American Industrial Hygiene Association Journal

ISSN: 0002-8894 (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/aiha20

Production of Vinylidene Chloride from the Thermal Decomposition of Methyl Chloroform

BRUCE T. GLISSON , BOBBY F. CRAFT , JAMES H. NELSON & HENK L.C. MEUZELAAR

To cite this article: BRUCE T. GLISSON , BOBBY F. CRAFT , JAMES H. NELSON & HENK L.C. MEUZELAAR (1986) Production of Vinylidene Chloride from the Thermal Decomposition of Methyl Chloroform, American Industrial Hygiene Association Journal, 47:7, 427-435, DOI: 10.1080/15298668691389991

To link to this article: https://doi.org/10.1080/15298668691389991

Am. Ind. Hyg. Assoc. J. 47(7):427 (1986)

Production of Vinylidene Chloride from the Thermal Decomposition of Methyl Chloroform*

BRUCE T. GLISSON[A], BOBBY F. CRAFT[B], JAMES H. NELSON[C] and HENK L.C. MEUZELAAR[D]
[A]National Semiconductor Corporation, 3333 W. 9000 S., West Jordan, UT 84084; [B]Department of Family and Community Medicine, University of Utah, Salt Lake City, UT 84112; [C]UBTL Incorporated, Deseret Research Company, Salt Lake City, UT 84108; [D]Department of Pathology, University of Utah School of Medicine, Salt Lake City, UT 84112

This study investigated the extent to which methyl chloroform undergoes thermal decomposition to form vinylidene chloride. The experiment was conducted under laboratory conditions that approximate those found in industrial environments. Methyl chloroform vapors at approximately the TLV concentration of 1910 mg/m^3 were passed through a heated quartz tube packed with glass or copper beads. In the presence of glass, the decomposition reaction began at 350° C and was essentially complete at 605° C. Vinylidene chloride was detected in nearly stoichiometric amounts. In the presence of copper, the reaction occurred initially at 180° C. At 442° C no methyl chloroform was detected. Once again, the conversion to vinylidene chloride was nearly complete. Two major conclusions have been derived from this study. First, under these experimental conditions, methyl chloroform undergoes thermal decomposition to yield substantial quantities of vinylidene chloride. Second, the dehydrohalogenation reaction proceeds at much lower temperatures in the presence of copper.

Introduction

Methyl chloroform, also referred to as 1,1,1-trichloroethane and alpha-trichloroethane, is a colorless, nonflammable liquid with an odor similar to that of chloroform. It has a vapor pressure of 127 torr at 25° C and a boiling point of 74.1° C at 760 torr. Since its introduction in 1951, methyl chloroform has been used widely as an industrial cold cleaning solvent. It is also present in many commercial products intended for use by the general public. In 1976 the National Institute for Occupational Safety and Health (NIOSH) estimated that 100 000 workers potentially were exposed to methyl chloroform vapors.(1)

The widespread acceptance of methyl chloroform generally is attributed to its relatively low toxicity, good solvent properties and nonflammable nature. It is an excellent solvent for greases, oils, waxes, tars and a wide range of other organic materials. It generally is considered to be the least toxic of the chlorinated hydrocarbons. Because of this, many industrial processes have substituted methyl chloroform for more toxic solvents such as carbon tetrachloride and trichloroethylene. The use of these other solvents has decreased considerably, while the demand for methyl chloroform has grown steadily.(2) Many of the applications of methyl chloroform have significant potential for the vapor to contact and be decomposed by hot surfaces or open flames. This is especially true when metal parts are cleaned in the vicinity of soldering or welding operations. Methyl chloroform is reported to have been recommended as a substitute solvent for trichloroethylene as a degreasing agent in welding shops.(3)

Toxicology

Methyl chloroform is a relatively minor skin and eye irritant, but repeated skin exposure may result in blisters or burning of the affected area. The first response to acute or chronic exposure is usually the depression of the central nervous system. Methyl chloroform is extremely volatile; at least six human fatalities have been reported regarding industrial exposure to high concentrations in poorly ventilated, confined areas. These deaths have been attributed to anesthesia or cardiac arrhythmia.(4)

Adams *et al.* reported that minor organic injury resulted from exposures exhibiting strong anesthetic effects.(5) Methyl chloroform has not demonstrated any carcinogenicity, but NIOSH has reported that congenital abnormalities have resulted in the offspring of experimental animals exposed to high concentrations. A study of an industrial population failed to detect any significant organic injury caused by methyl chloroform.(1)

Both the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) are expressed as 8-hr Time-Weighted Averages (TWAs) of 350 ppm or 1910 mg/m^3. The TLV was set at this level to minimize complaints about the odor and to reduce unnecessary prolonged exposure to chlorinated hydrocarbons.(6) NIOSH has recommended that a 15-min ceiling value of 350 ppm be adopted.(1) It generally is accepted that considerable variability exists in the odor threshold and, therefore, odor is not regarded as an adequate warning signal.

---

*This paper is adapted from a Master of Science thesis that was conducted at the University of Utah. The research was supported by the National Institute for Occupational Safety and Health (NIOSH), grant number 5-T15-OH07141-06 (Educational Resource Center), to the Rocky Mountain Center for Occupational and Environmental Health (RMCOEH), University of Utah. Laboratory facilities were provided by the U.S. Department of Labor, OSHA Analytical Laboratory, Salt Lake City, Utah.

Vinylidene chloride also is referred to as 1,1-dichloroethylene, vinylidine chloride, 1,1-dichloroethene, and vinylidene dichloride.(7) The available literature indicates that vinylidene chloride is considerably more toxic than methyl chloroform. It is extremely volatile, with a vapor pressure of 591 torr at 25° C.(4)

The acute effects of exposure to vinylidene chloride are typically depression of the central nervous system and hepatotoxicity. Typical symptoms of exposure to its vapors are continuous blinking, lacrimation, nasal irritation, excessive salivation, accelerated respiration, gasping, tremor, convulsions, lack of coordination, prostration and narcosis. The rat-oral LD_{50} was determined to be 200 mg/kg.(7) It has been noted that mice are more sensitive than rats to the hepatotoxic effects of this compound.(8) It also has been reported that concentrations as low as 50 ppm are lethal to some mice.(9) The LC_{50} (4 hr) was found to be 10 000-15 000 ppm in fed rats but only 500-2500 ppm in fasted rats. In addition, male rats were shown to be more susceptible than females to the hepatotoxic effects of vinylidene chloride.(10)

