U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
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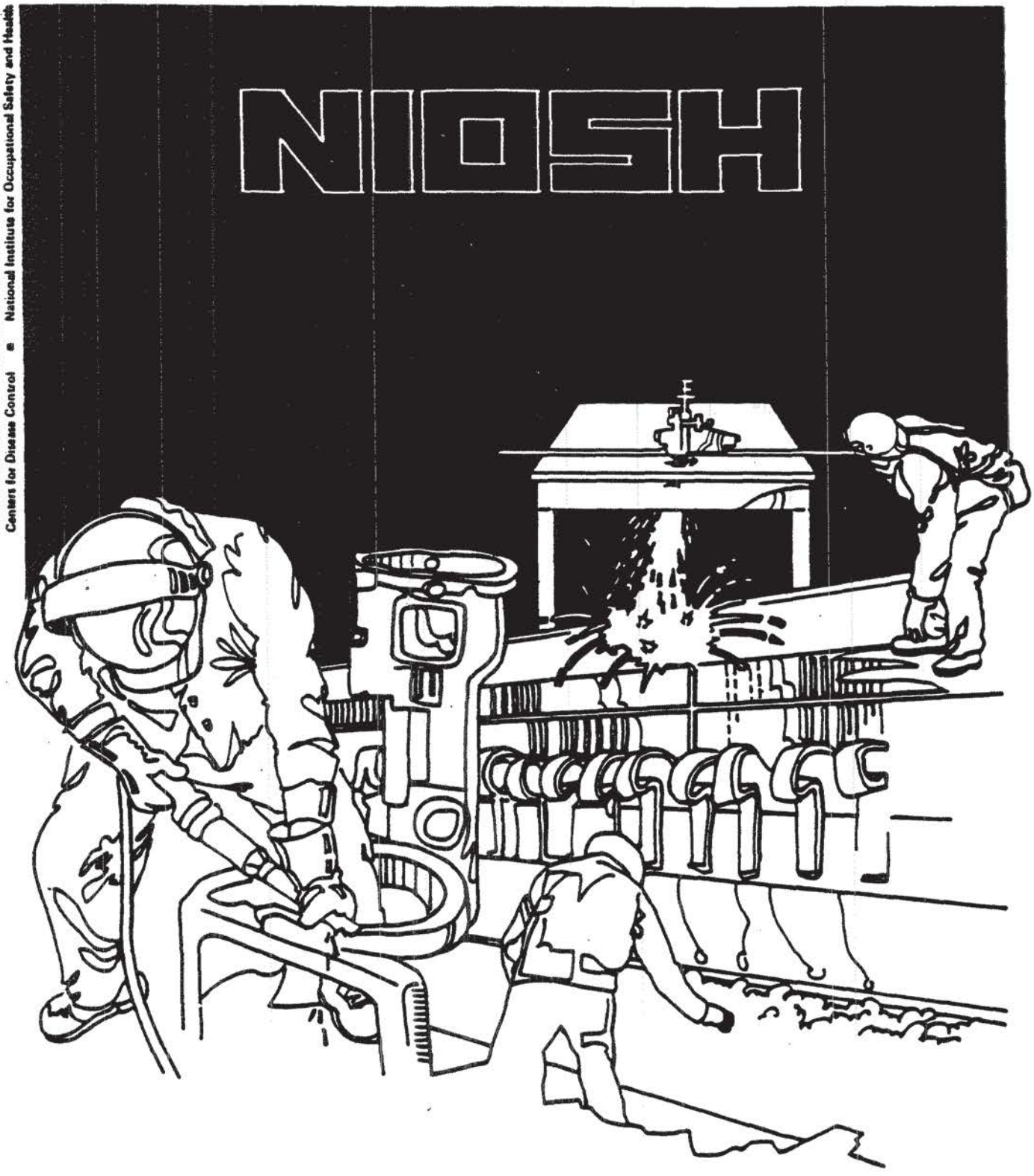
NIOSH



# Health Hazard Evaluation Report

HETA 85-407-1692
PARKWAY PRODUCTS, INC.
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.

HETA 85-407-1692
May 1986
PARKWAY PRODUCTS, INC.
CINCINNATI, OHIO

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## I. SUMMARY

In June 1985, the National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation from the management of the Parkway Products, Inc. plant in Cincinnati, Ohio. NIOSH was asked to evaluate a worker's exposure to 4,4'-methylene-bis-2-chloroaniline (MBOCA) during an accidental spill from a machine that mixes MBOCA with a polymer resin. The employee was sprayed over his torso and extremities with molten MBOCA while cleaning out a clogged hose from the MBOCA mixing machine. MBOCA is used as a curing agent for diisocyanate-based polymers (polyurethanes) and epoxy resin systems. This compound is suspected of being a human carcinogen on the basis of its chemical resemblance to benzidene and other known human bladder carcinogens, its carcinogenicity in multiple animal species, and its mutagenicity.

