NIOSH TECHNICAL REPORT

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
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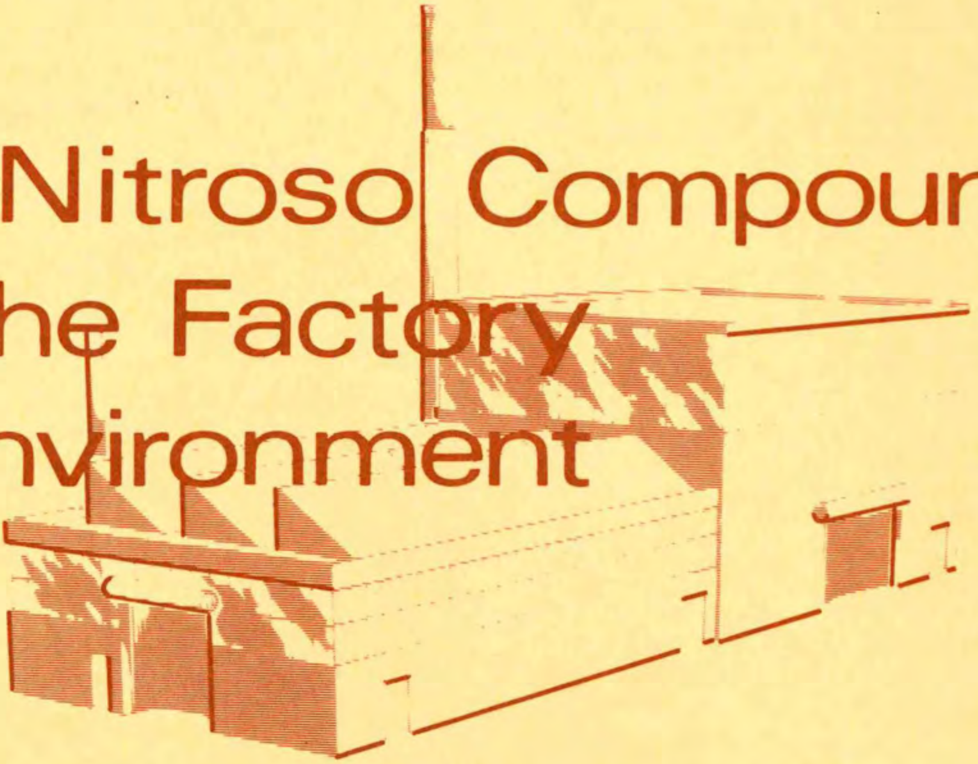
N-Nitroso Compounds in the Factory Environment



N-NITROSO COMPOUNDS IN THE FACTORY ENVIRONMENT

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DISCLAIMER

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PREFACE

Prior to 1975, the primary interest in the environmental occurrence of the carcinogenic N-nitroso compounds (N-nitrosamines) centered around nitrite preserved meats, foodstuffs, cheese products, fish, fish meal and biological samples. This emphasis began to shift when N-nitrosodimethylamine (NDMA), one of the more potent of these carcinogens, was found in the atmosphere near a facility producing rocket fuel in Baltimore, Maryland and in the atmospheres near dimethylamine plants in West Virginia and West Germany. Further discoveries of N-nitroso compound contamination in consumer and industrial products led to the speculation that workers in industries, that either manufacture or use these products, may be exposed to significant amounts of these carcinogenic agents. For example, the discovery of percent levels of N-nitrosdiethanolamine in some synthetic machine cutting fluids clearly pointed to the possibility of a significant exposure to this compound by some metal workers. These discoveries of N-nitroso compound contamination plus the increased understanding of the mechanisms by which these chemicals can be formed from their widely available precursors (amines and nitrogen oxides), has resulted in this study of worker exposure to N-nitroso compounds sponsored by the National Institute for Occupational Safety and Health (NIOSH).

When this study was initiated, adequate instrumental methods were available for detecting and quantifying N-nitroso compounds; however, environmental sampling and pre-analytical techniques were still being developed and validated. Until the development of the ThermoSorb/N nitrosamine air sampling cartridges, any discovery of N-nitro compounds in different industrial atmospheres had to be extensively examined for the possibility of artifact formation from co-sampled precursors. The artifact free ThermoSorb/N cartridges greatly reduced the need for this extra effort. These solid sorbent cartridges were also used to collect personal samples, a more accurate measurement of worker exposure, and to collect point source samples. Impinger traps containing aqueous potassium hydroxide (KOH) were not practical for this type of sampling. The real need for these artifact-free air sampling cartridges became apparent when nitrosamines were discovered in the rubber and leather industries . The atmosphere in these industries also contained the precursors to the discovered nitrosamines. The mobile on-site laboratory, constructed for use in this study, was initially required in order that samples could be examined as soon after collection as possible. This was necessary in order to both reduce the potential loss of the N-nitroso compounds, due to their chemical instability, and to minimize artifact formation by reducing the time between sampling and analysis. As the ThermoSorb/N cartridges became available they were used in this study along with the 1N potassium hydroxide (KOH) impinger air sampling method. When sufficient laboratory and field data validated the use of the ThermoSorb/N cartridges both the cumbersome 1N KOH impingers and the need for the on-site mobile laboratory were eliminated. As can be seen in the text of the study, the ThermoSorb/N cartridges were not used in the first part of this study and, towards the end of the study, 1N KOH impinger traps were phased out.

Towards the end of the study, methods were being developed for determining precursor amines in both air and bulk samples, and the nitrosating capacity of the sampled air. As these methods became more reliable they were included in this study in an effort to develop an understanding of the mechanism of N-nitroso compound formation in some of the plant environments. Unfortunately, these methods were not fully developed before this study ended. However, the data that were obtained on the amine and nitrosating capacity of the sampled air within tanneries has helped to explain how these atmospheres were contaminated with N-nitrosodimethylamine.

More research still needs to be done in order to understand the mechanism and circumstances that could give rise to worker exposure in those industries which use potential N-nitroso precursors. Those industries that use nitrosatable amines should be examined not only for N-nitroso compounds but also for precursors such as atmospheric NO_x and nonvolatile nitrosating agents. The researchers hope the results of this study and the methods which were developed will aid future investigations in understanding the circumstances of how workers are exposed to N-nitroso compounds and how to reduce or eliminate this exposure.

ABSTRACT

Under the NIOSH sponsored contract, a total of 55 on-site plant surveys were conducted in 40 separate United States manufacturing facilities. The industries surveyed were the azo dye, fish processing, cutting fluid manufacturers and users, rubber, tanning, detergent and surfactant and foundries. Airborne concentrations of Thermal Energy Analyzer (TEA™) responsive compounds were found in 25 of the 40 plants surveyed. The dye industry had airborne TEA responsive material as high as 40 μg/m^3, but they were not identified. A fish meal factory was found to contain N-nitrosodimethylamine (NDMA) at 0.06 μg/m^3. A plant that manufactured anionic, cationic, non-ionic and special surface active agents contained air levels of NDMA of 0.8 μg/m^3. In a chrome tannery NDMA was identified at 47 μg/m^3. The rubber industry contained levels of N-nitrosomorpholine as high as 248 μg/m^3. N-nitrosodiphenylamine (NDPhA), N-nitrosopyrolidine (NPYR) and NDMA were also detected in the work environment of tire plants.

Efforts to improve the worker environment in the tire plants through engineering controls and chemical substitution proved effective. Biological samples (blood, urine and feces) of the exposed population were obtained from the workers during two of the NIOSH surveys.

This study has resulted in an increased understanding of man's exposure to preformed nitrosamines. It is conceivable, from the information that has been generated in this study, that nitrosamine exposure as large as that in the tire and rubber industry may exist in other industries not yet surveyed.

ACKNOWLEDGMENT

The authors thank all of the participating manufacturing facilities for their generous cooperation and help in providing us with technical information and access to their facilities. We also acknowledge the assistance of our co-workers at the New England Institute for Life Sciences, Steven Fan, Ira Krull, Martin Wolf, Gordon Edwards, Ulku Goff, John Reisch, Jim Coombs and the many others who participated in one or more of the on-site surveys. We also thank Nancie Bornstein, who edited, organized and typed the numerous drafts and final version of this report.

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INTRODUCTION

AUTHORITY

The Williams-Steiger "Occupational Safety and Health Act of 1970" was passed into law "to assure safe and healthful working conditions for working men and women..." This Act established the National Institute for Occupational Safety and Health (NIOSH) in the Department of Health, Education, and Welfare (presently the Department of Health and Human Services) and the Occupational Safety and Health Administration (OSHA) in the Department of Labor. The Act provides for research, informational programs, education, and training in the field of occupational safety and health and authorizes the enforcement of standards.

NIOSH has been given the authority and responsibility under the Act to conduct field research studies in industry, evaluate findings, and report on these findings. Section 20(a)(1) of the Act mandates NIOSH to "conduct (directly or by grants or contracts) research, experiments, and demonstrations relating to occupational safety and health..." Section 20(c) provides the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for the purpose of conducting studies relating to responsibilities under the Act. For this purpose, NIOSH with the financial support of the National Cancer Institute established a contractual agreement with the New England Institute for Life Sciences to study worker exposures to N-nitroso compounds in industries where these compounds or their precursor chemicals are used.

BACKGROUND

Interest in the possible human health hazard that nitrosamines may pose began following the observation in animals of the toxic and carcinogenic effects of N-nitrosodimethylamine (NDMA) (1). The toxic effect of these compounds on humans was first reported by Freund in 1937 (2) who described the hepatotoxic effects of NDMA on two chemists that had been accidentally poisoned by this compound. Since these first findings, N-nitroso compounds have been studied extensively in experiments with laboratory animals. More than 100 of the 130 different N-nitroso compounds tested in animals have been shown to be carcinogenic (1, 3-5). N-nitrosodiethylamine, for example, has been tested for carcinogenic activity in the rat, African white-tailed rat, mouse, S.G. hamster, Chinese hamster, European hamster, guinea pig, rabbit, dog, pig, trout, grass parakeet and monkey, and has been shown to be carcinogenic in all these species.

The sites where tumors develop seems to depend upon the chemical structure of the N-nitroso compound, the animal being tested and on the route of administration. N-nitroso compounds have been shown to affect the bladder, bronchi, central nervous system, earduct, esophagus, eyelid, duodenum, forestomach, glandular stomach, hematopoietic system, intestine, jaw, kidney, larynx, lung, nasal cavity, oral cavity, ovary, liver, mammary glands, pancreas, pelvis, peripheral nervous system, pharynx, respiratory tract, skin, testes, tongue, trachea, uterus and vagina (4).

Many N-nitroso compounds are extraordinarily potent carcinogens. Three N-nitrosamines have been tested in dose response studies with rats. The apparent 'no effect level' at which no statistical difference between the test animals and the controls could be observed, was found to correspond to dietary levels of 1000 μg/kg (1 ppm) of N-nitrosodimethylamine (6), 1000 μg/kg (1 ppm) of N-nitrosodiethylamine (7), and 5000 μg/kg (5 ppm) of N-nitrosopyrrolidine (8). Thus, in a rat population of under 100 animals, between 1 and 5 ppm of these nitrosamines in the diet is marginally carcinogenic.

The comparative in vitro metabolism of N-nitrosodimethylamine is similar in both the human and rat liver (9). Furthermore, the rate of metabolism in human liver slices is comparable to that in the rat liver, with the levels of nucleic acid methylation being similar in the two species (10). In acute toxicity experiments with high doses, nitrosamines generally produce centrilobular necrosis in most animal species.

While many of these compounds have been demonstrated to be potent animal carcinogens, their carcinogenic risk to man (the probability that defined exposures to these chemicals will lead to cancer) has not yet been determined. In order to assess this risk it is first necessary to locate sufficient populations of exposed people.

Until as recently as 1975 the primary interest in human exposure to these carcinogenic compounds centered around their occurrence in nitrite preserved foods, cheese products, fish, fish meal, biological samples, tobacco, alcoholic beverages and in vivo formation from precursor chemicals. With the finding of NDMA in the atmospheres near manufacturing facilities producing and/or using dimethylamine (11-13) the emphasis on human exposure to these compounds began to shift to the workplace where it has been speculated that human exposure to these compounds may be the highest (11).

Further discoveries of N-nitroso compounds in cosmetics (14), tobacco smoke (15), indoor atmospheres under conditions of excessive tobacco smoking (16), in synthetic cutting fluids (17), and in some widely used herbicides (18), have further shifted the emphasis of the environmental search for human exposure to these compounds. It is now apparent that any situation where the precursors of these compounds (amines and nitrosating agents) may exist together, that there is a high likelihood of finding N-nitroso compounds.

Many secondary amines such as dimethylamine, diethylamine and morpholine are produced in large quantities for both industrial and consumer use. Products manufactured from these amines are used in agricultural chemicals, detergents, rust inhibitors, rubber additives, solvents, drugs, plastics, leather tanning, textiles, cosmetics and in synthetic cutting and grinding fluids (19). Given the widespread use of secondary amines and the ever present nitrogen oxides of an industrial society, the likelihood of N-nitrosamines being found in some products or in an industrial situation where these compounds may occur together, is high.

Until this study the human population groups that were identified as being potentially exposed to large amounts of carcinogenic N-nitroso compound included; chemical workers at a factory making unsymmetrical dimethylhydrazine from N-nitrosodimethylamine (12, 20), agricultural workers handling pesticides contaminated with nitrosamines (18), machinists using synthetic cutting and grinding fluids contaminated with N-nitrosodiethanolamine (17), and persons using facial cosmetics contaminated with N-nitrosodiethanolamine (14). During this present study three other groups: rubber chemical workers exposed to N-nitrosomorpholine and N-nitrosodiphenylamine (21); leather tanners exposed to N-nitrosodimethylamine in tannery air; and, workers in tire manufacturing exposed to N-nitrosodimethylamine and N-nitrosomorpholine (22) have also been discovered.

The discovery that some industrial workers are being exposed to relatively large quantities of N-nitroso compounds is a recent development which may have important implications in carcinogenesis. Minimizing exposure to these compounds could be a significant milestone in cancer prevention. Although direct evidence for the carcinogenicity of N-nitroso compounds in humans is lacking, the substantial amount of circumstantial evidence which does exist indicates that it is unlikely that humans will be the only species resistant to their carcinogenic assault. Recent advances in epidemiology and improvements in the environmental analysis of N-nitroso compounds may make it possible to determine what if any part, N-nitroso compounds contribute to cancer in man.

Until these epidemiological assessments can be made it must be assumed, on the basis of the many animal studies, that man will not be uniquely resistant to the carcinogenic action of N-nitrosamines. Since cancer produced from carcinogenic compounds is a delayed toxic effect, and since animal studies show dose related responses to these agents, it would be prudent to assume that any exposure to the carcinogenic N-nitrosamines constitute a risk. This study by the National Institute for Occupational Safety and Health (NIOSH) is the first attempt to determine workers' exposure to N-nitroso compounds in a variety of industrial facilities. The goal of this study is to assess the extent of worker exposure to these agents, how they are exposed and how to eliminate or reduce their risk.

SCOPE OF STUDY

The scope of this study was to determine, in selected industries, the extent of worker exposure to N-nitroso compounds in their place of employment. This study was limited to examining the workplace environment for those N-nitroso compounds for which analytical methods had been developed. This study was further limited in that only a few representative factories within an industry could be included in the survey. The N-nitroso compounds that were routinely searched for included those that were amenable to gas chromatography (GC) and a few nonvolatile N-nitroso compounds that were known or suspected to be present in a specific factory. Generally 7 volatile nitrosamines were included in the GC-TEA (Thermal Energy Analyzer) standard: N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodipropylamine (NDPA), N-nitrosodibutylamine (NDBA), N-nitrosopyrrolidine (NPYR) and N-nitrosomorpholine (NMOR). Other volatile nitrosamine standards were available in the event a volatile unknown compound was detected by GC-TEA. The nonvolatile compounds searched for were N-nitrosodiethanolamine (NDElA) and N-nitrosodiphenylamine (NDPhA). Unidentified TEA responsive compounds were not quantitated nor was any effort made to identify them. The industries selected for study were those which were known to use either N-nitroso compounds or to use chemicals which could serve as a precursor to these compounds. Again the scope of this study was limited to selecting only a few industries which could have N-nitroso compounds in their factory environments. The factory site visits consisted of on-site collection of area air samples and bulk samples. In most instances a mobile laboratory specifically designed and equipped for N-nitroso compound analysis was used on-site for the sample analysis. When warranted by the findings, re-visits were made to factories and an effort was made to determine why or how N-nitroso compounds were contaminating its environment. To a limited extent precursor amines and nitrosating agents were also examined.

CHEMISTRY OF N-NITROSO COMPOUNDS

The preparation of N-nitroso compounds in the laboratory has traditionally involved reactions between secondary amines and sodium nitrite under acidic conditions (23,24). These reaction conditions are the optimum for synthesizing N-nitroso compounds, however, they are not the only condition which give rise to these compounds. To the synthetic organic chemist, a yield of below 1% in a chemical reaction is generally of minimal interest. However, in assessing the importance of chemical carcinogens in the environment, any mechanism which can give rise to these compounds, even those reactions which proceed very slowly to give only a minimal yield, may be significant. Thus, the chemist concerned with the environmental distribution and occurrence of N-nitroso compounds must be equally familiar with the reactions which have high as well as low yields. This

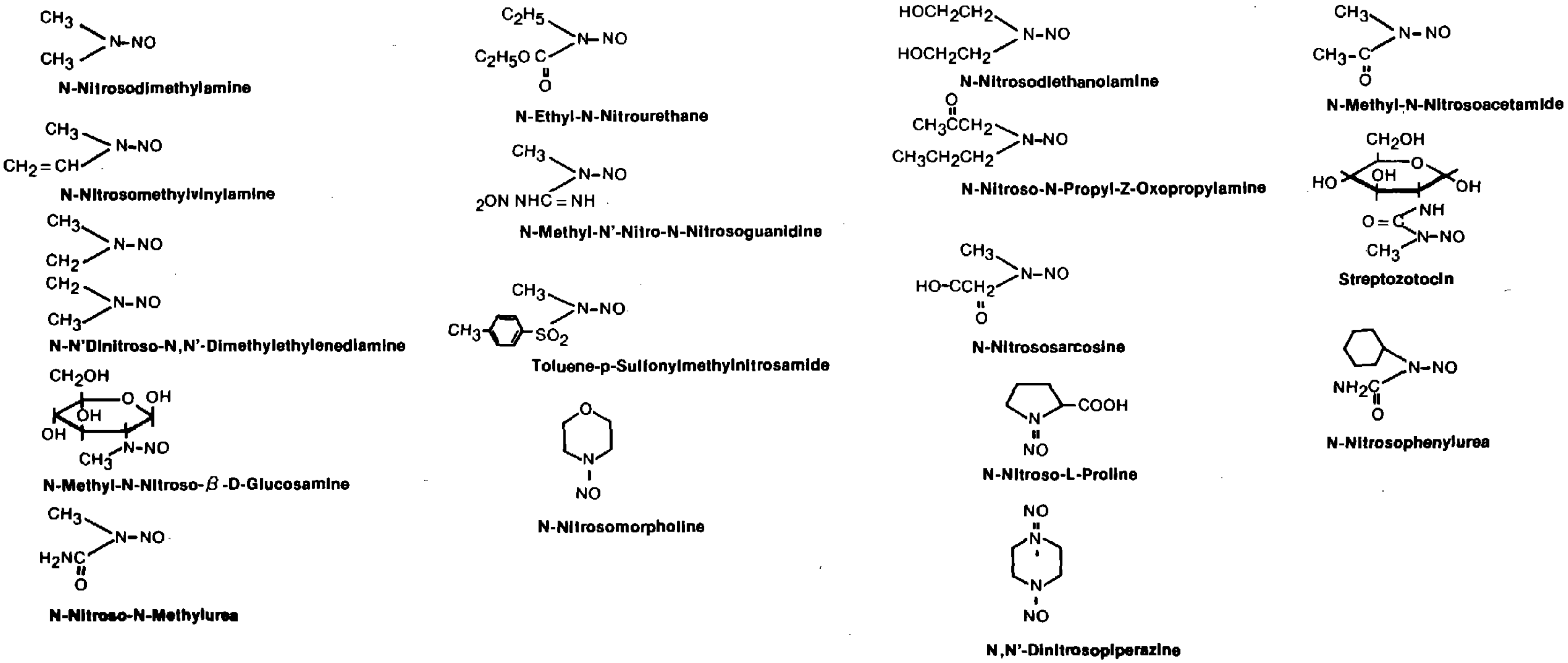


Figure 1. Structures of Representative N-Nitroso Compounds.
All of the compounds shown are known to be carcinogenic in animal experiments.

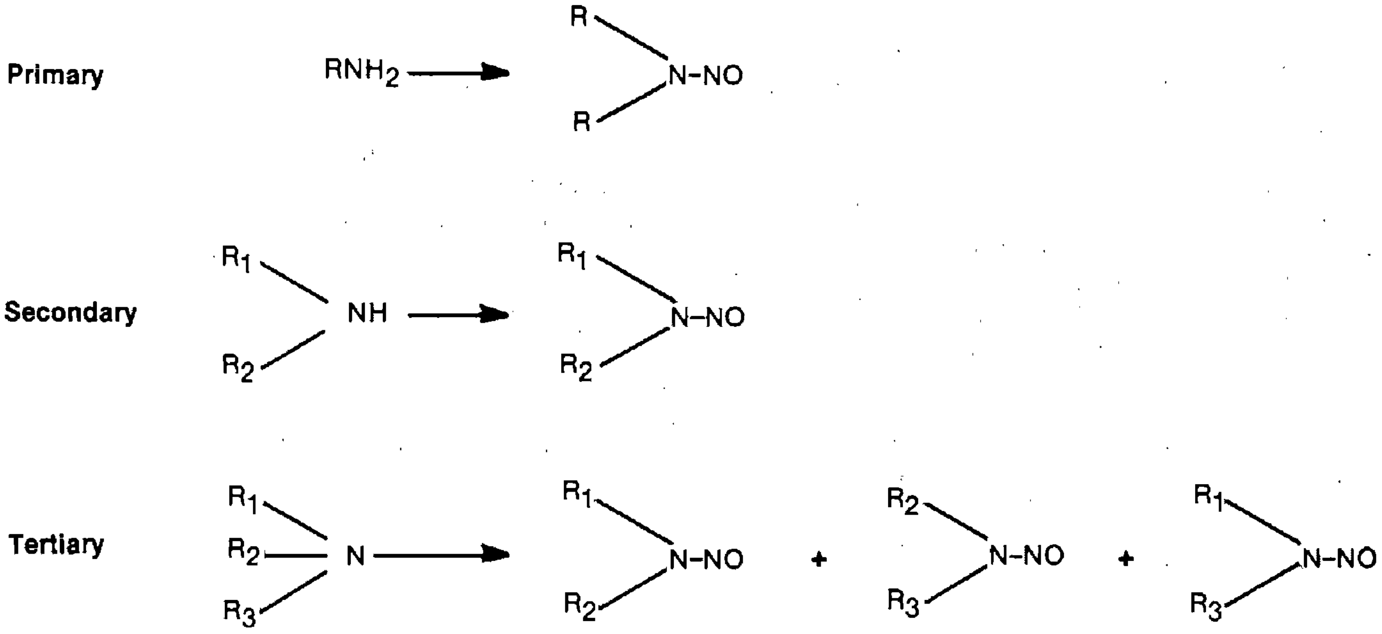
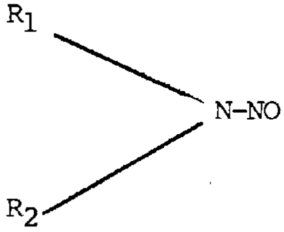


Figure 2. Diagramatic Representation of N-nitrosation of Primary, Secondary and Tertiary Amine Type Compounds. The yield and relative amounts of each product depend upon the reaction conditions, the nature of the R group, and other factors.

section discusses the chemistry and formation of N-nitroso compounds from this viewpoint.

N-nitroso compounds have the general formula:



where R_1 and R_2 can be virtually any organic group. For example, if R_1 and R_2 are alkyl groups, it is a dialkyl N-nitrosamine; if R_1 and R_2 contains a carboxylic acid group, it is an N-nitrosourea. The structures of some representative N-nitroso compounds are shown in Figure 1. N-nitroso compounds can be formed by the reaction of various precursor entities. The amino fragment, (R_1R_2N) can come from a primary, secondary or tertiary amine (see Figure 2). The nitrosyl group, NO, can be derived from nitrogen oxides (NO, NO_2, N_2O_4, or N_2O_3) or nitrite (nitrite salts of nitrous acid). N-nitrosation of the amine fragment can also occur via transnitrosation by other, more labile N-nitroso compounds. Depending on the reactants and the catalysts which are present, N-nitrosation can occur at either acidic, neutral or alkaline conditions. Some known N-nitrosation catalysts include formaldehyde chloral, ozone, and metal ions (25,26).

PRIMARY AMINES

Chemistry

The reaction of primary amine type compounds with nitrous acid principally yield compounds other than N-nitrosamines, however, it has been demonstrated that N-nitrosamines can be formed in low yields from primary amines (25-32). The yields of nitrosamines from some of the compounds investigated (30) were:

butylamine	-------	N-nitrosodibutylamine	0-1% yield
putrescine	-------	N-nitrosopyrrolidine	9.2% yield
lysine	-------	N-nitrosopipecolic acid	0.5% yield

The reaction of primary amines with nitrous acid has been reviewed (33), and although the reaction mechanism is not well understood, tentative reaction pathways have been proposed (31).

Sources

Primary amines such as methylamine, ethylamine, n-butylamine and ethanolamine are widely used in industry (19). While primary amines can be found in many foodstuffs (34-36) and in many products, a compilation of known primary amines in different matrices is not available.

SECONDARY AMINES

Chemistry

The kinetics of N-nitrosation of secondary amines have been recently reviewed (33, 37-39). The kinetics of nitrosation of secondary amines are very briefly summarized here: a reader wanting more depth should refer to references 33, 37-39. In a system containing nitrous acid ($HO\cdot NO$) as the nitrosating agent, the possible nitrosyl carriers are ($H_2O\cdot NO^+$), ($NO_2\cdot NO$) and NO^+). The nitrous acidium ion ($H_2O\cdot NO^+$) plays a significant role in acidic conditions. Therefore, it seems likely that at the dilute acidic conditions that are encountered in the environment, nitrous anhydride ($N_2O_3 = NO_2\cdot NO$) nitrosates secondary amines according to equations (1) and (2):

$$2HNO_2 \xrightarrow{fast} NO_2 \cdot NO + H_2O \ldots\ldots\ldots (1)$$

$$NO_2NO + R_2NH \xrightarrow{slow} R_2N - NO + HNO_2 \ldots\ldots (2)$$

For most secondary amines, equation (2) is rate limiting. The kinetic expression is thus:

$$\text{Rate} = k\ (HNO_2)^2\ (R_2NH) \ldots\ldots\ldots\ldots (3)$$

The reaction rate is pH dependent and has a maximum value at pH 3-4 (40). The rate constants for 14 secondary amines have been tabulated (39) from which it is observed that the ease of nitrosation increases as the basicity of the amine decreases.

In the presence of anions (x^-), XNO forms and these are efficient nitrosating agents (37). The effectiveness of the nitrosating species is in the following order (39):

$$NCS\cdot NO = I\cdot NO > Br\cdot NO > Cl\cdot NO > NO_2\cdot NO \quad \ldots\ldots\ldots\ldots (4)$$

Thiocyanate, iodide and bromide ions have all been demonstrated to increase the nitrosation rate for secondary amines (40-42).

The nitrosation of amides, such as methylurea and methylurethane, follows the kinetic expression:

$$\text{Rate} = k_2\ (\text{amide})\ (HNO_2)\ (H^+) \ldots\ldots\ldots (5)$$

The main nitrosating agent is probably the nitrous acidium ion ($NO{\cdot}OH_2^+$). The k_2 value of 21 amides has been tabulated (39). There is no simple rule, as there is for secondary amines, relating the ease of nitrosation to the properties of the amide.

Reaction by nitrites is usually very slow at neutral or alkaline pH due to the low equilibrium concentration of nitrous anhydride, however, in the presence of formaldehyde or chloral as a catalyst (25), an appreciable nitrosation rate for secondary amines is seen even at pH 6 to 11. Metal ions have also been demonstrated to catalyze the reaction under basic conditions (26).

Sources

Like primary amines, secondary amine type compounds are ubiquitous in the environment. Dimethylamine and diethylamine, for example, are also found in foodstuffs. Pyrrolidine is found in unburned tobacco, coffee extracts, defatted cocoa and several varieties of cheese (34-36). Diethanolamine, morpholine, dimethylamine, di-n-propylamine, di-n-butylamine are used widely in industry (19). A comprehensive compilation of the uses and occurrence of secondary amines is not available.

TERTIARY AMINES

Chemistry

One of the most remarkable myths in chemistry today is the notion that tertiary amines do not yield N-nitroso compounds (43). This myth has persisted for over 100 years since the work of Geuther (44) and has continued despite numerous studies demonstrating that tertiary amines readily form N-nitroso compounds. The subject and its history has been reviewed in the Journal of Chemical Education (45). It is this same fallacy that still allows the unrestricted world-wide use of synthetic cutting fluids, which contain up to 40% triethanolamine and 18% sodium nitrite; fluids which have been found to contain up to 3% of the corresponding N-nitroso compound, N-nitrosodiethanolamine (17). Aminopyrine, a widely used analgesic (not used in the U.K. or U.S.) has also been shown to form N-nitrosodimethylamine in yields as high as 30% (46-48).

Mechanisms for the N-nitrosation of tertiary amines have been proposed (49-51). The latter workers consolidated the mechanism, and proposed that the unshared electron pair on the unprotonated amine reacts with a nitrosating species to form a nitrosammonium ion (see Figure 3).The nitrosammonium ion then undergoes cis elimination of nitrosyl to form an immonium ion. At 100°C and low pH (pH-3), the immonium ion is hydrolyzed to give a carbonyl compound and a protonated secondary amine; the protonated secondary amine is then nitrosated to the corresponding N-nitrosamine. At 100°C and higher pH (pH-6) the immonium ion undergoes nucleophilic attack by free nitrites to form an unstable adduct which collapses to form a carbonyl compound and the nitrosamine.

The reaction of tertiary amine oxides with nitrous acid has also been shown to produce N-nitroso compounds. The mechanism for the amine oxides is similar to that for the tertiary amines (51).

Sources

Many tertiary amine type compounds which have been nitrosated and shown to produce an N-nitroso compound are used in industry (50).

OXIDES OF NITROGEN

Nitric Oxide (NO)

The reaction of nitric oxide (NO) with secondary amines in organic solvents, such as acetonitrile or ethanol has been shown to be slow, with a half-life of about 8 days (52). The reaction rate was shown to be independent of the amine basicity suggesting that some process, independent of the amine, is rate limiting. The presence of a small amount of air in the system resulted in complete conversion to the nitrosamine within a few minutes. It was concluded that nitrosation probably occurs via nitrogen dioxide (NO_2). Nitric oxide itself seems to be a poor nitrosating agent, probably because it is unable to abstract an amino-H atom to generate the dialkyl-amino radical, which might then combine with further nitric oxide (52).

Relatively small amounts of metal salts catalyze nitrosation of piperidine, piperazine and morpholine by nitrite (25,26) in organic solvents. Catalytic effects have also been demonstrated with ZnI_2, $ZnBr_2$, with the most effective catalyst being I_2. In these cases nitrosyl iodide (NOI) is the most likely nitrosating agent. The metal salt catalyzed reactions in organic solvents are substantially faster than N-nitrosamine formation by acidified nitrite.

Nitrogen Dioxide (NO_2, Nitrous Anhydride (N_2O_3) and Dinitrogen Tetraoxide (N_2O_4)

A commonly used technique for synthesizing N-nitrosamides in organic solvents involves the use of N_2O_3 and N_2O_4 (53). N-nitrosamines are also formed rapidly under these conditions (54). The possibility of these reactions being important in aqueous media (other than for nitrosation at pH 2-4) was not considered until recently (55). The omission may have arisen because N_2O_3 and N_2O would be expected to undergo rapid hydrolysis at pH >5 to innocuous NO_2^-.

$$N_2O_3 \xrightarrow{2HO^-} 2NO_2^- + H_2O \quad . . . . (6)$$

$$N_2O_4 \xrightarrow{2HO^-} NO_2^- + NO_3^- + H_2O \quad . . . . (7)$$

It has been shown that primary and secondary amines of widely different reactivity compete effectively with water and HO^- for both gaseous N_2O_3 and N_2O_4 (55). The amines which have been studied and shown to form N-nitroso compounds or the diazonium ion under these conditions include piperidine, morpholine, N-methylpiperazine, aniline, N-methyl-4-nitroaniline, p-nitroaniline, diphenylamine, 3,5 dinitroaniline, o-nitroaniline and

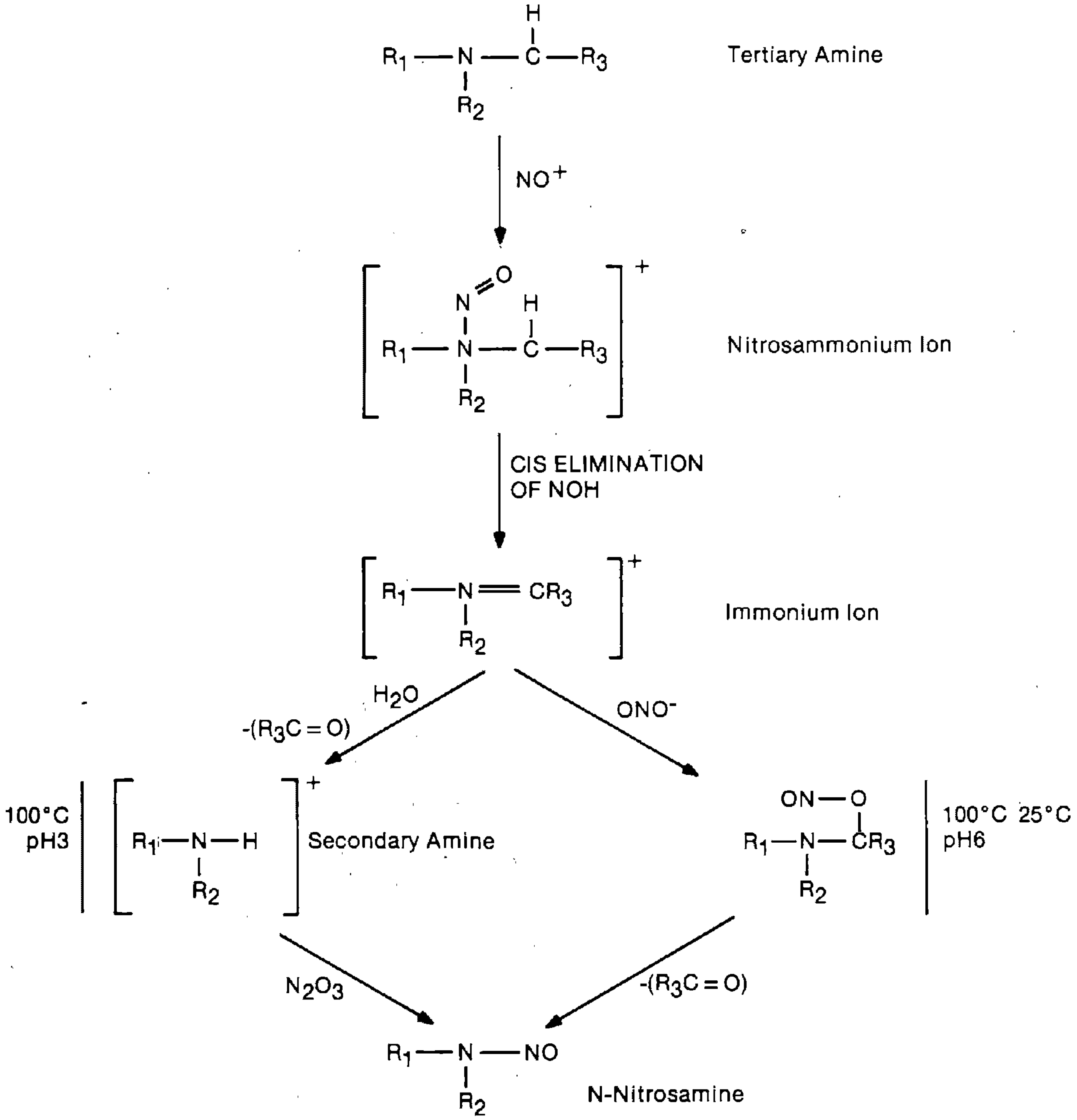


Figure 3. Proposed Mechanism of N-nitrosation of Tertiary Amines [after Smith and Loeppky (49) and Ohshima and Kawabata (51)].

2-chloro-4-nitroaniline. Two compounds did not react; 2,4 dinitroaniline (pK_A - 4.53) and N-methylacetamide (pK_A - 1.0).

N-nitrosation by oxides of nitrogen at neutral and alkaline pH has an important bearing on assessing human exposure to N-nitroso compounds, particularly as this route has been almost totally disregarded in the past. Those analytical techniques which have relied on basic pH to 'inhibit' nitrosation need further study to ensure the validity of the findings (56-59).

Sources

Nitrogen oxides, generally referred to as NO_x, are generated during high temperature combustion of fossil fuels. Approximately half the urban load of NO_x arises from mobile sources, primarily automobiles, with the remainder coming from stationary sources, primarily electric power utilities.

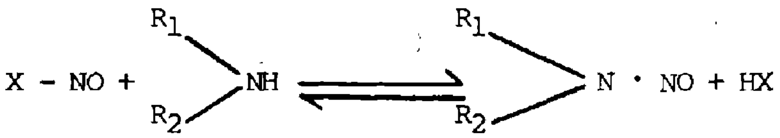
At temperatures above 1800°C, nitrogen fixation from nitrogen in the air becomes important. This route predominates in gas and oil fired systems, including NO_x emissions from gasoline and diesel engines. For thermodynamic reasons, nitric oxide (NO) is the predominant nitrogen oxide formed during high temperature combustion. As the exhaust temperature falls below 600°C, oxidation to NO_2 occurs. The chemistry of nitrogen oxides, and their occurrence in the environment has been reviewed (60).

Nitrite and Nitrate, Source

The availability of nitrite in the environment is an important factor in the occurrence of N-nitroso compounds. Sodium nitrite is produced industrially and is used in many industrial and commercial processes and products, including extensive application as an anti-corrosion agent. Nitrite is also widely used in the curing of meat, poultry and fish products to inhibit the growth of *C botulinum*, thereby preventing formation of its toxin.

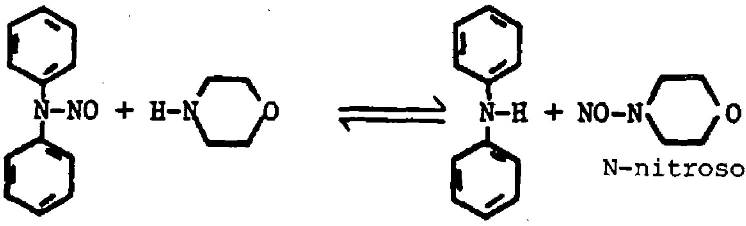
Transnitrosation

The term transnitrosation generally refers to reaction of the type:



$$X - NO + \begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>NH \rightleftharpoons \begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>N \cdot NO + HX \qquad \ldots\ldots (8)$$

For example:



N-nitrosodiphenylamine

N-nitrosomorpholine

Transnitrosation by aromatic nitrosamines has been reported to occur in both polar and non-polar solvents. Most commonly, the transnitrosating nitrosamine (for example, N-nitrosodiphenylamine (61) or N-nitrosocarbazole (62)) is heated with the amine substrate in the solvent (63,64). Transnitrosation in acid, in the presence of various catalysts, is also well known (65,66). This mechanism may be primarly responsible for the finding of high levels of N-nitrosomorpholine in Rubber Plant H (see Text).

ANALYTICAL METHODS

Introduction

To successfully determine the extent of environmentally occurring N-nitrosamines at the part-per-million (ppm) or the part-per-billion (ppb) level, it is essential that the analytical techniques that are chosen be sensitive, selective, free of false results and capable of dealing with a wide variety of sample types. Without such techniques, screening the environment for N-nitrosamines would be both costly and time consuming. The instrument system used in this study consisted of gas chromatography (GC) and high pressure liquid chromatography (HPLC) with sample detection by a TEA™ Analyzer. The TEA has been specifically designed for the detection of sub-nanogram amounts of N-nitroso compounds. The sample preparation and collection techniques were all designed to take advantage of the TEA detector.

In choosing the methods for screening the environment for N-nitrosamines we were also mindful of those factors which may adversely effect the analysis. False results, (i.e.) false positive or false negative findings of N-nitrosamines, can arise from either the creation or loss of these compounds due to the methods employed in sampling, sample preparation or detection. False results can be a problem in the analytical determination of any compound. However, in the case of N-nitroso compounds this problem is further aggravated by the multitude of reactants and reaction conditions that can give rise to these compounds. N-nitrosamines are relatively easy to make and are also fairly labile. They are sensitive to prolonged thermal treatment, as well as photochemical irradiation (67). In addition, certain N-nitroso derivatives are not stable to excessive conditions of pH (68). Most, if not all, N-nitroso compounds are decomposed by inorganic acids such as HCl, HBr, and HI (69).

TEA™ Analyzer

One of the most significant physical properties of N-nitroso compounds is the relative ease of the dissociation of the N-NO bond. For example, with N-nitrosodiphenylamine, the energy required to break the C-N bond is 105 kcal/mole, whereas the bond dissociation energy for the N-NO bond is only 11 kcal/mole. For other simple dialkylnitrosamines, the energy required for the N-NO bond dissociation is on the order of 40-60 kcal/mole. The relatively low energy requirement for the release of nitric oxide from N-nitroso compounds resulted in the successful development of the TEA Analyzer (70-74) as a N-nitroso compound detector for both gas and liquid chromatography.