The primary effects of chronic exposure to vinylidene chloride vapors appear to be liver and kidney damage. This has been demonstrated in rats, rabbits, guinea pigs and dogs exposed to concentrations as low as 25 ppm.(6) Animal studies have shown this compound to be carcinogenic in rats and mice. In rats, angiosarcomas, bronchioalveolar adenomas, breast cancer, and carcinoma of the zymbal gland have resulted from chronic exposure to 55 ppm.(11) Mice developed adenocarcinomas of the kidney after chronic exposure to 25 ppm; it was noted that male mice were especially susceptible.(12) It appears that exposure *via* inhalation offers considerably more potential for expression of vinylidene chloride's carcinogenicity than does oral administration.(13)

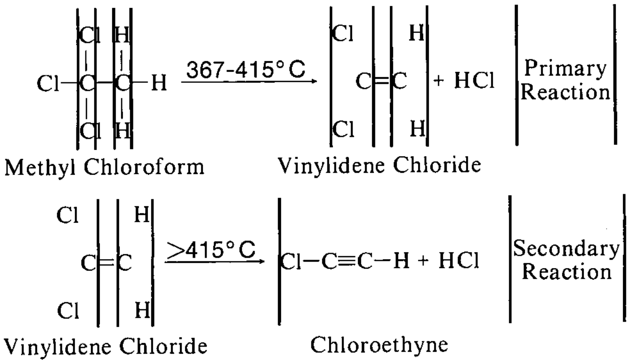
It has been suggested that the carcinogenicity of vinylidene chloride results from its biotransformation into highly reactive epoxide compounds. Reitz *et al.* reported that the carcinogenic effects of vinylidene chloride result only from exposures that cause massive tissue damage. It was noted that only a minimal amount of DNA alkylation or DNA repair synthesis occurred. This resulted in the speculation that the carcinogenic effects of vinylidene chloride result primarily from action upon nongenetic cellular components. Reitz suggested that protection against exposure capable of producing tissue damage should preclude any carcinogenic activity of vinylidene chloride.(14) In several bacterial studies, vinylidene chloride also has been shown to be mutagenic.(15,16)

To date, only one epidemiologic study has examined the effects of chronic exposure to vinylidene chloride in the absence of vinyl chloride. This study involved 138 employees who were exposed to TWAs ranging from 5 to 70 ppm for a minimum of one year. Two employees were found to have suffered hepatic damage, but in both cases alcohol consumption was a complicating factor.(17)

In 1984 the ACGIH TLV for vinylidene chloride was reduced and currently is expressed as a TWA of 5 ppm, or 20 mg/m^3, and a STEL of 20 ppm, or 80 mg/m^3.(18) These values have been set at levels that are believed will prevent observable toxicity.(19) Presumably, this refers to liver and kidney injury. There is no OSHA PEL for vinylidene chloride, although OSHA considers it to pose acute and chronic hazards. Based on carcinogenicity, NIOSH has recommended that occupational exposures be reduced to the lowest possible levels. NIOSH suggested the adoption of an 8-hr TWA of 1 ppm, or 4 mg/m^3, and a 15-min ceiling of 5 ppm, or 20 mg/m^3.(9) The odor threshold for vinylidene chloride is approximately 500 ppm. As a result, odor is unacceptable as a warning signal and vinylidene chloride is considered to have poor warning properties.(4)

Previous Studies

Several researchers have examined the thermal decomposition of various chlorinated hydrocarbons. The basic reactions involved in the decomposition of methyl chloroform are reported to be:(20)



Earlier experiments have included kinetic or mechanistic studies, studies of the effects of various catalysts for production purposes, and studies that focused on the toxic products formed during the degradations.(20-27) The latter type of study provides the information most relevant to industrial hygiene. In the case of methyl chloroform, however, earlier investigations have utilized techniques involving sealed vessels, inert atmospheres, or high vapor concentrations. Such experimental parameters failed to represent adequately typical industrial conditions and, therefore, have been of limited value from an industrial hygiene standpoint. For instance, even in a poorly ventilated room the contact time between solvent molecules and a hot surface will be of relatively short duration. The actual time will depend on the general movement of air in the room, the convective currents present in the vicinity of the heated surface, and the area of the heated surface. Pertinent conditions are not effectively addressed in closed-vessel studies. In addition, the atmosphere in industrial environments is composed largely of air and the concentrations of solvent vapors are usually low, even if they exceed allowable limits. It also has been suggested that excessively high vapor concentrations are not efficiently decomposed when flow techniques are employed.(28)

Earlier studies involving methyl chloroform neglected to examine the production of vinylidene chloride or other hydrocarbon products, focusing instead on the production of hydrogen chloride. It is possible that the investigators thought it was unnecessary to examine the production of vinylidene chloride since it has been suggested that the rate

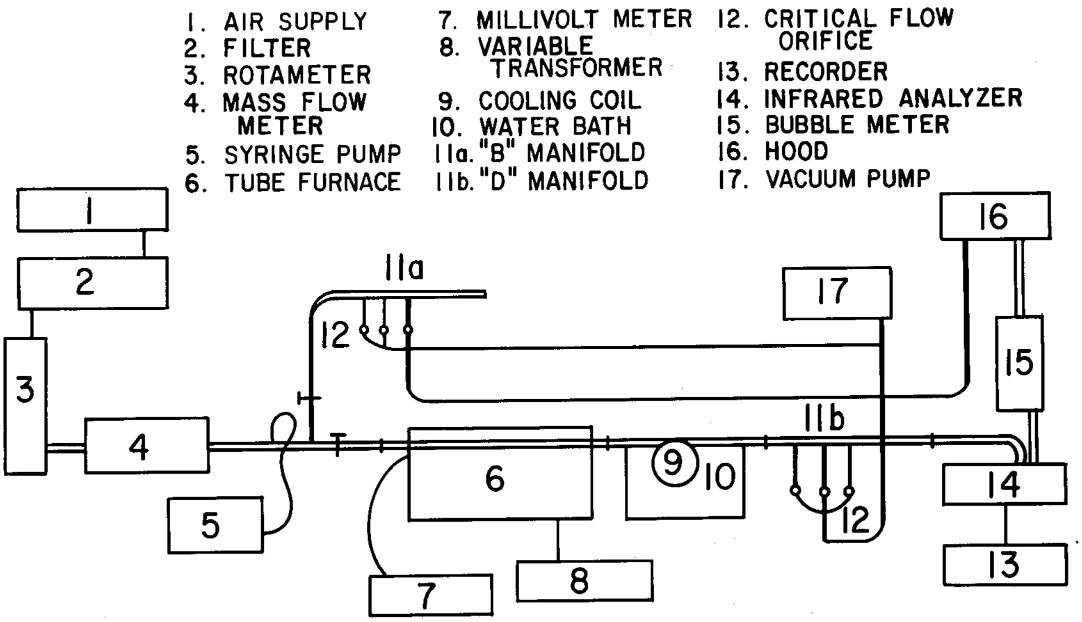


Figure 1 — System design.