On June 11-24, 1985, a NIOSH team conducted a medical and environmental evaluation at the plant. A medical history, an occupational history, a dermatological examination, serial serum liver and renal function tests, urinalyses, and urine MBOCA levels were obtained from this exposed worker over a two week period. The environmental evaluation consisted of a plant walk-through and a review of prior industrial hygiene data collected at that plant.

The serial urine determinations demonstrated that this exposed worker had urine MBOCA levels ranging from 1707 ppb (9 hours after the spill) to nondetectable (11 days after the spill). The earliest measurement was over 17 times higher than the maximum allowable urinary MBOCA concentration of 100 ppb permitted by the California Occupational Safety and Health Agency (Cal-OSHA). There is no federal standard for urinary MBOCA levels. The remaining blood and urine values were all within normal limits.

The environmental evaluation demonstrated that the production of MBOCA-cured polyurethane cast products involves potential dermatological exposure to MBOCA, and that good plant hygiene and work practices need to be enforced.

Based on the medical findings, the environmental results, and the available toxicological information, it is concluded that the health hazard from MBOCA exposure experienced by this worker at Parkway Products, Inc. did not result in any acute medical condition but that the long-term effects of this exposure can not be predicted. It was recommended that this worker receive an annual urine test for the presence of red blood cells and urine cytology screening for the detection of early bladder disease. Furthermore, recommendations to aid in providing a safer working environment and in avoiding future accidental spills are presented in Section VIII of this report.

KEYWORDS: SIC 3079 (molding primary plastics, for the trade), CAS No. 101-14-4, MBOCA, MOCA, 4,4'-methylene bis-2-chloroaniline, DACPM, Curaline M, Curene 442, Cyanaset, and renal effects.

## II. INTRODUCTION

In June 1985, the National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation at the Parkway Products, Inc. plant in Cincinnati, Ohio. NIOSH was asked by the management to evaluate a worker's exposure to an accidental spill of 4,4'-methylene-bis- 2-chloroaniline (MBOCA) from a MBOCA and polymer mixing machine. The urethane molder was sprayed with molten MBOCA while cleaning out a clogged hose from the MBOCA tank of the mixing machine. MBOCA is used as a curing agent for diisocyanate-based polymers (polyurethanes) and epoxy resin systems in order to achieve varying degrees of product hardness, flexibility and impact strength. This compound has been suspected of being a human carcinogen on the basis of its mutagenic properties, carcinogenic effects in rat, mouse and dog (including lung, hepatic, mammary gland and bladder tumors), and structural similarity to other known human carcinogens such as benzidine.(1,2)

On June 11-24, 1985, a NIOSH team conducted a medical and environmental evaluation at the plant. An initial medical and occupational history, a dermatological examination, multiple serum liver and renal function tests, and serial urine MBOCA, protein and red blood cell determinations were conducted over a two week period. The environmental evaluation consisted of a plant walk-through and a review of prior industrial hygiene data from that work site.

## III. BACKGROUND

Founded in 1946, Parkway Products, Inc. manufactures customized polyurethane products for industry such as precision aircraft parts. The process under investigation involves the molding of a MBOCA-cured urethane elastomer of varying tensile strength into a variety of commercial products. This process accounts for approximately 30% of the company's output. This plant employs approximately 142 workers with 70% involved in production work.

On December 20, 1984 and February 12, 1985, an industrial hygiene survey by the Industrial Commission of Ohio was conducted at the request of the company. The purpose was to evaluate potential solvent, nuisance dust and MBOCA exposure at the plant. On December 20, a single MBOCA air sample was taken in the MBOCA room where the substance is weighed and melted down. The air concentration was <0.005 ppm with the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value set at 0.02 ppm and the California-Occupational Safety and Health Agency (Cal-OSHA) standard set at 0.01 ppm (ppm indicates parts of MBOCA per million parts of air volume). The air concentrations of toluene diisocyanate, methylene chloride, methyl ethyl ketone, and nuisance particulates (total dust) measured at that time were also below the respective OSHA, NIOSH and ACGIH evaluation criteria.

During the last two years, urinary MBOCA monitoring of MBOCA-exposed workers has been conducted at this plant (Table 1). The analysis was conducted at Chromatics Laboratories Incorporated in Park Ridge, Illinois using a thin layer chromatography (TLC) technique until October, 1984, and subsequently, using the more sensitive high pressure liquid chromatography (HPLC) technique. (2) As can be seen in Table 1, all mean urinary MBOCA values were < 50 ppb. Two pre-accident urinary MBOCA levels for the worker under evaluation were < 10 ppb (July, 1983), and 65 ppb (August, 1983) using the TLC method.

