area and two breathing zone samples for CO were collected during metal pouring operations. Results indicate that the Skimmer was exposed to an average of 94 mg/M<sup>3</sup>, and that the Pourer was exposed to an average of 58 mg/M<sup>3</sup>. The general area sample, collected at the center of the pouring area, indicated an airborne concentration of 11 mg/M<sup>3</sup>.

6. Ammonia

One full shift breathing zone sample obtained from the Head Operator at the core production station a TWA ammonia concentration of 4 mg/M<sup>3</sup>.

7. Hydrogen Cyanide

Two breathing zone and one general area sample collected during metal pouring for HCN indicated exposure levels of less than 1 mg/M<sup>3</sup>.

8. Aromatic Amines

Results of five general area samples collected in the metal pouring area do not indicate the presence of aromatic amines. With an analytical detection limit of 0.1 mg/sample, results suggest that concentrations of the amines, if present, were below 1 mg/M<sup>3</sup>.

9. Respirable Free Silica / Respirable Dust

Two full shift samples were collected from the breathing zones of the workers involved with the shakeout operation. One sample had a respirable particulate weight of 1.78 mg/M<sup>3</sup>, with a free silica (quartz) content of 0.12 mg/M<sup>3</sup>. The other sample was reported as having a respirable particulate weight of 900 mg/M<sup>3</sup>, with a quartz content of 216 mg/M<sup>3</sup>, but the validity of this result is suspect. A third sample collected from the worker in the blast area for respirable dust and free silica showed 1.50 and 0.14 mg/M<sup>3</sup>, respectively.

B. Medical

1. First Survey - March 1981

For the purpose of analysis, employees were divided into three groups - Isocure workers, other core and molding workers, and other foundry workers (as defined in Methods section).

All workers but one were male. Isocure workers tend to be younger than other workers, but the difference was not statistically significant (Students's t Test). Nor was there a significant difference among the groups for allergic history or smoking (Fisher's Exact Test).

Table 7 also lists selected symptoms noted during the two days preceding the survey. (Other symptoms were not listed because of low frequency.) A high percentage of Isocure workers reported cough, but for other symptoms they tended to note a lower frequency than did other workers. None of these differences were statistically significant (Fishers's Exact Test).

Table 7 also lists the number of workers in various job categories who noted selected symptoms either frequently or occasionally during the three months preceding the survey. There are no significant differences between the groups for the occurrence of any symptom (Fisher's Exact Test). The symptoms most commonly reported overall were cough, eye irritation, stuffy nose, and headache.

In all, 15 of the employees who work or have worked with Isocure were interviewed. One of these reported having occasional high blood pressure. None of the others had a past history of any heart problems. None of the current Isocure workers had experienced any shortness of breath; two of the nine past Isocure workers had noted shortness of breath on a frequent basis and three had noted it occasionally. Some of the workers who had worked in the Isocure process prior to the placement of rubber seals on the apparatus noted the frequent occurrence, at that time, of hazy vision. Electric lights would appear to these workers to be encircled by halos. This lasted from one to four hours after leaving work.

2. Second Survey - March 1982

Of the 45 pulmonary function tests performed, six were excluded from analysis because of evidence of technical inadequacy of the tests. For three of these, the two best FEV-1 or FVC results differed by greater than 10%; for the other three, FVC had changed by greater than 10% between the two testing sessions.

For the 22 core and molding workers with adequate pulmonary function tests, FEV-1 had decreased by an average of 1.1% between the two testing sessions. The average drop for the four skimmers was 4.3%. In no instance did this drop exceed 10%, the largest drop being 9.5%. Table 8 lists the average change between pre- and post-shift values for the 26 workers tested on Monday morning. None of the differences listed are statistically significant (Student's t Test).

Table 9 summarizes the pulmonary function and questionnaire data for core and molding workers and for other workers. The means for FEV-1, FVC, and FEV-1/FVC are within the normal range. The means of FEV-1 and FVC for "other" workers are somewhat lower than for core and molding workers, but the differences are not statistically significant. Nor were there any significant differences between the groups for age, smoking, for years employed at either plant, or for the prevalence of cough, phlegm, shortness of breath, wheezing, and chest tightness, (Included in the "other" category is a worker with space-occupying lesions in the upper lobes of his lung that have not received a definitive diagnosis. Exclusion of this person's pulmonary function tests from the data does not result in statistical significance for any of the results).