at which vinylidene chloride is formed is equal to the rate of hydrogen chloride formation at temperatures below 415° C.[20] Phosgene is a potential chemical derivative of methyl chloroform. The presence of phosgene was not examined in this study, however, because earlier studies indicated it was not a significant product of the thermal decomposition of methyl chloroform.[22,23]

A previous study reported in the literature examined the photooxidation (UV) of methyl chloroform vapors in welding and the resultant production of phosgene. This study employed stabilized methyl chloroform (containing 3% aceto-nitrile and 2.5% isopropyl nitrate) and demonstrated that significant levels of phosgene were formed from the photodecomposition of methyl chloroform. The production of vinylidene chloride was not addressed in this research.[3]

System Design

The thermal degradation of methyl chloroform was examined in the presence of air; a flow technique was employed and the initial concentration of methyl chloroform vapors was approximately 1900 mg/m^3. The temperature range was 206-605° C. The effect of copper also was investigated.

Methyl chloroform was vaporized in a stream of compressed air and passed through a heated quartz tube containing either glass or copper beads. The organic vapors of interest (including reaction products) were collected on activated charcoal and analyzed by gas chromatography (GC) and coupled gas chromatography/mass spectrometry (GC/MS). Figure 1 offers a detailed schematic representation of the experimental design. Several important experimental considerations are presented in the following discussion.

A stream of filtered compressed air was regulated by means of a rotameter. A mass flow regulator was used to monitor the flow rate, which was maintained at approximately 6.2 L/min. Uninhibited methyl chloroform (Aldrich Chemical Company, Inc., 99% purity by volume, was introduced to the airstream *via* a syringe pump and solvent introduction apparatus. Uninhibited methyl chloroform was selected for this investigation because many different formulations of methyl chloroform are marketed commercially (*e.g.*, Chlorothene VG, Chlorothene NU, Chlorothane, Chloften, *etc.*). Since relatively low solvent concentrations were generated, the methyl chloroform readily vaporized, and it was not necessary to preheat the airstream. Beyond this point the system was divided into two branches. A vacuum-type stopcock was installed in each branch to allow for effective metering of the airflow through the furnace (a model 55-35 Lindberg Compact Tube Furnace). Airflow was maintained at approximately 0.7 L/min. The remainder of the solvent/air mixture bypassed the furnace and was routed through a collection manifold. Thus, samples of the initial solvent air mixture could be collected and analyzed. The design of the furnace tube is depicted in Figure 2. Although this experimental approach does not simulate flash pyrolysis conditions, attempts were made to minimize the initial temperature gradient and allow the air/solvent mixture to undergo an abrupt temperature transition. The entry portion of the tube was 6.4 mm o.d. until it reached the heated zone, where it expanded to 22 mm o.d. The heated zone of the tube was divided into three sections. The first, approximately 12.0 cm long, was packed with 3 mm diameter glass beads. It was designed to heat the air/solvent mixture as rapidly as possible. The second portion of the tube (7.0 cm) was not packed with beads in order to decrease the velocity of the airstream before it contacted the third zone. The third section (10.0 cm) was packed with either glass beads or copper beads (2-5 mm diameter). This was the area that was responsible for any observed catalytic effects of copper. Measurements of the furnace temperature were made with three Chromel-Alumel thermocouples (0.010 inch diameter). These were placed approximately 1.0 cm after the beginning of each of the three packing zones. The thermocouples were mounted externally on the tube and the temperature-sensing junctions were located in dimpled wells that projected into the airstream. The thermocouples were calibrated with a platinum resistance thermometer. All readings were taken using a Beckman Multimeter, which was sensitive to 0.1 mV or 1.0Ω. The maximum total error associated with the temperature measurements was determined to be ±5° C or ±1% at 500° C. Although attempts were made to minimize the temperature gradient along the length of the furnace, the center zone was 100-210° C hotter than the first zone and approximately 25° C hotter than the third. The magnitude of the temperature difference observed between the first and second thermocouples was attributed to the cooling effect of the airstream entering the furnace. The variation between the second and third thermocouple probably reflected the temperature gradient inherent to this particular tube furnace.

At 0.7 L/min the velocity through the packed sections was determined to be approximately 15-16 fpm. This approximates the slowest air velocity one would expect to find in a work environment. The residence times in the first and central zones of the furnace tube were calculated to be 1.6 sec and 2.3 sec, respectively. For the last zone, residence times were 1.3 sec for the glass beads and 1.2 sec for the copper beads (see Figure 2).

Upon leaving the furnace, the airstream passed through a modified glass gas chromatograph column that partially was submerged in a constant temperature (22° C) water bath. Immediately downstream, samples were collected using petroleum-base activated charcoal by means of a manifold equipped with three sampling ports. Each sampling port was equipped with a critical flow orifice. The air/solvent mixture exited the manifold and entered a Wilks MIRAN I Infrared Analyzer. A bubble meter located downstream from the infrared analyzer was used to determine the flow rate through the furnace and to calibrate the critical flow orifices. The air/solvent mixture then was exhausted to a canopy hood.

Samples were collected simultaneously from both manifolds (11a and 11b; Figure 1) to account for fluctuations in the initial concentration of methyl chloroform. Quantitative analyses were performed by GC. A representative chromatogram is presented in Figure 3. The front and back sections of each charcoal tube were desorbed and analyzed separately. No breakthrough was detected in any of the samples. Each sample was desorbed in 1 mL of carbon disulfide containing 1 uL of benzene per mL as an internal standard. A 20-foot × 1/8-inch stainless steel column packed with 10% Tergitol NP 35 on 80/100 Chromosorb P was used to achieve separation. A flame ionization detector (FID) was employed. A series of samples collected during a preliminary investigation involving glass beads was analyzed by GC/MS. These provided definitive identifications of the organic compounds that were present (see Figures 4-6).