Gas Chromatography-TEA

This system operates by catalytically pyrolyzing any N-nitroso compounds in the GC carrier gas. Figure 4 is the TEA Analyzer's operating schematic. All N-nitroso compounds present in the sample entering the pyrolyzer are cleaved at the N-NO bond, thereby releasing the nitrosyl radical (NO). The yield of NO is approximately stoichiometric for most N-nitroso compounds. Solvent vapor, pyrolysis products, and NO pass through an adsorbent which removes all materials other than the NO and permanent gases. The NO and carrier gas are then swept into a low pressure reaction chamber where ozone reacts with the NO to generate electronically excited nitrogen dioxide (NO_2*). The key reactions occurring in the pyrolysis and reaction chambers are:

$$\begin{aligned}
&RR'\text{-}N\text{-}NO && \xrightarrow[350\text{-}550^{\circ}C]{\text{pyrolysis}} \longrightarrow && R\ R'\text{-}N\cdot + NO \\
&NO + O_3 && \xrightarrow{\qquad\qquad} && NO_2^{*} + O_2 \\
&NO_2^{*} && \xrightarrow{\qquad\qquad} && NO_2 + h_{v}
\end{aligned}$$

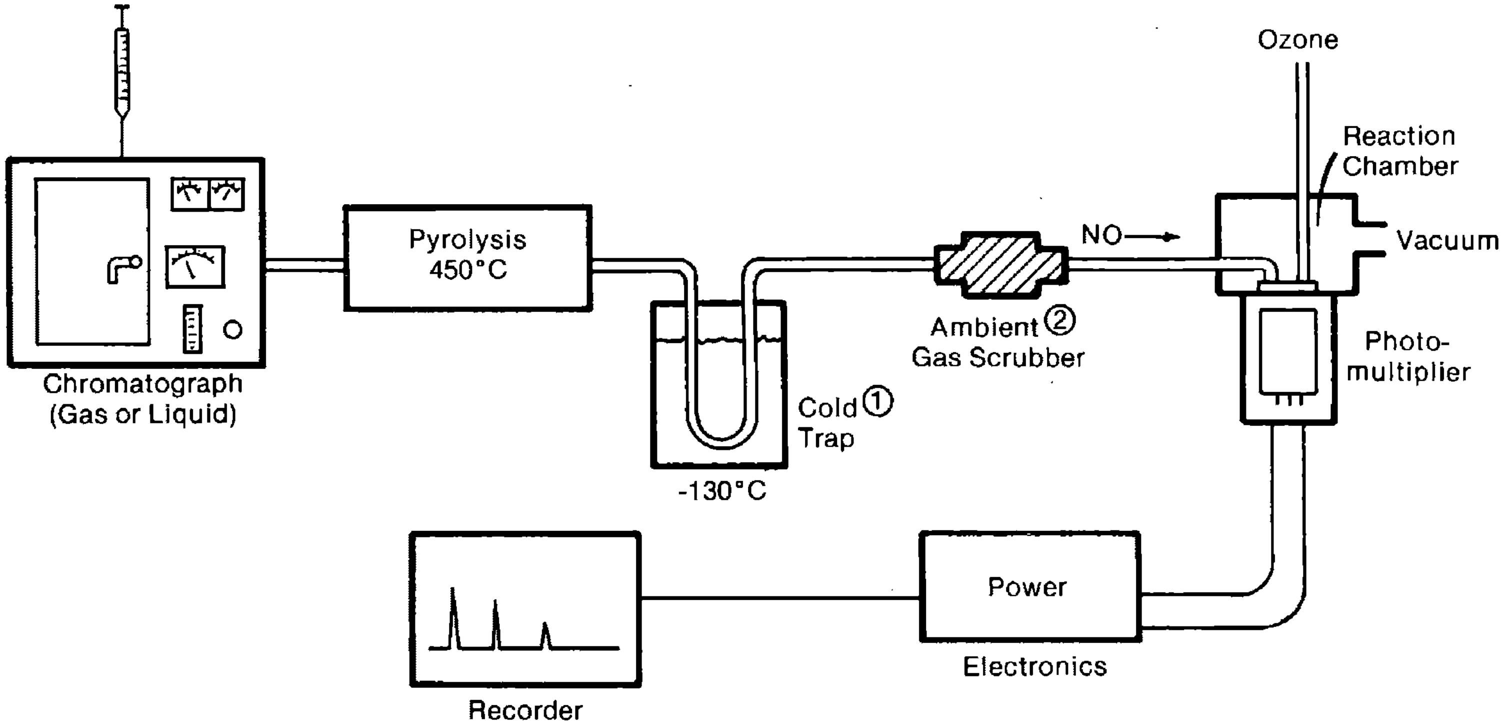
The excited NO_2* rapidly decays to the ground state with the concommitant emission of light near the infra-red region of the spectrum. The intensity of this emitted light is proportional to the amount of N-nitroso compound present in the sample. The TEA's selectivity for N-nitroso compounds is dependent upon pyrolysis occuring within a fraction of a second, NO passing through an adsorbant which removes other pyrolysis products from the gas stream and the NO reacting with ozone to produce a chemiluminescent reaction in the near infra-red region of the spectrum. Because of the TEA's selectivity and sensitivity, it is possible to chromatograph and quantitate N-nitroso compounds even in the presence of many other co-eluting compounds thus reducing, and in some instances eliminating, the need for sample clean-up procedures prior to chromatography. Detection limits, using the GC-TEA apparatus, are routinely less than 50 pg (50×10^{-12}g) for compounds such as NDMA or NPYR.

It should be mentioned that the TEA is not totally specific for N-nitroso compounds (75,76). Several other classes of organic compounds can also be detected using the TEA. These classes of compounds include, organic nitrites (O-NO), N-nitramines (N-NO_2), C-nitroso (C-NO), poly C-nitro (C-NO_2), nitrates (O-NO_2) and inorganic nitrites. It is also probable that other classes of organic compounds, e.g., S-nitroso and S-nitro, may also be detected by the TEA. Thus, the presence of a response by GC-TEA for a new sample cannot necessarily be taken as proof that the sample is an N-nitroso compound. Additional confirmation of positive results can be by either the use of specific chemical tests (77,78) or the use of high resolution mass spectrometry or by HPLC-TEA. High resolution mass spectrometry with continuous peak matching has been used as a confirmatory technique for the identification of N-nitroso compounds (73,79).

High Pressure Liquid Chromatography-TEA

The TEA in the HPLC mode operates on the same basic principle as previously discussed with regard to GC-TEA. However, here a liquid sample is swept through the catalytic pyrolyzer by argon carrier gas, with all organic materials being vaporized and/or pyrolyzed. Following the pyrolyzer, the LC solvents are condensed out of the gas stream in 300 ml vacuum cold traps.

At the low temperatures used in the cold traps, typically -80 to -120°C, only the carrier gas, the nitrosyl radical (NO), and a very few low molecular weight organic species pass through both cold traps and enter the



1 - Cold trap user with HPLC to remove solvent prior to O_3 + NO reaction chamber

2 - Ambient gas scrubber user with G.C. to remove pyrolysis products other than NO, carrier gas

Principal of Operation:

$NO + O_3 \longrightarrow NO_2^*$

$NO_2^* \longrightarrow NO_2 + IR$

Figure 4. TEA™ Nitrosamine Analyzer Operating Schematic

chemiluminescent reaction chamber. The remaining TEA operations are identical to those already described for the GC-TEA mode. With HPLC-TEA, the limits of detection for most N-nitrosamines are in the range of 0.1 - 1.0 ng per injection.

CHROMATOGRAPHY CONDITIONS

GC-TEA

The GC-TEA conditions used for the detection of volatile nitrosamine have been described by Fine and Rounbehler (72). A typical GC column consisted of a 14' x 1/8" stainless steel column packed with 10% Carbowax 20M containing 0.5% KOH on Chromosorb HP (80-100 mesh). The GC was usually operated at 150°C with argon gas as the carrier at a flow rate of 15 ml/min.

HPLC-TEA

HPLC-TEA was constructed by sequentially connecting a high pressure pump (Altex model 110), an injector (Waters), a Lichrosorb Si60 column (E. Merck Labs., Inc., 4 mm x 39 cm), and a TEA. The operation of an HPLC-TEA has been described (104). The samples were usually screened by using acetone as the elution solvent at 2 mL/min. If a TEA-responsive peak was detected at the non-retention volume (t_1), a less polar elution solvent would then be used until the peak was eluted to a capacity factor between 2-5. Capacity factor is defined as $(t_R - t_o)/t_1$, where t_R is the retention of the peak. The following varieties of solvent systems at 2 ml/min have been used in this study: (i) 100% acetone; (ii) 50% acetone, 50% hexane; (iii) 15% acetone, 85% hexane; (iv) 5% acetone, 95% hexane.

COMPOUND IDENTIFICATION

Use of N-nitroso Standards

Methods for the detection and analysis of known N-nitroso compounds using the TEA are relatively straight forward. As a general procedure, a mixture of volatile nitrosamines are used to calibrate an integrating recorder (Hewlett/Packard, Model 3380A) attached to the out-put signal of the TEA. The nitrosamines used for calibration usually include N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodipropylamine (NDPA), N-nitrosodibutylamine (NDBA), N-nitrosopiperidine (NPiP), N-nitrosopyrrolidine (NPYRR) and N-nitrosomorpholine (NMOR), however, many other nitrosamine standards were available. Most environmental samples examined by the TEA usually have, if any, only one or two chromatographic signals and as it often happens these signals correspond to well known nitrosamines such as NDMA or NDEA. Chromatographic comparisons of retention times and quantitation by both the GC-TEA and the HPLC-TEA using known standards, were generally used to confirm the presence of a N-nitroso compound. GC-mass spectral analysis was also used for additional confirmation when needed.

TEA-Responsive Unknown Compounds

As pointed out earlier, the TEA is not absolutely specific for N-nitroso compounds. When a TEA chromatographic signal is detected which does not match a known standard, the compound is labeled unknown until it can be structurally identified and an authentic standard obtained. Typically the methods used to identify unknown compounds consist of isolating a sufficient amount of the pure compound for mass spectral analysis (17). This does not constitute a particularly difficult problem if the unknown in the environmental sample is in high concentration and if some information is available which helps to identify it. An example of this was the finding of the nonvolatile nitrosamine N-nitrosodiphenylamine (NDPhA) in a chemical plant manufacturing this compound (21). However, if the quantity (estimated by assuming a molecular weight and comparing its molar response on the TEA to a known standard) of the unknown is in the low ng range, and the sample contains large amounts of co-eluting compounds, then the problems of identification can be formidable. This situation is further aggravated if the unknown compounds are nonvolatile and thus cannot be examined by GC-mass spectroscopy. While these identification problems are not insurmountable, they can be both costly and time consuming.

In order to avoid expending time and effort attempting to identify all unknown compounds which produced a TEA signal, simple screening methods were developed to help eliminate most of those unknowns which were not N-nitroso compounds (78). These methods can effectively distinguish N-nitroso compounds from all other TEA-responsive compounds with the only exceptions being a few C-nitro compounds. This greatly reduced the effort needed to examine environmental samples for N-nitroso compounds.

ARTIFACTS

False Negatives

The problems created by false negative results are generally more managable and of less concern than are the problems of false positive results. False negatives can arise from sample exposure to UV, sunlight or by acid degradation of the collected N-nitrosamine. Analytical controls, with N-nitrosamines added as internal standards, can be used to reveal any tendency of the sampling or analytical methods to degrade N-nitrosamines. As yet there is no evidence indicating that false negatives were a major problem with the methods used in this study. Photodegradation was minimized by either protecting the sample by light exclusion or by avoiding strong light sources when the samples were taken.

False Positives

The major sources of false positives are cross contamination and artifact formation of the N-nitrosamines. Another source of false positives is the TEA detection of unknown compounds, i.e., compounds which do not match a known standard. The compound is labeled unknown until it can be structually identified and authentic standards obtained. The problems due to artifacts in the analysis for N-nitrosamines have been reviewed recently (77). Control of contamination has been extensively discussed (80).

Because the techniques used in this study are highly specific for only compounds which can release the nitrosyl moiety, the overall problem of contamination is limited to those compounds. However, when performing routine analysis in the ppm-ppb range, the problems of contamination are still relevant, and for this reason, negative blanks are regularly used. False positives are generally caused by the inadvertant formation, during the sample collection, work-up or analysis, of precisely those nitroso materials for which one is sampling. If a N-nitroso compound is found in an entirely new sample situation, serious consideration must be given to the possibility that it may be a false positive. For example, Angeles, et al. (1978) have recently described the artifact formation of various N-nitrosamines during extraction of environmental samples (81). They have shown that inorganic nitrite in the solid phase can serve as an effective nitrosating agent for solutions of organic amines in non-aqueous solvents (CH_2Cl_2, CHClBr, Ch_2Br_2, etc.). A simple precaution to minimize the possibility of artifact formation is to use the bare minimum of analytical steps. This approach is feasible with the GC-TEA and HPLC-TEA methods of N-nitroso analysis, provided that the sample is in a form suitable for direct introduction into the apparatus. For example, aqueous pesticide formulations were directly introduced into both GC-TEA and HPLC-TEA in order to show that the NDMA present in the formulation was not an artifact of the sample preparation (18). In this case any possible artifact formation was limited to the chromatograph or detector conditions employed.

Possible sources of nitrosating agents which could be responsible for a positive artifact include: nitrite contamination of the sample itself (82,83), open column chromatography on nitrite contaminated packing materials for GC and LC columns (84), use of too high an injection port temperature in GC analysis of a complex sample (85), absorption of nitrogen oxides from ambient air (86), N-nitrosamine contamined deionized water (87) and organic solvents (88). The most frequent source of the amine precursors is the sample itself.

Use of Nitrosation Inhibitors

Analysts routinely add nitrosation inhibitors such as ascorbate (89), or sulfamic acid (14) to all samples prior to analysis. Nitrosation inhibitors are effective, because at the proper pH they compete with amines for available nitrite (90,91). Care is required to ensure that the inhibitor is added in excess so as to account for the available nitrite. If addition of an inhibitor decreases the amount of N-nitroso compound which is observed, it is possible that some or all of the N-nitroso material originally determined was due to artifact formation.

MOBILE LABORATORY

Because of the many problems associated with artifacts in the environmental analysis of N-nitroso compounds, it is essential that these determinations be carrried out as soon as possible following collection of the sample. For this and other reasons, a fully equipped mobile laboratory designed for the on-site analysis of N-nitroso compounds was constructed and used in this study (92). The mobile laboratory is self-contained with power generators, a fume hood, two TEA Analyzers, gas chromatographs, high performance liquid chromatographs, lab benches and essential laboratory equipment. All of the analytical procedures used in this study with the exception of GC-FID and GC-MS were incorporated in the mobile laboratory. Use of the mobile laboratory for on-site analysis not only made it possible to modify the survey protocols when needed but samples could be repeated or re-checked on the same day or while the laboratory was still within the vicinity of the factory being visited. The mobile laboratory greatly aided this study by providing on-site analysis, which allowed us to direct our sampling strategy and reduce the need for repeat visits to the same facility. This on-site laboratory and all of the analytical procedures were open to the personnel of the plants being visited giving them an opportunity to understand and participate in the study.

AIR SAMPLING METHODS AND ANALYSIS

The sampling strategy and methods evolved as new sampling techniques became available. Initially all air samples consisted of only area and process air samples collected by the use of diluted alkali (1N KOH) bubble traps (93) and Tenax™-GC cartridges (13). In later tests of these techniques it was discovered that artifact formation of N-nitrosamines could occur on Tenax™-GC and that the 1N KOH traps (also pH 4.5 phosphate-citrate/20 mM ascorbic acid traps) were temperature dependent and compound selective in trapping N-nitrosamines (160). While the problems with the wet traps were not catastrophic we felt that the formation of artifacts on the Tenax™-GC sorbent rendered it useless as a material for air sampling N-nitroso compounds (94,95).

In a comparison study of other possible N-nitrosamine air trapping sorbents it was discovered that the problem of artifact formation was common to all of the dry solid sorbents currently in use (95). For this reason, Thermo Electron, (Waltham, MA) independently developed an artifact resistant solid sorbent air trapping system for N-nitrosamines, ThermoSorb™/N (94). The ThermoSorb/N air sampling cartridges were designed specifically for the artifact resistant collection of airborne N-nitrosamines in atmospheres where their precursors are likely to co-exist. The ThermoSorb/N air sampling cartridges were further designed to minimize sample preparation, to collect samples close to specific processes along with area air samples, and for use as breathing zone air collectors.

Dilute Alkali (1N KOH) Traps

The use of (1N KOH) as a liquid scrubber for airborne N-nitrosodimethylamine was introduced after theoretical and practical problems had been raised concerning the previous method of cryogenic trapping (93). The wet air traps consist of vacuum traps (190 x 24 mm) containing 45 ml of a 1N KOH solution. Air is bubbled through these traps with a Bendix C115 air pump at a rate of approximately 2 L/min for about 3 hours, care being taken to avoid direct sunlight. The air flow rates were determined by reading the Bendix C115 rotameter which had been previously calibrated by use of Hasting 10L mass flow meter.

At the end of the sampling time the contents of the vacuum traps were extracted using 3 x 10 mL dichloromethane (DCM), dried over sodium sulfate and concentrated to a volume of approximately 1 mL, using a Kuderna-Danish evaporator at 52°C. The concentrates were then analyzed by GC-TEA and/or by HPLC/TEA. Analytical controls consisted of blank 1N KOH solvent controls and spiked N-nitrosamine recovery controls.

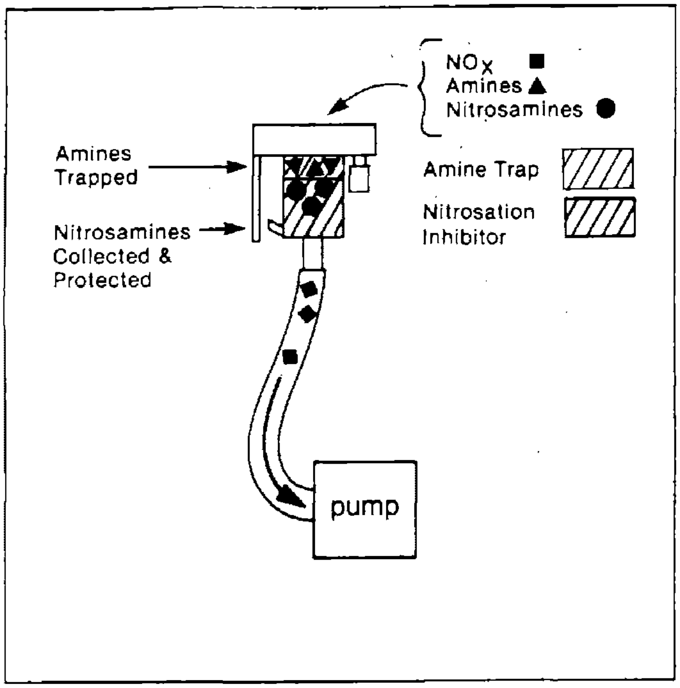
This trapping and analytical system works well for NDMA, with an efficiency of 80-90% (depending upon air temperature). However, N-nitrosodiethylamine (NDEA) is not trapped as well (40-50%) and for N-nitrosodipropylamine (NDPA) and N-nitrosodibutylamine (NDBA) less than 5% is trapped. N-nitrosomorpholine (NMOR) is trapped at close to 100% efficiency but unlike dimethylamine, morpholine (the amine precursor to NMOR) is also trapped with a high efficiency. The trapping of morpholine raises the possibility of artifact formation during the sampling via airborne nitrogen oxides of co-trapped transnitrosating agents. Despite the potential for artifact formation of NMOR there is no evidence that it has occurred in any of the samples taken in this study (21).

Tenax™-GC Cartridges

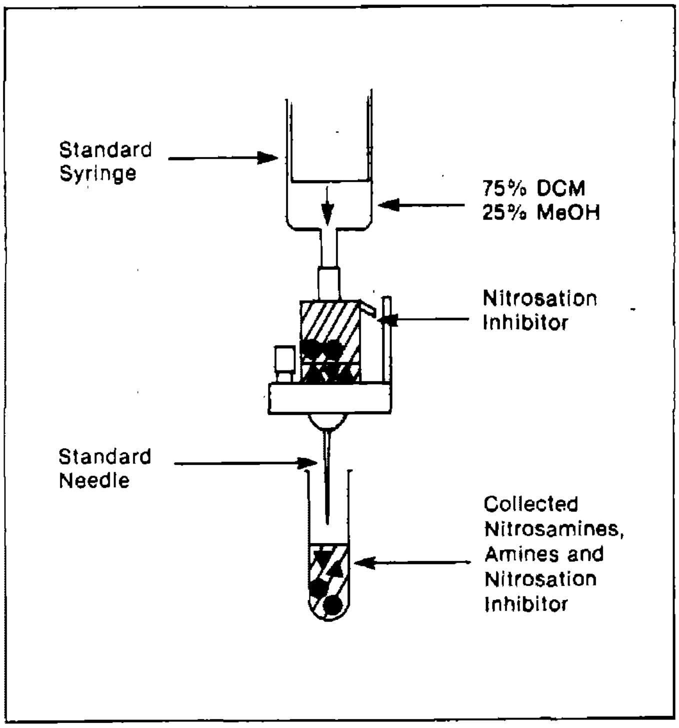
Sampling techniques for N-nitrosamines using Tenax were developed by Pellizzari et al., (96-98). Air is drawn through a 1 cm o.d. glass tube, 6 cm long, packed with pre-cleaned Tenax GC (35/60 mesh). Careful attention must be paid to the temperature of the air and the amount of air passed through the tube so as to ensure that breakthrough does not occur. The Tenax tubes are desorbed by heating in a stream of helium and cryogenically trapping the contents in a small volume gold lined trap held at -192°C. The cold trap is then flash heated, driving the contents directly into a capillary column (GC-MS) system. There are several drawbacks to this method. First, the Tenax may trap precursor amines and N-nitro compounds, which could form N-nitrosamines during the desorption and/or flash heating steps. Second, Tenax has a relatively small breakthrough volume for NDMA, often the N-nitrosamine of maximum interest. Third, Tenax has been demonstrated to be artifact prone in laboratory experiments (95).

ThermoSorb™/N Air Sampling Cartridges

These air sampling cartridges, manufactured by Thermo Electron Corporation, Waltham, MA, have been designed specifically for air sampling N-nitroso compounds (Figure 5). The cartridges, which are constructed of an opaque material, contain about 2 grams of sorbent in a 1.3 x 2.2 cm sample bed. The cartridges have a built on clip for personal sampling and have standard Luer fittings on both ends so that a second cartridge can be attached as a backup to check for sample break through during sampling. The standard Luer fittings also



Collection of nitrosamines in a nitrosating (NO_x + Amines → Artifacts) environment.



A schematic diagram of analytical preparation using the "Backflushing" technique.

Linearity Test

% RECOVERY

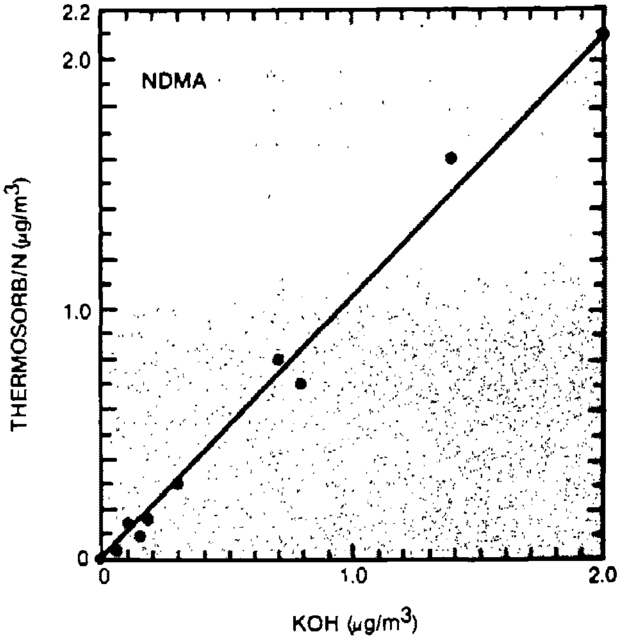
ng Spiked	1000 ng	500 ng	100 ng	25 ng
NDMA	106	94	103	112
NDEA	106	93	99	100
NDPA	100	94	104	89
NDBA	95	99	113	105
NPIP	98	101	103	108
NPYR	94	94	93	89
NMOR	97	92	95	98

Parallel ThermoSorb/N Air Sampling at Low Concentrations[8]

Sample No.	Volume of Air (liters)	NDMA μg/m³
1	886	0.17
2	1140	0.20
3	781	0.18
4	971	0.19
5	844	0.19

ThermoSorb/N Air Samplers sampling at 2 L/min overnight in an industrial environment.

Parallel ThermoSorb/N Air Samplers and 1N KOH impinger field data.



Number of Data Points = 44
Slope = 1.05
Correlation = 0.99
Substance Monitored = NDMA

Figure 5. ThermoSorb/N Operations Schematic and Performance Data

Results of *in-situ* Formation after Sampling 100 L of Air Containing 1 ppm NO + 1 ppmNO_2 at 2 L/min through Sorbents Spiked with 50 μg each of 5 Amine Standards

SORBENT	μg[a] of nitrosamine formed NDMA	NDiPA	NPIP	NPYR	NMOR
Dry					
activated charcoal	5.9	1.7	5.0	1.5	7.9
activated alumina	1.2	0.10	0.22	0.10	8.9
Florisil	0.59	ND[β]	0.20	0.21	8.1
silica gel	1.9	ND	0.56	0.58	9.0
Tenax GC	0.17	0.45	3.8	1.3	15.5
ThermoSorb/N	ND	ND	ND	ND	ND
Wet					
1N KOH	ND	ND	ND	ND	ND
pH 4.5 ascorbic acid	ND	ND	ND	ND	ND

[a] Each data point is the average of triplicate determinations.

[β] ND = None detected detection limit, 0.01 μg of nitrosamine.

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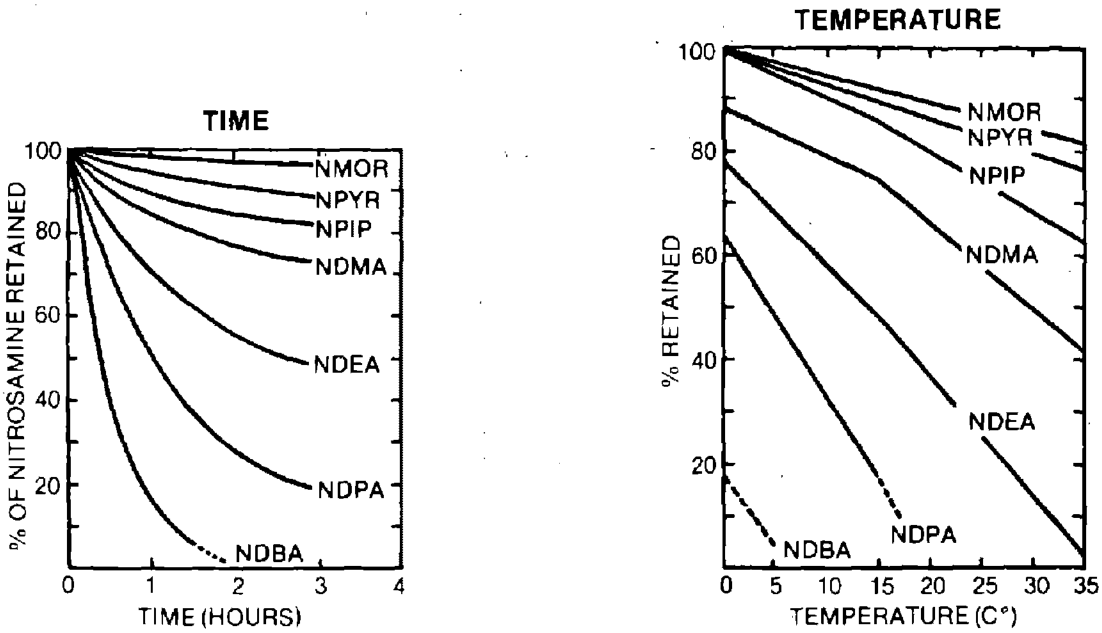
Nitrosamine Loss from Pre-Spiked Wet Impinger Air Traps as a Function of Time and Temperature. Air Flow Rate Held Constant at 2 L/min for 3 Hours through 45 ml of Solution (IN KOH on pH 4.6 Ascorbic Caid).



1. Nitrosamine Concentration Determined at 30-minute Intervals. Trap Maintained at 25°C.

2. Amount of Nitrosamines Retained by Wet Traps at Various Temperatures. Air Flow Rate Constant at 2 L/Min for 3 Hours.

Figure 6. ThermoSorb/N Artifact Comparison Tests

facilitate sample desorption by a solvent backflushing technique using standard syringes. The sorbent bed of these cartridges consist of an amine trapping agent followed by a magnesium silicate sorbent treated with an artifact inhibitor. Air, at flow rates of less than 100 mL/min to 4 L/min, can be drawn through the cartridges using standard battery operated air sampling pumps. For analysis, a polar solvent is backflushed through the cartridge with the first 2 ml collected. An aliquot (typically 5 μl) of the eluate is then examined by GC-TEA or HPLC-TEA for N-nitroso compound content. Solvents that have been used for backflushing these cartridges include acetone, methanol and a 25/75 mix of methanol in dichloromethane.

With this sampling and analytical system, N-nitrosodimethylamine (NDMA) can be detected at the 0.1 $\mu g/m^3$ concentration in air with a 200 L sample. Because of this sensitivity, concentration of the sample is not necessary, thereby further reducing any possibility of artifact formation by eliminating this step.

In comparison tests (see Figure 6) with other published methods for air sampling N-nitroso compounds, the ThermoSorb/N air sampling cartridge was found to be the only one that was both artifact free and accurate (94,95). These cartridges have been used in a variety of factory environments for the detection of the N-nitroso derivatives of dimethylamine, diethylamine, dipropylamine, dibutylamine, piperidine, pyrrolidine and morpholine.

Air Sampling For Amines and Airborne Nitrosating Potential

The apparatus used for the sampling are similar to that used for N-nitroso compounds except the sorbent in the ThermoSorb/A air sampling cartridge (Flouracil) was coated with either thiomorpholine or morpholine without added artifact inhibitors. Air was drawn through these cartridges at exactly 1 L/min for a total of 30 minutes. These cartridges were then backflushed with 4 ml of 1N KOH and aliquots of this eluate were then analyzed. Any N-nitrosothiomorpholine or N-nitrosomorpholine found on these cartridges and not found on the ThermoSorb/N cartridges would have been formed as a result of drawing a nitrosating agent, such as oxides of nitrogen, through the cartridge. Experiments at the Thermo Electron laboratories indicate that the formation of nitrosamines on surfaces coated with precursor amines by gas phase nitrogen dioxide can be a measure of the nitrogen dioxide concentration (See Figure 7). Analysis for N-nitrosothiomorpholine is similar to that for all other volatile N-nitroso compounds. The results of this analysis are, however, reported in equivalent nitrogen dioxide levels. These equivalent nitrogen dioxide levels are those concentrations which would produce an equivalent amount of N-nitrosothiomorpholine or N-nitrosomorpholine under experimental conditions.

Amine Analysis

The apparatus used for volatile amine analysis consisted of a gas chromatograph interfaced to a TEA Analyzer equipped with an oxidative catalytic pyrolyzer (See Figure 8). With this apparatus, all nitrogen containing compounds are quantitatively oxidized to produce stoichiometric amounts of nitric oxide radicals which are then detected via chemiluminescence. The gas chromatographic columns used with this system are similar to those used for

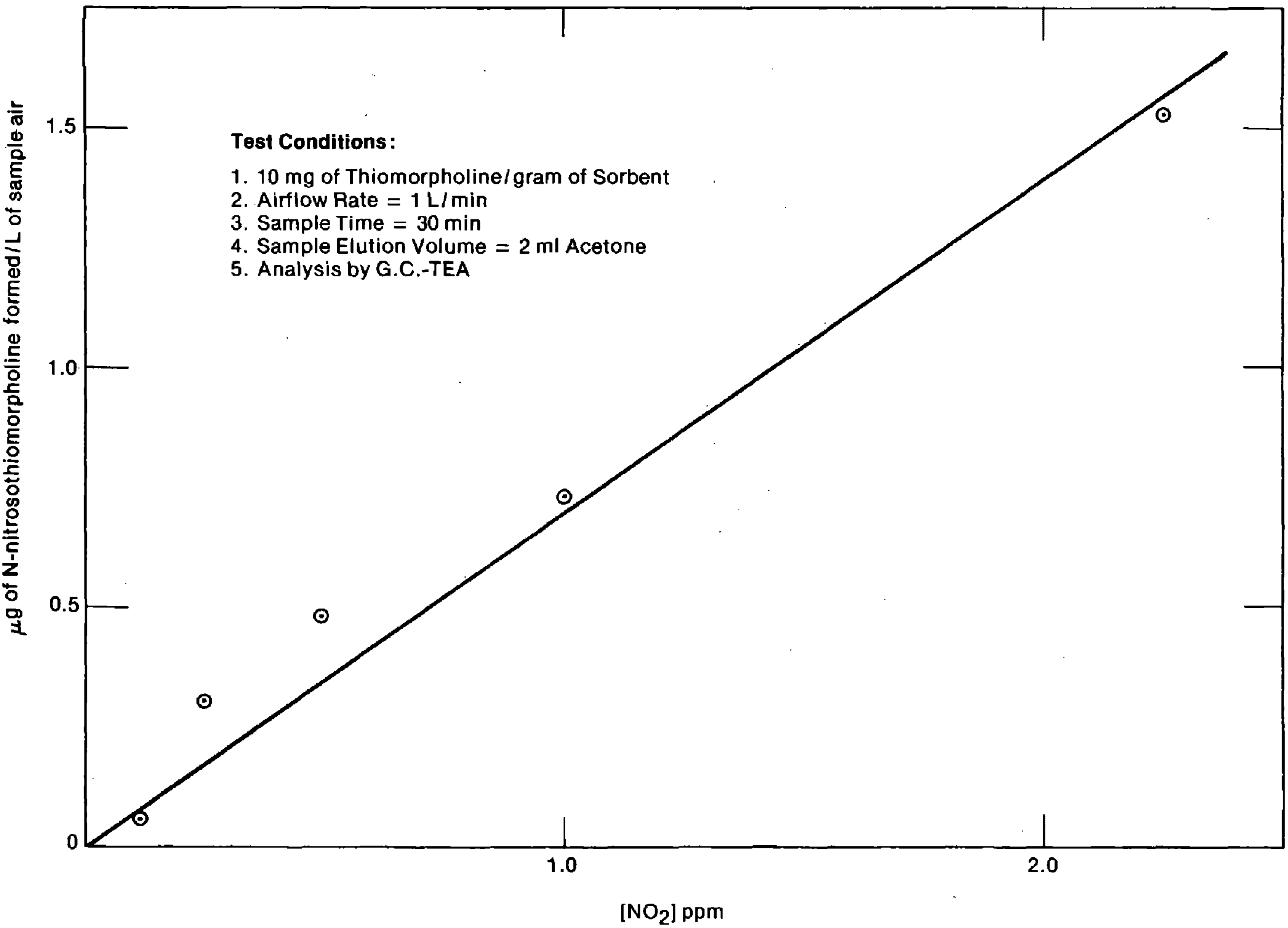
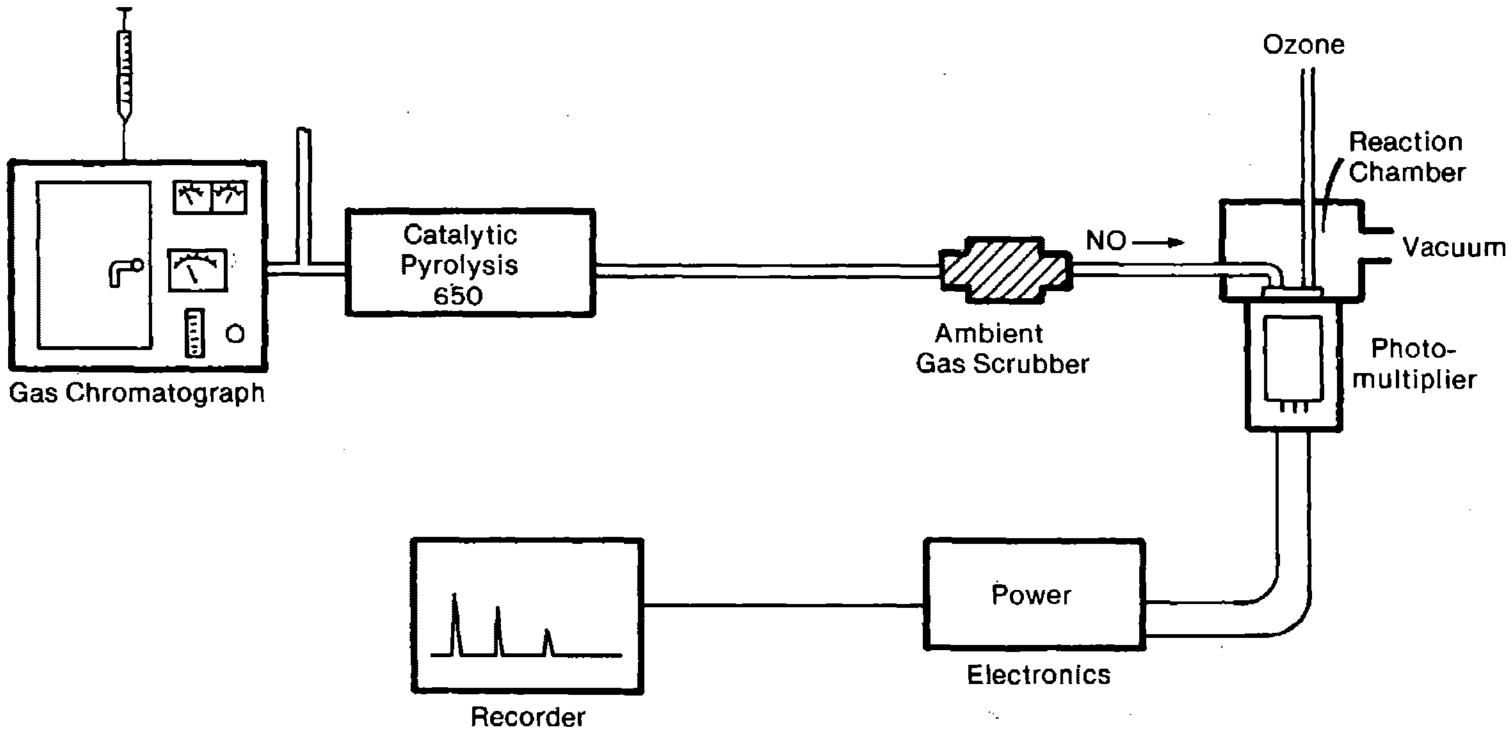


Figure 7. Formation of N-Nitrosothiomorpholine Due to Sampling Air Containing NO_2 Over Thiomorpholine Coater Sorbent



Principal of Operation:

$NO + O_3 \longrightarrow NO_2^*$

$NO_2^* \longrightarrow NO_2 + IR$

Figure 8. TEA Model 610 Nitrogen Analyzer Operating Schematic

nitric oxide radical which are then detected via chemiluminescence. The gas chromatographic columns used with this system are similar to those used for N-nitroso compound analysis. This system (TEA™ Model 610 nitrogen detector, Thermo Electron Corporation) is an absolute nitrogen detector which has no response for other than nitrogen containing compounds and its response for compounded nitrogen is molar. The detection limit for this system is better than 1 picogram of nitrogen per second (Figure 9).

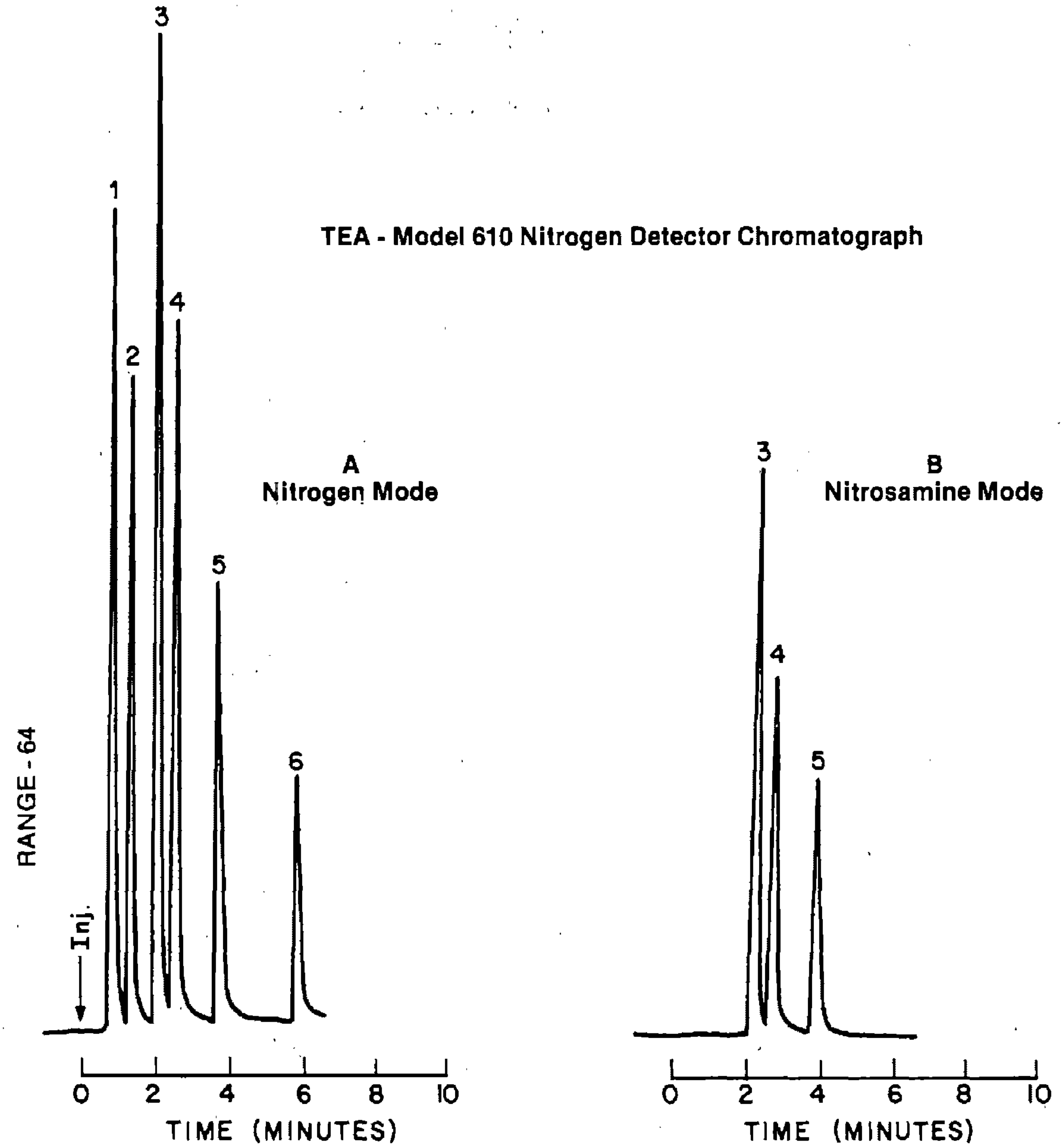
ANALYSIS OF BULK SAMPLES FOR N-NITROSAMINES

The analysis of N-nitrosamines in solid or liquid matrices has been reviewed recently (99-101). Several methods are available, both for volatile and nonvolatile N-nitroso compounds. For volatile N-nitrosamines, the most sensitive is distillation from mineral oil, followed by analysis on GC-TEA (105). This technique was selected as the method of choice in the FDA's meat screening program. Confirmation is by GC-MS or HPLC-TEA.

Distillation from Mineral Oil

The mineral oil distillation technique for the determination of volatile N-nitrosamines involves the use of readily available USP mineral oil, and can be used with samples as diverse as fish, meat, oil, bread, cheese, whole blood, laboratory animals, biological samples, and soil. A necessary condition for the successful application of the procedure is that the volatile N-nitroso compounds can be transferred, under vacuum, from the original sample to a receiving flask maintained at liquid nitrogen temperatures. The mineral oil procedure cannot be used for the analysis of nonvolatile N-nitroso compounds. A nitrosation inhibitor, such as ascorbic acid, sulfamic acid, or tocopherol (103) is typically added to the sample at the outset. Ideally, a combination of ascorbic acid (or sulfamic acid) should be used together with tocopherol, in order to ensure a lack of artifactual N-nitrosamine formation during the actual distillation step (104). If 10-30 grams of a sample is to be distilled, then approximately 0.5 grams of each of the nitrosation inhibitors would be added to the sample before homogenization. The homogenized sample plus inhibitors are added to a two-necked round bottom flask (500 ml), and about 60-70 ml of USP mineral oil is added to the sample so as to cover it completely. If the sample is dry, then 5-10 ml of water is added to the flask. The flask is attached to a vacuum distillation apparatus through the liquid nitrogen cold trap. A single cold trap, maintained at liquid nitrogen temperature, is sufficient to trap all volatile N-nitrosamines. The pressure is reduced to about 1.5 - 2.0 mm Hg throughout the system. The temperature of the distilling flask is then raised slowly over a period of over 40-50 minutes to a maximum of 110°C. This can be maintained for another 10-15 minutes, if less volatile N-nitrosamines are being determined.