Of the 39 individuals with adequate tests, eight had one or more abnormalities. In Table 10 these eight are compared to the remaining 31 for various characteristics. These two groups differ in such respects as age, seniority, smoking history, and in the percentage reporting cough. However, none of these differences are statistically significant. Of the eight individuals with abnormal tests, four have worked mainly in core and molding, and the others in burning and other foundry locations.

## VII. DISCUSSION AND CONCLUSIONS

### A. Discussion

#### MDI

The environmental investigation centered around the core and mold production areas, with emphasis on worker exposures to MDI and DMEA. All measured exposures to MDI were well within the NIOSH recommended standard for both time-weighted average and ceiling concentrations. The highest TWA concentration was less than 4% of the recommended standard, and ceiling concentrations were less than 10%.

None of the individuals who received Monday morning pulmonary function tests appeared to have occupational asthma. Not everyone was tested, however, including many not working due to lay-offs.

Since a person can be sensitized and still be asymptomatic, it is prudent to periodically perform pre- and post-shift pulmonary function tests on all employees with isocyanate exposure.

Because participants were not drawn strictly on a random basis, it is difficult to draw other conclusions from the pulmonary function data. The small group of employees with one or more abnormalities differed greatly from others tested in characteristics such as age and smoking. Hence, it is difficult to say how much of their pulmonary function deficit is due to their job as opposed to other factors such as smoking.

#### DME

Based on results of the first medical survey, it is apparent that workers in the core production area have, in the past, experienced hazy vision, difficulty breathing, cough, respiratory irritation, headache, sore throat, and eye irritation, which can be associated with the known short-term effects of exposure to DMEA. However, the current low prevalence of these health effects indicates that control measures installed or improved upon in the recent past, including placement of rubber seals at closure points on the metallic molds and local exhaust ventilation, have substantially reduced environmental concentrations. Tables 7 and 9 suggest that Isocure workers were not suffering any health effect, with the possible exception of cough, more than were other workers. Workers did report, however, that when leaks occurred in the process a very noxious odor was produced, which made breathing difficult, made the mouth feel dry, and necessitated leaving the area. Most of those who had worked with the Isocure process prior to the placement of rubber seals in the apparatus had noted the frequent occurrence of hazy vision, which is highly associated with DMEA and triethylamine. Other symptoms mentioned as associated with Isocure at that time were difficulty breathing and cough, which were associated with respiratory irritation, noxious odor, headache, sore throat, and eye irritation. These symptoms are also consistent with DMEA exposure. The fact that these symptoms were common previously and are uncommon now suggests that control measures taken in the interim have been effective. Another possible explanation is the discontinued use of TEA (although the greater volatility of DMEA does not support this theory).

No evidence was found in this study for cardiovascular effects. However, the number of workers involved in Isocure is so small that it would be statistically unlikely for an effect to be observed even if present. Current exposures to DMEA in this area average approximately 13 mg/M<sup>3</sup> (no OSHA or NIOSH recommended standard exists for DMEA). The lack of health effects among this group of employees suggests that these exposure levels may not be harmful. However, the lack of long-term health effect research dictates prudence when considering the acceptability of these levels.

### Formaldehyde

Formaldehyde has been shown to induce nasal cancer in rats and mice. Although humans and animals may differ in their susceptibility to specific chemical compounds, any substance that produces cancer in experimental animals should be considered a cancer risk to humans. Based on the animal studies, NIOSH recommends that formaldehyde be handled in the workplace as a potential occupational carcinogen. Safe levels of exposure to carcinogens have not been demonstrated, but the risk should be reduced by decreasing exposure. An estimate of the extent of the cancer risk to workers exposed to various levels of formaldehyde at or below the current standard has not yet been determined. In the interim NIOSH recommends that, as a prudent public health measure, engineering controls and stringent work practices be employed to reduce occupational exposure to the lowest feasible limit.