Results

The GC/MS analyses indicated that both vinylidene chloride and methyl chloroform were present in samples collected at temperatures of 500-625° C (as indicated by the second thermocouple). In addition, chloroethyne was detected in all samples collected at temperatures of 575° or greater. No chloroethyne was detected in samples collected at 500° or less. No limit of detection was determined for chloroethyne because no standards were available for calibration purposes. Trichloroethylene was detected in all samples, including a sample of the unreacted analytical reagent methyl chloroform. It was believed that the trichloroethylene resulted from a rearrangement of methyl chloroform within the mass spectrometer. Except for the carbon disulfide and benzene used in desorbing the samples, no other compounds were detected.

The results of the quantitative analyses are presented in Figures 7 and 8. In Figure 7, results are expressed as the percentage of the initial concentration of methyl chloroform that was not decomposed. Figure 8 depicts the formation of vinylidene chloride as a function of temperature. The axis labeled "Vinylidene Chloride Expressed as % Methyl Chloroform" indicates the percentage of the initial concentration of methyl chloroform that decomposed to form vinylidene chloride. The axis labeled "Vinylidene Chloride (mg/L)"

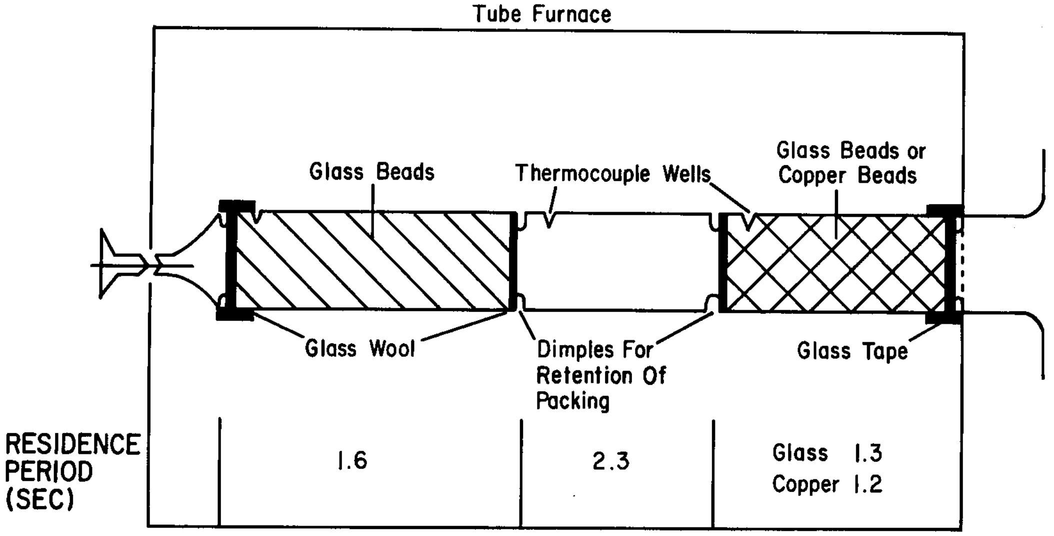


Figure 2 — Furnace tube design.

indicates the resulting milligrams of vinylidene chloride per liter of air normalized to an initial concentration of 1.910 milligrams of methyl chloroform per liter. This was intended to account for variations of the initial concentration of methyl chloroform. It should be noted that all graphs have been drawn by best fit by eye.

For the results of the investigation involving glass beads, the temperature values were derived from the second thermocouple (the one in the unpacked portion of the tube). For the evaluation of the effect of copper beads, the temperature values were derived from the third thermocouple. In a preliminary portion of this study, it was noted that at higher temperatures a greyish-black coating formed on the copper beads and on the wall of the tube in the immediate vicinity of the copper beads. This may be attributed to oxidation of the copper beads at higher temperatures. It was not known what effect, if any, this phenomenon would have on the decomposition reaction. Because of this, samples for the investigation of copper beads were collected as the furnace temperature was increased and prior to the initiation of the coating effect. This was done to eliminate any effect the surface coating may have had on the reaction at lower temperatures. The beads were considerably discolored at 332° C. At 442° C the beads and walls of the tube once again were coated with a greyish-black material.

Discussion

The results of the investigation involving glass beads indicate that methyl chloroform first began to decompose at approximately 350° C. These results also illustrate that the concentration of vinylidene chloride increased as a function of temperature until at least 605° C, although the rate at which it increased began to decline at approximately 570° C and above. The results of the GC/MS analyses confirm that, between 500-575° C, the secondary reaction producing chloroethyne began to occur to a noticeable degree. Although no samples were collected at temperatures greater than 605° C, one reasonably could hypothesize that the amount of vinylidene chloride exiting the furnace would decrease as temperature is increased further. At some point, chloroethyne might become the major component of the decomposition products.

The results of the investigation of the effect of copper indicate that methyl chloroform began to decompose at approximately 180° C. At 210° C, approximately 5% of the methyl chloroform had decomposed to form vinylidene chloride. This increased to 15% at 270° C, 50% at 325° C, and exceeded 95% at 442° C, the highest temperature investigated. No GC/MS analyses were performed on the samples derived from the experiments with copper. Therefore, the temperature at which the secondary reaction begins to occur was not determined.