At the end of the distillation, the distillate in the trap is thawed, and made up to a constant volume (usually 15 ml) with water. It is then extracted with 3 x 25 ml of dichloromethane (DCM), dried over 25 g of sodium sulfate, and the filter cake washed with DCM. A much more rapid extraction and drying procedure is to pour the 15 ml of water onto a Preptube™ (Thermo Electron), and then to flush the tube with 4-6 x 10 ml of DCM. The Preptube technique, not only solvent-solvent extracts the N-nitrosamines, but also dries the DCM.



A. Nitrogen Mode - Each peak is 5 ng of the following compounds:

1 Acetonitrile, 2 Pyridine, 3 N-nitrosodimethylamine, 4 N-nitrosodiethylamine, 5 N-nitrodipropylamine, 6 Aniline.

B. Nitrosamine Mode - The same amount of the same compounds as in A; however, only the nitrosamines are detected. Peaks 3, 4, and 5 and their response is one-half that in chromatograph A. Note: These nitrosamines contain 2 moles of nitrogen/mole of compound and thus will produce twice the response in the nitrogen mode.

Figure 9. Chromatograph of Various Nitrosamine and Nitrogen-Containing Compounds Detected by the Two Different Modes of Operation of the TEA™ Model 610 Nitrogen Detector.

Whichever extraction technique is employed, the DCM is concentrated on a Kuderna-Danish evaporator fitted with a Snyder column, with 0.2 - 0.3 ml isooctane being added as a "keeper". The water bath temperature is set at 52-53°C. The concentration is stopped when the final volume is about 0.5-1.0 ml. Aliquots of the final concentrate are injected directly into either GC-TEA or HPLC-TEA.

Solvent Extraction for Non-volatile N-nitrosamines

In this method (105), a 25 gram sample is blended to a uniform slurry in a stainless steel blender (Waring) containing liquid nitrogen. Acetonitrile (100 ml) is added in small portions (10 mls each) with additional liquid nitrogen. Powdered anhydrous sodium sulfate (5 grams) is then added, with additional homogenization, and the residual mixture allowed to warm to ambient temperature without stirring. The resultant acetonitrile slurry is gravity filtered through granular anhydrous sodium sulfate. The filter cake is washed sequentially with 2 x 15 ml portions of isooctane. If phase separation does not occur, it is facilitated by cooling to -20°C. The isooctane washings are discarded and the acetonitrile extract is taken to dryness under vacuum at 35°C. The residue is taken up in a few mls of a suitable solvent, such as DCM, transferred to a small concentration tube, and reduced to a final volume of about 0.5 ml with a stream of dry nitrogen in the cold. The solution is then used for both GC-TEA and HPLC-TEA analyses.

Analysis of Water Samples

Several studies have been reported with regard to the nitrosamine content of various water systems (106-111). The sensitivity obtained for most water analyses is less than 10 parts per billion. In the case of water samples, the extracts were routinely analyzed by both GC-TEA and HPLC-TEA in order to determine both volatile and nonvolatile N-nitroso compounds (112). There are basically two methods that can be used for the analysis of N-nitroso compounds in water samples. These are: 1) liquid-liquid extraction with an organic solvent, using either a separating funnel or a Preptube, and 2) adsorption on a sorbent material such as an XAD resin (113). In the liquid-liquid extraction method, water (50-100 mls) is repeatedly extracted with 3 x 10 ml of DCM. The combined extracts are dried over anhydrous sodium sulfate (5 grams), filtered and the sodium sulfate cake extracted further with 2 x 5 ml of additional, fresh DCM. The combined, dried extracts plus washings are concentrated on Kuderna-Danish apparatus, as decribed previously, using isooctane as a keeper, to a final volume of approximately 0.5-1.0 ml. Aliquots of the final concentrate are analyzed by both GC-TEA and HPLC-TEA.

A simpler and more rapid procedure would be to pour 15 ml of water on a Preptube, and wash the Preptube with 3 x 15 ml of DCM. The DCM can be concentrated for analysis. A single Preptube would provide enough sample to obtain a sensitivity of 0.08 μg/l. The sensitivity can be improved by combining the extracts from multiple Preptubes.

Analysis of Soil Sample

The analysis of soil for N-nitroso compounds has been reported (110). The mineral oil distillation procedure can be used to extract volatile N-nitrosamines from soils which are not amenable to solvent extraction. For solvent extraction the soil, together with suitable nitrosation inhibitors, such as ascorbic acid and tocopherol, is homogenized with a suitable extraction solvent. The solvent is then filtered and concentrated prior to analysis. An example is the extraction of NDPA from 50 grams of soil with 60 ml of DCM (113). The DCM is then poured through a Preptube, concentrated and analyzed according to standard procedures. Recovery of NDPA was 80% at the 4 ppb level, and 45% at the 1 ppb levels.

SOME SPECIFIC ANALYTICAL METHODS

Analysis of N-nitrosodiethanolamine

Analytical methods for N-nitrosodiethanolamine (NDElA), a relatively nonvolatile very polar N-nitrosamine, found in metal working fluids, have been described (14). The sample (5 grams) is weighed into a flask to which 250 mg of ammonium sulfamate is added. The mixture is stirred with a magnetic stirrer for 1 minute until all the ammonium sulfamate crystals are dissolved. Ethyl acetate (100 ml) is added, and the mixture is filtered through 40 g of anhydrous sodium sulfate, and this is further washed with 50 ml of ethyl acetate. Alternatively, the ethyl acetate solution can be filtered and dried simultaneously by pouring it through a Preptube. This crude ethyl acetate extract after concentration on a roto-evaporator can be directly analyzed by HPLC-TEA. Recoveries of NDElA have been found to vary from 7-110% depending on the nature of the particular sample, however, for one given sample, the recovery is consistent from analysis to analysis.

A recent development is to analyze the final extract by GC-TEA (114). In order for this to work, it is essential that the TEA furnace be attached to the outlet of the glass GC column without the effluent coming in contact with stainless steel. It is also essential that there be no cold spots between the column and the TEA furnace. This is critical to the GC analysis of NDElA, since even a small cold spot will tend to concentrate NDElA at that point. A glass lined injection port is also required.

Analysis of Silica Gel Cartridge for N-nitrosatable Amines (Method Used Only in Leather Plant E)

The sorbent used in the ThermoSorb cartridges was replaced by silica gel for the collection of volatile amines. After use the sample was eluted by back flushing the cartridge with 1.7 ml of pH 3 potassium biphthalate-HCl 0.02M buffer. The eluate was then nitrosated by the addition of 0.2 ml of a 10% solution of $NaNO_2$ in water and 0.1 ml of a 10% solution of sodium thiocyanate (NaCNS) in water. The NaCNS was added as a nitrosation catalyst. The sample was then incubated in a closed reaction flask at 50°C for 2 hours after which sulfamic acid was added to react with an excess $NaNO_2$. The contents of the reaction flask were then extracted with DCM and the DCM layer analyzed for N-nitrosamines by GC-TEA and HPLC-TEA.

Nitrosation of Bulk Liquid Samples for the Analysis of N-nitrosatable Amines

0.20 ml of the sample is added to 1.5 ml of pH 3 potassium biphthalate HCl 0.02M buffer. The reaction conditions, sample extraction and analysis is the same as described in the analysis of silica gel cartridges.

Analysis of Liquid Air Traps for N-nitrosatable Amines

The procedure is the same as that used for the nitrosation of bulk liquid samples, with the exception of the 1N KOH solution which is first neutralized by the addition of 1N HCl.

SITE VISIT PROTOCOL

The prime criteria for the selection of an industry to be surveyed were: 1) the possibility of formation of N-nitroso compounds from their precursors and 2) the use of products suspected of being contaminated with these compounds. A literature search was conducted on each industry selected. The literature search defined the process description and provided information on production records for the compounds of interest. The search also provided a background of epidemiological studies. In selecting a manufacturing facility within an industry, the contractor and the NIOSH project officer attempted to identify those manufacturing sites whose specific processes had the highest probability of worker exposure to N-nitroso compounds. The protocol of all site visits included the following:

- Prior notification by NIOSH to the plant management and labor unions of the purpose of the visit, and the date when the survey would be conducted.
- Pre-survey briefing of both the plant management and labor representatives at the plant site.
- A plant tour to familiarize the survey team with the specific manufacturing processes and scope of the facility.
- Selection of air sampling sites and identification of bulk samples to be collected.
- After the plant tour, area air sampling equipment was placed in the selected areas and bulk samples collected.
- During the three hours that the area air samplers were operating, 10-15 min high volume area air samples were taken in close proximity to specific processes.
- Using the mobile laboratory, on-site analyses were begun on the high volume process air samples as soon as they were collected.
- When the area air sampling was complete, on site analysis of the collected samples was started.

- After all sampling operations were complete, the survey crew discussed the preliminary findings with the plant management and labor representatives and, if needed, additional information about the plant or its processes was requested.

- After re-analysis and examination of the data at the laboratories of New England Institute for Life Sciences, a report of the results was submitted to NIOSH.

- If necessary, mass spectral confirmations were carried out in the laboratory of Dr. Klaus Biemann at the Massachusetts Institute of Technology in Cambridge, Massachusetts.

- The Final Report was sent to the plant, local and international union, NIOSH regional consultant, OSHA national headquarters and to NIOSHTIC (NIOSH computer information system).

FISH PROCESSING INDUSTRY

Two fish processing facilities were surveyed; a fish meal manufacturer and a frozen fish processing plant.

GENERAL DESCRIPTION

Several studies have indicated that N-nitroso compounds may be present in a variety of raw fish and fish meal products (115-119). N-nitrosodimethylamine (NDMA) has been found in fish meal with levels up to 0.5 µg/g and in other fish products with lower levels. Possible sources of amine precursors for NDMA and N-nitrosodiethylamine (NDEA), are; dimethylamine, triethylamine and trimethylamine oxide which have been found in fish. Levels as high as 400 µg/g of dimethylamine have been reported in Pacific Hake (119). It has also been found that the concentrations of these amines can increase in fish that have been stored under refrigeration. The source of the nitrosating agent needed to produce these N-nitroso compounds is unclear, however, fish meal is sometimes preserved with added nitrite and atmospheric nitrogen oxide could also be a source for this agent. There are no epidemiological studies indicating a worker exposure to a workplace related carcinogen in the fish processing industry.

FISH PLANT A

This plant, employing about 30 people, produces a fish meal and fish oil. The plant is located on a fishing pier in a single old building. The primary function of the employees are operation and maintenance of the plants equipment and machinery. There was little, if any, direct worker contact with either the raw fish or the fish meal product except when the fish meal was being loaded into trucks.

The plant receives raw fish and fish parts from other fresh fish processing plants and during the summer months large catches of whole menhaden are received for processing as well. The processing consists of grinding the raw fish and fish parts into finely divided pieces which are then dried to a course powder by tumbling the ground fish parts in steam heated drums. The dried fish meal is then moved by a conveyer belt to a separate storage building. The fish meal products are sold as feed for chickens, pigs, fur bearing animals and other livestock. At the time of the survey, the plant air had a heavy odor of fish, presumably amines.

SAMPLING STRATEGY

Air Samples

A total of six area air samples were collected using 200 ml vacuum traps containing 45 ml of 1N KOH. Air was sampled using Bendix C115 pumps at about 2 L/min for 3 hours.

Bulk Samples

Two bulk samples, one consisting of whole cod and pollack and the other consisting of dried fish meal product, were collected.

RESULTS AND DISCUSSION

The results of the analysis of the fish samples are indicated in Table 1. Small levels of NDMA were found in the raw fish sample No. 1, as well as in the dried fish meal sample No. 2. In addition, several of the air samples contained NDMA, as indicated in Table 2. No other N-nitroso compounds were identified.

Table 1

Results of Bulk Samples Fish Plant A

Sample No.	Type of Sample	Method of Analysis	NDMA* ng/g
1	Whole fish	GC-TEA (mineral oil)	0.2
2	Fish meal	GC-TEA (mineral oil)	2.7

* NDMA = N-nitrosodimethylamine. No other N-nitroso compounds were identified.

Table 2

Results of Air Samples Fish Plant A

Sample No.	Location	NDMA* $\mu g/m^3$
3	Near presses	0.03
4	Receiving area	0.01
5	Near fish grinder	0.01
6	By furnace	0.06
7	Outside plant	N.D.
8	By furnace	0.05

* NDMA = N-nitrosodimethylamine, no other N-nitroso compounds were identified.

** N.D. = None Detected - detection limit 0.01 $\mu g/m^3$

FISH PLANT B

This plant is one of the largest frozen fish processing plants in the United States. It is a new plant with modern loading and unloading facilities adjoining the plant itself. There are three floors in the processing and packaging plant, and there are approximately 1000 people employed when the plant is in full operation.

Frozen fish is received from a variety of foreign sources, such as Canada, Argentina, Japan, etc., as well as from fish processing factory ships. The fish is received frozen and is then cut into various sizes on the production lines. There were several production lines processing a variety of fish on the day of the site visit. The cut fish portions were dipped into a batter mix, dusted with a dry mix, and then deep fried at 390°C for approximately 30 seconds. After this step, the fish pieces are frozen in a liquid nitrogen operated freezer, and eventually packaged.

SAMPLING STRATEGY

Air Samples

A total of 16 area air samples were collected using 200 ml vacuum traps containing 45 ml of 1N KOH. Air was sampled using Bendix C115 air pumps at 2 L/min for three hours. The locations and results are contained in Table 3.

Bulk Samples

Six samples of fish and fish products were examined for nitrosamine content. The sample description and analytical results are contained in Table 4.

RESULTS AND DISCUSSION

There were no detectable volatile nitrosamines above the level of 0.05 $\mu g/m^3$ in any of the air samples (Table 3). All of the fish products contained contained low levels of N-nitrosodimethylamine (NDMA), ranging from 10 ppt to 200 ppt (parts per trillion). These results are indicated in Table 4.

SUMMARY AND CONCLUSIONS

While only two fish processing plants were visited in this study, the results indicate that there is no appreciable worker exposure to N-nitroso compounds. Further study of this industry does not seem warranted.

Table 3

Results of Analysis of Air Samples
Fish Plant B

Sample No.	Sample Location	N-nitroso Compounds
1	Second floor by No. 3 fish frier	N.D.*
2	Same location as sample No. 1	N.D.
3	First floor near fish cutting and breading operation	N.D.
4	Third floor near line 4 next to fish frier	N.D.
5	Third floor near line 4	N.D.
6	Control sample taken outside of plant on company property	N.D.

* N.D. - None Detected - detection limit for NDMA 0.05 $\mu g/m^3$.

Table 4

Results of Bulk Samples
Fish Plant B

Sample No.	Sample Description	NDMA* ng/g
7	Raw scallops.	0.05
9	Raw scallops, plus batter, and all cooking processes are completed, but before final freezing.	0.1
10	Raw, frozen pollack, after cutting.	0.1
12	Pollack, batter, and final frying processes, but before final freezing step.	0.2
13	Raw cod, after cutting	0.1
15	Cod, plus batter, and all frying processes, but before final freezing step.	0.1

* NDMA - N-nitrosodimethylamine. No other N-nitroso compounds were identified.

MANUFACTURERS AND USERS OF SYNTHETIC METAL WORKING FLUIDS

Several large and small machine shops that use metalworking fluids and two of the manufacturers of these fluids were included in this study.

GENERAL DESCRIPTION

Interest in possible worker exposure to N-nitroso compounds in association with metalworking fluids stemmed from a report stating that several brands of metalworking fluids, randomly selected from the local suppliers in the Boston area, contained N-nitrosodiethanolamine (NDElA). The reported concentration of NDElA in these products ranged from 0.02% to 3% (17). These findings are of concern because NDElA has been found to be an animal carcinogen. When it was fed to laboratory rats at an average daily dose of 600 mg/kg for 240 days, liver carcinomas were observed in 15 out of 16 rats and adenomas of the kidneys were found in four of these rats (120). Neoplasms of the nasal cavity and tracheal tumors were also observed in 39 out of 56 golden hamsters that were injected subcutaneously with a total dose of 15 mg of NDElA per kg body weight in either 7 or 27 subdoses over 78 weeks (121). Besides metalworking fluids, NDElA has been found in popular consumer cosmetics (14), and unburned processed tobacco (122).

During the past 30 years, cutting fluids or oils have been cited frequently in relation to cancer of the scrotum among machine operators and several cutting oils were found to be carcinogenic to laboratory animals (123). Cruickshank and Squire (124) first demonstrated the connection between cutting oils and cancer by noting that, of 34 cases of cancer of the scrotum seen in the previous 10 years, 12 cases have been occupationally exposed to cutting oils. Five years later, Mastromatteo (125) observed six cases of squamous-cell carcinoma of the skin at one metal machinery plant in Canada. In all cases, the time of exposure had been in excess of 20 years. The problem was first recognized in France by Tourenc (1964), who observed 21 cases of cancer of the scrotum in machine tool operators (126). Carteaud (127) observed eight cases of cancer of the scrotum in a region of Paris, and again all the cases were associated with employment as machine tool operators.

Many synthetic and semisynthetic metalworking fluids are formulated with sodium nitrite and triethanolamine as their major ingredients. The concentrations of these ingredients can be as high as 18% sodium nitrite to 45% triethanolamine. Commercial grade triethanolamine may also contain as much as 15% of diethanolamine as impurity. Thus the essential precursors for the formation of NDElA are present in these types of synthetic and semisynthetic metalworking fluids. During manufacture, heat is usually applied as an aid in dissolving the ingredients and after manufacture the metalworking fluids are frequently stored on the shelf for long periods. Under these conditions ample opportunity exists for NDElA to form from the precursors present in these metalworking fluids.

In the workplace where metalworking fluids are used, worker exposure is by both dermal contact and inhalation. Skin penetration studies with NDElA are currently under investigation by researchers associated with the Food and Drug Administration (FDA) and the National Institute of Occupational Safety and Health (NIOSH). NDElA is a relatively nonvolatile compound and it is not known whether the NDElA in the metalworking fluids will be vaporized or present as an aerosol in the air. It was the aim of this study to determine if NDElA constitutes a risk to workers either by dermal exposure or by inhalation. It was a further aim of this study to determine what effect dilution and use of these fluids may have on their NDElA content.

It is the opinion of the IARC working group on the Evaluation of the Carcinogenic Risk of Chemicals to Humans which met in Lyon, France, 10-15 October 1977 that "although no epidemiological data were available, N-nitrosodiethanolamine should be regarded for practical purposes as if it were carcinogenic to humans" (128).

METALWORKING PLANT A

This company is a multinational manufacturer with 112 plants located in 27 countries. It is the world's largest abrasives manufacturer producing raw materials and finished products such as grinding wheels, diamond products and sandpaper. It is also the world's leading producer of diamond drilling and coring bits for petroleum exploration, and mining. Other products include industrial ceramics, insulating sealants, chemical process products, medical and scientific tubing and safety products. In addition this manufacturer also produces synthetic metal working fluids, some of which are formulated using sodium nitrite and triethanolamine. This manufacturer's facilities for producing metalworking fluids are located in the New England area. The areas within this plant where the metalworking fluids are manufactured, and a machine shop located in a separate building were selected for this study.

Metalworking Fluids Facility

The plant, housed in one building, manufactures 18 different metalworking fluids. Currently, the plant produces 11 nitrite-free metalworking fluids and 7 regular metalworking fluids.

The metalworking fluids are formulated by mixing the ingredients in a blending tank. For the formulation of nitrite containing fluids, the powdered sodium nitrite is slowly dissolved in water and when the nitrite is completely dissolved, the remaining ingredients including triethanolamine are then added to the blending tank. The same blending tanks are used for the formulation of nitrite containing metalworking fluids and nitrite-free metalworking fluids.

Machine Shop

This facility performs many machine shop functions which include surface and finish grinding. The surface and grinding operation use coolants such as the synthetic metalworking fluids formulated with nitrite and amines.

SAMPLING STRATEGY

Air Sampling

A total of four area air samples were collected at this plant. Three of these were taken in the machine shop area and one was taken in the coolant (metal grinding fluid) manufacturing area. These samples were all collected using 1N KOH with an air flow of about 2 L/min with sample times of one hour.

Bulk Sampling

Twenty-three bulk samples were collected for N-nitroso compound analysis. Thirteen samples were from the coolant plant where the metalworking fluids are manufactured and ten were from the machine shop where these fluids are used. The samples from the coolant plant consisted of eight samples of metalworking fluid products and five samples of the raw materials used to manufacture these products. The product samples consisted of six different kinds of metalworking fluids, three of which were nitrite free and three that had been formulated with nitrite and amines. Three of the product samples consisted of different manufacturing batches of the same nitrite containing formulation. The raw ingredients sampled consisted of triethanolamine, diethanolamine, oleic acid amide, 1,3,5-trihydroxytriethyltriazine and process water.

The ten samples collected in the machine shop consisted of three metalworking fluid concentrates, five samples of in use (diluted in the metalworking machines) fluids and two miscellaneous samples consisting of a sample of steam condensate from the plant's heating system and a sample of waste grinding fluid from an outside dump site.

RESULTS AND DISCUSSION

At a detection limit of 0.1 $\mu g/m^3$, none of the air samples were found to contain any N-nitroso compounds (Table 5). The N-nitroso compounds most likely to be found in the air at this plant was N-nitrosodiethanolamine (NDElA), however, pure NDElA is a polar viscous oil compound which is not very volatile and unless it is present in a mist it probably will not vaporize out of aqueous grinding fluid solutions. Nine of the 13 bulk samples collected in the coolant plant contained NDElA with concentrations ranging from 0.2 µg/ml to 140 µg/ml (Table 6). Two of the five raw materials were found to contain NDElA, 0.8 µg/ml in the triethanolamine and 0.2 µg/ml in the diethanolamine. Two of the three nitrite-free fluids contained 4 µg/ml each of NDElA and all of the five samples of fluids formulated with nitrite and amines contained NDElA with levels ranging from 20 µg/ml to 140 µg/ml. Samples No. 9, 10 and 11 are all samples of different manufacturing batches of the same type of metal fluid, Fluid-203, these samples had the highest levels of NDElA. The variability of the NDElA concentration within the same formula of metalworking fluid may be due to product age, however this data was not obtained. The raw ingredients do not appear to be a major source for the NDElA contamination in the grinding fluids because the concentration of NDElA in these samples was less than 1 µg/ml. The evidence seems to indicate that the NDElA formed in the metalworking fluids after they were formulated.

Four of the 10 samples collected in the machine shop area were found to contain NDElA with levels ranging from 1.5 µg/ml to 470 µg/m (Table7). In the unused concentrated metalworking fluid samples only one was found contaminated with NDElA and its concentration was 470 µg/ml. This fluid contained nitrites and amines and is the same brand as the Fluid-203 sampled in the coolant plant. When Fluid-203 was diluted 20 to 1 and used in the grinding machine its level of NDElA was found to be nondetectable in one sample (Sample No. 6) and 11 µg/ml in sample No. 5. The concentration after dilution should have been about 25 µg/ml assuming a 20 to 1 dilution and no loss of the NDElA - Sample No. 8 is a sample of used grinding fluid, Fluid-E55, collected from a grinding machine. The sample contained 2 µg/ml of NDElA. The Fluid-E55 concentrate was not available for analysis and the concentration of this fluid in the grinder was not known. The outside water grinding fluids contained 1.5 µg/ml. It is apparent that NDElA is not formed in the dilute fluids during use in the machines. In fact, it appears that the original contamination decreases. Why the NDElA level in the used fluids should decrease is at present unknown. However, the grinding operation involves high temperatures which may decompose the fragile N-nitroso linkage of the NDElA and metal particles may be adsorbing surfaces thus decreasing the NDElA concentrations.

CONCLUSIONS

There were no N-nitroso compounds detected in the air, therefore, the N-nitroso compound contamination was limited to the grinding fluid. The exposure of the workers to N-nitroso compounds is mainly through skin contact with these fluids.

The nitrite-free grinding fluids contained low levels of NDElA, which might be due to cross contamination by sharing the same blending tank with nitrite-containing grinding fluids or through the slow absorption of nitrogen dioxide from the air. The regular grinding fluids which were formulated with sodium nitrite contained substantial amounts of NDElA. The grinding fluids used in the machines are normally diluted 20 times with water. The concentration of N-nitroso compounds is drastically reduced by dilution. Consequently, the concentrations of NDElA in the diluted fluids did not exceed 11 µg/ml.

Table 5

The Concentration of N-nitrosodiethanolamine (NDElA) in the Air Samples of Metalworking Plant A

Sample	Location	Nitrosamines in $\mu g/m^3$
1	14-inch o.d. grinder	N.D.*
2	Bryant Internal Grinder	N.D.
3	Entrance to Machine Shop	N.D.
4	Near top of blending tank in the coolant manufacturing plant	N.D.

* N.D. - Not detectable - detection limit 0.1 $\mu g/m^3$ (NDElA)

Table 6

N-nitrosodiethanolamine (NDElA) Analysis of Bulk Samples Collected in Coolant Plant

Metalworking Plant A

Sample No.	Sample Description	Use	NDElA μ g/ml
Raw Materials			
1	Triethanolamine 99%		0.8
2	Diethanolamine 85%		0.2
3	Oleic Acid Amide		N.D.*
4	1,3,5-trihydroxytriethyltriazine		N.D.
5	Process Water		N.D.
Nitrite-free Products			
6	Fluid-419 Semi-synthetic	General Purpose	N.D.
7	Fluid-658 Synthetic	High Performance	4.0
8	Fluid-810 Soluble Oil	Heavy Duty	4.0
Nitrite Containing Products			
9	Fluid-405 Synthetic Lot 792	General Purpose	140
10	Fluid-405 Synthetic Lot 781	General Purpose	110
11	Fluid-405 Synthetic Lot 7826	General Purpose	47
12	Fluid-203 Synthetic	Rust Inhibitor	20
13	Fluid-603 Semi-synthetic	High Performance	52

* N.D. - None detected, detection limit 0.1 μ g/ml (NDElA)

Table 7

N-nitrosodiethanolamine (NDElA) Analysis of Bulk Samples Collected in Machine Shop of Metalworking Plant A

Sample No.	Sample Description	Use	NDElA μg/ml
Unused Concentrate Fluids			
1	Nitrite free fluid concentrate	Turret Lathe Machine	N.D.
2	Fluid-203 Synthetic rust inhibitor	Grinding Machine	470
3	Fluid-607 Nitrite-free Soluble Oil	Unknown	N.D.*
Used Metalworking Fluids			
4	Fluid-203 diluted 20 to 1 in use for 2 weeks in grinding machine		N.D.
5	Fluid-203 diluted 20 to 1 in use for undetermined time in grinding		11
6	Fluid-607 diluted 20 to 1 in use for undetermined time in grinding		N.D.
7	Nitrite-free fluid concentrate in use for undetermined time in turret lathe		N.D.
8	Fluid-E-55 unknown composition in use in a 14' grinder		2
9	Grinding fluid waste from outside dumping site		1.5
10	Steam condensate from heating plant		N.D.

---

* N.D. - None detected - Detection limit 0.1 μg/ml (NDElA)

METALWORKING PLANT B

This plant has been manufacturing grinding fluids and lubricants for over 90 years in two adjacent buildings. One of these buildings, containing a number of 5000 gallon storage tanks, is used for raw material receiving and storage. The other building is used for formulating the metal working fluids. As needed, the stored aqueous sodium nitrite (40% solution) and aqueous triethanolamine (80% solution) are pumped from storage to an enclosed 5000 gallon blending tank in the formulation building. The facility also manufactures nitrite-free products and the material handling systems are independent of each other, thus preventing any possible cross contamination.

SAMPLING STRATEGY

Air Samples

No air samples were collected at this site.

Bulk Samples

A total of 9 bulk samples were collected for analysis, four of these samples were packaged products. Two were samples from the blending tanks, two were samples of raw materials and one was a small batch of grinding fluid prepared in the laboratory.

RESULTS AND DISCUSSION

The results of the NDElA analyses are summarized in Table 8. N-nitrosodiethanolamine was detected in every sample except the 40% sodium nitrite (Sample No. 6). The NDElA concentration ranged from 20 to 500 μg/ml.

The presence of N-nitrodiethanolamine (NDElA) in the sample metalworking fluid represents a potential health hazard from dermal contact. The occurrence of NDElA in the 80% triethanolamine is one obvious source of product contamination. However, the laboratory batch of Fluid-1500 Grinding Concentrate contained 7 times as much NDElA as would come from the triethanolamine alone, and the packaged product contained almost 90 times the level of NDElA expected assuming triethanolamine were the only source of contamination.

Table 8

Concentration of N-nitrosodiethanolamine in Grinding Fluids and Other Bulk Samples from Metalworking Plant B

Sample	Description	Concentration μg/ml
Packaged Product		
1	Fluid-E-55 Grinding Coolant	27
2	Fluid-1500 Grinding Concentrate	500
7	Fluid-2906 Grinding Coolant	90
8	Fluid-3100 Grinding Concentrate	63
Blending Tanks		
3	Fluid-E-55 Grinding Coolant	33
4	Fluid-2527 Grinding Coolant	90
Raw Materials		
5	80% Triethanolamine	22
6	40% Sodium Nitrite	ND*
Laboratory Batch		
9	Fluid-1500 Grinding Concentrate	66

*ND - None Detected - detection limit 1 μg/ml.

METALWORKING PLANT C

This plant has been in operation for 25 years (19 years at its present location). It performs precision grinding on metals and plastics. The building has 5000 square feet of space. The shop is equipped with 9 Centerless grinders, one Blanchard grinder, and two Hyprolap grinders. They have 9 employees; six of them are full time.

At the time of the site visit, most of the shop machines were in operation. It was also noted that the workers removed parts that were being ground from the machines using bare hands. This resulted in their hands being exposed to the grinding fluids.

SAMPLING STRATEGY

Air Sampling

Two area air samples, using 1N KOH and Bendix C115 pumps at a flow rate of 2 L/min, were set up on Cincinnati machines numbered 2M2H1Y-435 and 2M2H1L-1569.

Bulk Samples

The stock grinding fluids were shipped from the manufacturers in 55 gallon drums. Five drums of different grinding fluids were stored in the shop. The stock fluids were diluted 50 to 140 times to be used in the grinding machines. Five samples of the concentrated fluids were collected and five samples of the diluted in-use fluids were collected (see Table 9).

RESULTS AND DISCUSSION

The results of the grinding fluid analysis are presented in Table 9. At a detection limit of 0.3 µg/ml no NDELA was found in any of these grinding fluid samples. None of the air samples contained any N-nitroso compounds at a detection limit of 0.05 $\mu g/m^3$ for NDELA. The nondetection of any N-nitroso compounds in the air at this facility is not surprising since NDELA, the expected nitrosamine, is not very volatile. The nondetection of NDELA in the metalworking fluids is, however, surprising since most synthetic grinding fluids formulated with nitrite and amines have been found to contain this compound. Since the composition of the sampled metalworking fluids are unknown, the best explanation of our negative findings is that this facility did not use the nitrite-amine formulated metalworking fluids.

Table 9

Results of Analysis for N-nitrosodiethanolamine in Grinding Fluids from Metalworking Plant C

Sample No.	Sample Description	NDElA in μg/ml
Concentrated Fresh Fluids		
1	Exxon Rust Ban 392 Batch No. E4-18-77	N.D.*
2	Cutzol WS-15 Rust-Lich Inc.	N.D.
3	Teraco Spindura oil 22	N.D.
4	Cincinnati Milicron, Cimcool AL Batch No. 424	N.D.
5	White and Bagley RP Soluble 1999	N.D.
Used Diluted Fluids		
6	RP Soluble 1999 diluted 40 to 1	N.D.
7	Cutzol WS-15 diluted 50 to 1	N.D.
8	Cimcool AL diluted 50 to 1	N.D.
9	Cutzol WS-15 diluted 50 to 1	N.D.
10	Cutzol WS-15 diluted 50 to 1	N.D.

*N.D. - None Detected - detection limit 0.3 μg/ml.

METALWORKING PLANT D

This facility is a small family owned business which regrinds industrial machine knives. The company has been at its present location for 3-1/2 years. Total employment is five. The majority of work is performed on 3 Gockel longitudinal precision grinding machines. The blade to be reground is electromagnetically attached to the spindle of the machine. These Gockel machines are the only ones operating in the United States.

At the time of the visit, one Gockel machine was working on surface grinding of a steel blade. The grinding fluid used was White & Bagley E-55 which was diluted 100 to 1. The machine was equipped with an experimental Fishpin 1000 particulate separation device manufactured by Fisons Separator Products which trapped particles down to 3µM by centrifugation. The diluted grinding fluid was recycled and the particles removed by the Fishpin 1000 Separator. The fluid was never changed. New fluid was added to replace the fluid which was lost through evaporation or spilling. Because of the type of machine used, the fluid was not splashed into the air. The grinding fluid level was below the material being ground. As a result, the workers' skin contact with the grinding fluid was minimal.

SAMPLING STRATEGY

Air Samples

No air samples were collected at this site.

Bulk Samples

Two bulk samples were collected.

RESULTS AND DISCUSSION

N-nitrosodiethanolamine (NDElA) was detected in Sample 1 at a concentration of 20 µg/ml (Table 10). No detectable concentration of NDElA was found in the diluted fluid (detection limit 0.5 ug/ml).

The concentrated fluid contains 20 µg/ml of NDElA. However, the diluted grinding fluid did not contain detectable nitrosamines. Furthermore, the grinding fluid in the machine did not splash into the air. There is little chance nitrosamines would be detected in the atmosphere of this shop.

Table 10

Results of the Analysis of Bulk Samples for NDElA
Metalworking Plant D

Sample No.	Sample Description	NDElA in μg/ml
1	White and Bagley E-55	20
2	Diluted Grinding Fluid used in machine (100/1 dilution of White & Bagely E-55)	N.D.

N.D. - None Detected - detection limit 0.5 μg/ml

METALWORKING PLANT E

The facility is a gear and axle assembly plant. The total area of the plant is more than one million square feet. The plant operates three shifts with approximately 1200 employees on each shift.

Only two kinds of metalworking fluids were used in the plant with soluble oil type fluid, NP6058 being the most common one used. Synthetic fluids were required for a few machine operations. Cimcool Five Star B was used in these operations. Since some synthetic fluids are known to contain N-nitroso compounds, most of the effort of this study was concentrated on those machines which used this fluid.

SAMPLING AND STRATEGY

Stock Bulk Fluid

Three stock bulk fluids were sampled. Two were metalworking fluids and the other was a bactericide. The bactericide (Grotan) was added to the fluid when an odor developed in the metalworking fluid in the machine.

Stock Metalworking Fluid

The description of the diluted fluid samples collected from the machines is presented in Table 11. In total, six samples were collected. Five samples were from the machines using Cimcool Five Star B, while one sample was from the machine using the soluble oil type fluid NP6058.

Air Samples

In total, 5 area air samples were collected at this plant using 1N KOH and Bendix C115 pumps at a flow rate of 2 L/min. Four of the air samples were obtained around the machines which used Cimcool Five Star B. One of the air samples was collected in the Safety Office which was outside the machine operation area.

RESULTS AND DISCUSSION

Bulk Samples

The results of the analyses of the metalworking fluids are presented in Table 11. The synthetic metalworking fluid, Cimcool Five Star B, contained N-nitrosodiethanolamine (NDElA) at a level of 620 µg/ml. The soluble oil type metalworking fluid (NP6058) and the bactericide (Grotan) did not contain NDElA at a concentration above 1 µg/ml

The metalworking fluids were diluted from 10 to 35 times before being used in the machines. Generally, the concentrations of NDElA in diluted metalworking fluids collected from the machines were less than 5 µg/ml. This was lower than what was expected. For example, the stock Cimcool Five Star B (Sample No. 6) contained 620 µg/ml of NDElA. Upon dilution (10/1), the concentration of NDElA in Sample No. 6 should be 60 µg/ml. Instead, only 5 µg/ml of NDElA was found. The same pattern was observed in the other samples diluted from stock Cimcool Five Star B. These results indicated that additional NDElA was not formed from its precursors during machine operation. Furthermore, no other TEA responsive material was found in these diluted fluids, which also indicated that NDElA was not transformed to other N-nitroso compounds.

Air Samples

The results of air samples are presented in Table 12. A trace amount of NDElA was detected in one air sample (No. 3). This sample was collected in an area where diluted Cimcool Five Star B was being used. The concentration of NDElA in the fluid being used in the machines was 2 µg/ml. The negative findings in two air samples (Nos. 8 and 11), both of which were collected on machines using diluted Cimcool Five Star B, indicated that NDElA was not a general contaminant in the air of this facility.

Table 11

The Concentration of N-nitrosodiethanolamine (NDElA) in Machining Fluid from Metalworking Plant E

Sample No.	Sample Description	Dilution	NDElA μg/ml
Used Diluted Fluid			
2	Cimcool 5 Star B	10/1	2
6	Cimcool 5 Star B	10/1	5
7	Cimcool 5 Star B	35/1	3
9	Cimcool 5 Star B	26/1	ND*
10	Cimcool 5 Star B	24/1	ND
12	NP6058		1
Undiluted Fluids			
5	Cimcool 5 Star B		620
13	NP 6058		Trace
14	Grotan		ND

*ND - None Detected - detection limit 1 μg/ml.

Table 12

Results for the Air Samples Collected in Metalworking Plant E

Sample No.	Sample Location	NDElA Concentration μg/m^3
1	Safety Office	ND
3	Landis Grinder - 2959 BB13	Trace
4	Landis Grinder - 2959 BB13	ND
8	Ex-cello 900 HH7	ND
11	Barne No. 1 Unit 6 F2	ND

ND - None Detected - detection limit 0.1 μg/m^3.

METALWORKING PLANT F

The facility has been operated by its present owner since 1960. The plant is housed in one building which occupies 2 million square feet. Currently, the facility has an employment of 4300 with 4000 in the production area and 300 in the administration area. The plant is operated on a three shift basis with 2100, 1700 and 200 workers on each shift. The major products of the facility are automotive components, rear axles and control arms.

Only two kinds of metalworking fluids were used in the facility, both are soluble oil type fluids, Norton Wheelmate 810 and GC C-60. The metalworking fluids used in the machines were supplied by 11 central fluid reservoir systems. These reservoirs have a storage capacity of from 400 to 27,000 gallons each. Generally, the fluids in the central system are prepared as 3-5% emulsion by diluting the stock metalworking fluids with water. Once a week a bactericide, sodium hypochlorite, is added at 3 ounces/gallon to prevent odor.

SAMPLING STRATEGY

Bulk Samples

Only three samples were collected at the plant; two stock metalworking fluids and one fluid from the central system.

Air Samples

No air samples were collected at this plant.

RESULTS AND DISCUSSION

NDElA was not detected in any of the three samples at concentrations above 1 μg/ml (Table 13). The metalworking fluids used in this plant were nitrite-free soluble oil types, consequently, N-nitroso compounds were not likely to be found in this type of metalworking fluid.

Table 13

The Concentration of N-nitrosodiethanolamine in Metalworking Fluids from Metalworking Plant F

Sample No.	Sample Description	Results NDElA μg/ml
1	Wheelmate 810	N.D.
2	General Motors C-60	N.D.
3	Used Diluted General Motors C-60 Diluted 25/1	N.D.

N.D. - None Detected - detection limit 1 μg/ml.

METALWORKING PLANT G

The facility is an engine assembly plant, employing about 1700 hourly and 305 salaried workers. Only one metalworking fluid, Ford 3C66A, was used in the plant.

SAMPLING STRATEGY

Air Samples

No air samples were collected at this facility.

Bulk Samples

Two samples were collected in the plant. Sample one was obtained from the tank located in bay B-20, this fluid was diluted 24 to 1 from metalworking fluid Ford 3C66A. The other sample was a floor cleaning fluid, which was used for cleaning metal floor. Some floor cleaning fluids contain sodium nitrite as a rust inhibitor.

RESULTS AND DISCUSSION

No TEA-responsive peaks were detected in Sample No. 2, a floor cleaning liquid. The detection limit of the analytical method was 1 μg/ml.

The diluted Ford 3C66A, obtained from the filter tank, however, contained 10 μg/ml of N-nitrosodiethanolamine (NDElA). The stock fluid of Ford 3C66A was not sampled; it is not known whether NDElA was also present in the stock fluid.

METALWORKING PLANT H

The major products of this plant are automobile front and rear end suspensions. The facility was constructed in 1933 with the entire complex being completed in 1942. The plant consisted of 8 major buildings, occupying a total area of 2.5 million square feet. Currently, the facility has an employment of 7100 with 6300 employees in the production area and 800 employees in the administrative area. The plant was operated on three shifts with 3500, 3000 and 400 workers, respectively on the first, second and third shifts.

SAMPLING STRATEGY

Air Samples

No air samples were collected at this facility.

Bulk Samples

A total of seven bulk samples were collected for NDElA analysis. Three of the samples (Samples 2,4 and 6) were unused and undiluted metalworking fluids, three samples (Samples 1,3 and 5) were diluted, used metalworking fluids and one sample (Sample 7) was an ultrasonic testing fluid of unknown composition.

RESULTS AND DISCUSSION

The results of the analyses of stock and diluted bulk fluids are presented in Table 14. NDElA was present in only one sample, the stock ultrasonic testing fluid. No TEA-responsive material was detected in either stock or diluted Vantrol 710-W fluids.

Table 14

Concentration of N-nitrosodiethanolamine in Bulk Samples from Metalworking Plant H

Sample No.	Sample Description	NDElA μg/ml
Unused, Concentrated Metalworking Fluids		
2	Masolene DML DeMille Chem. Corp.	N.D.
4	Stuart HL-D5844 D.A. Stuart Chem. Co.	N.D.
6	Vantrol 710-W Van Stratten Chem. Co.	N.D.
7	Ultrasonic Testing Fluid Park Chem. Co.	1500
Used, Diluted fluids		
1	Masolene DML (diluted 100/1)	N.D.
3	Stuart HL (diluted 5/1)	N.D.
5	Vantrol 710-W (diluted 15/1)	N.D.

N.D. - None Detected - detection limit 1 μg/ml.

METALWORKING PLANT I

The facility was built in 1939, and is currently housed in one building, occupying a total area of 400,000 square feet. The major products of the plant were tools for metal stamping and die construction.

The metalworking fluids were supplied to the machines from two central cooling systems with capacities of 6000 and 1500 gallons, respectively. The fluid used in these central systems was Ford M589B. In addition, nine machines had their own fluid supply system, with a capacity of 20 gallons each. The fluid used was Ford M3C14AE.

Ford M97B14A, [formulated with tris-(hydroxymethyl)-nitromethane] was used as a bactericide in the metalworking fluid with 1-6 gallons added to each 1000 gallons of metalworking fluid.

SAMPLING STRATEGY

Air Samples

No air samples were collected at this facility.

Bulk Samples

In total, four bulk samples were collected for N-nitroso compound analysis. One sample was from a 6000 gallon central system. It consisted of a 24 to 1 dilution of Ford M589B. The second sample (Sample 2) was collected from a working machine (Pratt and Whitney Numeric Keller) which was supplied from the 6000 gallon central system. The third sample was Ford M3C14AE which is used without dilution in the band saws at this facility. The fourth sample consisted of a quench oil.

RESULTS AND DISCUSSION

N-nitrosodiethanolamine (NDElA) was detected in only one of the four samples collected (Table 15). This sample was collected from the Pratt and Whitney Numeric Keller and the fluid used in the machine was supplied from the central system. However, no TEA-responsive peaks were detected for Sample No. 1 collected from the central system. Samples 1 and 2 were both from the same metalworking fluid, M589B. Due to the limited number of samples collected and analyzed, no attempt has been made to explain the disparity between the results of Samples 1 and 2. However, it should be noted that the bactericide (M97B14A) does contain a C-nitro functional group, and that some C-nitro compounds are nitrosating agents. The method of the bactericide application might be important for the N-nitroso compound formation. For example, if the bactericide is added only to the machine fluid, then it is possible that N-nitroso compounds could be found in the sample collected from the machine but not from the central system.