### Other Substances

The environmental sampling strategy for CO, trace metals, ammonia, hydrogen cyanide, and free silica was designed to identify potential overexposures through collection of a limited number of samples. As a consequence, sampling results for these substances are only suggestive of potential problem areas and do not give definitive degrees of overexposure or, conversely, an absolute index of safe exposure. Two measurements were obtained for determination of exposure to CO during metal pouring. Results indicate concentrations in excess of the NIOSH recommended standard. The same sampling strategy (i.e., a limited number of samples collected) was used for ammonia and hydrogen cyanide. Results indicate that exposures to these substances are within their respective evaluation criteria.

### Free Silica

Three breathing zone samples collected for respirable free silica indicated excessive exposures in the shakeout area. While one of these samples showed extremely high free silica content (216 mg/M<sup>3</sup>) its validity is highly suspect. The other two samples collected in this area, reported at 0.10 and 0.12 mg/M<sup>3</sup>, are in excess of the OSHA and NIOSH-recommended standards. Although respiratory protection is required, employee exposures should be limited through engineering controls such as improved ventilation. Workers exposed to sand should be periodically screened for silicosis.

## B. Conclusions

From results of the environmental monitoring and the medical study, it appears that environmental conditions have improved in the recent past at the core production location. However, a continued

effort at exposure reduction should be made in this area in light of the recent research indicting formaldehyde as a suspect occupational carcinogen and the lack of information on the long-term effects of exposure to DMEA. Also, engineering controls should be considered in the shake out area toward reduction of exposure to free silica.

#### VIII. RECOMMENDATIONS

Based on results of environmental monitoring and the medical questionnaire, the following recommendations are made:

1. Management and union officials should inform employees of the potential carcinogenic properties of formaldehyde. The NIOSH Current Intelligence Bulletin #34, dated April 15, 1981, should be consulted for further information.
2. Based on results of the medical questionnaire indicating the continued occurrence of health effects suffered during leaks at the core production station, we recommend that in the event of leaks, the immediate area be evacuated until the leaks are located and repaired.
3. Observation of the catalyst (DMEA) recharge process indicated the potential for short-term exposures to relatively high concentrations of DMEA. We recommend that this area be evacuated during this procedure.
4. Beards should be prohibited on employees who are required to use respirators. Respirators cannot provide sufficient protection if facial hair interferes with proper seal.
5. Follow-up environmental sampling for CO should be conducted in the metal pouring area. While extensive sampling for CO in this area was not within the scope of the NIOSH evaluation, results of two samples indicated excessive exposure and warrant further investigation.
6. Exhaust ventilation in the shakeout area should be improved. Employee exposures to silica and dust should be reduced through engineering controls where feasible, rather than by respiratory protection.
7. Employees exposed to silica should receive pre-employment, and periodic examinations, including chest x-rays read by a physician trained in the ILO-UICC interpretation system for pneumoconiosis and pulmonary function tests. Any employee with symptoms of respiratory distress, x-ray evidence of silicosis, or pulmonary function impairment should be fully evaluated by a physician qualified to advise the employee whether or not he should continue working in a dusty trade.



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XI. DISTRIBUTION AND AVAILABILITY

Copies of this Determination Report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, Virginia 22151. Information regarding its availability through NTIS can be obtained from the NIOSH Publications Office at the Cincinnati address.

Copies of this report have been sent to:

1. Keokuk Steel Castings, Inc., Keokuk, Iowa
2. United Steelworkers of America
3. United Steelworkers of America, Local
4. OSHA, Region VII
5. NIOSH, Region VII

For the purpose of informing the "affected employees" the employer should post this report for at least 30 days in a prominent place(s) near where employees work.