By the classical definition, copper probably would not be considered to act as a true catalyst in the decomposition of methyl chloroform. While it is obvious that the initial dehydrohalogenation reaction proceeds at much lower temperatures when copper is present, it is uncertain if the copper emerges from the reaction chemically unchanged. Aside from the oxidation that appears to have occurred at higher temperatures, there is also the possibility that hydrogen chloride liberated during the course of the decomposition may have reacted with the copper. This was not examined during this study, but earlier reports suggest that hydrogen chloride may indeed react with metal packings. For the sake of the following discussion, however, the term "cata-

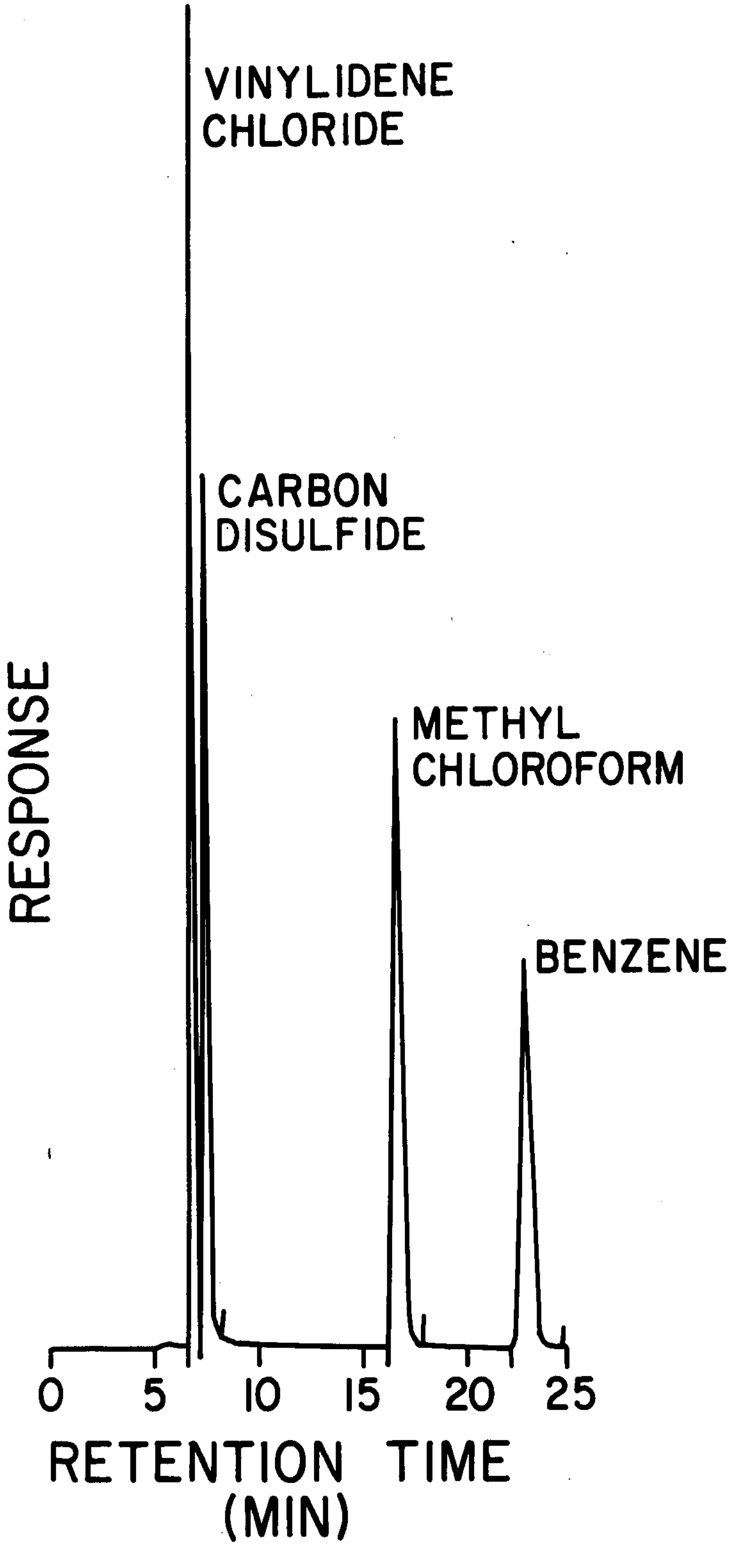


Figure 3 — Representative chromatogram.

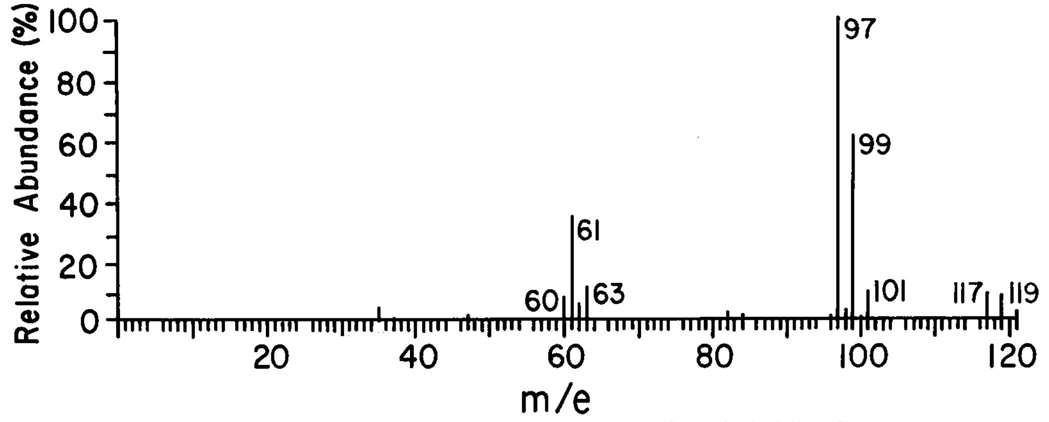


Figure 4 — Representative mass spectrum of methyl chloroform.

lytic" will be considered in a looser context and will refer only to the lowering of the initial temperature at which a reaction occurs.

Figures 7 and 8 clearly illustrate the catalytic effect that copper has on the decomposition of methyl chloroform. In the presence of copper, methyl chloroform began to decompose at a temperature approximately 170°C lower than when only glass was present. This difference is even more dramatic when one considers the following observation. The residence time in the decomposition zone was calculated to be approximately 3.6 sec for glass, compared to only 1.2 sec for copper. It is important that this inconsistency be considered when interpreting the results of this investigation. It seems probable that the catalytic effect of copper is substantially greater than indicated by the results of this experiment.

Although copper unquestionably catalyzes the initial decomposition reaction, it remains unclear as to whether or not it has a similar effect on the secondary reaction. It is possible that the decomposition of vinylidene chloride does not occur any earlier in the presence of copper than it does in the presence of glass. The results of the study involving copper indicate that the conversion of methyl chloroform to vinylidene chloride approaches 100% as the methyl chloroform is decomposed completely. Since no mass spectrometry analyses were performed for the experiments with copper, this study can offer no conclusions regarding this matter.