## IV. MATERIALS AND METHODS

### A. Medical

Four hours following the accident, the worker underwent a thorough medical and occupational interview, and a brief medical examination. Two sets of blood specimens were collected for liver and kidney function tests on the day of the accident and two days afterwards. In addition, a test for the presence of methemoglobin was performed on the second set of blood tests. The worker was then asked to collect a urine sample from every urinary void for the next week and a daily sample during the subsequent week. Plastic collection bottles containing 0.5 grams of citric acid preservative (for urine MBOCA determination) and bottles containing 0.5 grams of boric acid (for detection of protein and red blood cells in the urine) were provided to the worker. The worker was instructed to place all of his urinary sample bottles in the freezer until pickup by a NIOSH representative.

The liver and kidney function tests were obtained on the first and third day following the spill and analyzed at the MetPath Laboratory in Teterboro, New Jersey. A blood sample collected three days after the accident was analyzed for methemoglobin at the University of Cincinnati Hematology Laboratory within one hour of obtaining the specimen. An initial first day methemoglobin sample had to be discarded because of improper storage. The urine protein analysis used the dipstick method with a 6 mg/dl limit of detection (Chemstrip$^{tm}$ by Biodynamic Corporation). Also, a microscopic analysis of the urine for red and white blood cells was conducted at the MetPath Laboratory. The urinary MBOCA concentrations were obtained using the high performance liquid chromatography and the gas chromatography-mass spectrometry techniques at the Health and Safety Executive Occupational Medicine and Hygiene Laboratory, London, England. In addition, the urine MBOCA determinations were performed before and after acid hydrolysis of each sample.(3)

B. Environmental

On the day of the MBOCA spill, a walk-through of the plant was conducted by a NIOSH industrial hygienist and a medical officer. An assessment was made of all areas with potential MBOCA exposure to gain an understanding of the production process and to identify factors which could have led to the accident.

At the present time, there is no completely satisfactory method for monitoring the workplace environment for MBOCA. Air sampling data do not accurately reflect worker exposure because they do not estimate the fraction absorbed by the skin, which is an important route of exposure for MBOCA.(10) Wipe sampling can be a useful method for identifying contaminated surfaces, but these results indirectly reflect potential worker exposure. Therefore, no environmental monitoring was attempted for this health hazard evaluation. A concurrent project is underway at this company specifically directed toward developing better environmental monitoring techniques. The results of that study are pending.

## 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. However, it is 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 condition (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, medications or the 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 in this manner may 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 Occupational Safety and Health Agency (OSHA) occupational 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. Also, the OSHA standards may be required to take into account the feasibility of controlling exposures in various industries where the agents are used. By contrast, the NIOSH recommended standards 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.

A. Medical and Environmental

OSHA promulgated a standard for MBOCA on an emergency temporary basis in 1973 and on a permanent basis in January of 1974. In late 1974, the MBOCA standard was remanded for procedural reasons. The following year, ACGIH designated MBOCA as a suspect human carcinogen and set an air threshold limit value of 0.02 ppm with a caution about possible skin absorption.(4) Since then, California has been the only state to regulate MBOCA exposure using standards for air sampling (0.01 ppm), urine levels (100 ppb with a specific gravity adjustment to 1.019), and wipe samples (100 ug per 100 $cm^2$ of surface area).(5) The current ACGIH threshold limit value (TLV) for MBOCA air concentrations is still 0.02 ppm with no biological exposure index for urinary MBOCA.(6)

Although the animal studies clearly demonstrate the carcinogenicity of MBOCA, there is very little information on human exposure to this compound. In 1965, Mastromatteo reported urinary frequency and hematuria in 2 out of 6 MBOCA-exposed polyurethane workers with spontaneous resolution of the symptoms within a week.(7) Hosein writes of a MBOCA mixing machine accident identical to that of the worker under evaluation.(8) In this earlier case, the worker ingested MBOCA as well as experienced extensive skin contact during the spill. Although wearing protective gear, the worker suffered from conjunctivitis, "burning eyes" and an "upset stomach". Urinary MBOCA levels ranged from 1400 ug/gm creatinine (5 hours after the spill) to 30 ug/gm creatinine (23 hours after the spill) with an associated proteinuria from 220 mg/L to a trace amount.