Table 15

Results of the Bulk Samples Collected in Metalworking Plant I

Sample No.	Sample Description	NDE1A µg/ml
1	Ford M589B Diluted 24 to 1	N.D.
2	Ford M589B Diluted 24 to 1	16
3	Ford M3C14AE Used without dilution	N.D.
4	Quench Oil	N.D.

N.D. - None Detected - detection limit 1 µg/ml (NDE1A).

METALWORKING PLANT J

The facility is an engine assembling plant that has been in operation since 1955. The total area of the facility is 800,000 square feet. Total employment force in the plant was 3000 operators on three shifts with 1000 employees on each shift. A wide variety of metalworking fluids were used in the plant, which included synthetic material such as Cimcool Five Star, semisynthetics such as Texaco 2736 and Vantrol 510, and soluble oil types such as Cycleweld NP6058and NP6059. The metalworking fluids in these machines were supplied from 31 separate central systems. Each system contained metalworking fluids of different varieties, dilution and age. Because of wide varieties of fluids and large numbers of supply systems used, the facility was considered a suitable place to study the effect of dilution and age on nitrosamine content in the metalworking fluids during the machining operation.

SAMPLING STRATEGY

Air Samples

On December 13, 1977 six area air samples were collected in the production area of this plant. Because one of these samples was found to contain trace levels (less than 0.1 $\mu g/m^3$) N-nitrosodiethanolamine, a second visit was made to this plant on December 16, 1977 to re-check these findings and to determine if higher levels existed in this plants atmosphere. During the second visit five more air samples were collected in the same general area where the airborne NDElA was first found.

Bulk Samples

During the two visits a total of 14 bulk samples were collected. The samples collected on December 13, 1977 consisted of three unused undiluted metalworking fluids, one sample of a rust inhibitor (Alk-Ice NP6056) and eight samples of used diluted metalworking fluids. Two more used diluted metalworking fluids were collected on December 16, 1977.

RESULTS AND DISCUSSION

Bulk Samples

Four stock bulk fluids were sampled. Three of these samples were metalworking fluids, which covered three different types of formulations, i.e., soluble oil (Cycleweld, NP6058), semisynthetic (Vantrol 510), and synthetic (Cimcool Five Star).The other was a fluid (Alk-Ice NP6056), which was added to the water as a rust inhibitor for engine leak testing. The results of the analysis are presented in Table 16. Nitrite is not generally used in the soluble oil type metalworking fluids such as Cycleweld NP5068, however, a small amount of NDElA (6 $\mu g/ml$) was found in this sample. Higher concentrations of NDElA were detected in the semisynthetic and synthetic metalworking fluids at a level of about 100 $\mu g/ml$. The rust-inhibiting fluid (Alk-Ice NP6056) contained

4900 µg/ml NDElA as well as an equally large unidentified, TEA-responsive material.

The metalworking fluids are usually diluted 10 to 35 times when actually used on the machines. Since NDElA is detected in the stock metalworking fluid, the important question regarding the workers' exposure to NDElA concerns the fate of NDElA after it is diluted and used on the machines. Several possibilities exist. First, NDElA is chemically converted to other N-nitroso compounds. Second, NDElA is vaporized to the air. Third, NDElA decomposes to non-N-nitroso compounds. Furthermore, the precursors for NDElA formation are present in the metalworking fluid. It is possible that the machine operation environment could promote an additional formation of NDElA. One of the objectives of the present study is to assess all these possibilities.

NDElA was the only N-nitroso compound found in the fluids sampled from the machines (Table 16). The concentrations of NDElA in the used fluids were generally below 5 µg/ml. These low concentrations make it difficult to accurately determine what effects the length of usage has on the concentration of NDElA in these fluids. It does appear, however, that the NDElA levels in the fluids that have been used in machine operations decline. For example, Sample No. 2 (Vantrol 510) contained 98 µg/ml of NDElA and a 10 to 1 dilution of the measured concentration of NDElA (Sample No. 9) was only 2 µg/ml rather than the expected 10 µg/ml. From this result, it seems unlikely that NDElA is being formed from its precursors during machine operation. The fact that no other TEA-responsive compounds were detected indicates that the NDElA is not being converted to other N-nitroso compounds. The decrease in concentration of NDElA in the used metalworking fluids may be due to decomposition.

Air Samples

Air samples were collected in an effort to determine whether the loss of NDElA from the used metalworking fluid during machine operation was due to its vaporization to the air. The results of these air samples are presented in Table 17. Except for trace quantities detected in Sample No. 5, NDElA was not found in the plant's atmosphere. The detection limit of the method was 0.01 µg/m^3. In order to confirm the result of Sample No. 5, five more air samples were collected near the machine where this sample was collected. During the air sampling it was noted that metalworking fluids were being splashed into the air when the machines were in operation. The air inlet of Sample No. 22 was covered with a device that would prevent the liquid mist of metalworking fluid in the air from entering the impingers, but would, however, allow air to be pumped through the holes under the cover. The air inlets of the other air samples were not covered. Because Samples No. 21 and No. 22 were positioned next to each other, a comparison of analytical results could determine whether the metalworking fluid droplets in the air were contaminating the air samples.

Samples No. 20, No. 21 and No. 22 were all located near the same machine, a La Salle #66. NDElA concentrations in these air samples were all less than 0.1 µg/m^3. The fact that the quantities of NDElA found in Sample No. 22 were smaller than those found in Sample 21, indicate that contamination by metalworking fluid droplets in the air is possible if the air inlet of the impingers were not covered. NDElA was not detected in air samples collected about 20 ft away from the machine (Sample No. 23) thus indicating that the trace levels of NDElA present in the air near the operating machine did not constitute a general contaminant in the atmosphere of this engine plant.

NDElA was found in the stock metalworking fluids with levels ranging from 6 µg/ml to 5 mg/ml. The NDElA contamination in semisynthetic and synthetic fluids were much higher than in soluble oil type fluid.

Metalworking fluids used in the machine were diluted 10 to 35 times from the stock fluids. The concentration of NDElA was diluted accordingly. Furthermore, NDElA decomposed when metalworking fluids were used in the machines. Consequently, concentrations of NDELA in the diluted fluids were generally less than 5 µg/ml.

NDElA was not found in the general air environment of the plant. However, about 0.08 $\mu g/m^3$ of NDElA was present near the machine where NDElA concentration in the metalworking fluid was about 2 µg/ml.

Table 16

Results of Analysis for N-nitrosodiethanolamine in Metalworking Fluid Samples from Metalworking Plant J

Sample No.	Sample Description	Time of Use	NDElA in μg/ml
December 13,	Unused Fluids		
1	Chrysler Cycleweld NP6058	Unused	6
2	Vantrol 510	Unused	98
3	Cimcool Five Stars	Unused	140
4	Alk-ice NP6056	Unused	4900
	Diluted Fluids		
12	Texaco 2736 - 20 to 1	3 weeks	2
13	Vantrol 510 - 35 to 1	unknown	4
14	NP6059 - 15 to 1	unknown	2
15	NP6058 - 15 to 1	5 months	N.D.*
16	Cimcool Five Stars - 25 to 1	5 weeks	N.D.
17	Texaco 2736 - 20 to 1	5 months	1
18	NP6058 - 15 to 1	2 weeks	1
19	Vantrol 510 - 10 to 1	1 week	2
December 16,			
26	Texaco 2736 - 20 to 1	3 weeks	2
27	Texaco 2736 - 20 to 1	3 weeks	N.D.

* N.D. - None detected - detection limit 1 μg/ml

Table 17

Results of Air Samples Collected in

Metalworking Plant J

Sample No.	Machine	Location	Concentration of NDElA in $\mu g/ml^3$
December 13			
5	LaSalle #66	18S	Trace
6	Kruger #540	15N	N.D.*
7	Landis Grinder #035	7C	N.D.
8	Loswing	7B	N.D.
9	Bullard #31177	30P	N.D.
10		Personnel Office	N.D.
December 16,			
20	LaSalle #66	18S	Trace
21	LaSalle #66	18S	0.08**
22	LaSalle #66	18S	Trace
23	30' from LaSalle #66	18S	N.D.
24	Pump Stand	18S	0.04

* N.D. - None Detected - detection limit 0.01 $\mu g/m^3$ (NDElA).

** Sample may be contaminated from splashing metalworking fluid. See text.

SUMMARY OF METAL WORKING FLUIDS MANUFACTURERS AND USERS

Representative plants of the industries that produce and use synthetic or semisynthetic nitrite-amine type metalworking fluids were included in this study of worker exposure to N-nitroso compounds. Because of the discovery of N-nitrosodiethanolamine (NDElA) in some of these metalworking fluids, it was postulated that airborne levels of NDElA in metalworking plants that use these products could be high if this contaminant were appreciably volatized during use. It was also postulated that increased amounts of NDElA or other N-nitroso compounds, could result from the use of these fluids during hot machining operations. Worker exposure by skin contact with these NDElA contaminated products was considered to be a virtual certainty.

The result of this study reaffirmed the presence of NDElA in some of these synthetic nitrite-amine type metalworking fluids (Table 18). However, the concern that NDElA, or other N-nitroso compounds in these fluids, could become airborne and thus constitute a respiratory hazard to workers seems unfounded. Contrary to the speculation that further amounts of NDElA may be formed during the use of these products, less (than can be explained by simple dilution) was found in the working fluids sampled from operating machines. Several TEA-responsive compounds were discovered in some of the concentrated metalworking products. Again, due to the limitation of this study, none of these unknown compounds have been identified. It was observed that machine workers do have contact with metalworking fluids, but, until a NIOSH-sponsored study of skin absorption of NDElA is completed, assessment of this hazard is not possible. Human exposure to the NDElA in metalworking fluids could be limited by either re-formulating these products to remove the potential hazard or by providing greater worker protection during their use. Identification of the unknown TEA responsive compounds that have been discovered in some of these fluids should be undertaken in order to assess this potential hazard to workers in the event that they are identified as N-nitroso compounds.

TABLE 18

Summary of Bulk Metal Working Fluids Sampled During Survey of Metal Working Fluid Manufacturers and Users

Sample of Fluid	NDElA* ug/ml
Fluid - 419	N.D.**
Fluid - 658	4.0
Fluid - 810	4.0
Fluid - 405 Synthetic Lot 792	140
Fluid - 405 Synthetic Lot 781	110
Fluid - 405 Synthetic Lot 7826	47
Fluid - 203	20
Fluid - 603	52
Fluid - 607	N.D.
Fluid - E - 55	27
Fluid - 1500	500
Fluid - 2906	90
Fluid - 3100	63
Fluid - 2527	90
Exxon Rust Ban 392	N.D.
Cutzol WS-15	N.D.
Teraco Spindura Oil 22	N.D.
Cimcool AL	N.D.
RP Soluble 1999	N.D.
Cimcool 5 Star B	620
NP6058	Trace (<1ug/ml)
Wheelmate 810	N.D.
General Motor C-60	N.D.
Ford 3C66A (diluted 24:1)	10
Masolene DML	N.D.
Stuart HL-D5844	N.D.
Vantrol 710-W	N.D.
Ultrasonic Testing Fluid	1500
Ford M589B (diluted 24:1)	0-16
Ford M3C14AE	N.D.
Chrysler Cycleweld NP6058	6.0
Vantrol 510	98
Cimcool Five Star	140
Alk-ice NP6056	4900
Texaco 2736 (diluted 20:1)	2

* NDElA - N-nitrosodiethanolamine

** N.D. - None Detected

Three dye manufacturing facilities were surveyed for the presence of N-nitroso compounds.

GENERAL DESCRIPTION OF THE DYE MANUFACTURING INDUSTRY

N-nitroso compound precursors are used in the manufacture of dyes. Sodium nitrite, a well established nitrosating agent, and various amines are used in the synthesis of a large number of dyes. Azo dyes are synthesized by the coupling of an aromatic compound to a diazonium salt, which, in turn, is formed from the reaction between sodium nitrite and a primary aromatic amine such as aniline. To promote the coupling reaction, the coupling component usually carries either a hydroxyl or an amino functional group to activate the coupling site. The phenolic or anilinic compounds are normally used as the coupling agents in the synthesis of the water-soluble direct dyes. On the other hand, N-alkyl substituted anilines are used as the coupling agents to make the water-insoluble disperse dyes.

The most likely source of nitrosamine contamination in the azo dye synthesis is the reaction between sodium nitrite and secondary or tertiary amines. Sodium nitrite is an essential ingredient for the formation of diazonium salts, and is used in the production of every type of azo dye. The nitrosatable amines can be introduced during any stage of azo dye manufacturing in the following ways:

1. Secondary or tertiary amines may be present as an impurity in the primary amines.

2. Secondary or tertiary amines are used as the coupling agent, e.g. in the synthesis of the disperse dye.

DYE PLANT A

Plant A was constructed in 1965 and presently has two major buildings which occupy a site of about 137 acres. The plant employs 145 with 95 workers in the production area and the remainder in administration. At the time of this survey the plant was operating on three shifts with equal numbers of workers on each shift. The survey of this plant focused on its azo dye (disperse dye) production process.

Typically the production of azo dyes consists of diazotization and coupling. The first step, diazotization, is accomplished by reacting sodium nitrite with aromatic amine (usually aniline) at acid pH in cold aqueous solution. The resulting diazonium salt is drained to a coupling tub, where a coupling agent such as resorcinol or polyfunctional phenols had been added. After coupling, the dye is filtered in a press and dried as the finished product. Besides the basic diazotization and coupling reactions, additional diazotization-coupling cycles and phosphogenation reactions, which couples two dye components through a carbonyl bridge, are carried out to provide the dyes with the desired color and functional properties.

SAMPLING STRATEGY

Two separate site visits were made to this facility during which both air samples and bulk samples were collected for N-nitroso compounds.

Air Samples

Seven area air samples were collected on February 21, 1978. Three samples were taken near the diazotization tub, two near the coupling tub, and two near the filter press. The chemical intermediate being diazotized during the sampling time was 6-nitro-2-aminobenzothiazole. The air samples were collected during the time that the tubs and filter press were in operation.
The air sampling apparatus consisted of either midget impingers containing 15 ml of 1N KOH or 200 ml vacuum traps containing 45 ml of 1N KOH. Air was drawn through these traps at 1.5 L/min to 2 L/min using Bendix C115 air sampling pumps. On February 24, 1978, four more air samples were collected near the same diazotization tub and the intermediate being diazotized during this second sampling visit was the same as on February 21. These air sample locations and results are also presented in Table 19.

Bulk Samples

A total of 26 bulk samples were collected during the two visits. They consisted of 14 samples of raw materials used in the manufacture of dyes and 12 dye products. The sample descriptions and analytical results are presented in Table 20.

RESULTS AND DISCUSSION

Air Samples

A total of 11 area air samples were collected and examined for N-nitroso compounds. At a detection limit of 0.05 μg/m^3 for N-nitrosodimethylamine no volatile (GC-TEA amenable) N-nitroso compounds were detected. A nonvolatile TEA responsive compound was not further characterized and there is no other evidence indicating that it is an N-nitroso compound. The TEA can respond to any compound which releases NO upon pyrolysis and some of the dye chemical intermediate, such as 6-nitro-2-aminobenzothiazole, may show a response on the TEA. During the second visit to this plant air samples were collected in the same area where the unknown TEA responsive compound was formed. These samples, numbers 8-11, were free of any TEA responsive compounds. The air sample location and results are contained in Table 19.

Bulk Samples

No N-nitroso compounds were detected in any of the bulk samples.

Table 19

The Results of the Air Samples Collected on February 21 and 24
Dye Plant A

Sample No.	Process	Location	N-nitroso Compounds GC-TEA	N-nitroso Compounds HPLC-TEA
February 21				
1	Diazotization	On Tub K 314, 3rd floor	N.D.*	+**
2	Diazotization	6 ft. in front of Tub K 314, 3rd floor	N.D.	+
3	Diazotization	6 ft. in front of Tub K 314, 3rd floor	N.D.	N.D.
4	Coupling	On Tub K 314, 2nd floor	N.D.	N.D.
5	Coupling	4 ft. in front of Tub K 314, 2nd floor	N.D.	N.D.
6	Filter-press	6 ft. from Filter Press # 11 in Press Room	N.D.	N.D.
7	Filter-press	On Filter Press #11 in Press Room	N.D.	N.D.
February 24				
8	Diazotization	8 ft. in front of Tub K 312, 3rd floor	N.D.	N.D.
9	Diazotization	On Tub K 312, 3rd floor	N.D.	N.D.
10	Diazotization	8 ft. in front of Tub K 312, 3rd floor	N.D.	N.D.
11	Diazotization	On Tub K 312, 3rd floor	N.D.	N.D.

* None Detected - detection limit for NDMA 0.05 μg/m^3.

** + A nonvolatile TEA responsive compound was detected but not identified in these air samples. This compound was detected by HPLC-TEA only.

Table 20

Results of Bulk Sample Analysis for N-nitroso Compounds
Dye Plant A

Sample No.	Sample Description	N-nitroso Compounds	Unknown TEA Responsive Compounds
Raw Materials			
1B	N-(Cyanoethyl)-N-ethylaniline	N.D.**	-
3B	6-Nitro-2-aminobenzothiazole, 100%	N.D.	-
4B	2,4-Dinitro-6-bromoaniline	N.D.	-
5B	3-(Dihydroxyethyl)-amino-4-ethyl-acetanilide	N.D.	-
7B	N-Acetoxyethyl-N-cyanoethylaniline Fairlawn, NJ	N.D.	-
9B	3-(N,N-Dihydroxyethyl)aminobenz-anilide, 97%	N.D.	-
10B	3-(N,N-Dihydroxyethyl)amino-4-methoxyacetanilide, 90.7%	N.D.	-
11B	N-(Chloroethyl)-N-ethyl-m toluidine	N.D.	-
12B	N-(Hydroxyethyl)-N-ethyl-m-toluidine	N.D.	-
13B	N-(Cyanoethyl)-N-methylaniline, 99%	N.D.	-
14B	N-(Chloroethyl)-N-ethylaniline	N.D.	-
15B	Dichloro-p-nitroaniline	N.D.	+
16B	p-Nitroaniline	N.D.	-
17B	9-Chloro-p-nitroaniline	N.D.	+
Press Cake			
2B	Intrasil Rubine HBRS	N.D.	+
6B	Intrasil Navy Blue HGS	N.D.	+
		N.D.	+
Finished Product			
18B	Intrasil Navy Blue HGS	N.D.	+
19B	Intrasil Red FTS	N.D.	-
20B	Intrasil Scarlet HGF	N.D	+
21B	Intrasil Orange 2RA	N.D.	+
22B	Intrasil Red MG	N.D.	+
23B	Intrasil Navy Blue HRs	N.D.	+
24B	Intrasil Brown 3RF	N.D.	+
25B	Intrasil Rubine HBRS	N.D.	+
26B	Intrasil Red 2 GH	N.D.	+

** N.D. - No known N-nitroso compounds detected - detection limit for NDMA 0.5 μg/g.

Unknown TEA responsive compounds: + = a TEA response
- = no TEA response

DYE PLANT B

The facility was built about 1915. The plant site occupies about 600 acres and has 20 major buildings with a total area of two million square feet. The plant employs 700 people in the production area, 700 people in the administrative area, and 500 people for maintenance duty. The production employees work on three shifts, with approximtely 200 workers on each shift. The major products of the plant are dyes, pigments, pharmaceuticals, rubber and chemical intermediates. The present study focused only on azo dye production.

The production of the azo dye consisted of two major processes: diazotization and coupling. Sodium nitrite and aniline compounds were mixed in a diazotization tub with acid and ice added to provide the suitable pH and temperature. The resulting diazonium salt was drained into a coupling tub, where a coupling agent had been added earlier. After coupling, the dye was filter-pressed and spray-dried as the finished product. Besides the basic diazotization and coupling reactions, additional diazotization-coupling cycles might be carried out to provide the dyes with the desired color and functional properties.

SAMPLING STRATEGY

Air Samples

Four area air samples were collected in the dye plant (building 42); two near the diazotization tub, and two near the coupling tub. The dye being produced was Calcofast Brown MF. The sampling was done during the period the tubs were in operation. The air sample data are presented in Table 21. Air was sampled using midget impingers containing 15 ml of 1N KOH and 200 ml vacuum traps containing 45 ml of 1N KOH in series at ambient temperatures. Bendix C115 air sampling pumps were used to draw air at from 1.4 L/min to 1.8 L/min through the impingers for about three hours.

Bulk Samples

In total, six samples of finished dye products were collected for N-nitroso compound analysis. None of these dyes were produced using secondary or tertiary amines, however, sodium nitrite was used to form an intermediate diazonium salt. The sample results are contained in Table 22.

RESULTS AND DISCUSSION

Air Samples

The results of the air sample analysis are contained in Table 20. At a detection limit of 0.05 $\mu g/m^3$ for N-nitrosodimethylamine (NDMA) no N-nitroso compounds were detected. An unidentified TEA-responsive compound was detected in the air samples collected near the diazotization tub, however, there is no other evidence indicating that it is an N-nitroso compound. Other compounds that can liberate NO upon pyrolysis will be detected by the TEA.

Bulk Samples

At a detection limit for NDMA of 1 μg/g no TEA-responsive compounds were eluted in any of the bulk samples when examined by either HPLC-TEA or GC-TEA.

No N-nitroso compounds were found in either air or bulk samples collected in this plant.

Table 21

Results of Air Samples in Dye Plant B

Sample No.	Sample Location	N-nitroso Compounds
1A	12 ft. from Diazotization tube in 20D	N.D.*
2A	On the Diazotization tube in 20D	N.D.
3A	On the coupling tube in 23B	N.D.
4A	20 ft. from the coupling tube in 23B	N.D.

* N.D. - None Detected - detection limit for NDMA 0.05 $\mu g/m^3$.

Table 22

Results of Bulk Sample Analysis for N-nitroso Compounds
Dye Plant B

Sample No.	Sample Description	N-nitroso Compounds
1	Calcofast Orange YF	N.D.*
2	Calcofast Olive Brown G	N.D.
3	Orange II-3	N.D.
4	Oil Scarlet 2BL	N.D.
6	Calcofast Brown MF	N.D.
7	Calco Brown MF	N.D.

* N.D. - No N-nitroso compounds detected - detection limit for NDMA 1 μg/g

DYE PLANT C

The subsidiary of a large multinational drug and chemical manufacturing corporation produces a variety of dyes that are used in coloring textile materials. During this survey no data was obtained on the size of this facility or the number of employees involved in its dye manufacturing operations. Dyes are synthesized at this plant in large reaction kettles by first forming a diazonium salt which is later coupled to various amine containing coupling agents to produce the final product. The diazotization reaction involved reacting aromatic amines such as aniline with sodium nitrite at acid pH in cold aqueous solution. This area where the diazotization and coupling reaction reactions take place was selected for area air sampling for N-nitroso compounds. It was noted that this plant was free of any odors and that the manufacturing area was kept clean.

SAMPLING STRATEGY

Air Samples

A total of six area air samples were collected at this site. Four of these samples were located in the dye products areas, one in the quality control laboratory and one located outside about 250 feet from the production building. Two of the four air samples collected within the production area were located on the third floor adjacent to the diazotization reaction kettles and the other two were located on the second floor next to the coupling reaction kettles. The air sampling system consisted of 200 ml vacuum traps containing 45 ml of 1N KOH equipped with Bendix C115 air pumps. Air was sampled at 1.7 L/min for 2-2.5 hours.

Bulk Samples

Six bulk samples consisting of dye products were collected for N-nitroso compound analysis. The names of these products are contained in Table 23. No information about the structure, chemical composition or synthesis of these products was obtained.

RESULTS AND DISCUSSION

At a detection limit of 0.03 $\mu g/m^3$ by GC-TEA four of the six air samples were found to contain N-nitroso compounds. The compounds detected were N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA). The concentration of these compounds ranged from 0.03 $\mu g/m^3$ to 0.06 $\mu g/m^3$ for NDEA and 0.1 $\mu g/m^3$ of NDMA in sample No. 1 (Table 24). These amounts of nitrosamines in the plant's atmosphere are near the detection limit of the sampling and analytical methods and represent quite low concentrations of these compounds.

No N-nitroso compounds were detected in any of the bulk samples. Three bulk samples were found to contain TEA-responsive compounds, however, these unidentified TEA-responsive compounds were not further characterized.

Table 23

Results of Bulk Samples From Dye Plant C

Sample No.	Sample Description	N-nitroso Compounds
7	Acid yellow 4R	N.D.*
8	Metanilic acid	N.D.
9	Acid yellow 4R	N.D.
10	Acid yellow 4R	N.D.
11	O-anisidine omege	N.D.
12	Chlor yellow 5GL	N.D.

* N.D. - None Detected - detection limit for NDMA 1 μg/g.

Table 24

Results of Air Samples From Dye Plant C

Sample No.	Sample Location	N-nitroso Compounds in μg/m³ NDMA	NDEA
1	Diazotization kettle on third floor	0.1	0.05
2	Diazotization kettle on third floor	N.D.*	0.03
3	Coupling reaction kettle on second floor	N.D.	0.05
4	Coupling reaction kettle on second floor	N.D.	0.06
5	Quality Control Laboratory	N.D.	N.D.**
6	Outside - 250' from main building	N.D.	N.D.

* N.D. - None Detected - detection limit for NDMA 0.03 μg/m³.

** N.D. - None Detected - detection limit for NDEA 0.03 μg/m³.

NDMA - N-nitrosodimethylamine
NDEA - N-nitrosodiethylamine

CONCLUSIONS AND RECOMMENDATIONS OF THE DYE INDUSTRY

Worker exposure to known N-nitroso compounds via inhalation in the azo dye industry does not appear to be a serious problem in the three plant sites visited. It should be pointed out, however, that not all dye manufacturing processes involving all of the reaction conditions and raw material combinations have been examined. Reactions with primary amines such as aniline and sodium nitrite at acid pH produce diazonium salts, but if secondary or tertiary amines are also present, N-nitroso compounds can also be formed. Some of the samples collected in this study of the industry were found to contain TEA-responsive compounds. Estimates of the amounts of these compounds can be made assuming a molecular weight and assuming a molar amount of NO is released during the TEA-pyrolysis. While N-nitroso compounds will produce a TEA-response that is proportional to their molecular weight other compounds such as organic nitrites usually produce a TEA-response that is less than the theoretical amount of NO, thus making an estimate of their amounts impossible by this technique. Further characterization of these unidentified compounds using procedures such as mass spectrometry would be needed.

Because the reaction conditions used in producing diazonium salts can also result in N-nitroso compounds, if nitrosatable amines are present, and because most industrial grade amines are contaminated with other amines, this industry should be further studied for the possibility that other dye making operations will result in worker exposure to N-nitroso compounds. A further study should also include the identification of unidentified compounds that are found which produce TEA response.

RUBBER INDUSTRY

Products manufactured by the Plants chosen for this survey included: passenger car tires, aircraft tires, truck tires, industrial rubber products, rubber latex, consumer products and industrial chemicals used in the production of rubber products.

GENERAL DESCRIPTION OF THE RUBBER INDUSTRY

Rubber products such as tires and conveyor belts are made by processes that are analogous to baking pastries. Where flour is the main ingredient in pastries, natural and synthetic rubber are the main ingredients in rubber products. As with pastries, rubber is blended with whatever ingredients are needed to produce the desired product. The process starts with a recipe of ingredients which are then blended in a Banbury mixer followed by kneading the mix on a roller mill. The kneaded rubber is then either fed into an extruder, which is analogous to a meat grinder, equipped with a die to shape the ribbon of extruded rubber onto calender mills which press the rubber onto thin sheets of fabric. The tire is then constructed using the tread rubber from the extruder and the sidewall coated fabric from the calender mill. The raw tire is then baked (cured) in a press which imparts the tread design, shape and other fine detals to the tire. The curing step crosslinks the rubber polymer and to some extent exhausts certain of the additive ingredients. Other process steps also exhaust some of the additive ingredients into the Plants' atmosphere. The processes most likely to produce off-gasing of the rubber additive would be the extruder, calender and tire curing.

Rubber manufacturing facilities were surveyed for the presence of N-nitroso compounds because of their use of various amines, nitrosamines and other nitroso or nitro compounds in some of their rubber recipes. Many of these compounds are listed in the book, Materials and Compounding Ingredients for Rubber and Plastics (1965) (138). Examples of these compounds include: dibenzylamine, diethanolamine, N-nitrosodiphenylamine, N-methyl-N, 4-dinitrosoaniline, tetramethylthiuram disulfide, morpholine disulfide, and substituted p-phenylenediamines.

The basic ingredients used in the manufacture of rubber products are natural and synthetic latex. Natural Hevea rubber is a homopolymer of cis-1,4-polyisoprene and is obtained from several species of rubber yielding trees. Synthetic latex is produced from the polymerization of a variety of monomers. The most common of these monomers include: 1,3-butadiene, 2-chloro-1, 3-butadiene (chloroprene), 2-methyl-1, 3-butadiene (isoprene), etc. A synthetic rubber that is virtually identical with natural rubber is made from isoprene; the product formed is almost exclusively cis-1,4-polyisoprene. Formulations of natural rubber or synthetic latex usually include sulfur, accelerators, peptizers, antioxidants, carbon black and various fillers. Examples of products manufactured from rubber include: automotive tires, rain gear, footwear, adhesives, conveyor belts, automotive parts, seals and gaskets.

A further reason for including the rubber industry in this study was that epidemiological studies have indicated an excess mortality of the workers from certain specific cancers (139). The specific chemical or physical agents that may be causing the excess cancer deaths have not yet been identified.

RUBBER PLANT A

This facility produces synthetic latexes as its major product. The following latex compounds were being manufactured by this Plant: styrene butadiene copolymer, polybutadiene, butadiene-styrene-vinylpyridine copolymer, and butadiene-styrene-carboxylic acid copolymer.

The basic ingredients of latex are the monomers; styrene, butadiene, vinylpyridine, and carboxylic acids. Other ingredients are also used to control the polymerization of the monomers. Catalysts (peroxides or persulfate) are added to initiate the chain reaction. Emulsifier (sulfate or fatty acid) are added to promote the miscibility of water and oil soluble materials. Modifiers such as mercaptans, are added to control the chain length of the polymer. Inhibitors, nitrosophenylhydroxylamine or diethylhydroxylamine, are used to stop the polymerization.

The latex ingredients at this Plant were prepared in the solution area and pumped through pipes into the reactor. When the polymerization was completed, the contents of the reactor were pumped to a stripper where any unreacted monomers were removed by vacuum. The latex was then pumped to a storage tank.

At the time of this survey, this plant employed 240 workers, divided equally among three shifts.

SAMPLING STRATEGY

Air Samples

Five samples were collected using vacuum traps containing 45 ml of 1N KOH solution. Air flow rates were between 1.5 to 2 L/min using Bendix C115 air pumps with sampling times of approximately 3 hours (Table 25).

Bulk Samples

A total of 5 bulk samples were collected, see Table 26 for a description.

RESULTS AND DISCUSSION

No N-nitroso compounds were detected in any of the bulk materials examined or in the air in the area air samples.

Table 25

Air Samples Collected in Rubber Plant A

Sample No.	Location	N-nitroso Compounds Found
1	Solution area, on operating desk, near tank 105 and 113	ND
2	AO room, 1S, column F420	ND
3	Latex building, 1S, at the water meter near tank 303	ND
4	Control room, 2S, desk area	ND
5	Stripper house, 3S, on desk about 5 feet from No. 12 stripper	ND

*ND - None Detected, detection limit 0.05 μg/m^3 (NDMA).

Table 26

Bulk Samples Collected in Rubber Plant A

Sample No.	Monomer*	Catalyst	Emulsion	Inhibitor***	N-nitroso Compounds Found
1	B/S/COOH	Persulfate	Sulfate	--	ND****
2	B/S	SFS**	Fatty acid	DEHA/NPH	ND
3	B/S	SFS**	Fatty acid	SDD/NPH	ND
4	B/S	Persulfate	Rosin acid	-	ND
5	B	Persulfate	Rosin acid	-	ND

* B = butadiene; S = styrene, COOH = carboxylic acid,

** Sodium formaldehyde sulfoxalate

*** DEHA = diethylhydroxylamine; NPH = nitrosophenylhydroxylamine; SDD = sodium dimethyldithiocarbamate

**** ND - None Detected, detection limit 0.2 μg/g.

RUBBER PLANT B

This Plant has a production area of 800,000 square feet and an employment of 1000 with approximately 270 of these in the administrative area. The primary products of this facility, at the time of this survey, were rubber conveyor belts, rubber tubing, rubber hose, and rubber air shocks. The ingredients for all of these products were prepared in the chemical mixing room and batch fed into a Banbury machine for further mixing and milling. The batch stock from the mills was then fabricated into the various products via calendering, extrusion and fabric layer building operation. These products were then cured at elevated temperatures in various presses and molds. The survey for N-nitroso compounds conducted at this facility was focused primarily in the ingredient compound area.

SAMPLING STRATEGY

Air Samples

Four area air samples were collected using 1N KOH traps equipped with Bendix C115 air pumps operating at 2 L/min for about three hours. Three of these samples were collected in the manufacturing area and one sample, No. 4A, in the administrative area (Table 27).

Bulk Samples

Four bulk samples consisting of various amine type rubber ingredients were collected (Table 28).

RESULTS

Air Samples

Low levels, 0.07 to 0.14 $\mu g/m^3$, of N-nitrosodimethylamine (NDMA) were found in all four of the area air samples collected in this Plant (Table 27). These levels of NDMA are quite low and are comparable to levels reported to be present in the ambient air of downtown Baltimore (12,20). No attempt was made to determine the source of this NDMA, however, it is apparent from the data that its occurrence within the Plant's atmosphere is fairly uniform from area to area.

Bulk Samples

No N-nitroso compounds were detected in any of the bulk samples.

Table 27

Air Samples Collected in Rubber Plant B

Sample No.	Collection Method	Location	NDMA* Concentration (μg/m^3)
1	1N KOH	Mill weighing area	0.14
2	1N KOH	Banbury, loading area	0.14
3	1N KOH	Batch off mill area	0.10
4	1N KOH	Safety office	0.07

* NDMA - N-nitrosodimethylamine

Table 28

Bulk Samples Collected in Rubber Plant B

Sample No.	Description	N-nitroso Compound Found
1	Mixed aryl-p-phenylene diamines	ND*
2	Mixed diaryl-p-phenylene diamines	ND
3	Alkylated diphenylamines	ND
4	N-(1-3-dimethylbutyl)-N-phenyl-p-phenylendiamine	ND

* N.D. - None Detected - Detection limit 0.1 μg/g.

RUBBER PLANT C

This facility manufactures chemicals which are used as compounding ingredients in the manufacture of rubber products. Three separate buildings were sampled at this facility and three sampling visits were made - March 28, April 3, and May 24, 1978.

Building No. 1 produced N-nitrosodiphenylamine (NDPhA) and bismorpholine carbamylsulfenamide (BMCS). Building No. 2 was primarily used for the production of polymerized 2,2,4-trimethyldhydroquinoline (PTMDQ). Building No. 3 houses an employee lunch room, a maintenance and machine shop and the Plant's Safety Office. Building No. 3 is located adjacent to and between Building Nos. 1 and 2.

N-nitrosodiphenylamine is used in rubber compounding as a polymerization retarder, BMCS is on the other hand an accelerator and 2,2,4-trimethyl dihydroquinoline PTMDQ is used as an antioxidant. The possible nitrosamines that could be found in this plant include NDPhA, N-nitrosomorpholine (NMOR) and N-nitrosodimethylamine (NDMA). The nitrosamine, NDPhA will certainly be found since it is manufactured in the areas surveyed.

The floor plan of Building No. 1 is presented in Figure 10. The NDPhA production area is located in the east side of the building (rightside) and the BMCS production area is located about 100 feet away in the west side of the building.

NDPhA is produced from the reaction of diphenylamine and sodium nitrite in water that has been acidified with sulfuric acid. The reaction is carried out in a large (6'x8') reactor vessel. The starting chemicals for this product are located on the east third floor of Building No. 1 just above the reactor vessel on the second floor. These chemicals including water and sulfuric acid are fed by pipes to the reactor. When the NDPhA reaction is finished, it is emptied into a decantor located on the first floor. The NDPhA, being a water insoluble compound, is then separated from the aqueous layer, drained, dried on a hot roller and packed as the final product into drums. It was reported that 30,000 pounds of NDPHA were produced in this plant each month.

The equipment and starting chemicals for the BMCS production were also located in Building No. 1; however, they were located on the west side of the building. The amine precursors, morpholine and a 40% aqueous solution of dimethylamine, were stored on the third floor and fed to BMCS reactor on the second floor. After a BMCS production run, the reactor contents were centrifuged, transferred to the first floor and transported to the east side of the building for further drying. The BMCS drying station was in the same area and within a few feet of the NDPhA decanter and packaging area.

In its production area, this plant has approximately 120 employees operating three shifts of 40 employees each.

SAMPLING STRATEGY

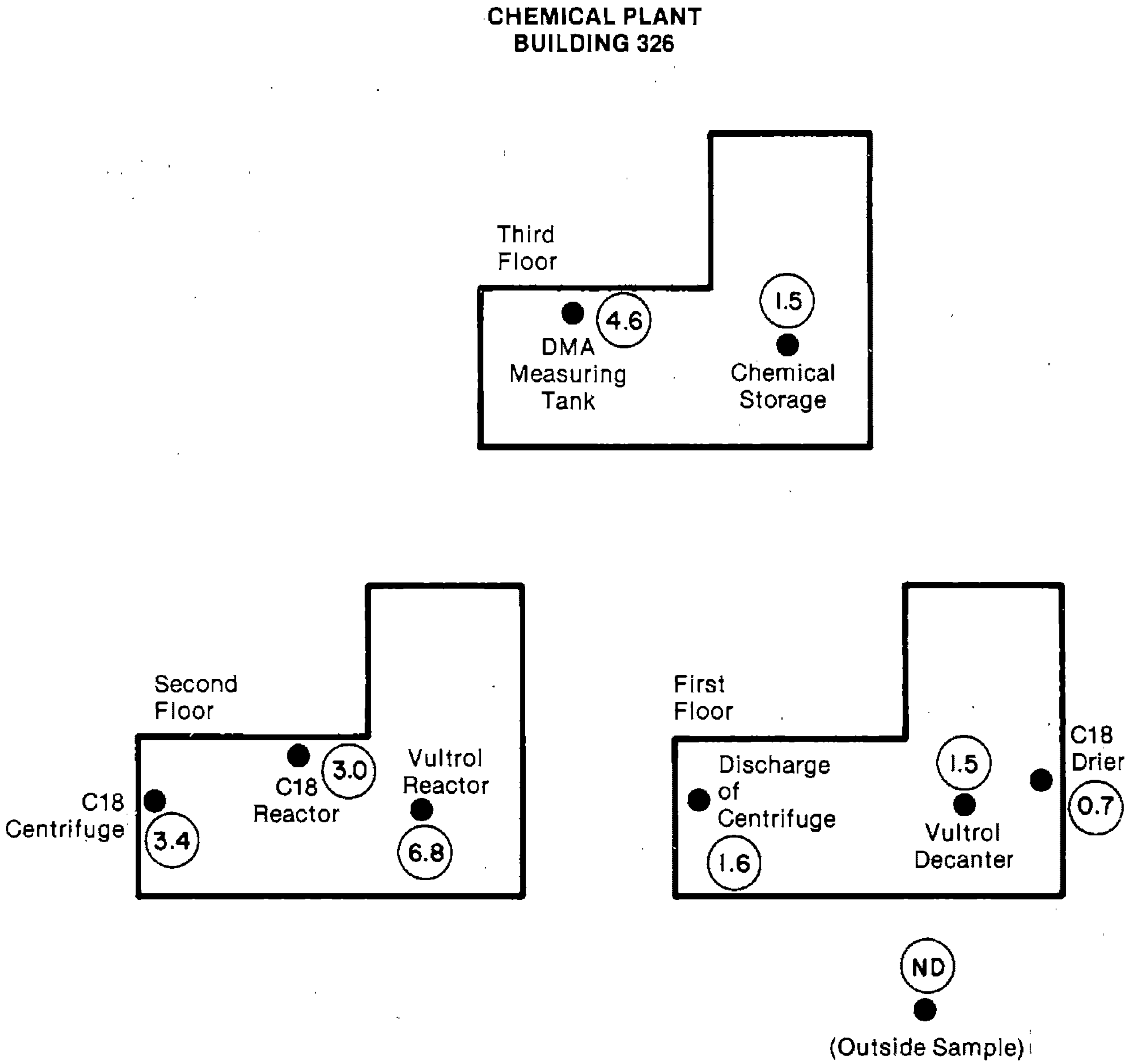


Figure 10. The Locations of Air Samples and Concentrations of N-nitrosomorpholine (μg/m³) in the Air Samples Collected on April 3, 1978, in Chemical Plant Building #1 of Rubber Plant C.

Air Samples

During the first visit to this Plant on March 28, 1978, five area air samples were collected in three separate areas; one in the employees lunch room, one in building No. 2 and three in building No. 1. In this initial air sampling no N-nitroso compounds were detected in building No. 2 where PTMDQ was being produced, however, three N-nitroso compounds were found in the air in Building No. 1 and two were found in the air of the lunch room. NDPhA and BMCS were being produced in Building No. 1 during the time that the air samples were collected. The nitrosamines found in these air samples were: N-nitrosodimethylamine (NDMA), N-nitrosomorpholine (NMOR) and NDPhA. The presence of NDPhA in these air samples was not unexpected since this compound is produced and packaged in Building No. 1. Smaller amounts of NDPhA and NMOR were also found in the employees lunch room.

In order to confirm these findings, ten more air samples were collected on April 3, 1978. One sample was taken in the safety office in the administrative building as a control. Another control was provided by sampling air outside the south side of Building No. 1. The other eight samples were obtained inside Building No. 1; three each on the first and second floors, and two on the third floor. During this sampling visit, the equipment for the NDPhA production was not in operation because it was being cleaned. While nitrosamines were not detected in either of the control samples (sample No. 6 and No. 7), NMOR, NDMA and NDPhA were again found in the other eight air samples collected inside Building No. 1.

The third visit to this Plant on May 24, 1978 was to obtain further air samples in the N-nitrosodiphenylamine production area. The primary purpose of this visit was to obtain air samples for GC-MS analysis for N-nitrosomorpholine and to determine if artifact formation of the discovered N-nitrosomorpholine could have occurred during sample collection or subsequent sample preparation. The sample for mass spectral analysis was obtained by combining the air samples collected in the 1N KOH traps. The artifact studies consisted of secondary amines spiking experiments and varying sample preparation techniques. One of these artifact experiments was the direct analysis of a dichloromethane extraction solution of a 1N KOH trap without further sample preparation or concentration.

Bulk Samples

On March 28, and April 3, 1978 a total of 15 bulk samples were collected along with the area air samples. Seven of these samples consisted of two chemical intermediates (raw materials) and five finished chemical products. The two raw material samples were morpholine and a 40% aqueous solution of dimethylamine. The five chemicals consisted of four samples of BMCS and one of PTMDQ-D. Five aqueous samples and three other miscellaneous samples consisting of two floor scrapings and a soil sample were also examined.

RESULTS AND DISCUSSION

Air Samples

Air samples were collected on three separate occasions in Building No. 1. On all three occasions NMOR was found in the air with levels ranging from 0.7 μg/m^3 to 6.8 μg/m^3 (Table 29). NDMA was also found in most of the area air samples with levels of from 0.05 μg/m^3 to 0.5 μg/m^3. Airborne NDPhA, with levels ranging from 0.2 μg/m^3 to 47 μg/m^3, was also found. This finding is not surprising since NDPhA is manufactured at this facility. Air Sample No. 11 indicated a level of 1230 μg/m^3 of NDPhA, however, this may be due to a spill of wash water containing NDPhA onto the air sampler.