It must be stressed that the results of this investigation should be interpreted with caution. The actual amount of vinylidene chloride produced at a given temperature is indicative only of the specific experimental parameters that were employed. Variation of such factors as residence time, surface area of the copper, the nature of the temperature gradient of the furnace, or even the use of different catalysts undoubtedly would affect the results obtained. In spite of this limitation, this study clearly addresses two items of primary interest to industrial hygienists. First, under conditions approximating those encountered in work environments, methyl chloroform undergoes thermal decomposition to yield substantial quantities of vinylidene chloride. Second, copper exerts a pronounced catalytic effect on the reaction. While the decomposition would not be expected to proceed to the extent that it does in the laboratory, the relative ease with which the reaction occurs (especially in the presence of copper) suggests that it at least has the potential of occurring in work environments. For instance, soldering operations typically employ temperatures of 425°C and greater and, in many cases, require that the material first be cleaned with a degreasing agent. This study demonstrates that greater than 90% of a given quantity of methyl chloroform can be converted to vinylidene chloride at these temperatures. Although it has been reported that in the presence of copper, industrial grade (inhibited) methyl chloroform releases less hydrogen chloride than technical grade,

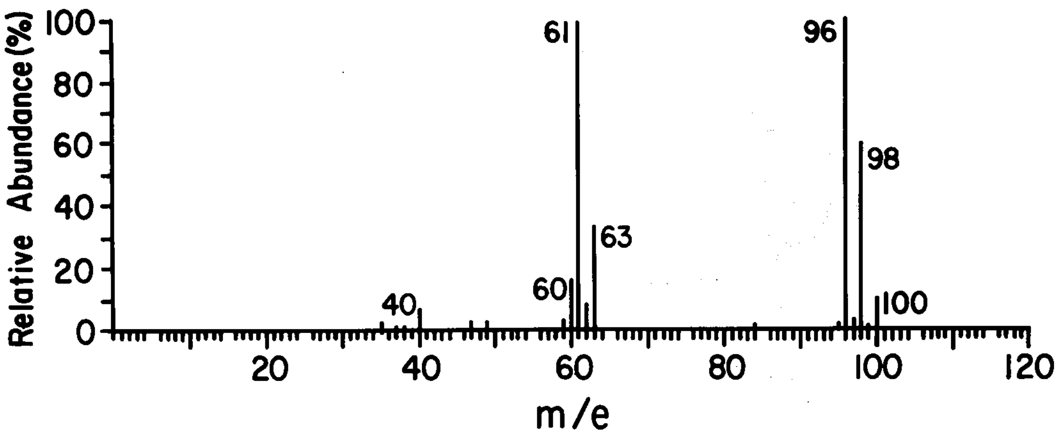


Figure 5 — Representative mass spectrum of vinylidene chloride.

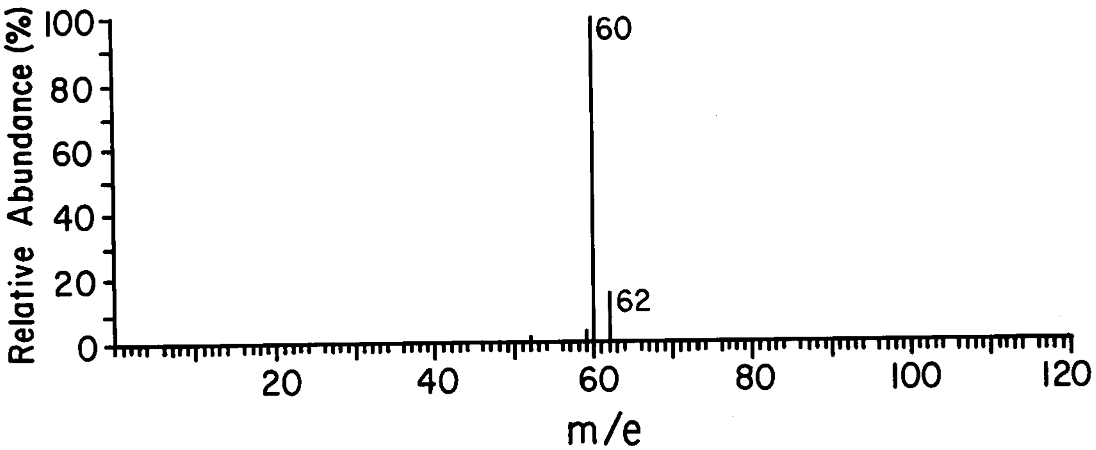


Figure 6 — Representative mass spectrum of chloroethyne.

it was not determined if the production of vinylidene chloride is similarly affected.[24] It is possible that the inhibitors effectively remove (or scrub) a portion of the hydrogen chloride that is produced but do not significantly alter the rate or extent of the decomposition reaction. One study has demonstrated that inhibited or stabilized methyl chloroform may undergo photodecomposition to yield significant quantities of phosgene, although to a lesser degree than the uninhibited form.[3] This information, however, may not be directly applicable to the present study. In a poorly ventilated area, even if only a small percentage of a TLV concentration of methyl chloroform decomposes, the resulting concentration of vinylidene chloride could be several times greater than the TLV currently proposed by the ACGIH. As a result, it is possible that significant overexposure to vinylidene chloride may occur. In addition, because excursion limits allow for considerable variability in actual exposure levels to methyl chloroform, the possibility of brief but high exposures to vinylidene chloride must not be overlooked. Even if hydrogen chloride theoretically does provide adequate warning properties, its reactive nature might result in lower airborne concentrations than would be expected. Therefore, it should not be considered to provide an adequate warning against overexposure to vinylidene chloride.

From the standpoint of controlled laboratory experimentation, this investigation was subject to several limitations. First, the temperature gradient inherent to the tube furnace made it difficult to determine the actual temperature at which the reaction occurred. In the investigation of copper, for example, the temperature reported for the reaction was the temperature at the front of the bed of copper beads. Beyond this point the temperature was thought to have decreased gradually. Additionally, it would have been preferable to have packed the center section of the tube with either glass or copper beads. This would have yielded more comparable results between the copper and the glass and would have provided a more accurate indication of the relative magnitude of the catalytic effect of copper.