In 1976, the Alberta, Canada government began urine monitoring of MBOCA exposed workers and discovered an average value of 200 ppb (38 individuals with a range of 0-1140 ppb) in March, and 80 ppb (25 individuals with a range of 0-480 ppb) in November.(8) The latter decline in the mean urine MBOCA level was attributed to improved control technology, and better worker protection and hygiene. A similar decline in urine MBOCA levels was observed in a screening program of polyurethane elastomer production workers in Great Britain.(9) After introducing improved ventilatory controls, the use of protective clothing and a greater emphasis on general factory hygiene over a five-year period, the mean monthly urine MBOCA concentrations from 10-15 exposed workers showed a decline from 118 ug/gm creatinine to 19. Furthermore, the biological monitoring program was extremely helpful in identifying those workers whose work practices were inadequate or who were being exposed to MBOCA from an unknown source.

Since no federal standard exists for urinary MBOCA levels, we will use the Cal-OSHA concentration of 100 ppb as a reference value. Note that there is no evidence to suggest that workers who have urine levels below this point will be safe from the toxic effects of MBOCA.

## VI. RESULTS AND DISCUSSION

### A. Medical

On June 11, 1985, a 30 year-old Caucasian male urethane molder was involved in a MBOCA spill. According to the worker, he did not release the pressure of a MBOCA and polymer automated mixing machine prior to opening and cleaning a clogged MBOCA delivery line. Approximately three gallons of molten MBOCA were sprayed on his chest, abdomen and extremities over a period of a few seconds. No accidental ingestion of the MBOCA occurred. He was wearing work pants and shirt with rolled up sleeves, a cartridge respirator, asbestos gloves and safety eye glasses. When the MBOCA spill occurred, the worker was immediately disrobed, showered and wrapped in a cloth sheet for transport to a nearby emergency room. Within approximately 45 minutes, he had the remaining MBOCA residue gently washed off with soap and water. Slight erythema and a burning sensation over the affected skin areas was noted by the attending physician at that time. The worker was given a clean set of clothes and returned to work in the non-MBOCA area of the plant. Another worker in protective clothing, gloves, and dust mask cleaned up the residual MBOCA on the ground by breaking up the crystallized MBOCA and sweeping away the material.

Four hours after the MBOCA spill, our initial medical evaluation revealed an employee in good general health with no skin erythema who complained of a mild "sunburn" sensation of the arms. There was no history of prior respiratory, hepatic or renal disease. The worker has smoked two packs of cigarettes per day for the last 15 years. The rest of the medical history

was unremarkable. During periodic contact with the worker in the two week period following the accident, no further symptoms were reported.

The laboratory results revealed normal renal and liver function tests, no methemoglobinemia, and the absence of protein and red blood cells in the urine. The serial urinary MBOCA levels are listed in Table 2. As can be seen, it took more than four days (>99 hours) for the urine values to fall below the Cal-OSHA environmental criterion of 100 ppb.

Environmental air and wipe samples for MBOCA were not obtained at the plant because these types of measurements correlate poorly with the actual body burden of MBOCA resulting from an acute dermal exposure.(2)

B. Pharmacokinetic Analysis

To calculate the biological elimination rate constant and half-life for MBOCA in this worker, the logarithmic concentrations of urinary MBOCA were plotted against time for both the HPLC (high performance liquid chromatography) and GCMS (gas chromatography/mass spectrometry) methods.(Figures 1 and 2) The elevation in the MBOCA concentration which occurred at the 434 hour mark was explained by the fact that the subject returned to work in MBOCA-exposed areas.

If the data points are fitted to a one compartment model, there is good agreement between the HPLC and GCMS methods. The half-life for both hydrolyzed and unhydrolyzed MBOCA samples is approximately 23 hours and the elimination rate constant is 0.0295 $hr^{-1}$. The best correlation (0.91) between the urinary MBOCA levels and time is observed when the data are expressed as ppb of MBOCA in urine unadjusted for creatinine using the HPLC method.(Table 3) When the creatinine correction is made, the correlation coefficient becomes 0.74 and the half-life is 20 hours. Assuming that no storage of MBOCA occurs in any physiological compartment of the body such as adipose tissue, approximately 94% of the initial MBOCA dose will be eliminated within four days.

C. Environmental

The production of MBOCA-cured urethane begins with the receipt of dry, prilled MBOCA (popcorn-sized pellets) from the chemical manufacturer. At Parkway Products, MBOCA is stored and handled in a specially constructed room isolated from the remainder of the plant. Air from this room is exhausted through high efficiency particulate filters. A single worker handles MBOCA which includes the removal of the material from the shipping container, the melting down of solid MBOCA, and the delivery of pre-measured quantities of MBOCA to the molders upon request.

After melting, the MBOCA is blended with an isocyanate prepolymer (e.g. Adiprene$^{tm}$) to form a moldable urethane. At Parkway Products, the dry MBOCA is melted and blended with the prepolymer in an automatic mixing machine or it is manually blended using a disposable container and a hand stirrer. Larger quantities are produced using the APC machine.