Raw Materials

N-nitrosodimethylamine (NDMA), at a concentration of 1.3 μg/g, was found in the 40% dimethylamine sample, No. 2 and N-nitrosomorpholine (NMOR), at a concentration of 0.8 μg/g, was detected in the morpholine sample No. 12. These nitrosamine levels may be typical of nitrosamine contaminations found in industrial grade secondary amines (140, 141). The results of all the bulk samples are summarized in Table 30.

Products

No N-nitroso compounds were detected in the sample of PTMDQ-D. Low levels of NMOR were found in both the wet cake BMCS (Samples No. 13 and 15) and dry cake BMCS (Samples No. 14 and 16). The dry cake BMCS samples contained almost twice as much NMOR as the wet cake, these samples were obtained from another plant. Among the four samples analyzed, the highest concentration of NMOR observed was only 1.0 μg/g (Table 30).

Water Samples

No N-nitroso compounds were detected in the samples of city water, sample No. 10, and service water, sample No.11. Traces of NMOR were found in the samples of steam condensate and waste water, these concentrations were 0.002 and 0.003 μg/g, respectively. NDPhA was, as expected, found in the aqueous phase of the decanter, and the level of NDPhA (732 ppm) observed was not surprising.

Miscellaneous Samples

The soil sample obtained outside Building No. 1 was found to contain 4.4 μg/g of NMOR and 47 μg/g of NDPhA. A scraping from the surface of the NDPhA reactor contained 5% of NDPhA. A very high concentration of NMOR (731 μg/g) was found in a floor scraping sample that had been obtained from the staircases between the first and second floors of Building No. 1. The Massachusetts Institute of Technology confirmed the presence of NMOR in this sample by GC-MS.

NMOR, NDMA and NDPhA were all found in the air samples collected inside Building No. 1. Since NDPhA was one of the major products manufactured in this Building, the finding of NDPhA was not unexpected. However, NMOR and NDMA constitute contaminants in the factory air. The precursors for these nitrosamines are presumed to be either the morpholine and dimethylamine intermediate or the final products made from these amines. Two ppb of NMOR was found in the steam condensate and from 0.4 - 1.0 ppm of NMOR was found in the product BMCS.

Table 29

The Concentrations of N-nitrosomorphline (NMOR) N-nitrosodimethylamine (NDMA), and N-nitrosodiphenylamine (NDPhA) in the Air Samples Collected in Rubber Chemical Plant C

Sample No.	Location	Concentration in μg/m^3		
		NMOR	NDMA	NDPhA
March 28, 1978				
4	Lunch room	0.07	ND	0.7
	Building #2			
5	PTMDQ washing area	ND	ND	ND
	Building #1			
1	NDPhA reactor	4.1	0.2	47
2	NDPhA decanter	4.6	0.05	12
3	Dimethylamine crystalized meter	0.9	0.2	0.8
April 3, 1978				
6	Safety office	ND***	ND	ND
7	Outside building #1, south	ND	ND	ND
	First Floor, Building #1			
8	BMCS drier	0.7	ND	0.3
9	NDPhA decanter	3.9	0.07	25
10	BMCS centrifuge discharge	1.6	0.1	ND
	Second Floor, Building #1			
11	NDPhA reactor	6.8	?*	1230**
12	BMCS centrifuge	3.4	0.3	0.2
13	BMCS reactor	3.0	0.3	0.9
	Third Floor, Building #1			
14	East wing of third floor	1.5	0.08	17
15	Dimethylamine crystalized meter	4.6	0.5	0.6
May 24, 1978				
3	NDPhA reactor area	5.8	ND	ND
10	NDPhA reactor area	4.0	ND	ND
11	NDPhA reactor area	4.3	ND	ND

* The presence of high concentration of NDPhA masked NDMA peak on GC-TEA.

** Possibly contaminated with fluid containing NDPhA.

*** ND - not detected

Detection Limit = 0.05 μg/m^3

Table 30

The Concentrations of N-nitrosodimethylamine (NDMA), N-nitrosomorpholine (NMOR) and N-nitrosodiphenylamine (NDPhA) found in Various Bulk Samples

Rubber Chemical Plant C

Sample No.	Sample Description	Concentration in μg/g NMOR	NDMA	NDPhA
(1) Starting Chemicals				
2	40% dimethylamine		1.3	
12	Morpholine	0.8		
(2) Products				
5	PTMDQ D	ND*	ND	ND
13	BMCS, wet cake	0.4		
14	BMCS, dry cake	0.7		
15	BMCS, wet cake other producer	0.5		
16	BMCS, dry cake other producer	1.0		
(3) Water Samples				
3	Aqueous phase, NDPhA decanter			732
7	Waste water	0.003		
8	Steam condensate	0.002		
10	City water	ND	ND	
11	Service water	ND	ND	
(4) Miscellaneous Samples				
4	Scraping from surface of NDPhA reactor			50,000
6	Soil, outside Bldg. #1	4.4		47
9	Scraping from staircases of Bldg. #1	731		15,000

*ND = not detected

Detection limit = 0.001 μg/g

Higher concentrations of NDPhA were generally observed in the east side of the building, where NDPhA was produced. Considering the concentration of NMOR found in the dirt on the staircase of Building No. 1, very little of this would be needed to produce the lunch room air level of 0.07 $\mu g/m^3$. The results of the artifact control experiments indicate no evidence that N-nitrosomorpholine was being produced as an artifact of either the air sample trapping techniques or the subsequent analytical procedures (21).

Airborne NDMA concentrations were highest in the area where dimethylamine was being stored. Morpholine was also stored in the vicinity of the dimethylamine tank, and, interestingly the concentration of NMOR in the air followed the distribution pattern of NDMA very closely, with NMOR levels being approximately 10 times higher than NDMA levels in most air samples. The further away from the dimethylamine and morpholine storage areas that the air samples were collected, the lower the airborne NDMA and NMOR levels. The only exception to this was a sample collected near the NDPhA decanter, Sample No. 9. The distribution of NMOR in Building No. 1 has been summarized in Figure 10. The presence of airborne NMOR and NDMA in this Plant could be explained by the reaction of morpholine or dimethylamine with a nitrosating agent present in the air. The formation of nitrosamines in air due to the nitrosation of secondary and tertiary amines by nitrogen oxides has been demonstrated (134-137,142). The possibility of nitrosating a secondary amine by a transnitrosation reaction with NDPhA in the air has not been studied and, therefore, it is not possible to determine whether this route might be a contributing factor to the nitrosamine contamination in this Plant's atmosphere.

A more likely site for the formation of NMOR and NDMA would be on the floor of the building. Morpholine and NDPhA present together on the floor could, by transnitrosation (61), produce NMOR. High levels of NMOR were indeed found in floor scraping from a staircase in this plant. The NMOR found the soil sample outside the east side of the building may have also been formed from the interactions of morpholine and NDPhA in the soil.

The finding of airborne NMOR in the lunch room of Building No. 3 could be due to workers transporting NMOR contaminated dirt from the floor of Building No. 1.

The scope of the present study did not generate sufficient information to allow the investigators to determine exactly how NMOR and NDMA were being formed in this plant. We can, however, speculate that these nitrosamines were most likely being formed from a reaction between their respective secondary amines with airborne nitrogen dioxides from the NDPhA reactor and by transnitrosation on the floor with NDPhA. NMOR contamination in the steam system and on the floor, might also be partly responsible for its presence in the air. Based on these assumptions, the following recommendations are made to reduce and hopefully eliminate the NMOR contamination in the air of Building No. 1.

* Discontinue the manufacture of NDPhA in buildings where secondary or tertiary amines are used or stored. To avoid transnitrosation, the floor should be cleaned frequently.

* If morpholine is used in the steam system as a rust inhibitor, its use should be discontinued, especially in areas where high nitrogen dioxide levels can be expected.

* Examine the possibilities that the amines are being nitrated in the air by the nitrogen dioxide being generated during the production of NDPhA.

* Regular sampling program to evaluate airborne concentrations of NMOR.

* This study was conducted prior to the NCI cancer-screening study of NDPhA which found the compound carcinogenic in rats at high doses.

RUBBER PLANT D

The part of this Plant that was surveyed produced aircraft and farm equipment tires. Due to the size of this Plant (building with 8 to 10 floors covering several acres) and the limitations of time, only the extrusion and the curing operations of one of the product lines was surveyed for the presence of N-nitroso compounds. The extrusion operations were located in Building 9A where approximately 20 workers were involved. At the time of this survey there was only one shift working from 6 A.M. to 2 P.M. The extrusion process starts with rubber batchstock from the storage area. This is first placed in a roller mill for warming and mixing, then it is milled to the proper size and moved to the extruder via a conveyor system. After extrusion the ribbon of uncured tire tread rubber is cooled in a water bath, cut to the desired length and then placed in trays (carding) to be later used for building tires.

The curing operations were located in Building 4A (Figure 11). These operations were divided into two separate areas, one for the curing of small tires, the other for the curing of large tires. In each of these areas there were many tire curing machines. The tires are cured individually in molds which force the crude tire to conform to the desired tire pattern while steam heat is used to accelerate the process. Two to three hours at temperatures of up to 300°F are required to complete the curing process.

SAMPLING STRATEGY

Air Samples

Area air samples were collected at this Plant on four separate visits. Two samples were collected on both March 27 and 29, 1978, 10 samples were collected on April 4, 1978 and 13 more on May 23, 1978. The four visits to this Plant were made to re-confirm the finding of N-nitrosomorpholine (NMOR) in the air samples and to obtain samples for GC-MS analysis. Some of the samples collected on May 23, 1978 were to determine if the discovered NMOR could have been formed as an artifact of the sampling or analytical methods. These artifact tests consisted of adding nitrosatable amines to the 1N KOH impinger traps and altering the analytical procedures to minimize the possibility of inadvertent formation of nitrosamines.

Bulk Samples

On March 27, 1978, two bulk samples were collected along with the area air samples. The two samples consisted of a rubber tread batchstock before it is milled and extruded and after is is extruded.

RESULTS AND DISCUSSION

This study focused on the manufacture of aircraft tires because, at this plant, a nitrosamine, N-nitrosodiphenylamine (NDPhA), is included in the compounding of some of the batchstock rubber used for making the tire treads. The process areas selected for air sampling included, batchstock rubber milling,

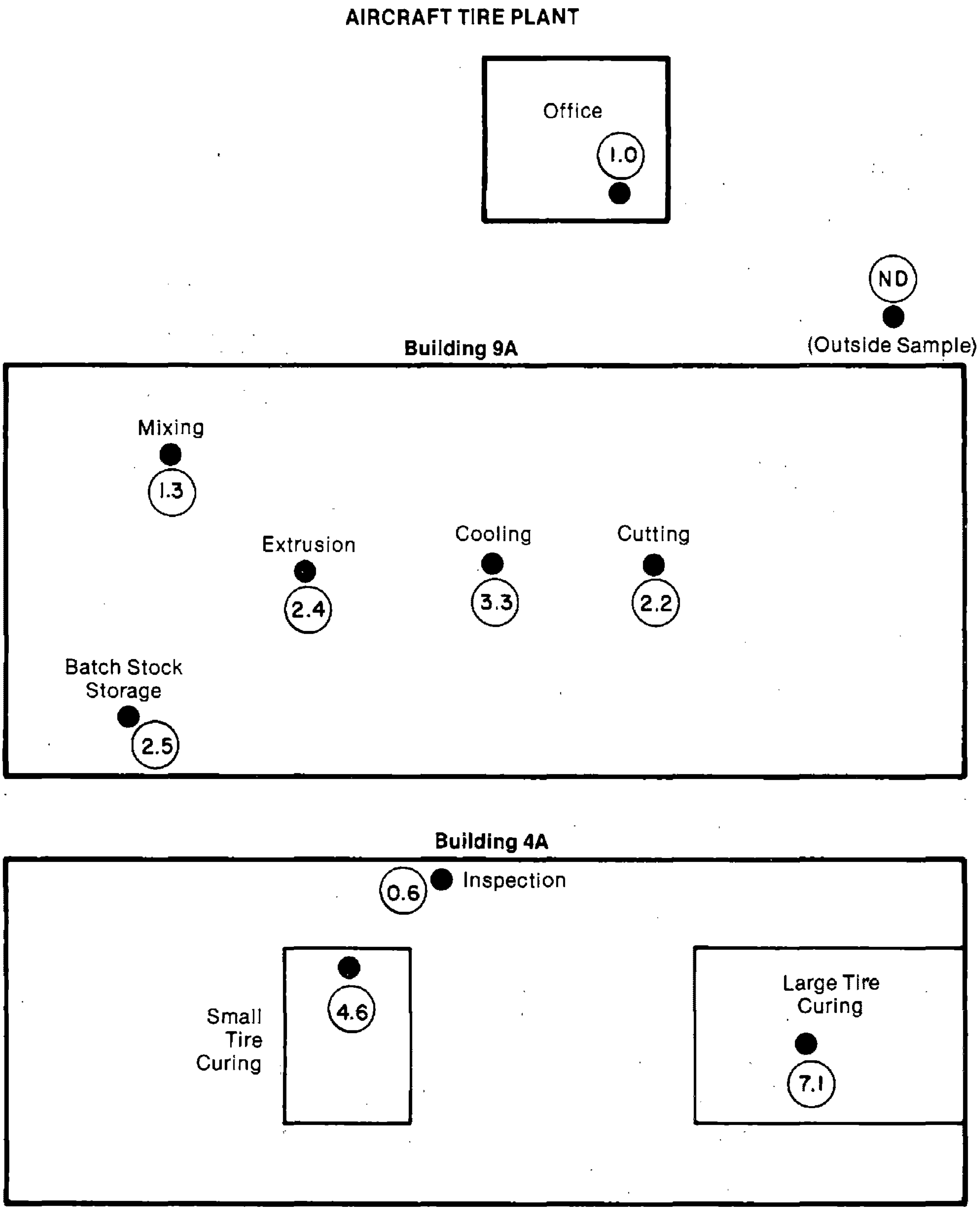


Figure 11. Location and Concentration (μ/m^3) of N-nitrosomorpholine in Rubber Plant D.

tire tread extrusion, rubber warm-up and mixing mills and the tire curing molds. During the first visit to this Plant one air sample was collected close to the tire tread extruder and a second sample was collected near the rubber batchstock warm-up mill in Building 9A. Two days later on March 29, 1978, two air samples were obtained near the tire curing presses in Building 4A. Airborne N-nitrosomorpholine (NMOR), at concentrations ranging from 1.7 to 4.9 μg/m^3, was found in these plant areas (Table 31). In order to confirm these findings and to sample other areas, 10 more air samples were collected during the following week, April 4, 1978. One of these samples was collected outside the factory as a control. A second control sample was placed in the administration building. This area, however, was connected to the process area being sampled by a 200' corridor. No nitrosamines were detected in the outside control sample but 1.0 μg/m^3 of airborne NMOR was found in the air in the administration area. The other samples collected during this visit were collected in the same areas of the previous visits. Five air samples were collected at various locations along the extrusion process and three were obtained in the curing area. While these samples were being collected a batchstock tire tread formulation containing NDPhA was being extruded and tires containing this rubber were being processed in the small tire curing molds. NMOR was again detected in every air sample with levels in the extruder area ranging from 1.3 μg/m^3 to 3.3 μg/m^3 and levels in the tire curing area ranged from 0.6 μg/m^3 to 7.1 μg/m^3.

The distribution of the airborne NMOR in the extrusion area was fairly uniform, however, this was not the case in the tire curing area (Figure 11). While the NMOR levels in the curing area were higher than in the extruder area, a level of only 0.6 μg/m^3 was detected in the tire finishing and inspection area. This area is located in close proximity to the curing area, but, it was noted that the windows in this area were open and that a window fan was drawing in outside air at the time that the sample was being collected.

Neither of the bulk samples of the batchstock rubber contained measurable levels of either NMOR or NDPhA. The detection limit for the analytical procedure used was 0.2 μg/g. Since NDPhA and a morpholine containing accelerator were compounded in this rubber sample we conclude that the analytical procedure used for this analysis either was inappropriate or that the NDPhA was not, as reported, compounded into this rubber mix.

Within the limited scope of this study, the source of the airborne NMOR was not ascertained. However, several posibilities can be postulated. The NMOR may be formed within the rubber by transnitrosation reactions involving NDPhA and either the morpholine accelerator or free morpholine. It is also possible that preformed NMOR may be present in the accelerator compound and this is being released during the mixing, extruding, and heating of the rubber. Some of the free morpholine outgasing from the rubber as the accelerator decomposes, may be reacting with airborne nitrogen oxides to form NMOR.

A fourth visit to this Plant on May 23, 1978 reconfirmed the earlier findings of airborne NMOR. During this sampling visit levels as high as 27 μg/m^3 of NMOR were found in close proximity to the tire tread extruder in Building 4A. A total of six area air samples were collected - four in the tire curing area and two in the extruder area. The levels of airborne NMOR in the

Table 31

The Concentration of N-nitrosomorpholine in the Air of Rubber Plant D

Sample No.	Location	NMOR Concentration ($\mu g/m^3$)
March 27		
1	North side of curing press H6	4.9
2	South side of curing press H6	2.2
March 29		
3	Extruder	1.7
4	Warm-up and mixer	2.2
April 4		
6	Outside the plant	ND*
14	Administrative office	1.0
	Building 9A	
10	Batchstock storage area	2.5
9	Warm-up and mixing	1.3
8	Extrusion	2.4
7	Cooling	3.3
5	Cutting	2.2
	Building 4A	
13	Large tire curing	7.1
11	Small tire curing	4.6
12	Inspection and finishing	0.6
May 23		
3	Large tire curing	2.3
5	Large tire curing	3.0
6	Extruder in building 4A 7:00 am to 9:32 am	27.0
7	Extruder in building 4A 9:40 am to 11:15 am	12.0
12	Large tire curing room	2.5
13	Large tire curing room	2.8

N.D. - None Detected - detection limit 0.05 $\mu g/m^3$.

extruder area were 12 and 27 μg/m^3 and in the curing area the levels ranged from 2.3 to 3.0 μg/m^3. The results of the artifact test air samples indicated that the sampling and analytical procedures used in this study were artifact free. A portion of these samples were examined by GC-MS and the presence of NMOR was confirmed.

RUBBER PLANT E

This Plant produces about 12,000 passenger and truck tires daily. The plant was built about 1935 and was later acquired by its present management. The plant has about 900,000 square feet of work space with 1350 people on its payroll, 1150 in production and 200 in administration. The Plant's employees work 3 shifts with about 450 on each shift.

SAMPLING STRATEGY

The principal areas surveyed for N-nitroso compounds were extruding and curing. In addition, an air sample was taken inside a small tire just as it came out of the curing press. In this survey an attempt was made to determine both the amount of N-nitroso compound in the areas sampled, and the process that may be responsible for this presence. To this end we located air samplers as close to suspected processes as possible and collected area air samples in the same general area. All of the area air samples were collected using both ThermoSorb/N air samplers and side-by-side 1N KOH impinger. The process air samples were collected using ThermoSorb/N air samplers alone. See Table 32 for sample location.

Air Samples

On September 19, 1978, a total of 20 air samples were collected at this Plant. Sixteen of these samples were area air samples collected by the use of both solid sorbents and 1N KOH solution. Two of these samples were collected by the use of Tenax™-GC solid sorbent, 11 were collected using ThermoSorb/N air sampling cartridges and seven were collected using 1N KOH impingers.

ThermoSorb/N air sample cartridges were used with both Bendix C115 air pumps and a 10 L/min metal bellows pump equipped with a Hastings mass flow meter. The air flow rates ranged from 2 L/min to 7 L/min depending upon the pump used.

The Tenax-GC tubes were also mounted on Bendix C115 pumps operating at about 3 L/min for about 3 hours. The Tenax-GC tubes consisted of glass tubes 20 mm x 80 mm packed with Tenax™-GC sorbent. The Tenax samples were collected in the small tire curing area next to samples No. 1A and No. 1B.

Fourteen of the air samples consisted of side-by-side sets of ThermoSorb/N air sampling cartridges and 1N KOH traps. These sets of pumps were used as area air samplers and were operated at 2-3 L/min for about 3 hours. The remaining four air samples were specific process samples taken using ThermoSorb/N cartridges and an air flow rate of about 7 L/min with sampling times of from 10 to 15 min.

RESULTS AND DISCUSSION

With the exception of sample 7B, all of the samples collected in this Plant contained N-nitrosomorpholine (NMOR) and three of them contained measurable amounts of N-nitrosodimethylamine (Table 32). The NMOR amount in the area air samples ranged from 0.25 $\mu g/m^3$ to almost 3 $\mu g/m^3$. The NMOR levels found in

Table 32

The Air Concentration of Nitrosamines in the Air of Rubber Plant E on September 18, 1978

Sample No.	Sample Type	Location	Nitrosamines in μg/m^3	
			NDMA	NMOR
1A	ThermoSorb/N	Center of north curing room	0.24	0.52
1B	1N KOH	" "	N.D.	0.24
2A	ThermoSorb/N	Z - calendar	N.D.	0.34
2B	1N KOH	" "	N.D.	0.64
3A	ThermoSorb/N	Center of truck tire curing	N.D.	1.1
3B	1N KOH	" "	N.D.	1.3
4A	ThermoSorb/N	East side of truck curing room near ceiling	N.D.	1.1
4B	1N KOH	" "	N.D.	1.1
5A	ThermoSorb/N	Truck tread extruder	N.D.	2.4
5B	1N KOH	" "	N.D.	2.0
6A	ThermoSorb/N	Warm up mill for truck tread extruder	N.D.	2.8
6B	1N KOH	" "	N.D.	1.9
7A	ThermoSorb/N	Outside near gate house	N.D.	0.08
7B	1N KOH	" "	N.D.	N.D.
8	ThermoSorb/N	Small tire curing in hot tire out of curing mold	N.D.	6.6
9	ThermoSorb/N	Inside a large air duct at north end of truck tire curing area	N.D.	0.24
10	ThermoSorb/N	Tire tread extruder where mill rubber enters the extruder	1.7	7.2
11	ThermoSorb/N	Exit of large tire tread extruder	1.7	8.5
T^1	Tenax-GC	Center of small tire curing	N.A.	N.A.
T^2	Tenax-GC	" "	N.A.	N.A.

N.D. - None Detected - Detection limit 0.1 μg/m^3 NDMA

N.A. - Not Analyzed

the air in close proximity to specific processes ranged from 6.6 $\mu g/m^3$ to 8.5 $\mu g/m^3$. A steel traction snow tire was removed from one of the curing molds and an air sample (Sample No. 8) was taken inside the body of this hot tire where NMOR was found at the 6.5 $\mu g/m^3$ level.

Samples No. 10 and No. 11 were both collected at the same tuber (tire tread extruder). Sample No. 10 was taken inside the hopper where the rubber from the mill enters the extruder. The levels found in the sample were 7.2 $\mu g/m^3$ for NMOR and 1.7 $\mu g/m^3$ for NDMA. Sample No. 11 was taken near the head of the tuber (exit of the large tire tread extruder) where the ribbon of rubber for tire treads is extruded. The levels found in this sample were 8.5 $\mu g/m^3$ of NMOR and 1.7 $\mu g/m^3$ for NDMA. An area air sample taken at this location contained 2.0 to 2.4 $\mu g/m^3$ NMOR, while NDMA was not detected.

From this data it appears that the airborne nitrosamines are being released into the air from the rubber. How or why the nitrosamines are in the rubber is not known at this time. However, the precursor amines, morpholine and dimethylamine are used extensively in rubber compounding ingredients as tertiary amine accelerators. Nitrosating agents such as N-nitrosodiphenylamine (NDPhA) and even sodium nitrite are also used in rubber compounding. The two Tenax-GC samples were sent to an independent laboratory for analysis by GC-mass spectroscopy. This laboratory reported that the samples were damaged in transit and as a result no data were obtained from these samples.

RUBBER PLANT F

This facility produces about 12,000 replacement passenger radial and bias belted tires per day. The Plant was built about 1929. The size of the Plant is about 1,300,000 square feet with 800 people on its payroll, 650 in production and 150 in administration. The Plant's employees work three shifts with about 250 on each shift.

SAMPLING STRATEGY

The principal processes surveyed for N-nitroso compounds were the extruding area and tire curing area. In addition, an air sample was taken inside a small tire just as it came out of the curing press. During this survey, the purpose was to determine not only the amount of N-nitroso compound in the area air samples but also where in the tire manufacturing process they may be coming from. To this end, air samples were taken close to suspected processes and collected area air samples in the same general area. Two curing areas were selected for sampling; one was a radial passenger tire curing room and the other curing area processed bias belted tires.

Air Samples

On September 20, 1978 a total of 20 air samples were collected at this plant, 14 were area air samples and six were specific process air samples. The air samples were collected by use of ThermoSorb/N air sampling cartridges, 1N KOH impinger traps and Tenax™-GC cartridges. Bendix C115 air pumps and a 10 L/min metal bellows pump equipped with a Hasting 102 mass flow meter were used to draw air through the air samplers. Air flow rates ranged from 2 L/min to 7 L/min depending on the pump used and the type of sample being collected. The Tenax-GC tubes were mounted on Bendix C115 pumps and air was drawn through them at about 2 L/min for about 3 hours. The Tenax tubes consisted of glass tubes 20 mm x 80 mm packed with Tenax™-GC sorbent. The Tenax-GC samples were collected near the 1010 extruder along with samples No. 13A and No. 13B.

Twelve of the air samples consisted of side-by side-sets of ThermoSorb/N cartridges and 1N KOH traps. These sets of samples were collected using Bendix C115 pumps operated at 2 to 3 L/min for about 3 hours. The remaining six air samples were taken using ThermoSorb/N air sampling cartridges and a high volume air pump. The air flow rate was about 7 L/min with sampling times of from 10 to 15 min.

RESULTS AND DISCUSSION

All of the air samples collected in this Plant contained N-nitrosomorpholine (NMOR) and 11 of them contained measurable amounts of N-nitrosodimethylamine. The NMOR amount ranged from 0.10 $\mu g/m^3$ to almost 4 $\mu g/m^3$ for the area air samples (Table 33). The NMOR levels found in the air in close proximity to specific processes ranged from 0.4 $\mu g/m^3$ to 9.2 $\mu g/m^3$ (Table 34). In the four process air samples, N-nitrosodimethylamine was found as high as 2.0 $\mu g/m^3$. A bias belted tire was removed from the curing mold and an air sample taken inside the body of the hot tire, NMOR was found at the 1.5 $\mu g/m^3$ and NDMA at 0.6 $\mu g/m^3$.

Samples No. 20 and No. 21 were both taken at the same tuber (1010 tire tread extruder). Sample No. 21 was taken inside the hopper where the rubber from the warm up mill enters the extruder while sample No. 20 was taken at the exit of the extruder where the extruded tire tread emerges. The levels found in these samples ranged from 1.5 to 9.2 $\mu g/m^3$ for NMOR and from ND (Not Detected) to 2.0 $\mu g/m^3$ for NDMA. The air at the entrace of the hopper contained less nitrosamines than did the air at the extruder exit.

In all cases the highest levels of nitrosamines were associated with both heating and increasing the surface area of the rubber stock.

Table 33

Results of Area Air Samples Plant F

			Nitrosamines in $\mu g/m^3$	
Sample No.	Sample Type	Location	NDMA	NMOR
1	Tenax	On top of 1010 extruder	NA	NA
2	Tenax	On top of 1010 extruder	NA	NA
12A	ThermoSorb/N	4 roll fabric calendar pull rod stand	0.16	0.17
12B	1N KOH	" "	0.18	0.08
13A	ThermoSorb/N	1010 extruder	0.15	3.9
13B	1N KOH	" "	0.10	3.2
14A	1N KOH	Banbury dump mill	ND	0.65
14B	1N KOH	" "	0.1	0.90
15A	ThermoSorb/N	Center of small tire curing	0.03	1.5
15B	1N KOH	" "	0.05	0.55
16A	ThermoSorb/N	Between curing press RC & QU	ND	0.62
16B	1N KOH	" "	UNK	UNK
17A	ThermoSorb/N	Roof of building E	ND	0.02
17B	1N KOH	" "	ND	ND

NA - Not Analyzed (sample saved for GC-MS analysis)

ND - None Detected - detection limit 0.05 $\mu g/m^3$ depending upon volume of air sampled.

UNK - lost sample

Table 34

Results of Process Air Samples Plant F

Sample No.	Sample Type	Location	Nitrosamines in µg/m^3 NDMA	Nitrosamines in µg/m^3 NMOR
18	ThermoSorb/N	4 roll gum calendar stock F32/F72 in process probe is 6" from rubber on rolls	0.16	2.9
19	ThermoSorb/N	No. 4 banbury drop chute from mezzanine level. Mixing T-26 snow tread stock at time of sample	ND*	0.41
20	ThermoSorb/N	Probe located 18" from exit of 1010 extruder and 3-4" from rubber stock T26/T55 being extruder (radial snow tread)	2.0	9.2
21	ThermoSorb/N	1010 extruder where rubber stock enters the hopper	ND	1.5
22	ThermoSorb/N	4.5/4.5 duplex extruder side wall tuber. At time of sampling T47/T55 radial side wall being extruded	1.4	1.1
23	ThermoSorb/N	Sample taken inside a bias belted tire. The tire had just been removed from a curing press	0.6	1.5

* ND - None Detected, detection limit 0.05 µg/m^3 (NDMA).

RUBBER PLANT G

The major products of this Plant are passenger tires, truck tires, recreational vehicle tires and mining tires. The original buildings were constructed in the 1890's and additions were added to them in 1942. The total floor size of the Plant is 1,656,896 sq. ft. This Plant employs 1736 people, of these, 1450 people work in production and 286 in administration. The Plant operates three shifts, five days a week.

SAMPLING STRATEGY

The principle areas surveyed for N-nitroso compounds were extruding and curing, however, air samples were also collected near surfaces of hot tires as they were released from the curing presses. This survey attempted to determine not only the amount of N-nitroso compounds in the area samples but also where in the process they may be coming from. To accomplish this air samples were collected close to suspected processes and area air samples near these proceses.

Air Samples

On September 22, 1978, a total of 21 air samples were collected at this Plant. Fourteen of these samples were area air samples collected by the use of ThermoSorb/N air sampling cartridges and 1N KOH solution. Two of these samples were collected by the use of Tenax™-GC solid sorbent. The other seven air samples were all collected close to specific processes.

The ThermoSorb/N cartridges were used with both the Bendix C115 air pumps and a 10 L/min metal bellows pump equipped with a Hastings mass flow meter. The air flow rates ranged from 2 L/min to 7 L/min depending upon the pumps used.

The Tenax-GC tubes were mounted on Bendix C115 pumps and air was drawn through them at about 3 L/min for about 3 hours. The Tenax-GC tubes consisted of glass tubes 20 mm x 80 mm packed with Tenax-GC solid sorbent. The Tenax-GC samples were collected on the first floor of Building No. 27 next to the No. 8 tuber, directly adjacent to samples No. 25A and No. 25B.

Twelve of the air samples consisted of side-by-side sets of ThermoSorb/N air sampling cartridges and 1N KOH traps. These sets of pumps were used as area air samplers and were operated at 2-3 L/min for about 3 hours. The remaining 7 air samples were collected using ThermoSorb/N cartridges and a high volume air pump. The average air flow rate was about 7 L/min with sampling times of from 10 to 15 min.

RESULTS AND DISCUSSION

Six of the 12 area air samples contained N-nitrosomorpholine (NMOR) ranging in amount from 0.03 $\mu g/m^3$ to 0.60 $\mu g/m^3$ (Table 35). Two of the samples also contained measurable amounts of N-nitrosodimethylamine (NDMA). In samples Nos.

25A and 25B N-nitrosodiethylamine (NDEA) was also found. The amount of NDEA found in sample No. 25A was 1.4 μg/m^3 compared to 0.13 μg/m^3 for No. 25B.

Four of the seven process air samples contained NMOR with amounts ranging from 0.73 μg/m^3 to 22.0 μg/m^3 (Table 36). The highest levels of 22 μg/m^3 was found near the No. 2 extrusion head. A sample taken directly on the surface of a hot recreational vehicle tire contained 1.4 μg/m^3 NMOR (Table 36). In all cases, the highest levels of nitrosamines were associated with processes involving both heating and increasing the surface area of the rubber stock. Analysis of some of the air samples by both GC-TEA and HPLC-TEA has detected several unknown TEA responsive compounds. Thirteen of the 19 air samples analyzed by GC-TEA, were found to contain two unknown peaks, one of which eluted from the GC-column between NDPA (N-nitrosodipropylamine) and NDBA (N-nitrosodibutylamine). When compared to NDPA the concentration of this unknown ranged from 0.1 μg/m^3 to 15 μg/m^3. The second unknown peak eluted from the GC after N-nitrosomorpholine, however, no attempt was made to quantitate this compound. A composite of the air samples was evaporated to dryness and the residue re-dissolved in DCM and analyzed by GC-TEA - no peaks were observed, i.e. the volatile compounds including the nitrosamines were lost during the evaporating. A fraction of this residue was adjusted to pH 3 and sodium nitrite added. Analysis of this reaction mixture revealed the presence of 4 peaks (N-nitrosodiethylamine) NDEA, (N-nitrosomorpholine) NMOR and 2 other peaks corresponding in retention time to the two unknown compounds. This test indicated the presence of nonvolatile nitrosamine precursors in the sample and that the two unknown TEA responsive compounds are indeed nitrosation products.

Table 35

Results of Area Air Samples - Rubber Plant G

Sample No.	Sample Type	Location	Nitrosamines in µg/m^3 NMOR	Other Nitrosamines
1	Tenax™	First floor, bldg. #27 near #8 tuber	NA	NA
2	Tenax™	First floor, bldg. #27 near #8 tuber	NA	NA
25A	ThermoSorb/N	First floor, bldg. #27 near #8 tuber	0.38	1.41 NDEA*
25B	1N KOH	" "	0.18	.13 NDEA
26A	ThermoSorb/N	D-unit near #39, #40	N.D.	N.D.
26B	1N KOH	" "	N.D.	N.D.
27A	ThermoSorb/N	#2 extruder, bldg. #27	0.49	N.D.
27B	1N KOH	" "	0.53	0.03 NDMA
28A	ThermoSorb/N	#4 tuber extruder	0.60	N.D.
28B	1N KOH	" "	N.D.	N.D.
29A	ThermoSorb/N	A-unit bldg. 28 near bagamatic presses	N.D.	N.D.
29B	1N KOH	" "	N.D.	N.D.
30A	ThermoSorb/N	C-unit row 5 near 9 and 10 heater room	0.03	N.D.
30B	1N KOH	" "	N.D.	N.D.

NA - Not Analyzed (sample saved for GC-MS analysis).

N.D. - None Detected, Detection Limit 0.01 µg/m^3 (NDMA).

* NDEA - N-nitrosodiethylamine

A & B samples are side-by-side samples.

Table 36

Results of Process Air Samples-Rubber Plant G

Sample No.	Sample Type	Location	NMOR $\mu g/m^3$
31	ThermoSorb/N	No. 8 extruder stock 10566/12605 in process	N.D.
32	ThermoSorb/N	No. 7 extruder stock 12766/13405	N.D.
33	ThermoSorb/N	No. 12 extruder head DTW extrusion stock 14005/14126	22.0*
34	ThermoSorb/N	Building 33, No. 40 press mining tires, tire size 15219-525	N.D.
35	ThermoSorb/N	No. 2 tuber warm up mill stock B20 14005/4	0.73
36	ThermoSorb/N	On surface of hot RV tire tire code 6479-762-RV	1.37
37	ThermoSorb/N	No. 4-T center stock feed mill stock 42066	0.97

N.D. - None Detected, detection limit 0.1 $\mu g/m^3$ (NMOR).

* HPLC-TEA analysis confirmed the presence of this compound.

RUBBER PLANT H

This tire plant produces bias-ply passenger, truck, and off-road tires 24 hours per day, 7 days per week. On the average, the Plant uses 6000 batches of rubber per month for passenger and off-road tires, and 2000-2,500 batches per month for truck tires. Batch weights range between 400-500 pounds each. During the manufacture of truck tire tread and bias-ply rubber approximately two pounds of NDPhA, a retarding agent which controls the time of rubber cure, are added to each rubber batch. In August 1979, short term workplace air samples (approximately 2 to 3 hours) of truck tire rubber batches were collected. On subsequent visits workplace air sampling was longer (approximately 5 to 7 hours), and included passenger tire rubber batches (65 to 75 percent of all batches sampled) which did not contain NDPhA. Nitrosamines found during these surveys were primarily in "hot process" areas where rubber is heated by friction and compression from milling, extruding, and curing operations. The milling and calendering temperatures range from 200-230°F, while extruding and curing operations range from 300-350°F. The term "process sampling" used in this report, refers to workplace air samples collected approximately one foot away from a tire manufacturing process. The word "calendering" refers to the sandwiches rubber onto nylon fabric to make the plies for bias-ply tires.

This study covers four separate survey visits made to this single tire plant. The results strongly suggest that NMOR may be generated by transnitrosation of morpholine by NDPhA when these two chemicals are used together. The chemical structure of four nitrosamine compounds found in this tire plant and three typical vulcanization accelerators and stabilizers used in the tire industry are in Figure 12.

Efforts to improve the worker environment through engineering controls and chemical substitution, and the results of a brief survey of biological samples (blood, urine, and feces) obtained from the workers during two of the NIOSH visits are also reported.

SAMPLING STRATEGY

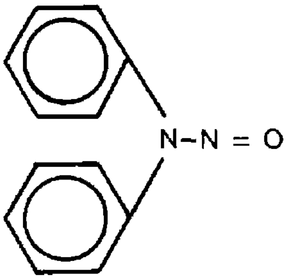
Air Samples

Airborne nitrosamines were collected with ThermoSorb™/N air samplers connected to battery-operated pumps (DuPont model P4000) which had been calibrated using 500 ml bubble burettes. The pumps were operated between 1.5 and 3.0 l/min. Air sampling times ranged from 1 to 8 hours. The air collectors were tightly capped and returned to the laboratory for analysis of nitrosamines. They were eluted with 2 ml of methanol:dichloromethane (1:3, v/v) - and directly injected into a gas chromatograph (GC) and/or high performance liquid chromatograph (HPLC), each equipped with a TEA™ Analyzer.

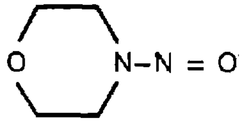
Biological Samples

Biological sampling was attempted at this plant because it had the highest levels of nitrosamines. There were three types of biological samples obtained from workers at the plant: urine, whole blood and feces. All urine and blood

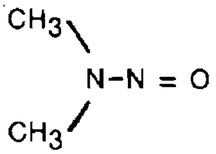
NITROSAMINES



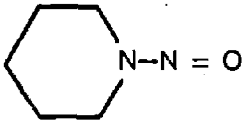
N-Nitrosodiphenylamine



N-Nitrosomorpholine

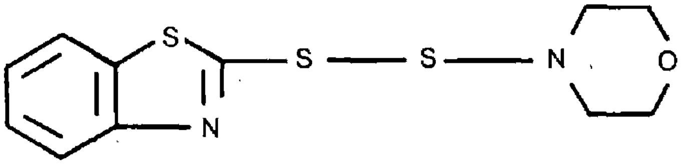


N-Nitrosodimethylamine

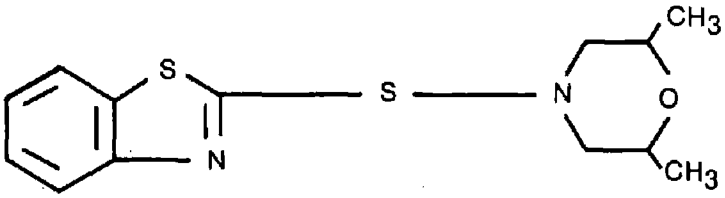


N-Nitrosopyrrolidine

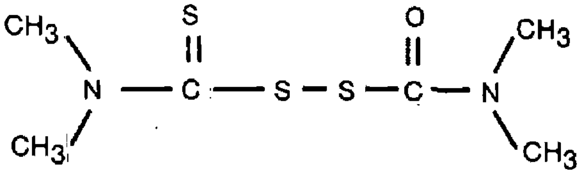
VULCANIZATION ACCELERATORS



4-Morpholino 2 Benzothiazole Disulfide



2(2,6-Dimethyl,4 Morpholinethio) Benzothiazole



Tetramethylthiuramdisulfide

Figure 12. N-nitrosamines Found in the Air of Rubber Plant H and Some Typical Vulcanization Accelerators and Stabilizers Used in the Tire Industry

samples were internally "spiked" at the factory with 1 μg/ml of a nitrosopiperidine (NPiP) standard. NPiP was used for spiking because it has a similar stability and recovery characteristic to nitrosomorpholine, and to provide a means of gauging the accuracy of the analytical methods. Due to the inability to perform homogenous mixing on site, the feces samples were not spiked until they were thawed upon return to the laboratory. Ethyl acetate extracts of urine samples were examined for the presence of N-nitrosodiethanolamine (NDElA), a metabolite of NMOR, by HPLC-TEA. All samples were immediately frozen at the plant (-80°C) and kept at this temperature until analysis.

Urine Samples

Analysis for NMOR. Ten ml of thawed urine were placed on a Preptube™ cartridge (Thermo Electron Corp.) and eluted with 60 ml of dichloromethane (DCM). The Preptube was pre-wet with DCM before receiving the sample. The resulting solution was concentrated to a volume of 1 ml at 55°C using a Kuderna-Danish apparatus. The concentrate was analyzed for NMOR by GC-TEA. Recoveries of the internal standard (NPiP) were typically 80-100%

Analysis of NDElA. Ten ml of the thawed urine were placed on another Preptube, pre-wet with ethyl acetate. The sample was washed with 60 additional milliliters of ethyl acetate and the effluent dried (rotary evaporator) to 1 milliliter. It was then analyzed by HPLC-TEA using a HN_2 column eluted with isooctane:dichloromethane:methanol (60:30:7). Recoveries for NDElA using this method were approximately 70%. The percent recovery was judged by an internal spike of N-nitrosodipropanolamine.

Blood Samples

Ten ml blood samples were analyzed for NMOR, using the method described for urine samples. Recoveries of the NPiP standard were more variable, ranging from 32 to 87%.

Fecal Samples

Twenty to 45 grams of samples were weighed out and ground to a fine powder in a blender containing liquid nitrogen. The resulting homogenate was placed in a 500 ml distillation flask with 50 milliliters of mineral oil (containing 1 mg/ml of -tochoperol (to prevent nitrosation during distillation) and allowed to thaw. The contents of the flask were mixed with 500 ng of NPiP to determine the recovery of the method. The feces samples were distilled under a vacuum of 2.2 torr at up to 130°C for 1 hour. Recoveries of NPiP were low, approximately 20%.