There were also several limitations with regard to industrial hygiene applications. The most obvious limitation pertains to how closely the experimental design and parameters approximate conditions found in typical work environments. As an initial investigation, however, a controlled laboratory experiment provided a pragmatic means of evaluating the subject. Future research efforts can be designed to determine the extent to which vinylidene chloride may form from the use of methyl chloroform in industrial settings. In addition, other laboratory experiments may be

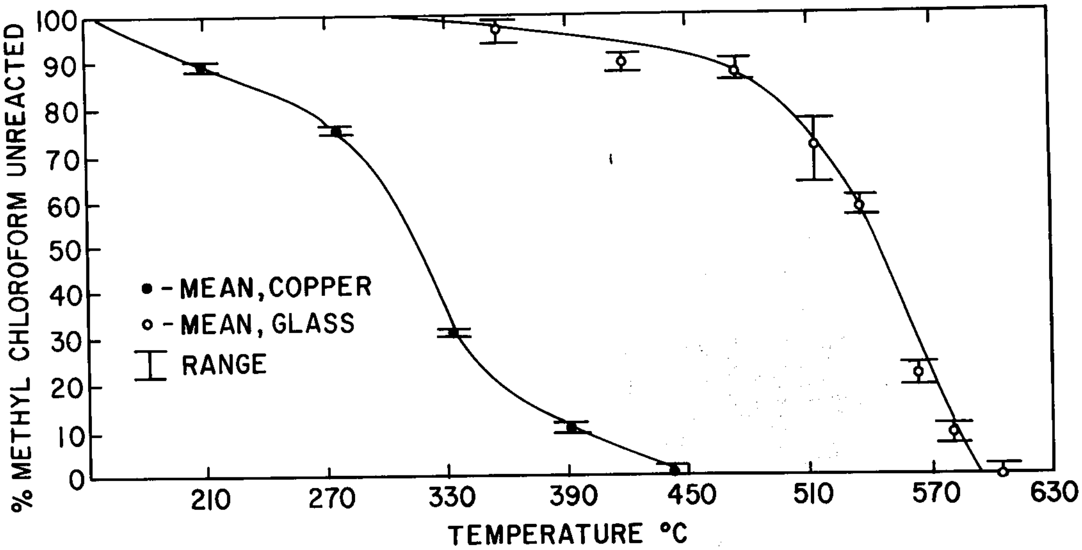


Figure 7 — The effect of copper as compared to glass. Decomposition of methyl chloroform.

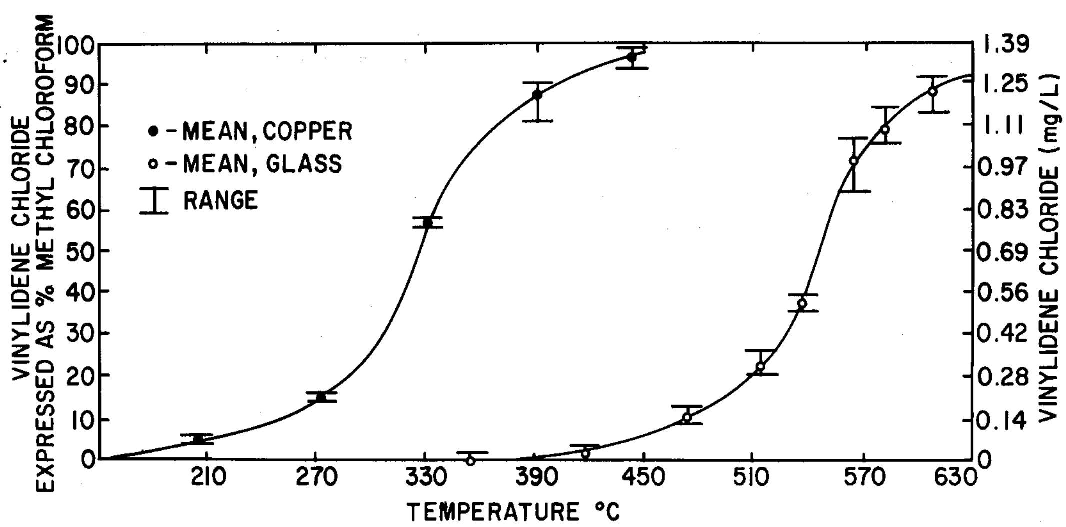


Figure 8 — The effect of copper as compared to glass. Formation of vinylidene chloride.

conducted to evaluate the catalytic effect (or lack thereof) of other metals.

Conclusions

The results of this experiment clearly demonstrate that vinylidene chloride is formed in significant amounts when methyl chloroform is decomposed thermally. In fact, under certain conditions the conversion may approach 100%. This information has important implications to the field of industrial hygiene, considering the much greater toxicity associated with vinylidene chloride.

In addition, the reaction has been shown to occur at much lower temperatures when copper is present. In the presence of copper, the conversion to vinylidene chloride was found to exceed 95% at 440° C compared to only 12% at 470° C in the presence of glass. Considering the widespread use of methyl chloroform and its numerous applications involving heat, it is entirely conceivable that this decomposition reaction occurs in industrial environments. Even if only 5% of a 1900 mg/m^3 concentration of methyl chloroform were decomposed, the resultant concentration of vinylidene chloride could be as high as 69 mg/m^3. This is greater than three times the TWA of 20 mg/m^3 and approaches the STEL of 80 mg/m^3 currently proposed by the ACGIH. Further research is needed to evaluate the extent to which vinylidene chloride is formed from the decomposition of methyl chloroform in actual work environments.

Acknowledgments

We gratefully acknowledge the cooperation and technical assistance provided by the OSHA Analytical Laboratory, especially Kevin Cummins, Carl Elskamp, Pat Hardy, Mike Shulsky, and Gerald Shultz. Special thanks to Donald E. Marano for suggesting this topic as a potential research project.