TABLE 1  
 Sampling and Analysis Methodology  
 March 1981

Keokuk Steel Castings  
 Keokuk, Iowa  
 HETA 80-081

<u>Substance</u>	<u>Collection Device</u>	<u>Flow Rate (lpm)</u>	<u>Duration(hrs.)</u>	<u>Analysis</u>	<u>Detection Limit(mg/sample)</u>	<u>Reference</u>
MDI	Glass Fiber Filter	1.0	6-8	HPLC *	0.00005	NIOSH Labs
Formaldehyde	Charcoal	0.2	6-8	Ion Chromatography	0.008	P&CAM 318
Dimethylethylamine	Silica Gel	0.2	6-8	Gas Chromatography	0.08	P&CAM 221
Free Silica	M-5 Filter	1.7	6-8	x-ray diffraction	0.03	P&CAM 259
Trace Metals	"AA" filters	1.5	6-8	ICP/Atomic Absorption	0.0005	NIOSH Labs
Aromatic Amines	Silica Gel	0.2	6-8	Gas Chromatography	0.1	P&CAM 168
Hydrogen Cyanide	Drager Long-term	0.05	6-8	Visual	----	----
Carbon Monoxide	Drager Long-term	0.05	6-8	Visual	----	----
Ammonia	Drager Long-term	0.05	6-8	Visual	----	----

\* High Pressure Liquid Chromatography

TABLE 2

Evaluation Criteria  
March 1981Keokuk Steel Castings  
Keokuk, Iowa  
HETA 80-081

Substance	Evaluation Criteria*(mg/M <sup>3</sup> )			Primary Health Effects
	NIOSH	OSHA	ACGIH	
Ammonia	35**	35	18	Intensely irritating to the mucous membranes, eyes, and skin. Chronic exposure may produce headache, salivation, burning of the throat, perspiration, nausea, vomiting, and substernal pain.
Aromatic Amines	***	***	***	The two major toxic effects of these compounds are methemoglobinemia and cancer of the urinary tract. Other effects may be hematuria, cystitis, anemia, and skin sensitization.
Carbon Monoxide	38.5	55.0	55.0	Causes tissue hypoxia by preventing the blood from carrying sufficient oxygen.
Dimethylethylamine	-----	-----	-----	May produce irritation of the skin and mucous membranes of the eyes, nose, throat and respiratory tract, producing cough, substantial distress and perhaps asthmatic-type symptoms.
Diphenylmethane diisocyanate	0.05	0.2**	0.2**	MDI is an irritant of the eyes and mucous membranes and a sensitizer of the respiratory tract, and can cause a chronic decrease in pulmonary function. In individuals who are sensitized to diisocyanates, exposure to extremely low concentrations can cause symptoms of asthma.
Formaldehyde	Lowest Feasible Limit	3.6	3.0**	In addition to recent classification as a suspect occupational carcinogen, formaldehyde gas is an irritant to the eyes and respiratory tract; solutions cause both primary irritation and sensitization.
Free Silica (respirable)	0.05	$\frac{10 \text{ mg/M}^3}{\% \text{ SiO}_2} + 2$		Silicosis; a pneumoconiosis due to the inhalation of silicon dioxide-containing dust, which is a disabling, progressive, and sometimes fatal pulmonary fibrosis characterized by the presence of typical nodulation in the lungs.
Hydrogen Cyanide	5.0**	11	10**	Inhalation, ingestion, or skin absorption of hydrogen cyanide may be rapidly fatal. Larger doses may cause the person to rapidly lose consciousness, stop breathing, and die. At lower levels of exposure a person may experience weakness, headache, confusion, nausea, and vomiting.

\* Values represent time-weighted average exposure limits for up to a 10 hr. work-day unless otherwise specified.

\*\* Ceiling concentration. Exposures shall not exceed this concentration.

\*\*\* A number of aromatic amines have been classified as cancer-causing agents, and thus all exposure should be avoided.

TABLE 3

Analytical Results; Diphenylmethane Diisocyanate  
March 1981Keokuk Steel Castings  
Keokuk, Iowa  
HETA 80-081