The blended urethane mix (prepolymer and MBOCA curative) is poured into a heated metal mold and permitted to cure either at room temperature or in an oven (depending on the desired physical properties). After a predetermined curing period, the mold is opened and the finished urethane part is removed. The finished part is inspected, trimmed, and prepared for shipment. The alloy metal molds are cleaned with methylene chloride and returned to storage for reuse.

In this plant, there are 2 automated MBOCA mixing machines with one worker assigned to each work station. During the last several years, there have been occasional accidental MBOCA spills from carrying the open bucket of molten MBOCA to the APC machine as well as during attempts to open and clean out the MBOCA line. According to the management, none of these incidents have been as extensive as the current spill. The worker in question has had two and a half years experience in operating this machine without any prior accidents.

The walk-through survey of the production area suggests that released pressure on the MBOCA feed tank prior to clearing the line should prevent this type of accident. These machines did not have built-in warning systems or lock devices which will prevent such an accident from occurring. The routine activity of refilling or servicing the MBOCA tank can lead to small spills. These spills can be readily cleaned up by breaking up the crystallized MBOCA on the ground and sweeping away the material. With the use of proper protective gear among the workers in the area and the isolation of this procedure, the clean-up should pose little risk of exposure to the workers. Those operators who refill or service the MBOCA feed tank wear protective gloves and a respirator which should preclude skin contact or inhalation exposure to MBOCA. Although the plant management recommends the use of protective workclothes, gloves, eye goggles, and foot covers, there does not seem to be enforcement of these practices (for example some men in the MBOCA room area were directly handling the buckets of molten MBOCA). Furthermore, there is no policy of routine wash down of the MBOCA operating areas nor enforcement of daily showering and change of workclothes. Finally, while there are safety

meetings twice a month involving both the the management and the employees, there is no educational component to update the workers on the hazards and proper handling of MBOCA.

## VII. CONCLUSIONS

This case investigation brings up various points concerning MBOCA hazards in the workplace. Based on the values from cases discussed earlier in the evaluation criteria section, we concluded that this worker experienced an extremely high dose of MBOCA as judged by his urinary MBOCA levels. There were no acute effects noted but possible long-term effects need to be monitored.

From the pharmacokinetics information, the half-life of MBOCA appears to be relatively short (approximately 23 hours). Monitoring of the urine MBOCA concentrations in exposed workers may miss peak levels due to an acute exposure unless the analyses of the urinary MBOCA are performed in a timely fashion.

Finally, further epidemiological studies are needed to fully address the issue of MBOCA carcinogenicity in humans. Currently, a prospective study of workers engaged in the production of MBOCA is being conducted by NIOSH investigators.(11) Based on the evidence currently available, NIOSH recommends that MBOCA be treated as a potential occupational carcinogen.(1)

## VIII. RECOMMENDATIONS

Because of the excessive exposure to MBOCA and the suspect carcinogenicity of this compound, we advise that the exposed worker receive continued medical surveillance for bladder cancer detection with annual urinalysis and urine cytology testing. It is also recommended that the following control measures be implemented: (1) Evaluate the current ventilation and isolation of MBOCA processes (mixing and transport), (2) Frequently wash the MBOCA operating areas, (3) Enforce the daily change in protective workclothes with in-plant laundering or disposable garments, (4) Enforce the use of impermeable gloves and safety goggles, (5) Encourage showering at the end of the work shift, (6) Continue monthly urine MBOCA monitoring of all exposed workers, and (7) Continue periodic safety meetings with an additional emphasis on the education of the workers on the hazards of MBOCA and the proper operation of the mixing machines.

## IX. REFERENCES

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## X. AUTHORSHIPS AND ACKNOWLEDGEMENTS

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## XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of standards Development and Technology Transfer, Publications 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, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati addresss. Copies of this report have been sent to:

1. Parkway Products, Inc., Cincinnati, Ohio
2. NIOSH, Region V
3. OSHA, Region V

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

TABLE 1

Urine MBOCA Levels among Exposed Workers prior to June 11, 1985 Spill

Parkway Products, Inc.