RESULTS AND DISCUSSION

Air Samples

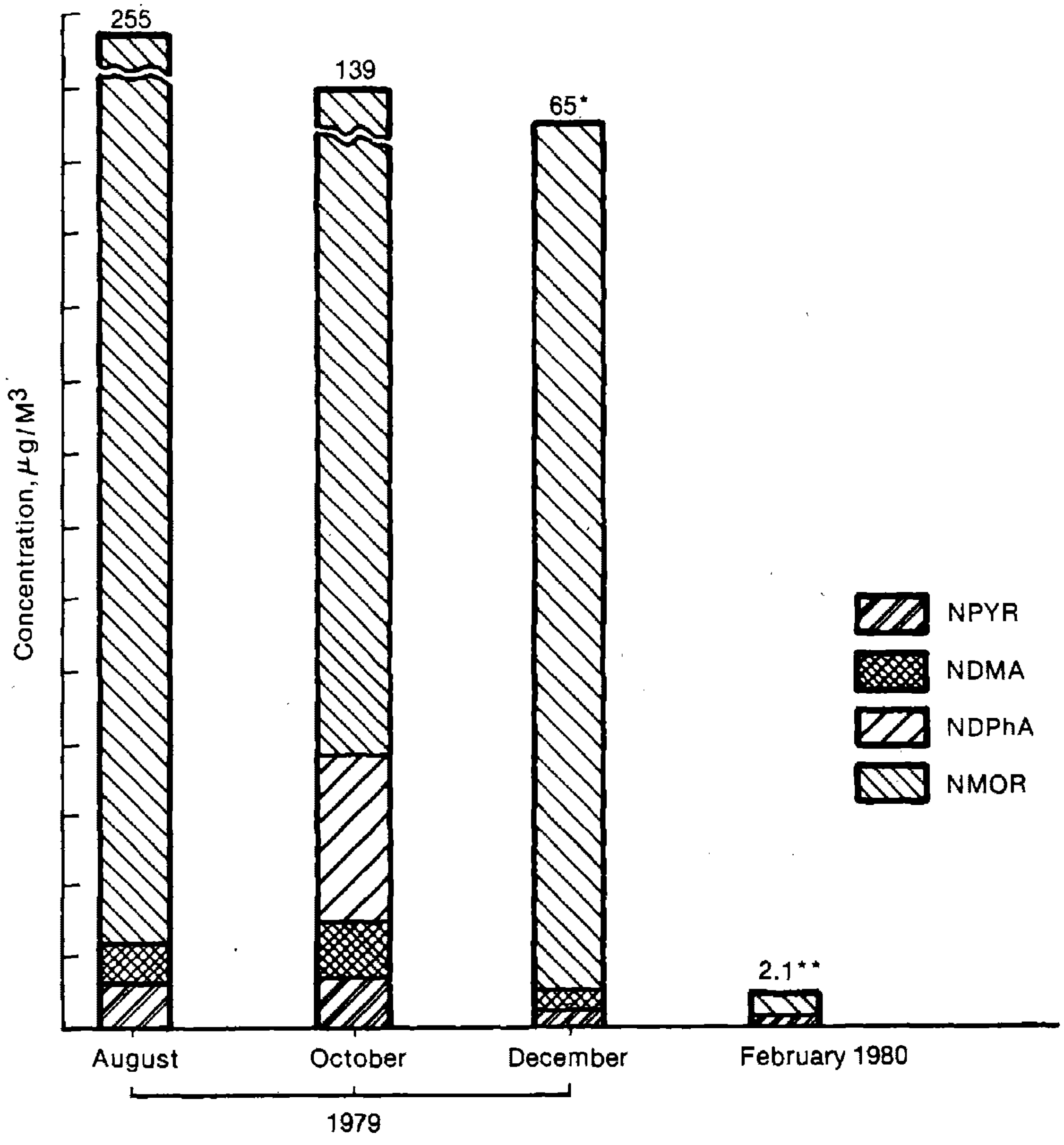
Airborne levels of NMOR, NDMA, and NPYR were found during the first visit to this tire manufacturing plant. One process air sample, collected at a feedmill, contained 250 $\mu g/m^3$ of NMOR. Maximum concentrations of NDMA and NPYR found in the hot process area were 4.4 $\mu g/m^3$ and 3.4 $\mu g/m^3$, respectively. Over the following 7 months, ventilation improvements and changes in chemical formulation of the rubber resulted in a 200-fold reduction in NMOR levels and elimination or reduction of other nitrosamines at most sites. Results are shown in Figure 13 and Table 37.

Personal (breathing zone) air samples obtained in October 1979, showed feed mill and calendering operators to be most heavily exposed to nitrosamines; one worker had a time-weighted average NMOR exposure of 25 µg/m^3. Workers in other hot processes such as warm-up mills, extruding machines, and curing processes were determined to have substantial personal exposure to airborne nitrosamines (Table 38). Personal exposures to airborne NMOR and NDMA were also detected in the truck tire building and tire shipping area. Although these nitrosamine levels are not very high (1.9 µg/m^3, 0.1 µg/m^3 NDMA), they demonstrate the residual effect of nitrosamines still volatilizing off from storage of freshly cured tires. When compared to passenger tire builders, truck tire builders on the average had 3 times the NMOR exposure even though 4 to 5 passenger tires could be built to every truck tire.

By November, 1979, there were strong indications that the source of the high levels of airborne NMOR was the thermal decomposition of the retarding agent NDPhA, and the subsequent reaction of its nitroso group with other rubber additives (preformed morpholine compounds). The results were most striking when two short term air samples were collected from the feedmill and calendering area - one rubber batch contained NDPhA, and the other did not. NMOR levels from the NDPhA batch were 14 times higher (120.3 µg/m^3) than the rubber batch without NDPhA. In December 1979, ventilation improvements (3-sided canopy enclosures and new fan motors) to the feed mills which process rubber for the calendering of bias-plies, and installation of local exhaust on the top and bottom of the tire tread extrusion machines, significantly reduced airborne nitrosamine exposure (Tables 37,38). By February 1980, a phthalimide derivative was substituted for NDPhA. In the feed mill and calendering area, this resulted in a 99.5% NMOR reduction in process sample concentration when compared to the August 1979 results, and a 96% NMOR reduction in the highest personal exposure when compared to the October results. In the same area, NPYR, which had measured 3.4 µg/m^3 in August and 3.9 µg/m^3 in October, was not detectable after removal of NDPhA. In general, the NPYR levels usually were detected when high levels of NMOR were found and were not detectable when NMOR levels diminished. The appearance and disappearance of NPYR seemed to be related to NDPhA, but the source of NPYR in these samples is not yet known. NDMA levels did not decrease substantially between August 1979 and February 1980. In fact, NDMA and NMOR levels increased slightly in the tire tread warm-up mill area. We suspect that the reason for the increase is due to a higher percentage of rubber stock containing NDMA additives on the day it was sampled, and also due to the continued use of NDPhA in truck tire tread.

NDPhA was detected in one process sample on the second survey and in two personal samples on the third survey. The fact that NDPhA was not detected more frequently was probably due to its high molecular weight and relatively low volatility.

On the fourth survey, process and personal nitrosamine samples were collected from rubber batches made at a Banbury (rubber batch mixer), where only



*Local exhaust improved - canopy inclosed on three sides.
**Rubber formulation change, N-Nitrosodiphenylamine not used.

Figure 13. Highest Reported Airborne N-Nitrosamine Levels in Feedmill and Calendering Area of Plant H

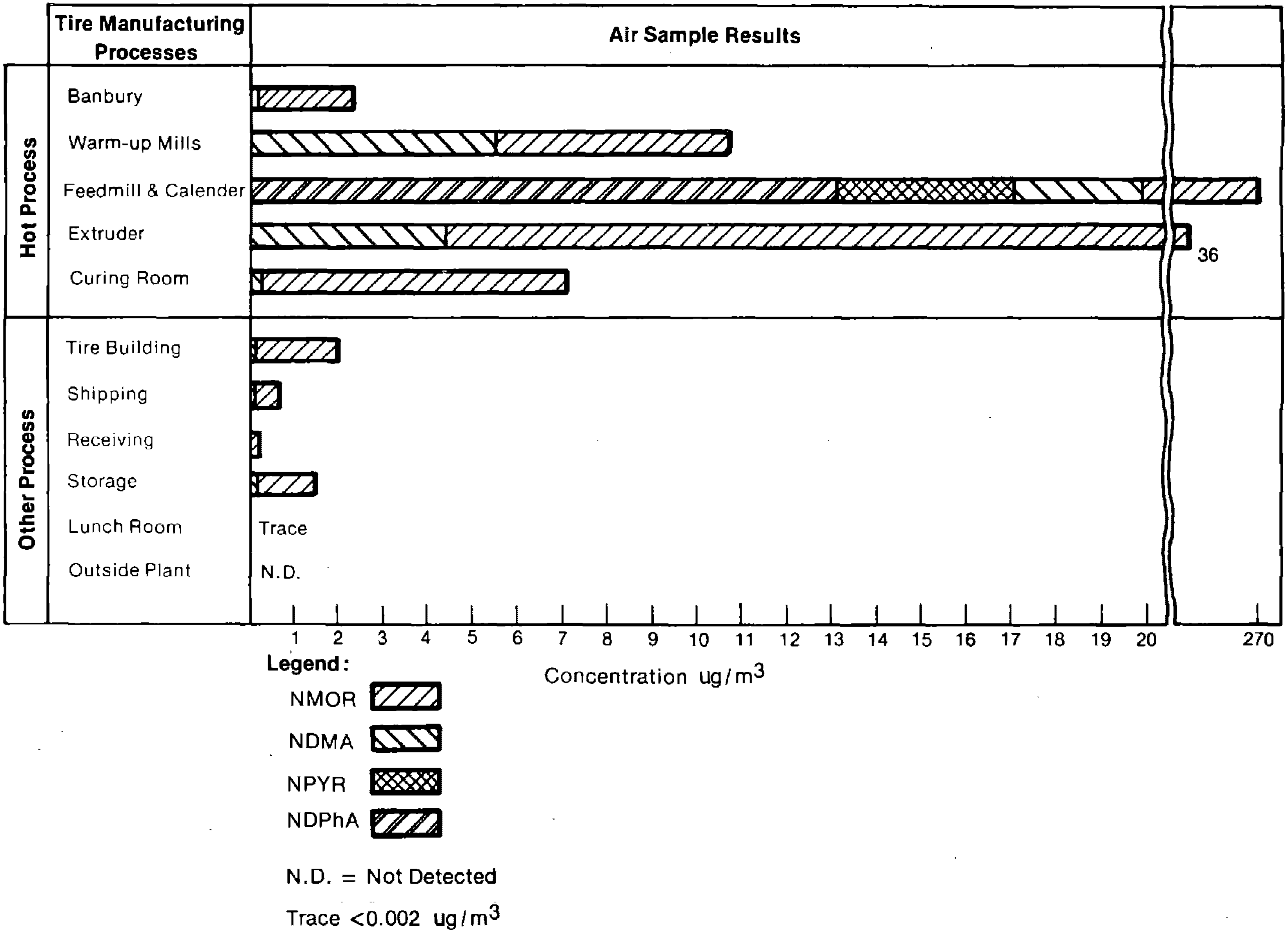


Figure 14. Concentration in $\mu g/m^3$ of N-Nitrosamine Found in Area Air Samples at Various Tire Manufacturing Processes in Rubber Plant H

Table 37
Area and Air Process Samples in $\mu g/m^3$
Rubber Plant H

Location	Nitrosamines	Aug. '79		Oct. '79		Dec. '79		Feb. '80	
		Highest/	Avg.	Highest/	Avg.	Highest/	Avg.	Highest/	Avg.
Banbury	NMOR	2.1	1.8	N.S.[2]	---	N.S.	---	0.3	---
	NDMA	0.1	---	N.S.	---	N.S.	---	0.1	---
	NPYR	N.D.[1]	---	N.S.	---	N.S.	---	N.D.	---
	NDPhA	N.D.	---	N.S.	---	N.S.	---	N.S.	---
Feed Mill & Calender	NMOR	250	160	120	64	63	25	1.3	1.0
	NDMA	1.9	1.5	2.9	1.6	1.1	0.4	0.8	0.3
	NPYR	3.4	2.3	3.9	2.0	1.0	0.6	N.D.	---
	NDPhA	N.D.	---	12	---	N.S	---	N.D.	---
Warm-up Mills	NMOR	5.2	3.5	N.S.	---	N.S.	---	14	4.6
	NDMA	0.7	0.4	N.S.	---	N.S.	---	5.5	2.7
	NPYR	N.D.	---	N.S.	---	N.S.	---	N.D.	---
	NDPhA	N.D.	---	N.S.	---	N.S.	---	N.D.	---
Extruders	NMOR	32	18	N.S.	---	N.S.	---	N.S.	---
	NDMA	4.4	---	N.S.	---	N.S.	---	N.S.	---
	NPYR	N.D.	---	N.S.	---	N.S.	---	N.S.	---
	NDPhA	N.D.	---	N.S.	---	N.S.	---	N.S.	---
Curing Room	NMOR	6.4	5.3	2.0	---	N.S.	---	N.S.	---
	NDMA	0.2	0.2	0.1	.07	N.S.	---	N.S.	---
	NPYR	N.D.	---	N.D.	---	N.S.	---	N.S.	---
	NDPhA	N.D.	---	N.D.	---	N.S.	---	N.S.	---
Tire Storage	NMOR	N.S.	---	0.6	---	N.S.	---	N.S.	---
	NDMA	N.S.	---	0.1	---	N.S.	---	N.S.	---
	NPYR	N.S.	---	N.D.	---	N.S.	---	N.S.	---
	NDPhA	N.S.	---	N.D.	---	N.S.	---	N.S.	---
Lunch Room	NMOR	N.S.	---	Trace	---	N.S.	---	N.S.	---
	NDMA	N.S.	---	.02	---	N.S.	---	N.S.	---
	NPYR	N.S.	---	N.D.	---	N.S.	---	N.S.	---
	NDPhA	N.S.	---	N.S.	---	N.S.	---	N.S.	---
Outside Plant	NMOR	N.S.	---	N.D.	---	N.S.	---	N.S.	---
	NDMA	N.S.	---	N.D.	---	N.S.	---	N.S.	---
	NPYR	N.S.	---	N.D.	---	N.S.	---	N.S.	---
	NDPhA	N.S.	---	N.D.	---	N.S.	---	N.S.	---

NMOR = N-nitrosomorpholine, NDMA = N-nitrosodimethylamine, NPYR = N-nitrosopyrrolidine, NDPhA = N-nitrosodiphenylamine

[1] N.D. = Not detected

[2] N.S. = Not sampled

Trace <.002 $\mu g/m^3$

Detection limit: 1 part per billion

Table 38
Personal Samples in μg/m^3
Rubber Plant H

Location	Nitrosamines	Oct. '79		Dec. '79		Feb. '80	
		Highest/Avg.		Highest/Avg.		Highest/Avg.	
Banbury	NMOR	N.D.[1]	---	N.S.[2]	---	N.S.	---
	NDMA	N.D.	---	N.S.	---	N.S.	---
	NPYR	N.D.	---	N.S.	---	N.S.	---
	NDPhA	N.D.	---	N.S.	---	N.S.	---
Feed Mill & Calender	NMOR	25	17	18	17	1.0	0.1
	NDMA	0.4	0.3	0.1	0.1	0.2	0.1
	NPYR	0.8	0.5	0.2	0.2	N.D.	N.D.
	NDPhA	N.D.	N.D.	13	9.9	N.S.	N.S.
Warm-up Mills	NMOR	0.8	0.8	N.S.	---	1.3	1.0
	NDMA	0.2	0.1	N.S.	---	0.5	0.4
	NPYR	N.D.	---	N.S.	---	N.D.	---
	NDPhA	N.S.	---	N.S.	---	N.D.	---
Extruders	NMOR	1.0	---	N.S.	---	N.S.	---
	NDMA	0.1	---	N.S.	---	N.S.	---
	NPYR	N.D.	---	N.S.	---	N.S.	---
	NDPhA	N.D.	---	N.S.	---	N.S.	---
Curing Room	NMOR	1.8	---	0.4	---	N.S.	---
	NDMA	0.1	---	0.3	---	N.S.	---
	NPYR	N.D.	---	N.D.	---	N.S.	---
	NDPhA	N.S.	---	N.S.	---	N.S.	---
Tire Building	NMOR	1.9	1.6	N.S.	---	N.S.	---
	NDMA	0.1	0.1	N.S.	---	N.S.	---
	NPYR	N.D.	---	N.S.	---	N.S.	---
	NDPhA	N.S.	---	N.S.	---	N.S.	---
Shipping	NMOR	0.6	---	1.7	1.3	N.S.	---
	NDMA	.04	---	0.1	0.1	N.S.	---
	NPYR	N.D.	---	N.D.	---	N.S.	---
	NDPhA	N.S.	---	N.S.	---	N.S.	---
Receiving	NMOR	N.D.	---	0.3	---	N.S.	---
	NDMA	N.D.	---	N.D.	---	N.S.	---
	NPYR	N.D.	---	N.D.	---	N.S.	---
	NDPhA	N.S.	---	N.S.	---	N.S.	---
Tire Storage	NMOR	N.S.	---	0.7	---	N.S.	---
	NDMA	N.S.	---	0.1	---	N.S.	---
	NPYR	N.S.	---	N.D.	---	N.S.	---
	NDPhA	N.S.	---	N.S.	---	N.S.	---

NMOR = N-nitrosomorpholine, NDMA = N-nitrosodimethylamine, NPYR = N-nitrosopyrrolidine, NDPhA = N-nitrosodiphenylamine

[1] N.D. = Not detected

[2] N.S. = Not sampled

starting ingredients such as natural and synthetic rubber, and waxes, were mixed. No retarding, accelerating, or stabilizing additives were added during this phase of mixing. The purpose of the environmental sampling was to determine if nitrosamines were being generated without rubber additives. Four samples were collected: three process, one personal. NMOR and NDMA were detected in two of the four samples, but at very low levels. The highest NMOR process sample was 0.27 $\mu g/m^3$, and 0.09 for NDMA. The personal sample was 0.24 $\mu g/m^3$ and 0.12 $\mu g/m^3$ for NMOR and NDMA, respectively. Thus, it seems that the majority, if not all of the nitrosamines are derived from rubber additives, either as a raw chemical contaminant, and/or from transnitrosation of various compounds during the final mixing and tire manufacturing stage.

In summary, nitrosamines were detected in every area of the tire plant sampled. Only outside the plant, next to the guard house, nearly 400 yards away, were nitrosamines not detected. Generally, highest nitrosamine levels were in the hot process areas, in particular, the feedmill and calendering area. With the exception of the guard house, the lowest nitrosamine levels found were in the receiving area (0.3 $\mu g/m^3$ NMOR) and lunch room (trace <.002 $\mu g/m^3$ NMOR). Results from the nitrosamine levels found throughout the plant, and over the past four surveys are in Figure 14. The tire building and tire storage areas were the only locations where appreciable NMOR levels were still off-gasing, after the tires had been cured. Personal NMOR exposures of truck tire builders were 3 times higher than personal NMOR exposures of passenger tire builders. NDMA, however, did not decrease in the tire tread warm-up mill area because there were no significant ventillation improvements and NDPhA continued to be used for truck tire tread. Nitrosamine results from rubber batches withoutadditives seems to indicate that natural and synthetic rubber, and other basic ingredients are not sources of significant levels of nitrosamines. Finally, over a 7-month period, process sample NMOR levels decreased 200-fold and personal sample NMOR exposure in the feedmill and calendering are decreased by 96%. NPYR was reduced to non-detectable levels. The reduction was due to improved ventilation and substitution of NDPhA with a phthalimide derivative.

Biological Samples

In December 1979, urine, and either blood, or stool specimens were collected from 15 non-smoking workers at the end of their work shift. Based upon environmental results from the previous two surveys, workers were selected according to high, medium and low nitrosamine exposure. The high exposure area was the feedmill and calendering area. The medium exposure areas were the truck tire tread warm-up mills, truck tire tread extrusion area, truck tire curing presses, and truck tire building area. The low exposure areas were receiving, shipping, passenger tire building, and Banbury area. Workers donating specimens for nitrosamine analysis were selected from at least one of these varied exposure areas. Results of analyses for nitrosamines were negative for all samples (detection limit = 1 ppb). Breathing zone nitrosamine measurements were taken simultaneously for all workers volunteering biological specimens. The time-weighted average (TWA) exposure for these workers ranged from 18.2 $\mu g/m^3$ to 0.78 $\mu g/m^3$ for NMOR; from 0.180 $\mu g/m^3$ to non-detectable for NDMA; and from 0.228 $\mu g/m^3$ to non-detectable for NPYR.

In February 1980, urine samples were obtained from nine workers for mutagenicity testing by the Ames Salmonella test. Four hundred milliliters from each specimen were put through an XAD-2 column and the adsorbed material was eluted. Methylene chloride extracts of the post-column urine eluate were made and tested for mutagenicity with the Salmonella/Mammalian Microsome Mutagenicity test. The TWA breathing-zone concentrations for nitrosamines nitrosamines taken from six workers donating urine specimens ranged from 1.3 $\mu g/m^3$ to 0.64 $\mu g/m^3$ for NMOR; and from 0.49 to 0.16 $\mu g/m^3$ for NDMA. NPYR was not detected in any environmental samples. The remaining three urine specimens were taken from truck tire builders for the purpose of monitoring mutagenic activity resulting from possible skin absorption (hands and forearms) of nitrosamines. None of the samples tested were mutagenic.

The negative findings for nitrosamines in these biological samples may reflect the fact that they were collected only during the last two visits, at which time the airborne nitrosamine levels had been greatly reduced. For example, assuming a respiration rate of 10 liters per minute, even the most exposed workers during the third survey (18 $\mu g/m^3$) would have breathed approximately 1 μg NMOR per kilogram body weight per shift. NMOR is relatively lipophilic, but even if all of this nitrosamine had been absorbed and evenly distributed in all body components, and none metabolized or excreted during the shift, its concentrations in blood (a relatively aqueous medium) would be below our detection limit (1 ppb).

These results are generally in agreement with previous reports (21) that NMOR and NDMA are present in tire factories. NDPhA and NPYR are reported here for the first time as being also present in tire factory air. What is unique about this factory is that NMOR was found at 250 $\mu g/m^3$ - a level higher than any nitrosamine ever reported, at that time, in any industrial site - and that its formation depended upon the thermal decomposition of NDPhA and the subsequent reaction of its nitroso group with preformed morpholine compounds. Company management response was effective in reducing nitrosamine levels first through improved ventilation, then by reducing or eliminating the use of NDPhA. However, NDMA is still a problem since it has remained above 1 $\mu g/m^3$ despite process changes that reduced NMOR levels. Laboratory testing or commercial grade amines has shown NDMA to be present as a contaminant (141). Most recently, NDMA has been shown to be generated from heated rubber stock containing a rubber accelerator tetra-methyl thiuram disulfide (143). The precursor chemicals and bulk process samples from this factory environment have not, as yet, been tested to confirm that these are the sources of the NDMA found. Transnitrosation of the nitroso group from NDPhA is known to occur under a variety of conditions (65,66). The nitrosation of the accelerators and stabilizers used in vulcanization (which are designed to break apart at elevated temperatures yielding the amines) was expected.

A second source of nitrosamine formation could be nitrosation of amines by NO_x, which has been clearly demonstrated in laboratory experiments (54,94,95). In industrial processes, NO_x was shown to be responsible for nitrosation of amines in foodstuffs dried with gas-fired burners (144), and also for the appearance of nitrosamines in diesel engine crankcase emissions (145). It is possible the NO_x could be nitrosating the amine rubber additives. It has been speculated that the source of NO_x is from the combustion of gasoline-powered forklift trucks used to transport rubber from one work station to another. Unfortunately, NO_x levels were not measured during any of the surveys to test this hypothesis.

A number of epidemiological studies conducted in the tire industry have shown workers to be at excess risk for cancer (146-148). In particular, excess cancer of the stomach and lung has been found in "hot process" areas in the tire plants (148). Although the majority of N-nitroso compounds have been shown to be animal carcinogens, including all nitrosamines found in this plant, they have not been directly associated with human cancer because no definable exposed population groups have been identified. Assessing the cancer risk for nitrosamine exposure among tire workers is confounded by past exposure to potential carcinogenic agents such as asbestos, benzene, beta-naphthalamine, and polynuclear aromatic hydrocarbons from carbon black.

SUMMARY AND CONCLUSIONS OF THE RUBBER MANUFACTURING INDUSTRY

Eight facilities manufacturing rubber and related products were surveyed for worker exposure to N-nitroso compounds. Seven of these facilities were found to be contaminated with one or more of these compounds; N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosopyrrolidine (NPYR), N-nitrosomorpholine (NMOR), and N-nitrosodiphenylamine (NDPhA). All of these nitrosamines are known animal carcinogens. Six plants were contaminated with N-nitrosomorpholine, three with N-nitrosodimethylamine, two with N-nitrosodiphenylamine, one with N-nitrosodiethylamine and one with N-nitrosopyrrolidine. The most wide spread N-nitroso contaminant found in these plants was NMOR. This compound was found in air, soil, floor scraping, steam condensate and compounding chemicals.

Air samples containing NMOR varied in amount from just detectable (0.02 $\mu g/m^3$) to as much as 250 $\mu g/m^3$. The highest level discovered (751 $\mu g/g$) was found in a floor scraping taken inside a chemical plant (Rubber Plant C) that manufactured chemicals that are used in rubber products. The level of NMOR found in air samples taken in the rubber tire factories were highest near processes that heated the rubber stock. These hot processes include; Banbury mixing, milling, extrusion, calendering and tire curing, of these processes tire tread extrusion was consistently associated with the highest levels of airborne NMOR.

The finding of N-nitrosodiphenylamine (NDPhA) in a chemical plant (Rubber Plant C) that manufactured this compound was expected, however, the discovery of NMOR and NDMA in this plant was unexpected. The exact reason why these other N-nitroso compounds are in the air, soil, floor scraping and products of this plant are not known. It can be speculated that the morpholine and the dimethylamine used in Plant C could be nitrosated via transnitrosation or airborne nitrogen oxides to produce these N-nitroso derivatives. It was observed that the bismorpholinecarbamylsulfonamide (BMCS) (a morpholine containing compound) wet cake was dried in close proximity to the NDPhA reactor, this reactor used sodium nitrite and acid condition to make NDPhA. It was observed that nitrogen oxides from this reaction are released into the air near the BMCS wet cake drying area. It is possible that nitrosation reaction involving NO_x and either the BCMS or unreacted morpholine may result in the formation of NMOR. What ever speculated process is responsible for the nitrosamine contamination, it is clear that the needed precursor amines are present in this plant along with nitrosating agents.

Some of the compounding ingredients used in making rubber tires were found to contain NMOR as a contaminant. Analysis of 4 morpholinyl-2 benzothiazole disulfide (MBD), revealed the presence of 3 to 4 mg/kg of NMOR. This compound is formulated as an accelerator for the tire curing process. Rubber Plant E which has NMOR in its air, uses a similar morpholine type accelerator in its tire compounding. The annual use of this NMOR contaminated accelerator by Rubber Plant E was reported to be 0.25×10^6 kg. Vaporization of this NMOR contamination during heating or extrusion of rubber stock formulated with this curing accelerator may in part explain the occurrence of NMOR in the air at this plant. The free amine morpholine was also discovered as an impurity in these accelerators (9 g/kg). This amine when volatized into the air during tire production may contribute to the airborne NMOR via N-nitrosation by atmospheric nitrogen oxides. Rubber Plant G did not use morpholine type accelerators and, with few exceptions, was found to be relatively free of airborne contamination of NMOR. The most likely explanation for the high (250 $\mu g/m^3$) levels of NMOR in the air of Rubber Plant H is the transnitrosation of either morpholine or the compounded morpholine based accelerator by NDPhA. In those Plants that use NDPhA, transnitrosation may be the dominant reason for the nitrosamine found in them. A recent study of nitrosamine formation in compounded rubber conducted by the Rubber Manufacturers Association indicates that transnitrosation is a major factor.

Removing the NMOR and morpholine contamination from the rubber curing accelerator chemicals could reduce the airborne levels of NMOR. If further air sampling indicated that NMOR is still present in the air, then serious consideration should be given to the possibility that the morpholine released during curing or heating processes is reacting with airborne nitrogen oxides, or some, as yet, unidentified nitrosating agent. In Plant H, it was demonstrated that reformulation of the stock rubber to remove the NDPhA and better engineering controls substantially reduced the airborne nitrosamine levels.

THE LEATHER INDUSTRY

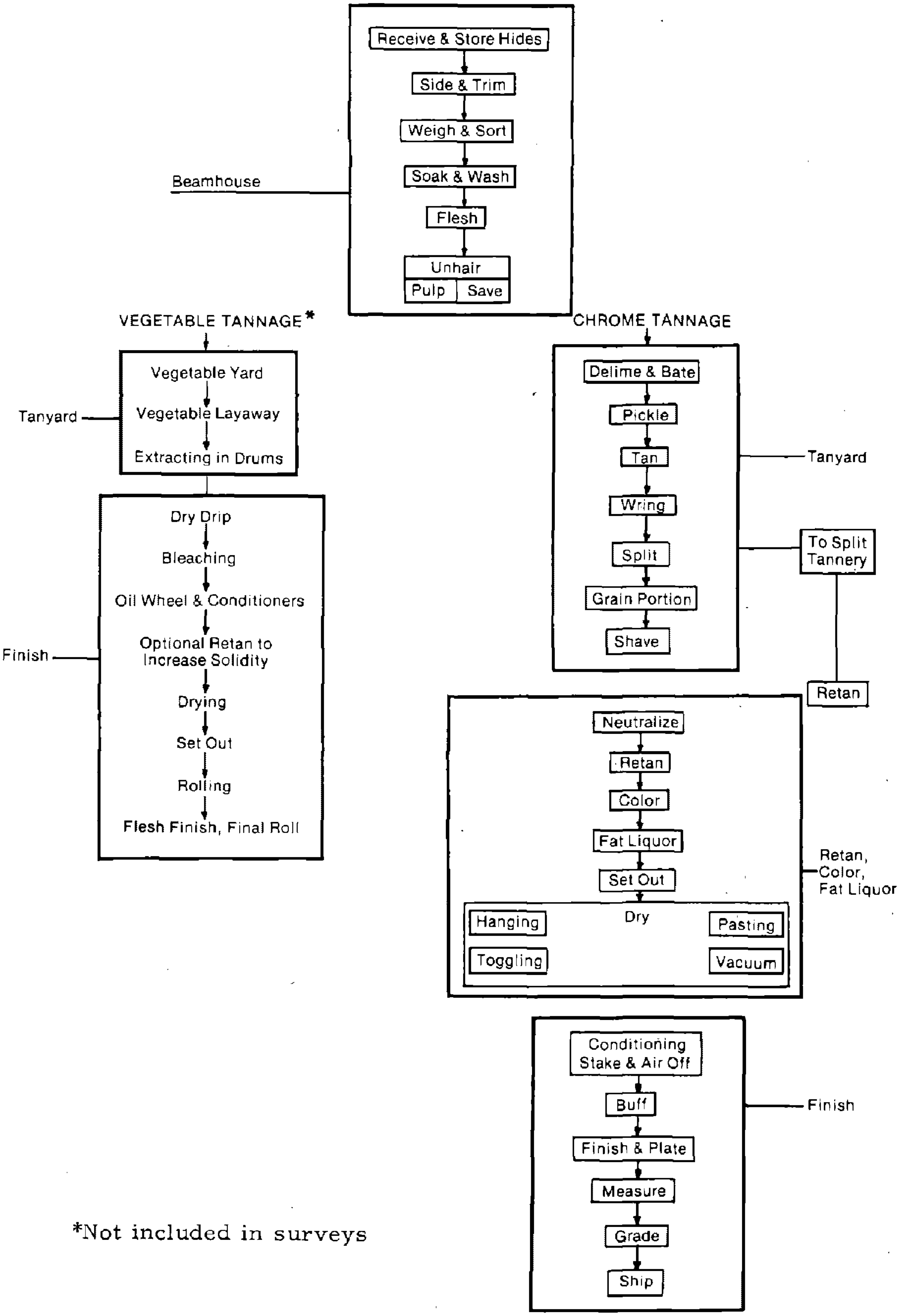
The activities of the leather industry included in this survey consisted of leather tanning, leather finishing, and a hand sewn shoe operation.

Several studies have indicated an increased risk of bladder and nasal cancer in the leather and leather products industries. The relative risk for bladder cancer for men employed in the leather industry was found to be 2.25 compared to a control population (129). In this same study, an excess (2.65) was associated with leather finishing and associated processes. An increased risk of nasal cancer was found among finishing room workers in the leather boot and shoe industry in England (130). The agents responsible for these cancer excesses have not been identified but it has been postulated (129) that a single adsorbable carcinogen may cause the tumors at the site of contact, the upper respiratory tract, and the site of excretion. In addition, amines such as dimethylamine sulfate are used in the manufacture of leather (19). These amines could be contaminated with nitrosamines or could give rise to these compounds. In the finishing operation of a tannery a great variety of chemicals including solvents and dye stuffs are used, some of these could be either contaminated with N-nitroso compounds or could serve as precursors.

GENERAL DESCRIPTION OF THE TANNING INDUSTRY

It has been estimated that as many as 25 million hides were processed in the U.S. in 1976 (131). In 1972 approximately 520 (132) tanneries were engaged in both the finishing and tanning operations. The leather tanning and finishing industry ranges from small one-man or family-owned companies, to large operations that are subsidiaries of even larger corporations. Most of these tanning and finishing operations are located in New England, mid-Atlantic states, New York and the Chicago - Milwaukee area. Over 35 states have one or more leather producing facilities (132). The total number of workers employed in the tannery industry has been estimated to be 25,700 with over 200 tanneries employing 20 or more workers (132).

The processing of hides and skins into leather requires over 300 separate chemical and mechanical operations (133). Some leather-making operations can be described as preparatory; that is, putting the skin into the proper conditions for a step in the process that is to follow. Others, on the other hand, affect major changes in the properties or appearance of the finished leather. All of these operations are interrelated in a step by step process from raw hides to the final product. Figure 15 outlines the typical process for tanning and finishing leather.



*Not included in surveys

Figure 15. Typical Process for Tanning and Finishing Leather

LEATHER TANNERY PLANT A

The facility was built during 1955 on the same site as a previous tannery. The plant site occupies 10 acres and has two major buildings with a total of 160,000 square feet and an enclosed air volume of about 110,000 cubic meters. The plant employs about 240 people in a three shift operation in the production area and 40 people in the administrative area. The only products of this plant are finished leather cow hides with an annual production of 500,000 hides. These hides are produced in a wide variety of colors with many different finishes and special treatments. The tannery building is a U-shaped structure with the salted hide receiving facilities at one end and the final finishing facilities at the other (Fig. 16). The tanning process is similar to the general tanning process that has been previously outlined. This study included the entire leather tanning and finishing production of this plant. Air samples were taken at all stages of the process. Bulk samples included; waste water, process water, some chemicals used in the process and samples of untanned and tanned cowhides.

The most likely source of nitrosamine contamination within this plant was the beam house where the secondary amine dimethylamine sulfate (DMAS) was being used in the unhairing process. Chemical agents which could serve to nitrosate the dimethylamine sulfate to form N-nitrosodimethylamine have not been identified as a part of this tanning operation. However, since many of the products used in the tanning process are complex mixes of chemicals marketed under trade names, these agents may be present as components or contaminants, or they may be present in the hides or process water.

SAMPLING STRATEGY

Air Samples

Six air samples were collected on April 11, 1978; one near the re-liming second unhairing process; one at the border between tanning and splitting and shaving; one at the end of the hide drying oven; one in the center of the paste wash off area; one located in the midst of the open drums of chemicals used in the doping area and one located near the spray finishing area. The six air samples represent a limited cross section of the air in the tannery.

N-nitrosodimethylamine (NDMA) was found in all of the air samples with amounts ranging from 6 $\mu g/m^3$ to 33 $\mu g/m^3$ (Table 39). The highest level of NDMA was found in sample No. 2 which was located at the border between tanning and splitting and shaving (Figure 16). The average amount of NDMA found in the plant air was 13 $\mu g/m^3$. The finding of this level of NDMA in the plant air engendered a return visit to the site. The plant was re-visited on April 13, 1978 at which time 20 air samples were taken. Sixteen air samples were taken using vacuum traps containing 45 ml each of 1N KOH and 4 air samples were taken using Tenax-GC cartridges. Three of the air samples (1N KOH traps) were placed outside on the perimeter of the plant grounds. The Tenax-GC cartridges were used to provide an alternative means of confirming the presence of NDMA in the plant air.

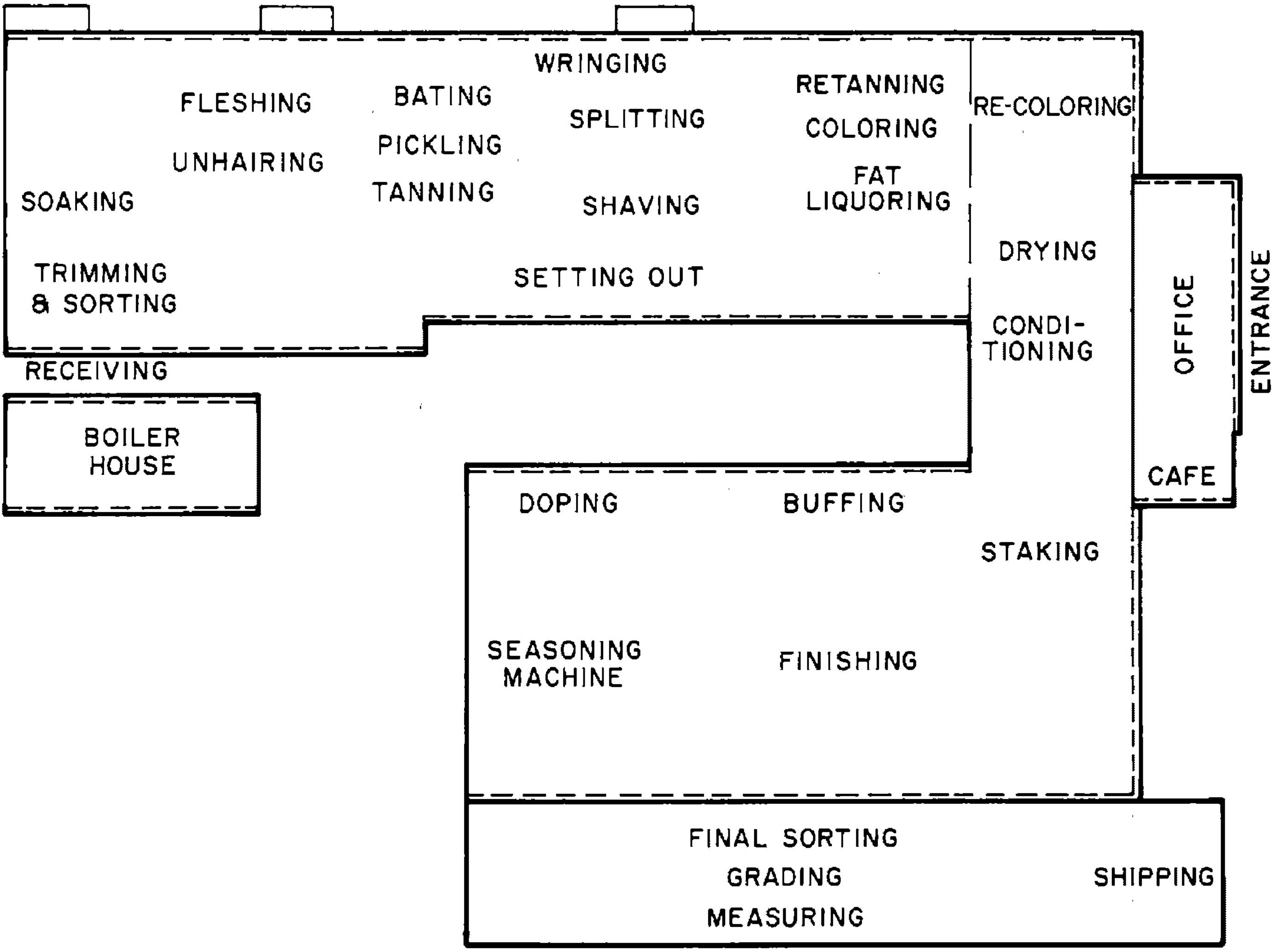


Figure 16. Process Flow Diagram for Leather Plant A

Analysis of the air samples taken on April 13, 1978 revealed the presence of NDMA in all the areas sampled with the exception of samples taken outside the plant. The NDMA levels ranged from nondetectable, less than 0.05 $\mu g/m^3$ outside the plant, to 47 $\mu g/m^3$ in the re-tanning area. The Tenax-GC cartridges were placed in two locations; the border between tanning and splitting (the high area of April 11, 1978), and doping area. The 2 Tenax-GC samples collected in the doping area contained 4 GC-TEA responsive peaks: NDMA and N-nitrosomorpholine (NMOR) were identified by GC-TEA and HPLC-TEA as two of the compounds. Air sample No. 5, a 1N KOH trap collected in the doping area on April 11, 1978, also contained 4 GC-TEA signals two of which were identified as NDMA and NMOR (2 $\mu g/m^3$) by GC-TEA and HPLC-TEA. The other two Tenax-GC sample tubes were sent to Research Triangle Park Institute for GC-MS analysis. These samples were lost due to damage in transit. The pertinent data for the air samples are described in Table No. 39. The names given to the sample location were supplied by plant personnel.

JUNE 1, 1978 SAMPLING

On June 1, 1978, the tannery was re-visited to gather further air and bulk samples from the tannery process. The purpose of this visit was: 1) to re-confirm the presence of N-nitrosodimethylamine (NDMA) in the air; 2) to obtain a sample of NDMA for gas chromatography mass spectral (GC-MS) analysis; 3) to attempt to determine if the air contained a nitrosating compound which could nitrosate other secondary amines in 1N KOH; 4) and to determine, if possible, the source of this compound. To this end, 14 area air samples and 14 bulk samples were collected and analyzed.

Samples were collected by drawing air at a rate of approximately 2 L/min through the following trap arrangement:

1. 45 ml of 1N KOH in glass impingers
2. 45 ml of 1N KOH spiked with 2 mg each of piperidine and pyrrolidine
3. 1N KOH traps with high volume air pumps which operate at a rate of 4 L/min.

The air traps containing 45 ml of 1N KOH are similar to the traps used on previous sampling visits. The 1N KOH traps with the 2 added nitrosatable amines were examined for N-nitrosopiperidine and N-nitrosopyrrolidine as well as NDMA, and the high air volume 1N KOH traps were collected for GC-MS analysis. Bulk samples were obtained in plastic bottles, securely capped and labeled.

On April 11, 1978, 8 bulk samples were collected along with the area air samples. Four of these bulk samples were chemical products used in the finishing (doping) area of the tannery. These samples were randomly selected from a list of products and were supplied by plant personnel (see Table 40). Sample No. 11 is a sample of chrome tanned leather scrapings. These scrapings are produced during the shaving process, a process which adjusts the thickness of the chrome tanned leather. The actual sample came from a pile of dry scrapings at the bottom of the conveyor belt. Sample No. 12 is waste ammonia detergent paste wash-off solution. This operation occurs at the end of the first drying step and is intended to remove the paste used to glue the hides on flat drying racks. Samples No. 13 and No. 14 were both obtained from the tannery waste water outlets at the municipal waste water treatment plant. The waste water from the tannery enters the waste water treatment plant in two separate lines. One of the waste water lines is from the beam house and the other is waste water from the remainder of the tannery. According to plant personnel the total amount of waste water from the tannery entering the treatment plant averages 1 million gal/day with about 350,000 coming from the beam house.

On April 13, 1978, five bulk samples were collected during a return visit to the tannery. Samples Nos. 25 and 26 are samples of chemicals and chemical mixes used in the plant steam system to protect the system against scale build up and rust. These samples were taken because amines and nitrites are commonly used as rust inhibitors and steam may have been used to heat some of the wet processes.

The composition of sample No. 25 is:

1. 15 lbs of Betz Formula 100 (Poly-Sperse) boiler water dispersant
2. 15 lbs of Betz Formula CL-2 (Chelant) boiler water conditioner
3. 3.5 lbs of Betz Formula NA-6 (Neutramine) condensate neutralizing amine
4. 4 lbs caustic soda (Sodium Hydroxide)
5. 1.5 lbs Betz Corragen (Sodium Sulfite)
6. Water to a total volume of 55 gal.

Sample No. 26 is the amine used in the system, Betz Formula NA-6 (Neutramine).

Sample No. 27 is the 36.5% dimethylamine sulfate solution (Rohm & Haas lot No. 2-1584) used in the unhairing process. This sample was of interest because of the possibility of NDMA contamination.