<u>SAMPLE #</u>	<u>DATE</u>	<u>TYPE</u>	<u>LOCATION/OPERATION</u>	<u>DURATION</u>	<u>VOLUME (M<sup>3</sup>)</u>	<u>CONCENTRATION (ug/M<sup>3</sup>)</u>
MDI 1	3-10	BZ*	Core/Head Operator	15:48-22:20	0.392	0.79
MDI 2	3-10	BZ	Core/Stripper	15:54-22:19	0.385	Less than 0.52**
MDI 3	3-10	BZ	Sm. Mold/Head Operator	16:11-22:25	0.374	0.80
MDI 4	3-10	BZ	Lg. Mold/Head Operator	16:07-22:21	0.374	0.59
MDI 10	3-11	BZ	Metal Pour/Skimmer	06:07-08:17	0.130	1.77
MDI 11	3-11	BZ	Core/Head Operator	08:10-13:15	0.305	Less than 0.66
MDI 12	3-11	BZ	Sm. Mold/Head Operator	06:27-13:12	0.405	Less than 0.49
MDI 13	3-11	BZ	Core/Sm. Blwr Operator	08:13-13:14	0.301	Less than 0.66
MDI 14	3-11	BZ	Core/Head Operator	06:30-13:11	0.401	Less than 0.50
MDI 15	3-11	BZ	Metal Pour/Skimmer	06:02-09:01	0.179	1.12
MDI 16	3-11	BZ	Lg. Mold/Head Operator	06:22-13:10	0.408	0.71
MDI 20/C	3-11	Area	Core	08:25-08:35	0.010	Less than 20.0
MDI 21/C	3-11	Area	Core	10:57-11:07	0.010	Less than 20.0
MDI 100	3-12	BZ	Core/Sm. Blwr Operator	06:03-13:14	0.431	0.67
MDI 101	3-12	BZ	Core/Head Operator	06:06-13:55	0.469	Less than 0.43
MDI 103	3-12	BZ	Sm. Mold/Head Operator	06:17-13:17	0.420	0.55
MDI 104	3-12	BZ	Lg. Mold/Head Operator	06:20-13:19	0.419	Less than 0.48
MDI 105	3-12	BZ	Metal Pour/Pourer	06:37-13:35	0.418	0.74
MDI 106	3-12	BZ	Metal Pour/Skimmer	06:39-13:30	0.411	0.68
MDI 110	3-12	Area	Metal Pour	14:20-14:30	0.010	Less Than 20.0

\* BZ = Breathing Zone Sample

\*\*"Less than" values based on sampled air volume and analytical limit of quantification (0.2 ug/sample) or detection (0.05 ug/sample).

TABLE 4  
 Analytical results; Formaldehyde  
 March 1981

Keokuk Steel Castings  
 Keokuk, Iowa  
 HETA 80-081

<u>SAMPLE #</u>	<u>DATE</u>	<u>TYPE</u>	<u>LOCATION/OPERATION</u>	<u>DURATION</u>	<u>VOLUME (M<sup>3</sup>)</u>	<u>CONCENTRATION (mg/M<sup>3</sup>)</u>
FD 1	3-10	BZ*	Lg. Mold/Head Operator	16:07-22:20	0.075	0.29
FD 2	3-10	BZ	Core/Stripper	15:54-22:19	0.071	0.50
FD 3	3-10	BZ	Core/Head Operator	15:50-22:20	0.060	0.18
FMD 10	3-11	BZ	Lg. Mold/Head Operator	06:22-13:15	0.089	0.36
FMD 11	3-11	BZ	Sm. Mold/Head Operator	06:27-13:50	0.074	0.43
FMD 12	3-11	BZ	Core/Head Operator	06:30-13:53	0.081	0.41

\* BZ = Breathing Zone Sample

TABLE 5  
 Analytical results; Dimethylethylamine  
 March 1981

Keokuk Steel Castings  
 Keokuk, Iowa  
 HETA 80-081

<u>SAMPLE #</u>	<u>DATE</u>	<u>TYPE</u>	<u>LOCATION/OPERATION</u>	<u>DURATION</u>	<u>VOLUME (M<sup>3</sup>)</u>	<u>CONCENTRATION (mg/M<sup>3</sup>)</u>
SGT 4	3-11	BZ*	Core/Head Operator	08:10-13:55	0.064	26.5
SGT 5	3-11	BZ	Core/Sm. Blwr Operator	08:13-13:57	0.064	18.8
SGT 8	3-12	BZ	Core/Sm. Blwr Operator	06:03-13:14	0.081	8.6
SGT 20	3-12	BZ	Core/Head Operator	06:06-13:55	0.012	14.8
SGT 6	3-12	BZ	Core/Sm. Blwr Operator	06:08-13:14	0.065	11.3
SGT 13	3-12	BZ	Core/Sm. Blwr Operator	06:09-13:16	0.072	4.2
SGT 11	3-12	Area	Core	06:11-13:25	0.059	8.8
SGT 10	3-12	BZ	Core/Sm. Blwr Operator	06:11-13:27	0.045	15.3
SGT 100	3-12	BZ	Core/Head Operator	09:16-13:55	0.052	5.3