Cincinnati, Ohio

HETA 85-407

July 1983 through May 1985

| Date of sample | Number of workers sampled | Urine MBOCA (ppb) | | |
|---|---|---|---|---|
| | | Mean | Std. Dev. | Peak Value |
| July 1983 | 3 | <10.0 | ---- | <10.0 |
| August 1983 | 4 | 20.0 | 30.0 | 65.0 |
| May 1984 | 3 | <10.0 | ---- | <10.0 |
| August 1984 | 3 | 16.7 | 20.2 | 40.0 |
| October 1984 | 3 | 16.3 | 10.6 | 26.0 |
| December 1984 | 3 | 35.0 | 15.7 | 51.0 |
| January 1985 | 3 | 5.3 | 0.5 | 5.8 |
| February 1985 | 3 | 23.1 | 21.3 | 46.5 |
| April 1985 | 3 | 36.1 | 22.4 | 61.4 |
| May 1985 | 6 | 43.8 | 32.1 | 97.9 |

| | |
|---|---|
| 100 ppb | ...Environmental Criteria (Cal-OSHA) |
| 10 ppb | ...Limit of detection |

Note: ppb = parts of MBOCA per billion parts of urine volume.
All results corrected to a specific gravity of 1.024.
Prior to October, 1984, the method of analysis was thin layer chromatography. Subsequent results were obtained using the high pressure liquid chromatography technique.

TABLE 2

Serial Urinary MBOCA Levels for a Urethane Worker Following a MBOCA Spill

Parkway Products, Inc.

Cincinnati, Ohio

HETA 85-407

June 11-14, 1985

| Time after exposure* (hours) | Urine MBOCA (ppb) | | | | Adjusted urine MBOCA** (ug/gm creat) | | | |
|---|---|---|---|---|---|---|---|---|
| | HPLC-UH | GCMS-UH | HPLC-H | GCMS-H | HPLC-UH | GCMS-UH | HPLC-H | GCMS-H |
| 9 | 1707 | 1659 | 2746 | 3132 | 2169 | 2107 | 3488 | 3979 |
| 18 | 1148 | 1096 | 1309 | 1395 | 1395 | 1331 | 1591 | 1694 |
| 18 | 1734 | 1864 | 2170 | 1910 | 2237 | 2405 | 2799 | 2464 |
| 23 | 691 | 794 | 1218 | 1792 | 585 | 673 | 1031 | 1517 |
| 29 | 1345 | 1472 | 2321 | 2844 | 2301 | 2518 | 3972 | 4866 |
| 33 | 498 | 585 | 1207 | 1180 | 1300 | 1527 | 3153 | 3082 |
| 42 | 700 | 752 | 1495 | 1517 | 380 | 408 | 812 | 824 |
| 54 | 385 | 376 | 695 | 724 | 1194 | 1163 | 2152 | 2244 |
| 61 | 417 | 373 | 782 | 1018 | 267 | 238 | 500 | 651 |
| 67 | 447 | 495 | 707 | 855 | 1843 | 2044 | 2917 | 3528 |
| 67 | 281 | 273 | 601 | 512 | 170 | 165 | 363 | 309 |
| 77 | 156 | 159 | 269 | 368 | 104 | 106 | 179 | 245 |
| 99 | 109 | 125 | 172 | 254 | 78 | 90 | 123 | 182 |
| 143 | 21 | 13 | 37 | 48 | 19 | 12 | 33 | 42 |
| 149 | 33 | 33 | 56 | 42 | 17 | 17 | 28 | 21 |
| 219 | 20 | 15 | 35 | 25 | 9 | 7 | 17 | 12 |
| 358 | nd | nd | nd | nd | nd | nd | nd | nd |
| 404 | nd | nd | nd | nd | nd | nd | nd | nd |
| 412 | nd | nd | 9 | 9 | nd | nd | 5 | 5 |
| 434 | 8 | 9 | 13 | 6 | 24 | 26 | 38 | 19 |

100 ppb ...Environmental Criteria (Cal-OSHA)

5 ppb ...Limit of detection

* MBOCA accident = time 0.

** Adjustment for potential dilutional effect.

Note: ppb = parts of MBOCA per billion parts of urine volume.
ug/gm = microgram of MBOCA per gram of creatinine.
HPLC-UH = high performance liquid chromatography, unhydrolyzed sample.
GCMS-UH = gas chromatography/mass spectrometry, unhydrolyzed sample.
HPLC-H = high performance liquid chromatography, hydrolyzed sample.
GCMS-H = gas chromatography/mass spectrometry, hydrolyzed sample.
nd = non-detectable value.