Sample No. 28 was a piece of the raw salted cowhide as it is received at the tannery. This sample was examined for both NDMA and the possibility that it contained a nitrosating agent which could form NDMA in the presence of dimethylamine under acid conditions.

Sample No. 29 is a sample of the process water from the re-lime pit where dimethylamine sulfate is used. It contained the following:

1. 1.5 gal of 36.5% solution of dimethylamine sulfate
2. 350 lbs of lime

Table 39

The Concentration of N-nitrosodimethyamine (NDMA) in Tannery Air Plant A

Sample No.	Collection Method	Sample Location	μ g/m^3 NDMA
Date: April 11, 1978			
1	1N KOH	2nd step in unhairing	13.2
2	1N KOH	Border between tanning, splitting and shaving	32.8
3	1N KOH	End of drying over	11.1
4	1N KOH	Paste washing off	8.2
5	1N KOH	Doping area	6.5*
6	1N KOH	Spray finishing	6.0
Date: April 13, 1978			
15	1N KOH	Hide house	5.6
16	1N KOH	Border between tanning, splitting and shaving	23.7
17	1N KOH	Border between tanning, splitting and shaving	35.8
18	1N KOH	Middle of beam house	27.3
19	1N KOH	Start of beam house	26.5
20	1N KOH	Wringing area	37.5
21	1N KOH	Coloring and fat-liquoring	47.2
22	1N KOH	Color set-out	19.3
30	1N KOH	Buffing and sorting room	3.5
31	1N KOH	Seasoning room	3.5
32	1N KOH	Spray booth next to pill box	6.5
33	1N KOH	Shipping room	1.4
34	1N KOH	Lunch room	0.1
35		Outside, N.E. corner 100 ft from building	N.D.
36	1N KOH	Outside W.S.W. 50 ft from building	N.D.**
37	1N KOH	Outside W.N.W. 50 ft from building	N.D.***

Table 39 (continued)

Sample No.	Collection Method	Sample Location	$\mu g/m^3$ NDMA
Date: June 1, 1978			
38	1N KOH	Chemical room	1.1
39	1N KOH	Chemical room	1.3
40	1N KOH	Catwalk above retan	1.9
41	1N KOH	Catwalk above retan	2.5
42	KOH and amine spike	Catwalk above retan	3.1
43	KOH and amine spike	Catwalk above retan	3.7
44	1N KOH	Re tanning	2.0
45	1N KOH	Re tanning	2.2
46	1N KOH	Catwalk above chrome tanning	3.4
47	1N KOH	Catwalk above chrome tanning	2.5

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* 2.0 $\mu g/m^3$ of N-nitrosomorpholine was found in this sample.

** N.D. - None Detected, detection limit 0.05 $\mu g/m^3$ (NDMA).

*** Sample lost during analysis.

Table 40

The Concentration of N-nitrosodimethylamine in Tannery Bulk Samples Plant A

Sample No.	Material Tested	ng/g NDMA
Date: April 11, 1979		
7	Azo rubine dye	N.D.
8	Penetrator L-219	N.D.
9	Nigrosine blue L	N.D.
10	Polar sol 5	N.D.
11	Chrome tanned leather scraping	N.D.
12	Ammonia paste wash	N.D.
13	Beam house waste water	4
14	Tanning house waste water	6
Date: April 13, 1978		
25	Boiler rust inhibitor mix	N.D.
26	Betz formula NA-6	N.D.
27	Dimethylamine sulfate	500
28	Salted cowhide trimmings	N.D.
29	Process water re-line pit	1.4
Date: June 1, 1978		
	Chemicals	
48	P-nitrophenol	N.D.*
49	KITO-40	N.D.
50	Fresh brine	N.D.
	Process Water	
51	Bating solution	N.D.*
52	Bating solution	N.D.
53	Pickling solution	N.D.
54	Chrome tanning solution	N.D.
55	Chrome tanning solution	N.D.
56	Final rinse from chrome tanning	N.D.
57	Final rinse from chrome tanning	N.D.
59	Wash out of coloring (2nd)	N.D.
60	Final rinse fatliquoring	N.D.

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* N.D. - None Detected, detection limit for chemicals - 0.1 ng/g (NDMA).

** N.D. - None Detected, detection limit for process water - 0.1 ng/g (NDMA).

3. 1.5 gal of Tek-wet surfactant

4. 18,000 lbs of water
   *Note: the re-lime pit was in operation when the sample was taken and the solution was reported to be about 20 hours old. Tek-Wet is supplied by Hamblet & Hayes Co., Salem, MA.

The results of the analysis of the bulk samples are described in Table 40.

RESULTS AND DISCUSSION

Bulk Chemical Samples

At a detection limit of 0.2 µg/g, only one of the chemicals was found to contain a TEA-responsive compound, N-nitrosodimethylamine (NDMA). This was found in a sample of dimethylamine sulfate. The amount of NDMA found was 0.5 µg/g (500 ppb) (Table 40).

According to plant personnel 27 gallons of dimethylamine sulfate are used each day in the unhairing process.

None of the bulk samles from the June 1, 1978 survey contained measurable amounts of NDMA (Table 40).

Process and Waste Water Samples

At a detection limit of 0.04 µg/g the ammonia paste wash solution (Sample No. 12) contained no TEA-responsive compounds (Table 40). At a detection limit of 0.001 µg/g the unhairing process water sample was found to contain 0.0014 µg/g NDMA. This process water also contained the NDMA contaminated dimethylamine sulfate.

Both of the waste water samples contained NDMA. The beam house sample No. 13 had 0.004 µg/g and the tanning house sample No. 14 had 0.006 µg/g. The amount of water used by the entire tannery was reported to be 1 million gal/day. 20 grams of NDMA would be required to produce 0.006 µg/g in 1 million gallons of water. Three other TEA responsive compounds were detected after separation on HPLC but not identified.

Leather Samples

At a detection limit of 0.015 µg/g for chrome tanned leather scrapings and a detection limit of 0.04 µg/g for salted cowhide trimmings no TEA-responsive compounds were found. The salted cowhide was further examined by placing a one gram piece in 5 ml of sulfuric acid (pH 3) containing 50 mg dimethylamine hydrochloride for 4 hours at 25°C - this test was to determine if the cowhide sample contained any material which could nitrosate dimethylamine under the chosen condition. At a detection limit of 0.04 µg/g no TEA responsive compounds were formed.

Air Samples

Two N-nitroso compounds, N-nitrosodimethylamine (NDMA) and N-nitrosomorpholine (NMOR) were found in this plant's atmosphere. The NDMA was found in the atmosphere at all stages of production with the highest level of 47 $\mu g/m^3$ being found in the wet process area in the center of the re-tanning, coloring and fatliquoring process. The NMOR at 2 $\mu g/m^3$ was found only in the air in the leather surface finishing (doping) area. The source for the NDMA seemed to be within the beam house and re-tanning area with other areas containing less NDMA depending upon their distance from the beam house area. Dimethylamine sulfate (DMAS) is used in the beam house area in the hide unhairing process. This process is carried out in large open vats at high pH and could, presumably, liberate free dimethylamine (DMA) when these paddle vats are in operation, and/or when the hides are removed. A potential source for the NMOR was not identified; however, morpholine is used in waxes that may be applied to the leather surfaces and this process may result in releasing either preformed NMOR or the morpholine precursor.

Only NDMA was found in the bulk samples. The highest level of 500 parts per billion (ppb) NDMA was found as a contaminant in the 36% solution of dimethylamine sulfate with only 1.4 ppb being found in the unhairing process water. The other bulk sample that contained NDMA (4-6 ppb) were the waste water streams from the tannery. At a detection limit of 0.5 ppb, no N-nitroso compounds were found in any of the other bulk samples of chemicals, leather and process water, thus the largest amount of NDMA in this plant is airborne.

The discovered airborne NDMA seems to have no other source except its formation either in the air (134-136)or on surfaces (137) with subsequent release to the atmosphere. The amount of dimethylamine sulfate that is used on a daily basis in the unhairing process could, if completely converted to NDMA, provide over 200 times the combined amounts of NDMA found in the waste water and air of this plant (approximately 100 g of NDMA per day). The preformed NDMA contaminant of NDMA and the 1.4 ppb NDMA in the unhairing process water can account for only 1.0% of the estimated 20 g/day of NDMA in the waste water.

In order to form the NDMA from the dimethylamine sulfate a nitrosating agent would be required and because NDMA was found primary in the plant's atmosphere, this needed nitrosating agent would have to be airborne. The only obvious source for an airborne nitrosating agent was the exhaust gas from the propane operated fork lift trucks in the beam house area. During operation the combustion products in the exhaust of these vehicles will contain oxides of nitrogen. Secondary amines and some oxides of nitrogen will form N-nitroso compounds in both the gas phase and on surfaces (134-137). This proposed explanation for the presence of the NDMA could account for both the airborne levels and for its appearance in the waste water. In this plant, process water from several of the operations was allowed to drain on to the floor into run-off trenches. During the draining of this process water, surface held NDMA would be flushed into the waste water stream.

During the first two visits in April, a strong amine-like odor (presumably dimethylamine) was detected inside the beam house area. This odor was absent during the June visit. The tannery had, however, by this time discontinued its use of dimethylamine sulfate. The propane operated fork lifttrucks were still in use in the beam house. The airborne levels of NDMA at this time was only 10% of what had been found during the April visits. This drop in airborne NDMA levels may be due to 1) discontinuing the use of dimethylamine sulfate and 2) better ventilation due to warmer outside temperatures. The residual airborne NDMA may be due to its slow release from all of the contaminated surface within the plant.

The amount of NDMA found in the tannery air during the June 1, 1978 visit ranged from 1.1 $\mu g/m^3$ to 3.7 $\mu g/m^3$, this is about 10% of what had been found on previous visits (Table 39). The 1N KOH traps with the added piperidine and pyrrolidine did not contain the N-nitroso derivatives of these compounds at detection limits of 0.001 μg/ml. GC-MS confirmation for NDMA was obtained on samples collected using 1N KOH.

LEATHER TANNERY B

This Plant has been operating at its present site for about 50 years. A new beam house is being added and a new waste water treatment facility has been completed. The site occupies about 20 acres and has one major building with all tanning operations taking place on the ground level (Figure 17). The Tannery has an empty loft and cafeteria above the unhairing operation, otherwise it is essentially a single story structure. The plant employs 75 people in the production area and 7 people in administration. The only products of this plant are unfinished leather hides with an annual production of 25,000 hides. The hides produced at this facility are chrome tanned and dyed to a variety of colors. The final finishes are applied to the hides at a separate facility. The tanning of leather at this plant is similar to the wet processes of Plant A, however, they have recently discontinued the use of dimethylamine sulfate in their unhairing process.

SAMPLING STRATEGY

Air Samples

On October 11, 1978 a total of 20 air samples were collected and analyzed for N-nitroso compounds (Table 41). With the exception of one outside air sample, all of the samples were collected within the tannery. The air samples were collected by drawing air through 1N KOH impinger traps at a constant rate of 2 to 4 liters/min, depending upon the pump used, for 15 minutes to 3 hours. The volume of air sampled for each site varied from 40 to 600 liters.

Bulk Samples

Along with the air samples, 4 bulk samples were collected and analyzed (Table 42). The samples consisted of 2 waste water samples, one sample of steam condensate and one sample of floor scrapings from the dye room near the re-tanning area. At a detection limit of 0.2 ng/g, no NDMA was found in any of the aqueous samples and at a detection limit of 3 ng/g no NDMA was found in the floor scraping sample.

RESULTS AND DISCUSSION

N-nitrosodimethylamine (NDMA) was found in the atmosphere of this plant at all stages of production except the new beam house area. The highest level of 8 $\mu g/m^3$ was found in a loft above the unhairing process (Table 41). In the production area, 2.8 $\mu g/m^3$ was found in a sample taken in the dye room with the remainder of the samples ranging in amount from 0.03 $\mu g/m^3$ to 1.2 $\mu g/m^3$. The further away from the unhairing process that the air samples were taken, the lower the levels of NDMA found. NDMA is either being made as an artifact in one or more of the wet tanning operations, or it is present as a contaminant in the building. Past use of dimethylamine sulfate may have resulted in surfaces being contaminated with NDMA which is now slowly leaching out. The finding of 2.8 $\mu g/m^3$ of NDMA in the small dye room near the coloring area with levels of

0.1 - 0.2 μg/m^3 just outside this room (a 15- to 30-fold difference) suggests that there may be a source (contamination) for the NDMA within the dye room.

The highest level of 8 μg/m^3 in the unused loft above the unhairing process is hard to explain unless the levels of NDMA in the plant were higher in the past. This plant does not presently use dimethylamine sulfate in its unhairing process. The only potential nitrosating agent identified in any of the processes (except dyeing) was the antifungal agent paranitro-phenol. Some of the dyes used by this plant contained C-nitro groups which could transnitrosate dimethylamine to form NDMA, however, an air sample taken inside one of the coloring drums was no higher in NDMA than the air outside of it.

Another possible source for either the dimethylamine or a nitrosating agent was the steam used to heat some of the process water. However, at a detection limit of 0.2 ng/g no NDMA was found in this steam condensate. The waste water from both the beam house and the tanning area when analyzed for NDMA also proved negative at a detection limit of 0.2 ng/g. As with Tannery A, this plant also used propane operated fork-lift vehicles which emit nitrogen oxides into the plant atmosphere.

The source of the NDMA in this plant is not obvious, and if it is being produced in the tanning process, then a source for the dimethylamine is needed to explain this. A sample of a wood beam taken from the loft above the unhairing area was found, by United States Department of Agriculture personnel, to contain up to 25 part per million of NDMA. This finding suggests that NDMA may be slowly leaching into the plants atmosphere from the structure. This finding also suggests that NDMA levels may have been higher in the plants atmosphere in the past.

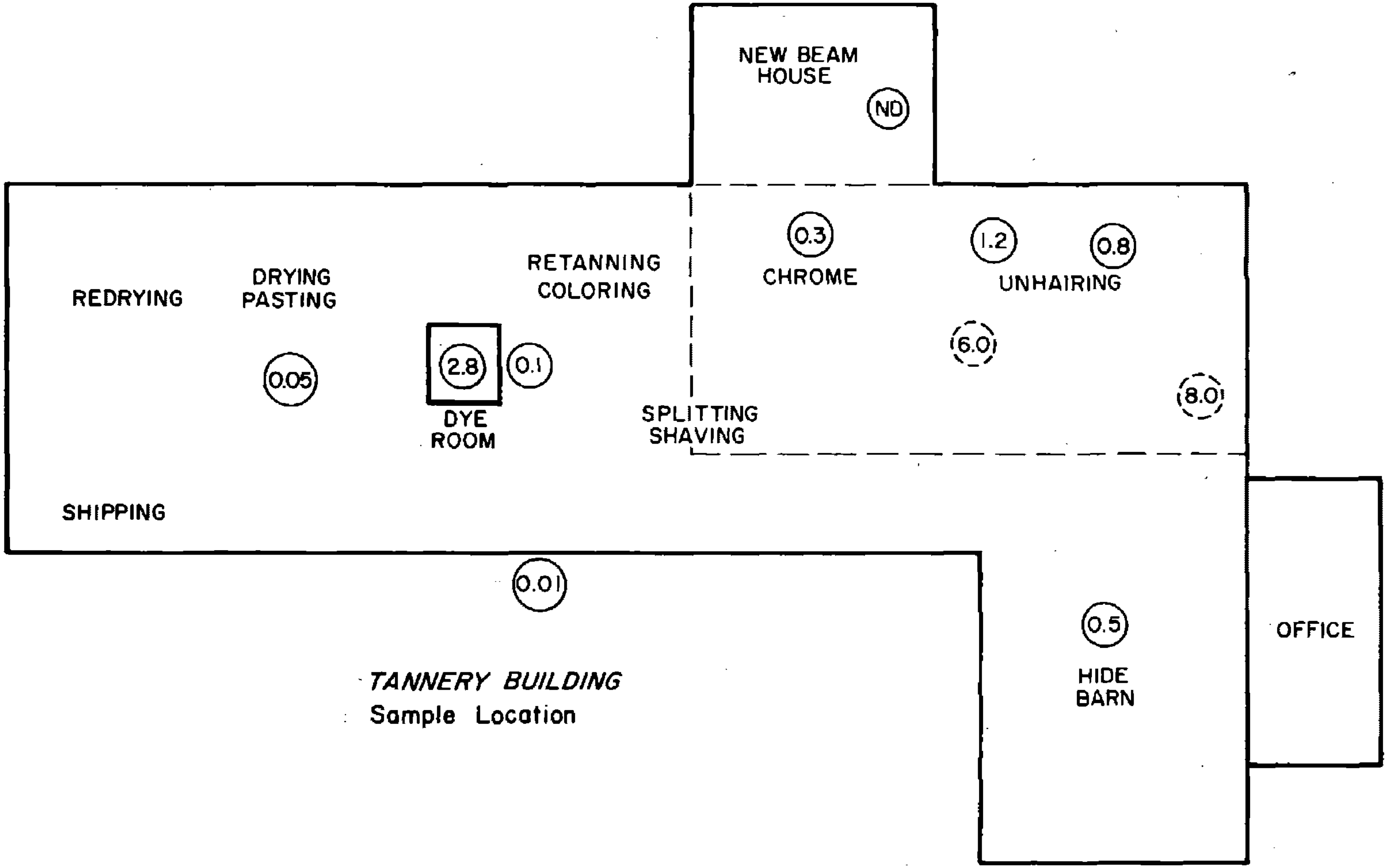

Figure 17. Air Sample Locations within Leather Plant B. The circled numbers refere to μg/m^3 of N-nitrosodimethylamine

Table 41

Results of Air Sampling in Leather Plant B

Sample No.	Collection Method	Sample Location	NDMA μg/m^3
1A	ThermoSorb/N	Hide barn	0.4
1B	1N KOH		0.6
2A	ThermoSorb/N	Unhairing	0.7
2B	1N KOH		0.8
3A	ThermoSorb/N	Chrome tanning	0.3
3B	1N KOH		0.3
4A	ThermoSorb/N	Re tanning	0.1
4B	1N KOH		0.15
5A	ThermoSorb/N	Pasting	0.03
5B	1N KOH		0.06
6A	ThermoSorb/N	Center of drying	0.03
6B	1N KOH		0.05
8	ThermoSorb/N	New beam house	N.D.**
9	ThermoSorb/N	Outside tannery	Trace
10	ThermoSorb/N	Dry room	2.8
11	ThermoSorb/N	Loft above unhairing	6.6
12	ThermoSorb/N	In retanning drum	0.15
13	ThermoSorb/N	Loft above unhairing	6.0
14	ThermoSorb/N	Loft above unhairing	7.9

** N.D. - None Detected, detection limit 0.02 μg/m^3 (NDMA).

A & B samples are duplicate except for the collection sorbent.

Table 42

Results of Bulk Samples in Leather Plant B

Sample No.	Material Tested	NDMA ng/g
15	Waste water from acid area	N.D.*
16	Waste water from beam house	N.D.
17	Steam system condensate	N.D.
18	Floor scraping from dye room	N.D.**

* N.D. - None Detected. Detection limit 0.2 ng/ml.

** Detection limit 3 ng/g.

LEATHER TANNERY PLANT C

The primary function of this plant consists of surface finishing leather that had been previously chrome tanned and re-colored (dyed) at Plant B. The process used at this plant included mechanized sanding, texturing, surface chemical coating and spray-dyeing of the leather. There were no wet operations associated with this plant and neither dimethylamine sulfate nor fork lift trucks were being used. Because this plant's operations were geographically separated from the wet tanning processes it was possible to determine whether or not the leather finishing part of tanning could have been contributing to the NDMA previously found in the atmosphere of Plant A - a full tannery.

The plant's operations were located in the top floor of a three-story brick building and occupied about 40,000 square feet. There were 55 employees in the production area and five in administration.

SAMPLING STRATEGY

On October 12, 1978, after a brief plant tour, 17 air samples were collected and analyzed on site, using a mobile laboratory, for N-nitroso compounds. These samples were collected using both ThermoSorb/N air sampling cartridges and impinger traps containing 1N KOH. The air sampling rates for the individual traps ranged from 2 to 4 L/min with sample volume ranging from 40 to 300 L. Since, upon analysis, no N-nitroso compounds were found in the air samples (Table 43), no bulk samples were collected. These air samples were all collected within the production area and at all of the leather finishing processes.

RESULTS AND DISCUSSION

Because the wet (Beam House) and dry (leather finishing) processes of Plant A were located within the same one-story building in close proximity to each other, it was not possible, prior to this study of Plant C, to determine the relative contribution of each separate process to the airborne NDMA levels found in Plant A. In spite of the fact that many of the chemicals and processes used at this Plant (Plant C) were similar to those used at Plant A, no airborne N-nitroso compounds were found. It is apparent from this study that other similar leather finishing operations may not be a primary source for airborne N-nitroso compounds. It is concluded from this data that the wet operations of Plant A were the major, if not the only, contributor of the NDMA found in that Plant's atmosphere.

Table 43

Results of Air Sampling in Leather Plant C

Sample No.	Collection Method	Sample Location	N-nitroso Compounds Detected
15A	ThermoSorb/N	Spray booth area	N.D.*
15B	1N KOH		N.D.
16A	ThermoSorb/N	Dye storage area	N.D.
16B	1N KOH		N.D.
17A	ThermoSorb/N	Entrance to dryer off sprayer	N.D.
17B	1N KOH		N.D.
18A	ThermoSorb/N	Entrance to dryer off seasoning	N.D.
18B	1N KOH		N.D.
19A	ThermoSorb/N	Exit of dryer from seasoning	N.D.
19B	1N KOH		N.D.
20A	ThermoSorb/N	Stick dryer	N.D.
20B	1N KOH		N.D.
21	ThermoSorb/N	6" above brush roller on seasoning process	N.D.
22	ThermoSorb/N	Dryer near sprayer	N.D.
23	ThermoSorb/N	Hanging inside buffer	N.D.
24	ThermoSorb/N	Inside exit of drying furnace off seasoning	N.D.
25	ThermoSorb/N	Exit of dryer for spray finish	N.D.

* N.D. - None Detected, detection limit 0.05 μg/m^3 (NDMA).

A & B samples are duplicate.

LEATHER TANNERY PLANT D

This plant has been producing chrome tanned leather since 1971. The manufacturing facility has 40,000 square feet of floor space divided into 8 work areas, salted hide receiving and hide soaking, hide processing, wet hide wringing, storage, hide shipping, chemical laboratory, chemical processing and hide process control area. With 134 employees, the Plant produces about 22,000 chrome tanned hides per week operating on 19 out of a possible 21 shifts.

At this plant, unhairing, bating, pickling and chrome tanning are all done in the same hide processor - one after the other. The hide processors have the appearance of large cement mixers and operate by constantly tumbling the hides in the process solution. The hides are moved to the hide processors by an overhead conveyor system. The Plant does not use dimethylamine sulfate except on an experimental basis.

Most of the chemical tanning operations in this plant are automated so that there is little reliance on worker batchmixing of chemicals. The various process waters are heated directly by steam. The Plant's air heating system consists of nine large gas heaters which heat the air by direct combustion. The total air exchange was reported to be 20 - 30,000 ft^3/hr. Waste water from the Plant was reported to be about 270,000 gal/day.

SAMPLING STRATEGY

The sampling strategy used at this site was to collect area and process air samples along with process water samples to be analyzed for the presence of N-nitroso compounds and their precursors. The precursors analyzed for were nitrosatable amines and potential nitrosating agents. The process air samples were taken to determine if any specific process could be contributing to the airborne N-nitrosodimethylamine found in the area air samples. The process water samples were examined for both N-nitroso compounds and amine precursors. These amine precursors were determined by nitrosating a portion of the sample and examining it for N-nitroso compounds. Airborne nitrosating agents, such as nitrogen dioxide (NO_2) were determined by drawing the air sample through a ThermoSorb/A air sampling cartridge that had morpholine added to the sorbent. The amount of N-nitrosomorpholine formed on these cartridges is proportional to the airborne levels of (NO_2).

Wet Air Traps

Impinger traps consisting of glass vacuum traps (190 x 24 mm) equipped with a Bendix C115 air pump and 45 ml of a liquid sorbent were used to sample air with flow rates of about 2 L/min for 3 hours.

The various liquid sorbents used were:

- 45 ml 1N KOH
- 45 ml 1N KOH with 30 mg each of piperidine, pyrrolidine and morpholine added to the trap

- 45 ml of potassium biphthalate-hydrochloric acid 0.02 M buffer solution

- 45 ml of pH-4 phosphate-citrate 0.02 buffer solution

The 1N KOH traps were the standard traps used throughout this study. However, for this survey, one of these (Sample NO. 7-K) had nitrosatable secondary amines added to determine if there were any airborne nitrosating agents which could produce an artifact in the trap. The pH-3 and pH-4 acid traps were used to trap airborne amines.

Dry Solid Sorbent Traps

These traps consisted of 15 mm i.d. x 20 mm length cartridges containing about 1.5 grams of a dry sorbent. The air samples were drawn through these cartridges using either a Bendix C115 air pump or a 10 L/min metal bellows air pump equipped with a 10 L/min Hastings mass flow meter. The air was sampled at a constant rate for each trap at 2 to 6 L/min for 5 to 200 minutes.

The solid sorbent cartridge used were:

- ThermoSorb/N air sampling cartridge

- ThermoSorb/A air sampling cartridge

- ThermoSorb/A air sampling cartridge with 30 mg of morpholine coated onto the sorbent.

The ThermoSorb/N air sampling cartridges were used to sample both area and process air samples for N-nitroso compounds. The ThermoSorb/A air sample cartridge is an amine trap and was used to determine both the amount of nitrosatable airborne amines and as an indicator of nitrosating agents in the sampled air. The nitrosating capacity of the sampled air can be estimated by measuring the amount of N-nitrosomorpholine (NMOR) produced in the morpholine coated sorbent in the ThermoSorb/A air sample cartridge. Morpholine, when coated on a surface, can be directly nitrosated to form NMOR by atmospheric nitrogen dioxide. The amount of NMOR formed is proportional to the square of the concentrations of the airborne nitrogen dioxide $(NO_2)^2$.

Bulk Samples

Along with the air samples, 8 bulk samples were collected and examined for N-nitrosamines and nitrosatable amines. Samples were taken from each of the wet processes: chrome tanning, basification, pickling, bates, unhairing and hide soaking. Samples of condensed steam and waste water from the plants waste water treatment facility were also obtained.

RESULTS AND DISCUSSION

This Tannery was visited on January 16, 1979 and a total of 21 air samples and 8 bulk samples were collected and analyzed for the presence of N-nitroso compounds and their precursors. N-nitrosodimethylamine (NDMA) was found in all air samples with the exception of the background control placed outside the Plant (Table 44). The amount found ranged from 0.2 $\mu g/m^3$ in the sulfide stripping room to 2.1 $\mu g/m^3$ at the hide processing. A higher value of 3 $\mu g/m^3$ on the boiler water treatment deck is suspect due to a possible error in pump calibration. All other areas range in amount from 1 to 2 $\mu g/m^3$ with a mean of 1.5 $\mu g/m^3$. These findings indicate a fairly uniform distribution of NDMA in the plant atmosphere. The process air samples (Table 45) contained levels of NDMA that were at or below the mean level in the Plant, indicating that these processes were not the primary source for the airborne NDMA. Sample No. 7-K, a 1N KOH impinger with added nitrosatable secondary amine, contained N-nitrosodimethylamine but none of the added amines had been converted to their respective compounds thus indicating that the traps were artifact free.

None of the process water samples contained measurable amounts of NDMA, however, after nitrosation, 1.4 to 2.5 ng/ml of NDMA were found in three of the eight samples (Table 46). Assuming that the amine precursor was dimethylamine, then these three processes may have been a source for this compound. The results of nitrosating three of the air samples indicates that there are NDMA amine precursors in the air (Table 47).

All of the morpholine spiked solid sorbent tubes, except the unspiked control, were found to contain N-nitrosomorpholine thus indicating that the sampled air did indeed contain a nitrosating agent (Table 48). The relative nitrosating capacity ranged from 41 parts per billion (ppb) of NO_2 outside the plant to 4200 ppb on the boiler water treatment deck. The nitrosating capacity of the air as measured by this technique, reflects only the relative nitrogen dioxide levels in the plant air.

In summary, the reason for the NDMA found in the air of this tannery may include the following:

1. An unsampled product or process is responsible.
2. The NDMA was formed at some other time in the past and we are measuring residual levels in the air.
3. Some of the processes are releasing dimethylamine into the air and it is being nitrosated by the detected airborne nitrosating agent.

As far as the airborne nitrosating agent is concerned, if it is nitrogen oxides produced by combustion, at least 3 sources may be responsible for its presence:

1. The gas fired direct air heaters.
2. The propane operated fork-lift trucks.
3. The combustion system of the steam boiler under the boiler water treatment deck.

The level of 4200 ppb of NO_2 inside this Plant is quite high and may be the result of the gas fired direct air heaters.

Table 44

Results of Air Samples in Leather Plant D

Sample #	Collection Method	Sample Location	μg/m³ NDMA
1-S	ThermoSorb/N	Outside of north end of building	N.D.
2-S	ThermoSorb/N	Middle of hide processing	2.1
2-K	1N KOH		2.0
3-S	ThermoSorb/N	Hide soaking	1.6
3-K	1N KOH		1.4
4-S	ThermoSorb/N	Center of Blue hide wringer	0.8
4-K	1N KOH		0.7
5-S	ThermoSorb/N	Boiler water treatment deck	1.1
5-K	1N KOH		3.3**
1-U	ThermoSorb/A	Boiler water treatment deck	1.2
7-K	1N KOH		2.0
6-S	ThermoSorb/N	South end of hide processing	N.D.
6-K	1N KOH		1.7
7-S	ThermoSorb/N	Control (no air sample)	N.D.
10-S	ThermoSorb/N		N.D.

* N.D. - None Detected, detection limit 0.05 $\mu g/m^3$.

** - Sample may be high due to incorrect pump calibration.

Table 45

Results of Process Air Samples in Leather Plant D

Sample No.	Collection Method	Sample Location	NDMA μg/m^3 NDMA
8-S	ThermoSorb/N	Inside hide processor #9 chrome tanning in process	1.0
11-S	ThermoSorb/N	Inside hide processor #17 chrome tanning in process	1.3
12-S	ThermoSorb/N	Inside hide processor #5 pickling in process	1.0
13-S	ThermoSorb/N	Inside hide processor #3 unhairing in process	1.2
14-S	ThermoSorb/N	Sulfide stripping room	0.23

Table 46

NDMA in Leather Plant E Process Water Before and After Nitrosation

Sample	NDMA ng/ml Before Nitrosation	NDMA ng/ml After nitrosation
Chrome tanning	N.D.	1.4
Unhairing	N.D.	2.3
Soaking solution	N.D.	2.5
Basification	N.D.	N.D.
Pickling solution	N.D.	N.D.
Bates solution	N.D.	N.D.
Plant waste water	N.D.	N.D.
Steam condensation	N.D.	N.D.

N.D. - None Detected, detection limit 0.01 ng/ml.

Table 47

NDMA Amine Precursors in the Air of Leather Plant D

Sample No.	Sample Type	NDMA $\mu g/m^3$	$\mu g/m^3$ of NDMA after sample nitrosation
P-C	pH-4 citrate buffer	2.1	5.5
A-P	pH-3 HCl buffer	2.2	5.1
Silica-1	silica gel	N.A.*	5.2

* N.A. - Not Analyzed

Table 48

Nitrosating Agent in the Air of Leather Plant D

Sample No.	Sample Location	m^3 of air sampled	ppb of NO_2* in the air
1-S	Outside plant air	.49	41
2-S	Hide process area	.52	360
4-S	Blue hide wringer	.48	1300
5-S	Boiler water treatment deck	.33	4200
6-S	Hide process area	.30	710
8-S	Inside hide processor #9 chrome tanning in process	.07	140
1-U	Control - unspiked (no morpholine)ThermoSorb	0.42	0
10-S	Control - unused morpholine spiked ThermoSorb	0	0
11-S	Inside hide processor #8 chrome tanning in process	.03	410
12-S	Inside hide processor #5 pickling in process	.03	300
13-S	Inside hide processor #3	.03	250
14-S	Sulfide stripping room	.06	2200

All air nitrosation measurements were made by measuring the amount of morpholine converted to N-nitrosomorpholine on morpholine spiked ThermoSorb air sampling cartridges. N-nitrosomorpholine was not detected in any of the morpholine spiked 1N KOH traps, thus indicating that these traps are artifact free.

*Concentration of NO_2 required to produce an equivalent level of N-nitrosomorpholine in laboratory experiments.

LEATHER TANNERY E

This tannery was started in 1935 as a full tannery producing finished leather from raw hides. The company was expanded in 1973 and its operation was changed from a full tannery to a re-tanning and finishing operation. The plant building has two stories with 150,000 sq ft of floor space. The company receives chrome tanned hides from other parts of the country which it re-tans, re-colors, and finishes into leather which is then used for shoes and belts. The plant processes about 8 - 10,000 hides/day employing 560 people on three shifts. Dimethylamine sulfate is not used in this plant. However, they do have propane operated fork-lift trucks.

SAMPLING STRATEGY

The sampling strategy consisted of collecting both area and process air samples along with process water samples, to be analyzed for the presence of N-nitroso compounds and their precursors. The precursors analyzed for were nitrosatable amines and nitrosating agents. The process air samples were collected to determine what, if any, specific processes were contributing to the airborne nitrosamines found in the area air samples. The process water samples were examined for both N-nitroso compounds and amine precursors. The amine precursors in both air and water samples were determined by nitrosating a portion of the sample and then examining it for the formation of N-nitroso compounds. Airborne nitrosating agents, such as nitrogen oxides, were determined by drawing the air through solid sorbents containing morpholine and measuring the amount of N-nitrosomorpholine produced per cubic meter of air and from this, calculating the airborne NO_2 levels.

In order to accomplish the sampling strategy objectives, the following types of air traps were used:

1. 45 ml of 1N KOH
2. 45 ml of 1N KOH with 30 mg each of piperidine, pyrrolidine and morpholine added
3. 45 ml of pH-3 potassium biphthalate-hydrochloric acid 0.02 M buffer
4. 45 ml of pH-4 phosphate-citrate 0.02 M buffer

Dry Solid Sorbent Traps

These traps consisted of 15 mm i.d. x 20 length cartridges containing about 1.5 grams of dry sorbent. The air samples were drawn through these cartridges using either a Bendix C115 air pump or a 10 L/min metal bellow air pump. The air samples were collected by drawing air through the traps at a constant rate for each trap of 2 to 6 L/min for 5 to 200 minutes. All air flow rates were calibrated using a Hasting 10 L/min mass flow meter. The types of solid adsorbent traps used were:

- ThermoSorb/A amine air sampling cartridge

- ThermoSorb/A air sampling cartridges with added morpholine
- ThermoSorb/N air sampling cartridges with added dimethylamine
- ThermoSorb/N air sampling cartridges

The 1N KOH trap is the standard trap used throughout this NIOSH sponsored study. The pH-3 and pH-4 acid traps were used to trap both airborne amines and N-nitroso compounds.

RESULTS AND DISCUSSION

This plant was visited on February 5, 1979 and a total of 21 area air samples were collected and analyzed for the presence of N-nitroso compounds (Table 49). Except for sample Numbers 2B and 5B, no N-nitrosamines were detected. Samples 2B and 5B were 1N KOH traps. Sample No. 2B was found to contain 0.25 $\mu g/m^3$ of N-nitrosomorpholine (NMOR) while sample Number 5B contained 0.05 $\mu g/m^3$ of N-nitrosodimethylamine (NDMA) and 0.12 $\mu g/m^3$ of NMOR. These levels of N-nitrosamine are from 1/10 to 1/100 of that found in other tanneries. The air nitrosation capacity was found to be lower in this plant than the outside parking lot (Table 50), however, during the time the outside air sample was being collected there was truck traffic in the parking lot. The highest level of nitrosating capacity within the plant, 480 parts per billion (ppb) NO_2, was found in the splitting department. It was observed that propane driven fork lifts were being operated within this area and these may have contributed to the higher levels of nitrogen oxides in the air.

Table 49

Results of Air Samples in Leather Plant E

Sample No.	Collection Method	Location	N-nitrosamine $\mu g/m^3$ NDMA	N-nitrosamine $\mu g/m^3$ NMOR
1A	Thermosorb/N	Dye weighing room	ND*	--
1B	1N KOH		ND	ND
2A	ThermoSorb/N	Season area 1	ND	--
2B	1N KOH		ND	0.25
3A	ThermoSorb/N	Splitting department	ND	--
3B	1N KOH		ND	ND
4A	ThermoSorb/N	Color house by sample mills	ND	--
4B	1N KOH		ND	ND
5	1N KOH	Downstairs by dual spray	0.05	0.12
6	ThermoSorb/N	Bypasting unit	ND	--
7	ThermoSorb/N	Outside control	ND	--
8	pH-3 buffer	Color house by sample mills	ND	ND
9	pH-4 buffer	Color house by sample mills	ND	ND
10	ThermoSorb/N	Color house by sample mills	ND**	ND
11	ThermoSorb/A	Color house by sample mills	ND	ND

* N.D. - None Detected, detection limit 0.02 $\mu g/m^3$.

All ThermoSorb/N tubes except Sample No. 10 were spiked with 500 µg of morpholine to determine the nitrosating capacity of the air.

** Sample 10 was spiked with 35 µg of dimethyalmine to determine if it could form NDMA as an artifact.

NDMA - N-nitrosodimethylamine, NMOR - N-nitrosomorpholine.

Table 50

Nitrosating Agent in the Air of Leather Plant E

Sample No.	Location	m^3 of air sample	ppb of NO_2* agent in the air
1	Dye weighing room	0.576	270
2	Season area 1	0.421	210
3	Splitting department	0.432	480
4	Color house by sampling mills	0.625	100
6	B-pasting area	0.360	85
7	Parking lot outside plant	0.065	850

All air nitrosation measurements were made by determining the amount of morpholine converted to N-nitrosomorpholine on morphline spiked ThermoSorb/A air sampling cartridges.

* Concentration of airborne NO_2 required to produce an equivalent level of N-nitrosomorpholine in laboratory experiments.

LEATHER TANNERY PLANT F

This leather tannery is located in the mid-west. It produces fully tanned and finished leather from calf hides and pig skins. The Plant's buildings occupy approximately 8 acres and the main production building has seven floors. The operations typically found in leather tanneries are in use at this facility. The Plant employs approximately 300 workers and operates one shift. The area in this Plant where N-nitroso compounds are most likely to be found is the beam house area where dimethylamine sulfate (DMAS) is used. DMAS is used in the hide unhairing operation to gently loosen hairs from the hides. These loosened hairs are later removed from the skin by mechanical means during the unhairing operation. DMAS serves as a catalyst to loosen the hair and is added to the unhairing solution at 1% of the weight of the skins. The hide unhairing solution has a pH of about 12 thus most of the DMAS may be in the form of the free amine and not the sulfate salt.

A further reason for suspecting the presence of N-nitroso compounds in the beam house is the use of propane operated fork-lift trucks in this area. Exhausted gases from these vehicles can contain high levels of oxide of nitrogen and, as stated, these oxides of nitrogen can serve as nitrosating agents. If sufficient levels of both dimethylamine and oxides of nitrogen are present in the air, then N-nitrosodimethylamine (NDMA) can be formed. The formation of NDMA may occur both in the atmosphere and on surfaces, with its subsequent release to the air. In order to test this hypothesis, air samples were collected during July 22-24, 1980 to measure airborne dimethylamine, N-nitrosodimethylamine and for the presence of an airborne nitrosating agent. During a prior sampling visit to this plant in January of 1980, as part of a NIOSH epidemiology study, six air samples were collected using ThermoSorb/N air sampling cartridges. NDMA was found in all the sampled areas with levels ranging from 0.3 $\mu g/m^3$ to 10.8 $\mu g/m^3$ (see Table 51).

SAMPLING STRATEGY

After a brief plant tour, sample sites were selected within the beam house and wet operations for area sampling for N-nitroso compounds and their precursors. Six sites within the beam house were identified as sample stations. These sites were sampled for three consecutive days at approximately the same time of day. Figure 18 is a floor plan of the wet operation area showing the location of the sample stations and the area where the fork-lift trucks operated. All sample stations were sampled for N-nitroso compounds, amines and airborne nitrosating agents.

A total of 5 bulk samples were also collected during the survey. These samples consisted of fresh hide unhairing process water containing added dimethylamine sulfate (DMAS), hide unhairing process water without added DMAS, four-day old hide unhairing water containing DMAS, a 40% aqueous solution of the DMAS used in the unhairing process and a water sample from a floor puddle near the unhairing machine. All of these samples were analyzed for both dimethylamine (DMA) and N-nitrosodimethylamine (NDMA) content. These samples were to determine if NDMA was being formed in the unhairing process, on the floor surface or if it was a significnt contaminant in the 40% aqueous DMAS.

Air Sampling for N-nitroso Compounds

All N-nitroso compound air samples were collected with the artifact free ThermoSorb/N air cartridges and battery-driven air pumps. Typically, the air pumps were operated at from 1.5 L/min to 2.0 L/min for 7-8 hours.

Air Sampling for Amines and Airborne Nitrosating Potential

The apparatus used for the sampling are similar to that used for amine compounds except the sorbent in the ThermoSorb/A cartridges consisted of thiomorpholine coating the sorbent. Air was drawn through these cartridges at exactly 1 L/min for a total of 30 minutes. These cartridges were then backflushed with 4 ml of 1N KOH. Aliquots of this eluate were then analyzed for both volatile amines and for N-nitrosothiomorpholine. Any N-nitrosothiomorpholine found on these cartridges would have been formed as a result of drawing a nitrosating agent, such as oxides of nitrogen, through the cartridge.

Amine Analysis

The apparatus used for volatile amine analysis consisted of a gas chromatograph interfaced to a TEA equipped with an oxidative catalytic pyrolyzer. With this apparatus, all nitrogen containing compounds are oxidized to produce nitric oxide radicals which are then detected via chemiluminescence. The gas chromatographic columns used in this system was a 4' x 1/4" 2 mm i.d. glass column packed with Carbopack B/4% Carbowax 20 M/0.8% KOH with 15 ml/min argon gas temperature programmed from 60°C to 180°C at 10°C/min (Supelco, Inc.).

Analysis of Bulk Samples

Aliquots of these samples were analyzed by GC-TEA in either the nitrosamine operating mode or the total nitrogen mode. The sample preparation consisted of diluting the sample 100-fold with 1N KOH for amine analysis and 10-fold for N-nitroso compound analysis.

RESULTS AND CONCLUSIONS

N-nitrosodimethylamine (NDMA) was found in the air at all sample sites ranging in level from 0.1 µg/m^3 in the tan yard to 6.6 µg/m^3 in the center of the unhairing area (Table 52). While the amounts of NDMA found at each site varied from as much as 1.2 µg/m^3 in the bating area on the first day to 5.5 µg/m^3 in the same area on the third day of sampling the daily mean of all sampling sites was 2.9 g/m^3 ± .5 µg/m^3. Dimethylamine (DMA) was also found at all sample sites with airborne concentrate varying from 33 µg/m^3 near the fleshing machine to 653 µg/m^3 in the center of the unhairing vats (Table 52). The variability of the airborne DMA may be attributable to the operation of the hide unhairing vat paddles. On occasion the hides are tumbled in the unhairing solution by use of the paddles, and during this operation it was noted that the amine-like odor increased. The mean amount of airborne DMA was 291 µg/m^3 ± 110 µg/m^3.