\* BZ = Breathing Zone Sample

TABLE 6  
 Analytical results; Trace Metals  
 March 1981

Keokuk Steel Castings  
 Keokuk, Iowa  
 HETA 80-081

SAMPLE #	DATE	TYPE	LOCATION/OPERATION	DURATION	VOLUME (M <sup>3</sup> )	Al	CONCENTRATION (mg/M <sup>3</sup> )				
							Ca	Cr	Fe	Mg	Mn
M 2	3-10	Area	Metal Pouring	16:27-22:30	0.545	0.010	0.022	0.003	0.256	0.001	0.043
AA 51	3-12	Area	Crane Cab	06:24-12:07	0.515	-----	0.107	ND*	0.350	0.008	0.136
S 8	3-11	BZ**	Metal Pour/Pourer	06:03-13:45	0.693	-----	0.029	ND	0.202	0.010	0.062
S 9	3-11	Area	Small Mold/Pre Mix	06:33-13:53	1.100	-----	0.018	ND	0.200	0.006	0.003
S 11	3-11	BZ	Metal Pour/Skimmer	06:07-13:45	0.687	-----	0.036	0.007	0.277	0.010	0.070

\*ND = None Detected

\*\*BZ = Breathing Zone Sample



TABLE 7

Results of Questionnaire  
March 1981Keokuk Steel Castings  
Keokuk, Iowa  
HETA 80-081

	<u>Isocure (6 workers)</u>	<u>Other Core and Mold (24 workers)</u>	<u>Other (19 workers)</u>
Mean Age (years)	31	42	41
Males	6 (100%)	23 (96%)	19 (100%)
Smokers	2 (33%)	11 (46%)	15 (79%)
Known Allergies	1 (17%)	0 (0%)	2 (11%)
Symptoms Reported For The Two Days Preceding Survey:			
Headache	0 (0%)	9 (38%)	10 (53%)
Cough	5 (83%)	10 (42%)	11 (58%)
Stuffy Nose	3 (50%)	15 (62%)	12 (63%)
Shortness of Breath	0 (0%)	7 (29%)	8 (42%)
Skin Irritation	1 (17%)	4 (17%)	5 (26%)
Eye Irritation	1 (17%)	6 (25%)	11 (58%)
Blurry Vision	0 (0%)	1 (4%)	1 (5%)
Sore Throat	2 (33%)	7 (29%)	4 (21%)
A Cold	1 (17%)	5 (21%)	5 (26%)
Symptoms Reported For The Three Months Preceding Survey:			
Headache	2 (33%)	14 (58%)	8 (42%)
Cough	3 (50%)	12 (50%)	12 (63%)
Shortness of Breath	0 (0%)	9 (38%)	5 (26%)
Stuffy Nose	3 (50%)	10 (42%)	12 (63%)
Eye Irritation	2 (33%)	12 (50%)	12 (63%)
Blurry Vision	1 (17%)	2 (8%)	3 (16%)
Skin Irritation	3 (50%)	7 (29%)	5 (26%)
Sore Throat	1 (17%)	6 (25%)	3 (16%)

Table 8

Pulmonary Function Tests  
Shift Changes

Keokuk Steel Castings, Inc.  
Keokuk, Iowa  
March 1982

	<u>Pre-shift mean</u> (26 workers)	<u>Post-shift mean</u> (26 workers)	<u>Mean change</u>
FEV1 (liters)	3.60 (0.832)*	3.56 (0.857)	-0.04
FVC (liters)	4.60 (0.955)	4.57 (0.956)	-0.03
FEV1/FVC	0.78 (0.074)	0.78 (0.072)	0.00

\*Standard deviation.