References

1. **National Institute for Occupational Safety and Health:** *Criteria for a Recommended Standard: Occupational Exposure to 1,1,1-Trichloroethane (Methyl Chloroform)* (DHEW/NIOSH Pub. No. 76-184). Cincinnati, Ohio: Government Printing Office, 1976.
2. **Mark, H.F., D.F. Othmer, C.G. Overberger, G.T. Seaborg, M. Grayson and D. Eckroth, eds.:** *Kirk-Othmer Encyclopedia of Chemical Technology,* vol. 5, 3rd ed. New York: John Wiley and Sons, 1978. pp. 728-731.
3. **Dahlberg, J.A., V.O. Christiansen and E.A. Eriksson:** On the Formation of Phosgene by Photooxidation of Methyl Chloroform in Welding. *Ann. Occup. Hyg. 16*:41-46 (1973).
4. **Clayton, G.D. and F.E. Clayton, eds.:** *Patty's Industrial Hygiene and Toxicology,* vol. 2B, 3rd ed. *Toxicology.* New York: John Wiley and Sons, 1981. pp. 3502-3510.
5. **Adams, E.M., H.C. Spencer, V.K. Rowe and D.D. Irish:** Vapor Toxicity of 1,1,1-Trichloroethane (Methyl Chloroform) Determined by Experiments on Laboratory Animals. *Am. Ind. Hyg. Assoc. J. 1*:225-236 (1950).
6. **American Conference of Governmental Industrial Hygienists:** *Documentation of the Threshold Limit Values,* 4th ed. Cincinnati, Ohio: ACGIH, 1980. pp. 269-270.
7. **National Institute for Occupational Safety and Health:** *Registry of Toxic Effects of Chemical Substances,* Vol. 2. (DHEW/NIOSH Pub. No. 83-107). Cincinnati, Ohio: Government Printing Office, 1981-82. p. 278.
8. **Short, R.D., J.M. Winston, J.L. Minor, J. Seiffer and C.C. Lee:** Effect of Various Treatments on Toxicity of Inhaled Vinylidene Chloride. *Environ. Health Persp. 21*:125-129 (1977).
9. **National Institute for Occupational Safety and Health:** *Vinyl Halides Carcinogenicity* (DHEW/NIOSH Pub. No. 9-102). Cincinnati, Ohio: Government Printing Office, 1979.
10. **Jenkins, L.J. and M.E. Andersen:** 1,1-Dichloroethylene Nephrotoxicity in the Rat. *Toxicol. Appl. Pharmacol. 46(1)*:131-141 (1978).
11. **Lee, C.C., J.C. Bhandari, J.M. Winston and W.B. House:** Carcinogenicity of Vinyl Chloride and Vinylidene Chloride. *J. Toxicol. Environ. Health 4(1)*:15-30 (1978).
12. **Maltoni, C.:** Recent Findings on the Carcinogenicity of Chlorinated Olefins. *Environ. Health Perspect. 21*:1-5 (1976).
13. **U.S. Department of Health and Human Services/Public Health Service/National Institutes of Health:** *National Toxicology Program Technical Report No. 228, Carcinogenesis Bioassay of Vinylidene Chloride in F344 Rats and B6C3F Mice (Gavage Study)* (NTP-80-82). Research Triangle Park, N.C.: National Toxicology Program, 1982. p. 72.
14. **Reitz, R.H., P.G. Watanabe, M.J. McKenna, J.F. Quast and P.J. Gehring:** Effects of Vinylidene Chloride on DNA Synthesis and DNA Repair in the Rat and Mouse: A Compara-

tive Study with Dimethylnitrosamine. *Toxicol. Appl. Pharmacol. 52(3)*:357-370 (1980).

15. **Bartsch, H., C. Malaveille, R. Montesano and L. Tomatis:** Tissue Mediated Mutagenicity of Vinylidene Chloride and 2-Chlorobutadiene in Salmonella Typhimurium. *Nature 255*:641-643 (1975).
16. **Baden, J., R. Whurton, B. Hitt, M. Brinkenhoff, U. Simmons and R. Mazze:** Mutagenicity of Volatile Anaesthetics. *Fed. Proc. 35*:410 (1976).
17. **Ott, M.G., W.A. Fishbeck, J.C. Townsend and E.J. Schneider:** A Health Study of Employees Exposed to Vinylidene Chloride. *JOM 18(11)*:735-738 (1976).
18. **American Conference of Governmental Industrial Hygienists:** *TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-1984.* Cincinnati, Ohio: ACGIH, 1982. p. 40.
19. **American Conference of Governmental Industrial Hygienists:** *Documentation of Threshold Limit Values.* 4th ed. Cincinnati, Ohio: ACGIH, 1982. pp. 433-434.
20. **Barton, D.H.R. and P.F. Onyon:** The Pyrolysis of 1,1,1-Trichloroethane. *J. Am. Chem. Soc. 72*:988-995 (1950).
21. **Barton, D.H.R. and K.E. Howlett:** The Kinetics of the Dehydrochlorination of Substituted Hydrocarbons. Part III. The Mechanisms of the Thermal Decomposition of Ethyl Chloride and of 1:1-Dichloroethane. *J. Chem. Soc.*:165-169 (1949).
22. **Sjoberg, B.:** Thermal Decomposition of Chlorinated Hydrocarbons. *Svensk. Kem. Tidsk. 64*:63-79 (1952).
23. **Crummet, W.D. and V.A. Stenger:** Thermal Stability of Methyl Chloroform and Carbon Tetrachloride. *Ind. Eng. Chem. 48*:434-436 (1956).
24. **Mochida, I., J. Take, Y. Saito and Y. Yoneda:** Linear Free-Energy Relationships in Heterogeneous Catalysis. VI. Catalytic Elimination Reaction of Hydrogen Chloride From Chloroethanes on Solid Acids and Bases. *J. Organ. Chem. 32*:3984-3989 (1967).
25. **Mochida, I. and Y. Yoneda:** Dehydrochlorination and Dechlorination of Chloroethanes on Chromia Catalyst. *J. Organ. Chem. 33(5)*:2163-2165 (1968).
26. **Mochida, I. and Y. Yoneda:** Elimination Reaction of Hydrogen Chloride From 1,1,2-Trichloroethane on Ion-Exchanged Molecular Sieves. *J. Organ. Chem. 33(5)*:2161-2163 (1968).
27. **Mochida, I. and Y. Yoneda:** Linear Free Energy Relationships in Heterogeneous Catalysis. I. Dealkylations of Aklylbenzenes on Cracking Catalysts. *J. Catalysis 7*:386-392 (1967).
28. **Noweir, M.H., E.A. Pfitzer and T.F. Hatch:** Thermal Decomposition of Carbon Tetrachloride Vapors at Its Industrial Threshold Limit Concentration. *Am. Ind. Hyg. Assoc. J. 34(1)*:25-37 (1973).

15 August 1984; Revised 13 January 1986