Figure 1

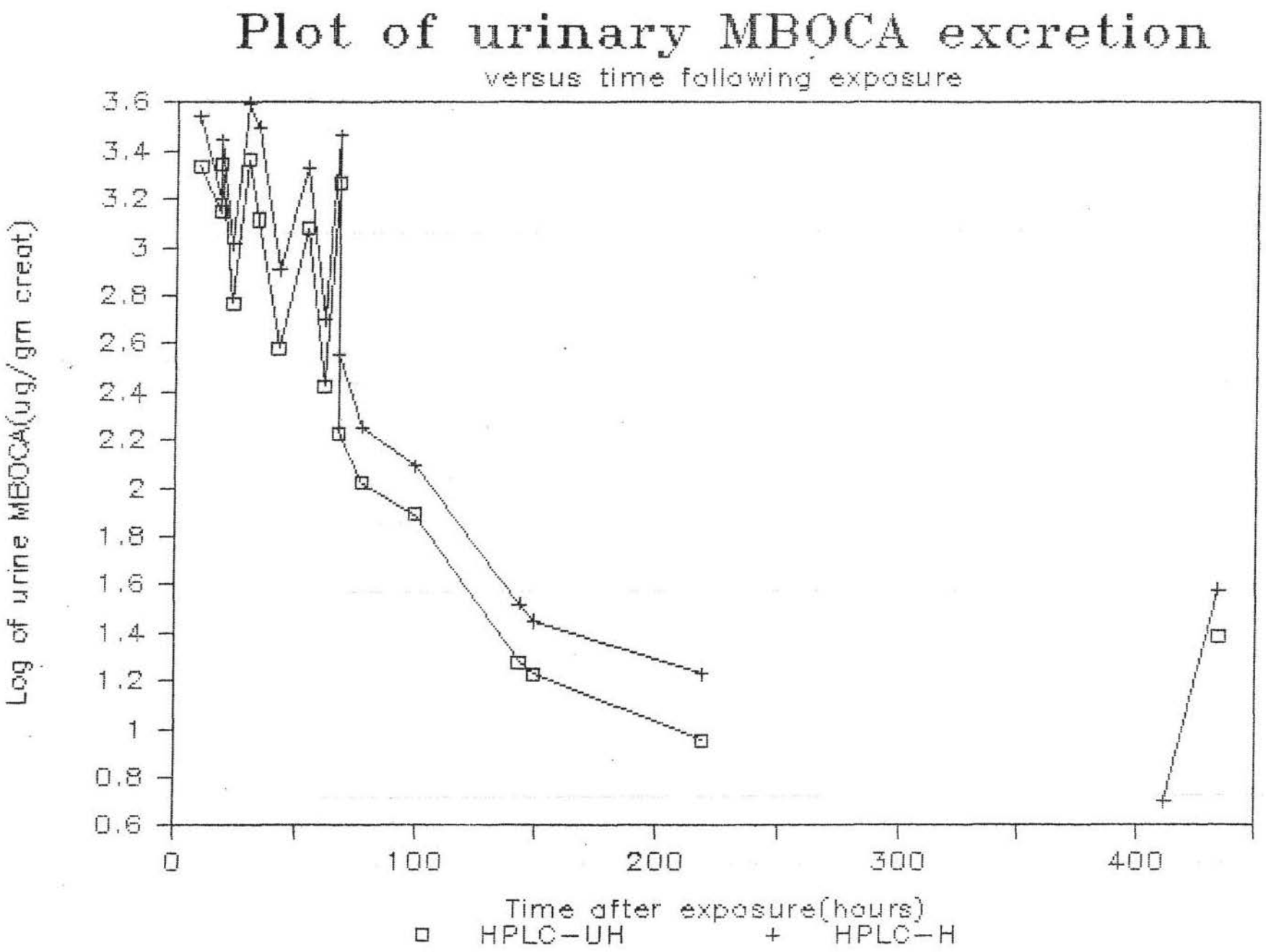
Plot of urinary MBOCA excretion
versus time following exposure
Log of urine MBOCA(ug/gm creat)
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0
100
200
300
400
Time after exposure(hours)
HPLC-UH
HPLC-H

TABLE 3

Logarithmic regression analysis of time following an acute exposure to MBOCA versus urinary MBOCA concentrations using different laboratory techniques.*

Parkway Products, Inc.