Table 9  
Pulmonary Function Test and Questionnaire Results

Keokuk Steel Castings, Inc.  
Keokuk, Iowa  
March 1982

	Core and Molding (22 workers) <sup>1</sup>	Other (17 workers) <sup>2</sup>
mean FEV1 (liters)	97 (15.879) <sup>3</sup>	91 (15.831)
mean FVC (liters)	101 (14.062)	93 (14.921)
mean FEV1/FVC	0.78 (0.0750)	0.80 (0.0547)
mean age (years)	41	36
mean pack years	20	24
mean years at plant	5	5
mean years at Kast Metal	16	13
number with <sup>4</sup>		
cough	10 (38%)	7 (37%)
phlegm	4 (15%)	3 (16%)
shortness of breath	1 (4%)	1 (5%)
wheezing	3 (12%)	6 (32%)
chest tightness	5 (19%)	1 (5%)

<sup>1</sup>Includes one female

<sup>2</sup>Includes one black

<sup>3</sup>Standard deviation

<sup>4</sup>Includes 4 core and molding workers and 2 other workers with inadequate pulmonary function tests

Table 10

Comparison of Workers With Abnormal and Normal  
Pulmonary Function TestsKeokuk Steel Castings, Inc.  
Keokuk, Iowa  
March 1982

	<u>Abnormal test</u> <u>(8 workers)</u>	<u>Normal test</u> <u>(31 workers)</u>
mean age (yrs.)	45	38
mean years at plant	5	5
mean years at Kast Metals	19	14
mean pack years	33	19
number with		
cough	5 (62%)	11 (35%)
phlegm	1 (12%)	6 (19%)
shortness of breath	0 (0%)	1 (3%)
wheezing	1 (12%)	8 (23%)
chest tightness	0 (0%)	5 (16%)

APPENDIX A

SAMPLING AND ANALYTICAL METHODOLOGY FOR MDI

ANALYTICAL REPORT: NIOSH ORGANIC METHODS DEVELOPMENT SECTION

KEOKUK STEEL CASTING, INC.

HETA 80-081

MARCH 10-12, 1981

Seventeen time-weighted average samples and three 10-minute ceiling samples were collected. The samples were collected with 13 mm glass fiber filters impregnated with a reagent, N-p-nitrobenzyl-N-propylamine. The reagent can react with MDI to form a urea derivative, MDIU. The samples can collect MDI both aerosol and vapor forms. There were 9 field blanks.

For analysis, each impregnated filter was treated with 1 ml of dichloromethane, and a 50- $\mu$ l aliquot of the resulting solution was analyzed by high pressure liquid chromatography with an ultraviolet detector set at 254 nm. Injections of aliquots from two samples were bracketed by injections of high and low standards. Heights of peaks corresponding to the urea derivative were measured and recorded. The quantities of MDI which corresponded to the quantities of MDIU detected were determined from calibration curves based on the standards which bracketed the samples.

Five control samples were prepared by adding known quantities of MDI in dichloromethane solution to impregnated filters. The control samples were analyzed by HPLC. Quantities found were corrected for a recovery of 0.98.

Quantities for field samples were not corrected for recovery. The average recovery at the 0.781 ug level of MDI was not significantly different from 1.000 for  $\alpha = 0.05$ . A recovery curve suggested recoveries at the level of the field samples were not significantly different from 1.000 for  $\alpha = 0.05$ .

The retention time for a peak corresponding to MDIU for a selected field sample was confirmed by the use of authentic MDIU. A quantity of authentic MDIU in solution was added to a solution of the field sample. HPLC analysis of an aliquot of the solution gave rise to a larger peak at the retention time of MDIU.

Work was performed with a solution of a selected field sample to determine whether unreacted reagent, N-p-nitrobenzyl-N-propylamine, was present. A known quantity of MDI (10.1 ug) in dichloromethane was added to the solution of the field sample. A result of HPLC analysis indicated a recovery of 104%.

The relative standard deviation of measurement of each of the following levels of MDI was less than 7%: 0.20, 0.32, 0.47, and 0.65 ug. The lower quantitation limit for MDIU was estimated to be 0.20 ug MDI per sample. The detection limit for MDIU was estimated to be 0.05 ug/sample.

Three of the nine field blanks gave detector responses, but were below the detection limit. Consequently, no blank correction was necessary for all field samples.