Cincinnati, Ohio

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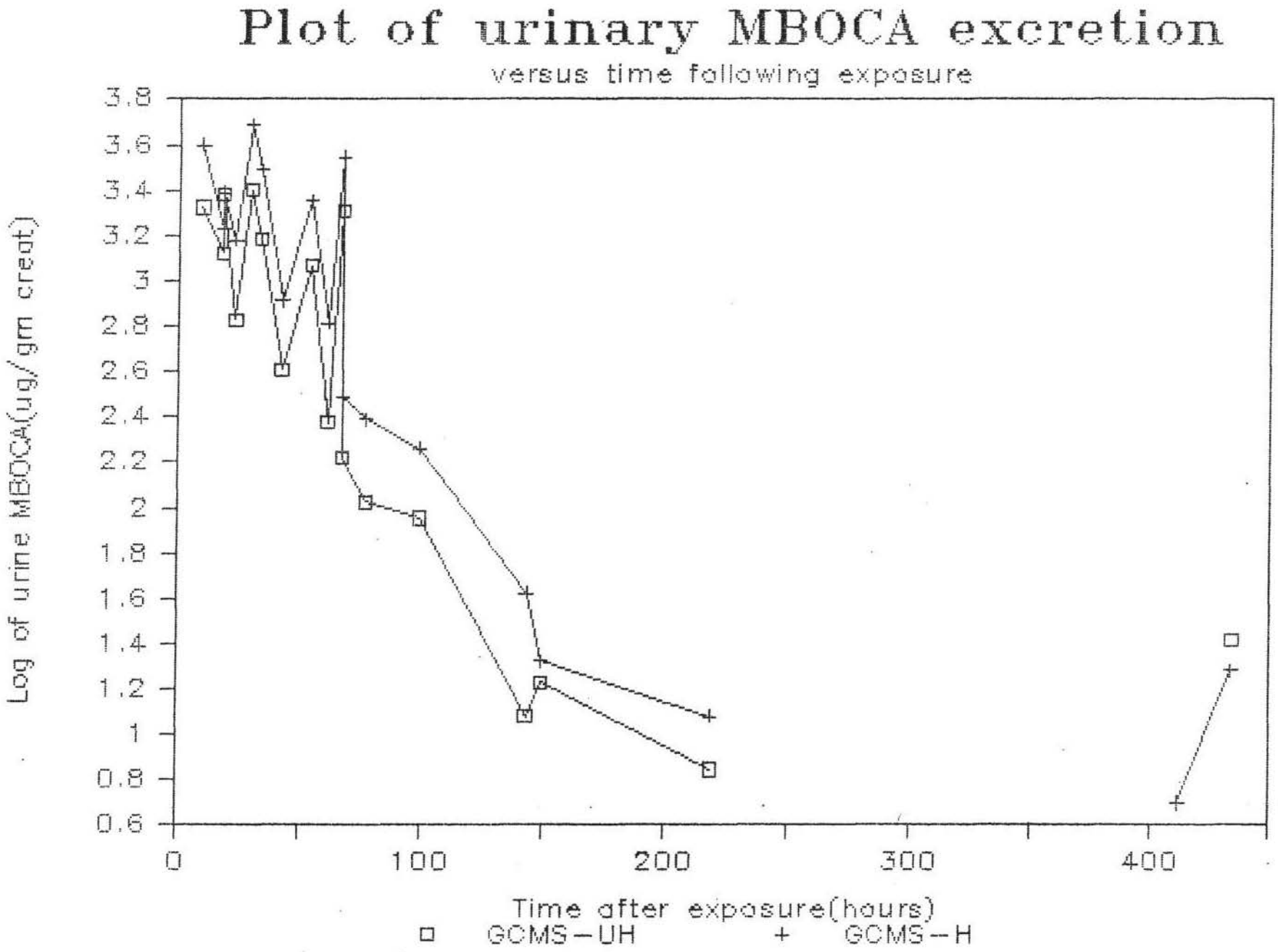
$Y = b + m(\ln X)$

| Y | X | b y-intercept | m slope | R regression coefficient |
|---|---|---|---|---|
| **Urine MBOCA (ppb):** | | | | |
| HPLC-UH method | Time (hours) | 3122.72 | -650.60 | 0.91 |
| HPLC-H method | " | 4669.85 | -949.81 | 0.91 |
| GCMS-UH method | " | 3209.48 | -666.43 | 0.90 |
| GCMS-H method | " | 5148.42 | -1043.86 | 0.89 |
| **Urine MBOCA (ug/gm creatinine):** | | | | |
| HPLC-UH method | Time (hours) | 4030.28 | -812.10 | 0.74 |
| HPLC-H method | " | 6144.13 | -1208.14 | 0.69 |
| GCMS-UH method | " | 4145.71 | -829.37 | 0.71 |
| GCMS-H method | " | 6691.44 | -1307.96 | 0.66 |

Note: ppb = parts of MBOCA per billion parts of urine volume.
ug/gm = microgram of MBOCA per gram of creatinine.
HPLC-UH = high performance liquid chromatography, unhydrolyzed sample.
GCMS-UH = gas chromatography/mass spectrometry, unhydrolyzed sample.
HPLC-H = high performance liquid chromatography, hydrolyzed sample.
GCMS-H = gas chromatography/mass spectrometry, hydrolyzed sample.
* For calculations, only the data points for <200 hour mark were used because the values beyond this mark were infrequent and approached the limit of detection (5 ppb).

Figure 2


Plot of urinary MBOCA excretion
versus time following exposure
Log of urine MBOCA(ug/gm creat)
3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0
100
200
300
400
Time after exposure(hours)
GCMS-UH
GCMS--H

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