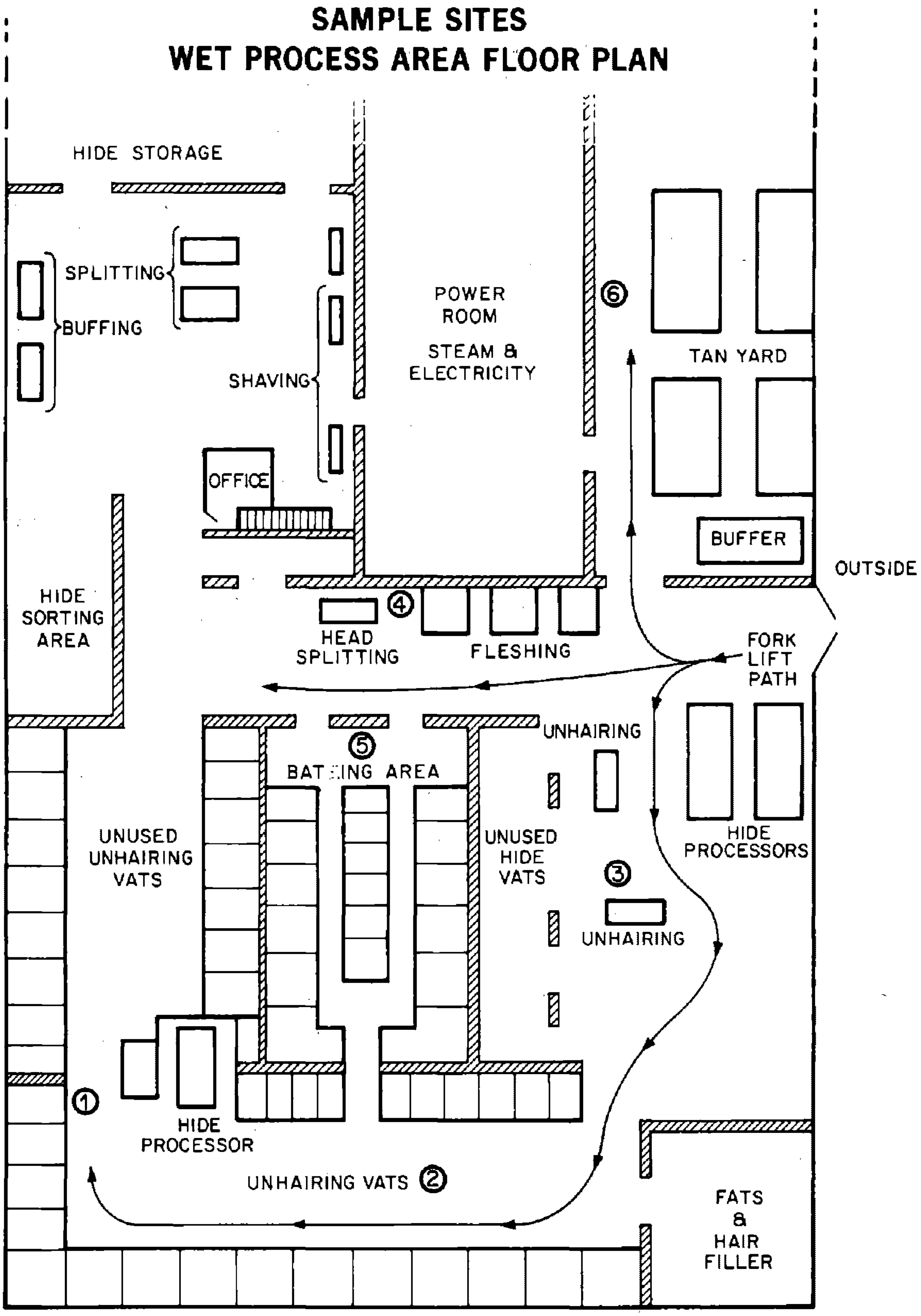

Figure 18. Leather Tannery Plant F Sample Sites

Table 31

Air Sample Analysis for Nitrosamines
January 1980

Leather Tannery Plant - F

Sample No.	Sample Location	$\mu g/m^3$ NDMA
1	Bating Pit	5.3
2	Dehairing	10.8
3	Dehairing	7.8
4	Tan Yard	0.3
5	Color Run	1.0
6	Dehairing Line	10.1

* NDMA - N-nitrosodimethylamine

Table 52

Analysis of Air Samples Collected on July 22, 23, 24, 1980 for N-nitrosodimethylamine (NDMA) and Dimethylamine (DMA)

Leather Tannery - F

Results in $\mu g/m^3$

	7/22		7/23		7/24	
Sample Location	NDMA	DMA	NDMA	DMA	NDMA	DMA
1. Unhairing Vats	4.6	510	3.8	290	5.4	663
2. Center of Unhairing Area	4.3	228	4.1	132	6.6	481
3. Fleshing Machine	1.1	33	1.1	334	1.3	183
4. Head Splitting	1.0	45	1.1	91	1.2	644
5. Bating Area	1.2	270	4.0	166	5.5	405
6. Tan Yard	N.S.*	N.S.	0.2	64	0.1	36

* N.S. - Not Sampled

Table 53

Results of Air Nitrosation Capacity in Equivalent Levels of Airborne Nitrogen Dioxide (NO_2)* Samples Collected on July 22-24, 1980

Leather Tannery - F

Sample Location	Results in part per billion**		
	7/22	7/23	7/24
1. Unhairing Vat	97	35	42
2. Center of Unhairing	34	44	33
3. Fleshing Machine	41	97	64
4. Head Splitting	97	106	63
5. Bating Area	36	97	106
6. Tan Yard	NS***	64	71

* Equivalent to measured NO_2 levels that experimentally produce the observed amount of nitrosamine formed on the nitrosation capacity cartridge.

** 1 ppb of NO_2 is approximately 2×10^{-9} g of NO_2/liter of air

*** N.S. = Not sampled

Table 54

Results of Analysis of Bulk Samples for N-nitrosodimethylamine (NDMA) and Dimethylamine (DMA)

Samples Collected on July 23, 1980

Leather Tannery - F

Sample Description	NDMA (μg/ml)	DMA (μg/ml)
1. Floor Water near unhairing	N.D.*	120
2. Fresh hide unhairing solution containing dimethylamine sulfate	N.D.	790
3. Hide unhairing solution - no dimethylamine sulfate added	N.D.	8
4. 4-day old hide unhairing solution containing dimethylamine sulfate	N.D.	630
5. 40% solution of dimethylamine sulfate	N.D.	120,000

* N.D. - None detected - detection limit 0.5 μg/ml

Airborne nitrosating agents were also found at all sample sites ranging from equivalent NO_2 levels of 33 parts per billion (ppb) in the center of the unhairing vats to 106 ppb in the head splitting and bating area (Table 53). The mean amount of this nitrosating agent was 58 ppb ± 16 ppb. The highest levels of 106 ppb are not unusual and do not represent a particularly high level of NO_2. Some of this detected nitrosating agent may be due to outside ambient levels of NO_2, however, it was observed that on occasion one to two propane driven fork-lift trucks were operating within the sample area. These samples, like the amine samples, were collected for only 30 minutes, and as a result the mean levels do not represent a daily average.

The results of the bulk samples are contained in Table 54. At a detection limit of about 0.5 μg/ml no NDMA was found, however, all of these samples contained DMA with levels ranging from 8 μg/ml in the unhairing process water without added DMAS to 120,000 μg/ml in the 40% aqueous DMAS solution. When calculated as DMAS, the 120,000 μg/ml of DMA represents approximately a 40% solution. It is apparent from these findings that the airborne NDMA is not a result of its being formed in the unhairing process water.

In summary, airborne levels of NDMA were found in association with its precursor amines and an airborne nitrosating agent. From the evidence it appears that low levels of airborne oxides of nitrogen and dimethylamine can result in the formation of N-nitroso dimethylamine. Whether or not this reaction is taking place in the gas phase or on the building surface, or both, has not yet been determined. Cited experimental evidence (134-137), however, indicates that either of these possibilities could be responsible for the formation of NDMA.

LEATHER TANNERY PLANT G

This leather tannery located in the midwest near Plant G has been at its present location since 1931. The chrome tanning operation of this plant is new and utilizes hide processors to process about 35,000 cattle hides per week. The company employs between 325 - 350 workers. It does not use dimethylamine sulfate (DMAS) in its leather tanning process. A total of 6 air samples were collected in the wet process area using battery operated air pumps and ThermoSorb/N air sampling cartridges. About 180 L ± 10 of air was collected at each site giving a detection limit of 0.1 $\mu g/m^3$ for N-nitrosodimethylamine NDMA.

RESULTS AND DISCUSSION

No N-nitroso compounds were found on these air sample cartridges. See Table 55 for results and sample locations.

Table 55

Air Sample Analysis for Nitrosamines

Samples Collected during January 1980

Leather Tannery Plant - G

Sample #	Sample Location	N-nitroso Compounds Detected
1	Hide Processors	N.D.*
2	Beam House	N.D.
3	Tan Yard	N.D.
4	Tan Yard	N.D.
5	Color & Fat Liquoring	N.D.
6	Color & Fat Liquoring	N.D.

* N.D. - None detected, detection limit for N-nitrosodimethylamine = 0.1 $\mu g/m^3$

LEATHER TANNERY PLANT H

This tanning company, a side leather tannery, was established in 1872 in a small town located in the midwest. In 1900 the Company moved to its present location where the daily capacity was about 300 hides per day. Over the years the Company has grown considerably and today the plant processes 6800 hides per day - enough leather each year to make uppers for millions of pairs of shoes. Due to the increase in production, in 1966, the company moved the finishing operation to a new plant site, about 1/2 mile up the street. The plant site is made up of 68 acres with three major buildings containing 270,000 sq. ft. of production space. The Company moved a substantial portion of its operation to Texas in July of 1979.

Presently there are 394 full-time employees at the Plant. Of the 394 employees, 293 are in production. There are 3 shifts in operation. the first shift, 6:00 a.m. - 2:00 p.m., has 165 employees; second shift, 2:00 p.m. - 10:00 p.m. has 95 employees; third shift, 10:00 p.m. - 6:00 a.m. has 33 employees. With the exception of 4 white females, all production employees are male Caucasians. Only during the war years was there a substantial number of females hired. The turnover rate in the production area is very low, with many employees working for the Company 10-15 years or longer. In addition, there have been many family members employed by the company.

The tannery produces fully tanned and finished leather cow hides. Most of the operations typically found in leather tanneries are in use at this facility (Figure 15). Interest in surveying this plant for the presence of N-nitroso compounds and the possibility that workers may be exposed to these agents is due to the non-use of dimethylamine sulfate (DMAS). This tannery burns the hair off the hides in hide processors. This plant was included in this study in order to obtain a comparison between DMAS users and a plant which does not use DMAS in its process.

SAMPLING STRATEGY

Several sample sites were selected for area sampling for N-nitroso compounds and the nitrosation capacity The general areas selected for sampling were the beam house, retan, color and fatliquoring and the tan yard. Six sites within the plant were identified as sample stations. These sites were sampled during the intial walk-through survey of April 24, 1979. All sample stations were sampled for N-nitroso compounds, and airborne nitrosating capacity.

Air Sampling for N-nitroso Compounds.

All N-nitroso compound air samples were collected with ThermoSorb™/N air cartridges and the DuPont 2500 pump. Typically, the pumps were operated at from 1.5 to 2.0 Lpm for approximately 3 hours. After air sampling, the adsorbed compounds were quantitatively removed by back-flushing the cartridge with a 2.0 ml solution of 25% methanol in methylene chloride (7). Aliquots of the 2.0 ml eluate were then examined for N-nitroso compound content by either gas or liquid chromatography. In either case the TEA™ Analyzer is used for analysis.

RESULTS AND DISCUSSION

N-nitroso compounds were not detected in the April 24, 1979 walk-through survey (Table 56). The Company does not use dimethylamine sulfate in the dehairing process thus reducing the probability of nitrosamine formation. This plant was also selected for an epidemiological study.

Airborne nitrosating agents were found at all the sampling sites during the April 24, 1979 survey. The equivalent NO_2 levels of 26 parts per billion (ppb) in the fatliquor weigh-up area to 370 ppb in the beam house (Table 56). The average level of nitrosation capacity was 94 ppb. The highest level of 370 ppb is not unusual and does not represent a particularly high level of NO_2. Some of this detected nitrosating agent may be due to outside ambient levels of NO_2. These samples represent short term events, and, as a result they do not represent a daily average for this airborne nitrosating capacity.

The lack of dimethylamine sulfate (DMAS) in the dehairing process supports the theory that the non-use of this compound results in reduced levels of N-nitrosodimethylamine (NDMA). From the previous work that has been conducted in tanneries it can be shown that those plants which use DMAS have significantly increased levels of NDMA.

Table 56

Analysis of Air Samples Collected April 24, 1979
For Nitrosamine and Nitrosation Potential at Leather Plant H

Sample Number	Area Sample Location	Nitrosamines	Equivalent NO_2 PPB
1	Retan, Color, Fatliquor	N.D.*	28
2	Retan, Color, Fatliquor	N.D.	31
3	Beam House	N.D.	370
4	Tan Yard	N.D.	69
5	Dye Room	N.D.	38
6	Fatliquor Weigh-up Area	N.D.	26

* N.D. - Nondetectable - detection limit 0.05 $\mu g/m^3$

SHOE FACTORY PLANT I

This plant manufactures hand-sewn men's shoes with 125 employees in manufacturing and 5 in administration. The total floor space of the plant was about 50,000 sq ft, with about one-half of it for manufacturing. The factory occupied part of the first floor of a large building where other undetermined activities were located.

Hand sewing is the simplest form of shoe manufacturing, requiring few chemicals and glues. About 10% of all shoes made in this country are hand sewn. The largest percentage of shoes (60%) are made by cementing the leather. Welt construction accounts for 25% of all shoe manufacture (this is the oldest method of making high grade shoes) and the remaining 5% are made by other techniques including hot melting the sole to the uppers.

The manufacturing operation at this plant can best be described as hand crafting with little reliance on machines. Fully tanned and finished leather is received at the plant where it is then cut into various shoe parts using press dies (clickers). The shoe parts are then hand sewn using shaped forms (lasts) into finished shoes. Glue is occasionally used to temporarily secure the leather parts to the lasts and water is used to soften the leather, thus making it easier to stretch and shape the shoe over the last. There were no obvious sources of N-nitroso compounds at this plant.

SAMPLING STRATEGY

Air Samples

Five area air samples were collected at various locations along the shoe assembly line. One air sample was taken in the office area and one air sample was taken in the rubber sole stock storage area.

Bulk Samples

Four bulk samples were taken of process water and rubber sole stock. The process water samples were taken from a leather wetting tank, and a pail of water used to soak leather parts. The rubber sole stock samples were taken from a pile of foam rubber used to make rubber soles. The rubber sole stock was found to be free of TEA responsive compounds. The detection limit for NDMA was 0.5 $\mu g/g$.

RESULTS AND DISCUSSION

At a detection limit of 0.01 $\mu g/m^3$ there were no N-nitroso compounds in any of the area air samples (Table 57). At a detection limit of .001 $\mu g/g$ the two samples of leather soak water contained 9.6 ppb and 4 ppb of N-nitrosodimethylamine. At a detection limit of 0.2 $\mu g/g$ no N-nitroso compounds were detected in the bulk rubber sole materials (Table 58). These low levels of NDMA are probably of no real concern. The source for the NDMA in the water samples was not determined, however, it may have been leached out of the leather during soaking. The results of this plant survey indicate that only minor amounts of NDMA are associated with the manufacture of hand-sewn shoes. Other shoe manufacturing operations such as the hot melt or those that cast rubber parts to the shoe have not been surveyed.

Table 57

Results of Air Sampling in Leather Plant I

Sample No.	Collection Method	Location	N-nitroso Compounds Detected
2A	1N KOH	Cutting room	N.D.*
3A	1N KOH	Middle of hand sewing	N.D.
4A	1N KOH	Pre-fit area	N.D.
5A	1N KOH	Office area	N.D.
6A	1N KOH	End of fitting area (wetting tank area)	N.D.
7A	1N KOH	Exit from dryer	N.D.
10A	1N KOH	Rubber sole stock storage	N.D.

* N.D. - None Detected, detection limit 0.05 μg/m^3 (NDMA)

Table 58

Results of Bulk Samples in Leather Plant I

Sample	Material	N-nitroso Compounds Detected
1	15 iron Red crepe sole American Built rite	N.D.*
8	30 iron Black crepe sole Castelnovo Bariano (RO)	N.D.*
9	Leather soak water	9.6 ppb (NDMA)
11	Wetting tank water	4.3 ppb (NDMA)

* N.D. - None Detected, detection limit 0.2 μg/g (NDMA).

LEATHER INDUSTRY SUMMARY

A total of nine separate faclities were surveyed for the presence of N-nitroso compounds and two of these were re-surveyed. Four of the nine plants were found to have airborne levels of N-nitroso compounds greater than 0.5 $\mu g/m^3$. N-nitrosodimethylamine (NDMA) was the primary nitrosamine found associated with the tanning industry with the highest levels being found in those tanneries which used dimethylamine sulfate in the hide unhairing process. Table 59 summarizes the operations of each plant and the highest level of NDMA found in that plant. It can be seen from Table 59 that the use of dimethylamine sulfate (DMAS) is associated with the highest amounts of airborne NDMA. Five of the nine plants were found to have measurable amounts of airborne NDMA. However, the level of 0.05 $\mu g/m^3$ in the atmosphere of Plant F is insignificant compared to the 47 $\mu g/m^3$ found in the atmosphere of Plant A. This level of 47 $\mu g/m^3$ of airborne NDMA exceeds the previous high for any factory surveyed, the high of which was a finding of 36 $\mu g/m^3$ in the air adjacent to a rocket fuel manufacturing facility (20). Plants B and F have NDMA in their atmosphere, 8 $\mu g/m^3$ and 3 $\mu g/m^3$ respectfully, and at the time each was surveyed they were not using dimethylamine sulfate in their unhairing operations. However, Plant B had used DMAS in the recent past and analysis of wood samples of the plant's structure indicated a high level of NDMA in the structure itself (25 ppm, confirmed by USDA). The airborne levels of NDMA found in Plant B may be the result of past use of DMAS and the observed NDMA may be leaching out of the structure wood. In Plant F, DMAS had only been used on an experimental basis and perhaps residual amounts of this are responsible for finding NDMA in its atmosphere. Plant F also had a high level of an airborne nitrosating agent (assumed to be nitrogen dioxide) and small amounts of an NDMA precursor (presumably dimethylamine) were found in samples of process water. The other four plants, C, G, H and I were free of any NDMA contamination. Plant I produces only hand-sewn shoes thus the negative NDMA finding is not surprising and Plant C only finished leather that had been tanned elsewhere. It is significant that both Plants G and H, full tanneries, do not use dimethylamine sulfate and do not have measurable amounts of NDMA in their atmospheres.

The finding of N-nitrosodimethylamines in tanneries is directly associated with their use of dimethylamine sulfate and the evidence indicates that it is being produced as a result of dimethylamine being nitrosated by airborne nitrogen oxides. Dimethylamine was found, along with NDMA and a nitrosating agent, in the atmosphere of Plant F. A precursor amine compound for NDMA was discovered upon nitrosating air samples from Plant D - suggesting airborne dimethylamine. This same Plant D also had both NDMA and a high level of a nitrosating agent in its atmosphere. The concentration of nitrogen dioxide needed to experimentally produce the same amount of N-nitrosomorpholine as produced on the morpholine-coated nitrosation capacity air samples used in Plant D, would have to be 4 to 5 parts per million. The use of open gas flame heaters to heat this Plant's atmosphere would certainly result in high levels of airborne nitrogen oxides. Neither Plants A or B were examined for airborne amines or for the capacity of their air to form N-nitroso compounds. However, it was noted that these Plants, along with Plants D, E, F, G and H all used propane driven fork lift trucks operating within their Plants. The exhaust from these vehicles can contribute to higher levels of nitrogen oxides within the Plant's atmosphere. Plant H had measurable levels of an airborne nitrosating agent (NO_x) as determined by the formation of N-nitrosothiomorpholine on an air nitrosation capacity ThermoSorb/A cartridge. Plant H did not use DMAS and no NDMA was found in its atmosphere.

Because none of the process water samples or other bulk samples were found to contain significant amounts of any N-nitroso compounds, it cound be concluded that worker exposure will be via inhalation. We also conclude that the source for the airborne NDMA in these tanneries is due to nitrosation of dimethylamine, in either the gas phase or on surfaces, by airborne oxides of nitrogen.

Further studies involving N-nitroso compounds in tanneries should include:

- Nitrogen oxide measurement
- Airborne amine measurement
- Simulated atmosphere studies of the formation of N-nitroso compounds using precursor levels of amines and nitrogen oxides that approximate actual levels measured in tanneries.
- Identification of the sources of other N-nitroso compound precursors within the leather tanning industry
- Possible methods to eliminate or reduce the levels of N-nitroso compounds found in these atmospheres.
- Breathing zone measurement of N-nitroso compounds
- Biological sampling

Table 59

Summary of NDMA Findings and Plant Operation of the 9 Leather Manufacturers

Plant	Description of Operation	Uses DMAS* for unhairing	Highest Level of Airborne NDMA
A**	A full tannery	Yes	47 $\mu g/m^3$
B	A partial tannery producing re-tanned leather for finishing at Plant C	Has recently discontinued its use	8 $\mu g/m^3$
C	A leather surface finishing operation - no tanning	No	0
D	Produces chrome tanned leather for re-tanning and finishing at Plant F	Used only on an experimental basis	3 $\mu g/m^3$
E	A re-tanning and finishing operation	No	0.05 $\mu g/m^3$
F	A full tannery	Yes	10.8 $\mu g/m^3$
G	A full tannery	No	0
H	A full tannery	No	0
I	A manufacturer of hand-sewn mens' shoes	No	0

* DMAS - Dimethylamine sulfate

** 2.0 $\mu g/m^3$ of N-nitrosomorpholine was found in air samples collected in the finishing area of this plant.

SOAP, DETERGENT AND SURFACTANT INDUSTRY

General Description of the Soap, Detergent and Surfactant Industry

Interest in surveying this industry for the presence of N-nitroso compounds and the possibility that workers may be exposed to these agents is due to its production of amine cationic surface active agents (149). This industry also produces anionic detergents and soap. The production of anionic detergents and soaps, from arylalkylsulfonates, fats, waxes and oils of plants and animals, does not involve the use of amines and therefore seems an unlikely source for N-nitroso compounds. However, in the production of cationic surface active agents, primary, secondary and tertiary amines are used. These amines could, if a suitable N-nitrosating agent were present, give rise to N-nitroso compounds. Sources for nitrosating agents include airborne oxides of nitrogen, drying towers, a process where combustion gas may be passed over products and gas driven lift trucks. As evidence that N-nitroso compounds may be associated with this industry, 0.15 $\mu g/m^3$ of NDMA was found in an outside air sample collected adjacent to a cationic detergent manufacturing facility in Jersey City, New Jersey. This facility was manufacturing cationic surfactants at the time that Thermo Electron Corporation, under contract to EPA, made this finding. Because of this finding and the known use of nitrosamine precurors, this industry was included in this study of worker exposure to N-nitroso compounds.

While this study has been limited to the manufacture of surfactants, the use of the cationic surfactants by other industries could result in worker exposure to N-nitroso compounds. Amine containing cationic surfactants have been used for: corrosion inhibitors, ore benefaction, solvent extraction of uranium ores, asphalt emulsifiers, bacteriocides, fabric softeners, antistatic agents, acid washing of wool, dye leveling agents, dye fixatives for direct cotton dyes, dry cleaning additives, hair rinses and shampoos, pigment dispersion agents in paint, sanitizing, antiseptic lotions, mouthwashes, additives to paper, motor oil additives, additives to metal pickling baths, textile finishing and textile softeners (149-150).

SURFACTANT PLANT A

This plant, located in a residential area on the East Coast, was built in 1910. At the present, the plant occupies 4.2 acres with 72,000 sq. ft. of production space and a separate 40,000 sq. ft. of warehouse space. A variety of chemical products including anionic, cationic, non-ionic and special surface active agents are manufactured at this facility. The plant operates three shifts five days per week employing 104 in the production area and 25 in the administrative area. Of interest at this facility was the secondary amines. The type of cationic compounds produced at this facility include: germicidal quarternaries, germicidal specialties and non-germicidal quarternaries.

The germicide quarternary compounds are of the alkyldimethylbenzylammonium chloride type. The synthesis of these compounds includes the use of dimethylamine (DMA), a precursor for N-nitrosodimethylamine (NDMA). The germicide specialty products include n-alkylisoquinolinium bromides, n-alkyldimethyl benzyl ammonium saccharinates and n-alkyl dimethyl ethylbenzyl ammonium cyclohexylsulfamates. The non-ionics are of the n-alkyldimethylamine oxide type. The non-ionic amine oxides are used in cosmetics and househould and janitorial products. The specialty products of this plant include a variety of tertiary amines that are produced using dimethylamine, for example, n-alkyl dimethyl-amine. These compounds are intermediates for later use in the synthesis of quarternaries and amine oxide products. Other amine type surfactants produced at this facility include alkanolamines and diethanol amides. These non-ionic compounds are used in a variety of products including shampoos, bubble baths and dishwasher detergents.

SAMPLING STRATEGY

Air Samples

After the plant tour, 11 area air sample sites were selected. Eight of the air sample sites were located within the product manufacturing area. The other sites included, the quality control laboratory, the warehouse, the plant boiler room and an outside control sample. ThermoSorb/N air sampler cartridges and battery driven air pumps (DuPont 2500 and Bendix C115) operating at 1.5 to 2 L/min were used to collect the air samples. The volume of air sampled at each site varied from 273 to 370 liters.

Bulk Samples

No bulk samples were examined at this facility.

RESULTS AND DISCUSSION

Nine of the 11 air samples were found to contain N-nitroso dimethylamine (NDMA) with levels ranging from 0.07 $\mu g/m^3$ to 0.8 $\mu g/m^3$ (Table 60). The sample collected in the warehouse area and the sample collected outside the plant were both negative. The NDMA findings in this plant were not surprising since NDMA had been found outside the plant on a previous occasion and the amine precursor, dimethylamine, is used at this plant. A nitrosating source for the NDMA was not observed within the plant, however, the plant is located in an urban area and local vehicular traffic may account for airborne oxides of nitrogen at levels sufficient to act as the nitrosating agent.

Table 60

Airborne N-nitroso Compounds
Surfactant Plant A

Sample No.	Sample Location	N-nitroso Compound $\mu g/m^3$ NDMA*
1	Production area for amine containing compounds	0.20
2	Dimethylamine distillation area	0.30
3	Secondary sulfuric acid scrubber for dimethylamine removal	0.26
4	Product Packaging Area	0.80
5	Boiler Room	0.15
6	Sulfation Area	0.16
7	Chemical Mixing Tank	0.10
8	Control Laboratory	0.26
9	Feinc Area	0.07
10	Warehouse Area	N.D.**
11	Outside Air Control Sample	N.D.

* NDMA = N-nitrosodimethylamine

** N.D. = none detected - detection limit for NDMA = 0.03 $\mu g/m^3$

SURFACTANT PLANT B

This plant employs 250 workers in the production area, 50 in management and operates three shifts, five days per week, producing synthetic laundry detergents and soaps. It has been in operation since the 1940's and does not produce cationic surfactants. The raw materials used at this facility consist of linear alkyl benzenes, fatty alcohols, oleum, sulfuric acid, sodium hydroxide and a variety of additives and perfumes. The manufacturing process consists of sulfating the alkyl benzene or fatty alcohols followed by neutralization with sodium hydroxide. Dyes and other additives are then added and the product dried via hot air in a drying tower. Perfumes, admixes and softening ingredients are then added to the dry product prior to packaging. The final product is warehoused for later distribution to retail outlets. The only amine used at this facility is the cationic surfactant Di-tallow dimethyl ammonium chloride. This softening agent is added to some of the products.

The drying tower used to dry the products is heated by direct oil heat. During our intial plant tour we observed several propane driven fork lift trucks. These trucks would exhaust oxides of nitrogen into the atmosphere of this plant.

SAMPLING STRATEGY

Air Samples

At this plant on March 19, 1980, eight area air samples were collected and analyzed for N-nitroso compounds. The volume of air sampled at each site varied from 100 to 358 liters. ThermoSorb/N air samplers were used in each case.

RESULTS AND DISCUSSION

No N-nitroso compounds were found in this plant's atmosphere (Table 61). However, after inspecting the plant's manufacturing processes, these results are not surprising since the only amine used by the plant is the cationic surfactant Di-tallow dimethyl ammonium chloride. This compound is manufactured at a separate facility and is shipped to this plant for use as an additive to its final product.

Table 61

Airborne N-nitroso Compound
Surfactant Plant - B

Sample No.	Collection Method	Sample Location	N-nitroso Compound Detected
1	ThermoSorb/N	MSG Table Area	N.D.*
2	ThermoSorb/N	5th Floor Finished Products	N.D.
3	ThermoSorb/N	4th Floor Finished Products	N.D.
4	ThermoSorb/N	3rd Floor Packing Room Line 9	N.D.
5	ThermoSorb/N	Soap Process Near Neutralizer	N.D.
6	ThermoSorb/N	2nd Floor Soap Processing	N.D.
7	ThermoSorb/N	Glueing operation on packing line	N.D.
8	ThermoSorb/N	Warehouse Unit Load Former	N.D.

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* N.D. - None detected, detection limit 0.03 μg/m^3

SURFACTANT PLANT C

This plant, located on the East Coast, is a complex of multi-storied buildings which occupy 22.9 acres and was constructed in 1820. The plant employs 1200 in production and 600 in administration and R&D. The plant operates three shifts, five days per week, producing anionic detergent, and soaps, cleansers and personal care products. One of the shampoos produced in the personal care products area of the plant contains an alkanolamine in its formulation. The raw materials used at this facility include linear alkyl benzenes, fatty alcohols, oleum, sulfuric acid, sodium hydroxide and a variety of dry additives and perfumes. The manufacturing process consists of sulfonating the alkyl benzenes or fatty alcohols followed by neutralization with sodium hydroxide and after the addition of dyes and additives, the product is dried via hot air in a drying tower. Perfumes, admixes and softening ingredients are then added to the dry product prior to packaging it. The product is then warehoused for later distribution to retail outlets.

The drying tower is heated by direct oil heat. During our initial plant tour we observed several propane driven fork lift trucks which could contribute oxides of nitrogen to the plant's atmosphere.

SAMPLING STRATEGY

Air Samples

Using battery-driven air pumps (Model DuPont 2500 and Bendix C115) operating at 1.5 to 2 L/min and ThermoSorb/N air cartridges, 11 area samples were collected at this facility. The sites chosen for sampling (See Table 62 for locations) were selected during the initial tour. All of the sites sampled were, with the exception of an outside air control, within the manufacturing areas of this plant. The sample sites were typical of the operations within an anionic detergent producing facility.

RESULTS AND DISCUSSION

No N-nitroso compounds were found in this plant's atmosphere on the day that it was sampled. These findings were, however, expected since this facility did not use any volatile amines in its processes.

Table 62

Air Sample Location and Analytical Results
Surfactant Plant C

Sample No.	Sample Location	N-nitroso Compounds
1	Liquid Detergent Manufacturing Area	N.D.
2	#4 Product Packing Line	N.D.
3	#2 Product Packing Line	N.D.
4	Soap Kettle House	N.D.
5	#10 Dryer	N.D.
6	Minor Ingredients Room	N.D.
7	#3 Product Packing Line	N.D.
8	Shampoo Production Area	N.D.
9	F-Tower Computer Area	N.D.
10	Under Premix Blower Pump	N.D.
11	Outside Air Control Sample	N.D.

*N.D. - None detected - detection limit for NDMA = 0.03 $\mu g/m^3$

SUMMARY OF SOAP, DETERGENT AND SURFACTANT INDUSTRY

Three surfactant manufacturing plants were included in this survey, two of which, Surfactant Plants B and C, produced anionic detergents and soaps and one of which, Surfactant Plant A, produced cationic surface active agents. N-nitrosodimethylamine was found in the atmosphere of plant A with levels ranging from non-detectable in a separate warehouse to 0.8 $\mu g/m^3$ within the product packaging area. No N-nitroso compounds were found within plants B and C.

The negative findings for N-nitroso compounds within plants B and C are not surprising since the needed amine precursors are not a part of anionic detergent manufacturing processes. In manufacturing cationic surface active agents, on the other hand, nitrosatable amines, such as, dimethylamine and secondary alkanolamines, are widely used. Since only one cationic detergent manufacturing facility was surveyed and N-nitroso compounds were found in its environment, other such manufacturing facilities should be surveyed in order to determine the actual extent of possible worker exposure to these compounds.

General Description of the Iron and Steel Casting Industry

Metal castings are produced by pouring molten metal into refractory molds where it solidifies into the desired shape and contour. This industry has been in existence since 1845. The first steel castings were made using sand molds to produce horseshoes and loam molds to produce steel church bells (152). In the United States there are now approximately three hundred foundries ranging in size, according to production, from 10 to 100 tons of castings produced per month, to those which are capable of producing several thousand tons of castings per month. These foundries can be either highly specialized, producing specific types of castings, or easily adaptable to the production of a wide variety of castings. While foundries may differ in product line or specific production methods, they all use molds and molten metal to produce the desired casting.

The material most widely used to make molds and cores (cores are used to exclude metal from areas of the final casting) is silica sand. The refractory molds are fabricated using sand containing binders and patterns to imprint the desired shape of the casting in the sand. Binders are materials that are compounded into the sand mix which act to hold the sand in the desired shape.

Some of the sand binding materials include the following: sodium bentonite, cereals, water, clay, phenol formaldehyde resins, isocyanates, oils and amine catalyzed resin systems. Interest in surveying this industry for the presence of N-nitroso compounds centers around the sand core fabrication process that utilizes amines as a part of the sand binding system. These cores are made by injecting sand, containing amine catalyzed binding agents, into molds followed by injection of the amine catalyst. This interest stems from an OSHA report of November 15, 1978 stating that N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA) were found in the atmosphere of a foundry (see Foundry E in this report). The reported levels of NDMA were from 0.1 - 0.8 $\mu g/m^3$ and from 0.1 - 1.4 $\mu g/m^3$ for NDEA. These nitrosamines were found in air samples collected in the sand core production area where amine catalysts were being used. The amine being used by this foundry was reported to be triethylamine (TEA).

Other amines that may be found in the sand core process include dimethylamine (DMA), trimethylamine (TMA), N-ethyldimethylamine (EDMA), and diethylamine (DEA). Some of these amines may also be present as contaminants in the actual amine being used or they may be produced when hot metal is poured into the molds. In any event, all of these amines can serve as nitrosamine precursors. Compounds such as dimethylamine and diethylamine (secondary amines) have been demonstrated to form their corresponding nitrosamines from atmospheric oxides of nitrogen. Tertiary amines such as N-ethyldimethylamine and triethylamine are, on the other hand, less likely to form nitrosamines under the same conditions. As for the oxides of nitrogen, these can be produced by the combustion of natural gas used to heat hot shell cores to fuse sand grain together and by air contacting hot metal in the metal pouring area.

Five foundries were surveyed for the presence of N-nitroso compounds, and three of these facilities (Foundries A, B and E) used the amine catalyzed sand binding process in their sand core operation. The other two foundries (C and D) did not use amines in their manufacturing operations.

FOUNDRY A

This plant occupies several acres and has four separate buildings. The largest of these buildings is the green mold area where the casting are poured. This area is approximately 60 x 80 ft. with a ceiling height of 20 ft. The core making building is separate from the casting operation and occupies about 10,000 sq. ft. The shell core production is located in this area. The plant started operating in 1947 and presently has a work force of 200 with 25 in management. The plant produces about 6000 tons of castings per year. The Ashland processes (the core process that uses amines) has been in operation for 3 years producing cores for about 10-15% of their castings. This process was reported to use about five (200 lb) tanks of dimethylamine per month. The reason the plant gave for using the Ashland process was that it is more economical and faster than the core making processes that it replaces.

SAMPLING STRATEGY

After a brief plant tour, several sample sites were selected for area air sampling for N-nitroso compounds and precursor amines. The two general areas selected for sampling were the shell core production building, where the Ashland process is also located, and the main metal casting building, where the iron and steel castings are poured. Within these areas a total of six sample sites were established. Two battery operated pumps, one equipped with a ThermoSorb/A air sampling cartridge for trapping amines, the other, a ThermoSorb/N cartridge for N-nitroso compounds, were placed side by side at each sampling site. These pumps were then operated for approximately 2 to 3 hours with air sampling rates of 1.5 L/min to 2 L/min.

The three sites sampled in the shell core area were the hot shell core machine, the Ashland amine core process, and the core storage area. It was requested that the smaller of the two Ashland core machines be operated for approximately 45 min during the sampling periods. During this time we detected an ammonia-like odor within the building. The shell core machines were fully operational using open flame natural gas to heat the cores to the proper temperature. While the air samples were being collected we also obtained a composite sand sample from waste sand around the shell core machines. The three sample sites within the metal casting area were selected such that a cross section of the atmosphere would be sampled. We did not detect any ammonia-like odor in this area and were told that none of the amine containing cores were being used during the sampling time. We observed several potential sources of nitrogen oxide within this area, these included the electric furnace and the hot casting.

The amine samples were collected to determine if the sampled atmospheres contained any amines which could give rise to N-nitroso compounds. Amines that could give rise to these compounds would be secondary amines such as dimethylamine, diethylamine, morpholine, etc.

RESULTS AND DISCUSSION

N-nitroso compounds were not detected in this plant's atmosphere (Table 63). These negative findings were surprising since the plant reported using dimethylamine in its cold core making operation - an operation which is about 6' from a hot shell operation. The hot shell operation, which uses multiple gas jets to heat the shell cores, should produce high levels of oxides of nitrogen. The combination of oxides of nitrogen and dimethylamine in the atmosphere should, to some extent, result in the formation of N-nitrosodimethylamine (NDMA). However, we did not find any dimethylamine in the plant's atmosphere (Table 64) and this perhaps explains why we did not collect any NDMA.

The plant personnel reported that dimethylamine was used in its core making operation, and an ammonia like odor was detected in the air near this operation - suggesting that an amine was being used, but we were unable to detect any dimethylamine. We also were unable to detect any N-nitroso compounds in the casting area. However, none of the amine formulated sand cores were being used on the day that we were sampling.

We did find dimethylamine, trimethylamine, and N-ethyldimethylamine in the bulk samples of sand collected in the shell core area (Table 65). The presence of these amines in the sand samples and not in the air samples is hard to explain at this time. However, this sample does suggest that either these amines were used in the past or that the amines in the sand core process can give rise to these compounds.

Table 63
Nitrosamine Results - Air Samples
Foundry A

Sample No.	Collection Method	Sample Location	N-nitroso Compounds Detected
1	ThermoSorb/N	Amine Core Making Operation	N.D.*
2	ThermoSorb/N	Shell Core Operation	N.D.
3	ThermoSorb/N	Core Storage Area	N.D.
4	ThermoSorb/N	Near Electric Furnace	N.D.
5	ThermoSorb/N	Sand Shakedown Area	N.S.**
6	ThermoSorb/N	Green Sand Molding	N.D.

* N.D. - None detected - detection limit = 0.1 μg/m^3 for N-nitrosodimethylamine.

** N.S. No sample - air pump failed during sampling

Table 64

Amine Results - Air Samples
Foundry A

Sample No.	Collection Method	Sample Location	Amines* Detected			
			DMA	TMA	DEA	TEA
1	ThermoSorb/A	Amine Core Making Operation	ND**	ND	ND	ND
2	ThermoSorb/A	Shell Core Operation	ND	ND	ND	ND
3	ThermoSorb/A	Core Storage Area	ND	ND	ND	ND
4	ThermoSorb/A	Near Electric Furnace	ND	ND	ND	ND
5	ThermoSorb/A	Green Sand Molding	ND	ND	ND	ND

*<u>Amines</u>

DMA - Dimethylamine
TMA - Trimethylamine
DEA - Diethylamine
TEA - Triethylamine

**ND - None detected - detection limit 0.5 μg/m^3 for dimethylamine

Table 65

Bulk Sample Results
Foundry A

Sample Description	μg/g* of Amines Found	
Core Making Sand Collected from Sand Deposits on Shell Core Operations and Ashland Process Machine	Methylamine	= 2.6
	Dimethylamine	= 1.2
	Trimethylamine	= 3.8
	N-Ethyldimethylamine	= 14.2
	Triethylamine	= 0.2
	Morpholine	= 0.8

* μg/g = part per million

FOUNDRY B

This Foundry was started in 1906 and presently has 143 employees producing cast iron and steel products. The main plant operations are housed in one building with the sand core operation separated by about 100 ft from the metal casting area. The approximate size of the plant is 400 ft x 400 ft with the metal casting area occupying about 1/2 of this area. The management of this plant reported using an amine sand core process. This process is not in operation on a daily basis and was not being operated while we were sampling. This plant also produces metal casting molds using sand binder systems containing phenolic type resins called Pep-Set and a process called Isocure.

SAMPLING STRATEGY

Air Sampling

Six sample sites were selected for area air sampling for N-nitroso compounds and their precursor amines. The two areas selected for sampling were, the sand core production area where the hot shell core, amine sand core, and the Pep-Set molding are located, and the metal pouring area where the castings are produced. Within the sand core area, air sampling pumps were placed near the Isocure process (not in operation during sampling), the amine sand core finishing area and the Pep-Set operations. Other sample sites were the center of the molding room and an outside air control sample.

At all sites, two battery operated pumps, one equipped with a ThermoSorb/N air sampling cartridge and the other with a ThermoSorb/A air sampling cartridge were placed side by side. These sample pumps were operated for approximately 3 hours at air flow rate of from 1.5 to 2 L/min. While these pumps were operating, a composite sample of waste sand was collected near the shell core process machinery.

During the survey none of the amine sand cores were being used in the metal casting area and none of the sand core processes were in operation.

The amine samples were collected to determine if the sampled atmospheres contained any amines which could give rise to N-nitroso compounds. The amines that could give rise to these compounds include secondary amines such as dimethylamine, diethylamine and morpholine.

RESULTS AND DISCUSSION

N-nitroso compounds were not found in this plant's atmosphere (Table 66). These findings were unexpected since the facility was reported to use dimethylamine in its sand core making operations. However, this process was not in use while we were at this facility. The hot shell core operation, which would be a source of nitrogen oxides, was also not in operation during our visit. We did not find any nitrosatable amines in the plant's atmosphere (Table 67) and this may explain the negative findings for N-nitroso compounds.

We did not find any N-nitroso compounds or amines in the metal casting area, however, the amine formulated sand cores were not being used on the day that we sampled.

Four amines, trimethylamine - 2 μg/g, N-ethyldimethylamine - 19 μg/g, triethylamine - 0.4 μg/g, and morpholine - 0.04 μg/g were found in the composite sand sample. With the exception of the morpholine, the other amines are tertiary amines, these are less likely to give rise to any N-nitroso compounds by direct reaction with oxides of nitrogen.

Table 66

Nitrosamine Air Sample Results

Foundry B

Sample No.	Collection Method	Sample Location	N-nitroso Compound Detected
16175	ThermoSorb/N	Isocure Area	N.D.*
16177	ThermoSorb/N	Amine Sand Core Process	N.D.
16179	ThermoSorb/N	Core Finish Area	N.D.
16181	ThermoSorb/N	Pep-set Mold Production	N.D.
16183	ThermoSorb/N	Center of Mold Room	N.D.
16185	ThermoSorb/N	Outside Air Control	N.D.

*N.D. - None detected - detection limit for N-nitrosodimethylamine = 0.1 μg/m^3

Table 67

Amine Air Sample Results

Foundry B

Sample No.	Collection Method	Sample Location	Amine Detected DMA	 TMA	 DEA	 TEA**
16176	ThermoSorb/A	Isocure Area	N.D.*	N.D.	N.D.	N.D.
16178	ThermoSorb/A	Amine Sand Core Process	N.D.	N.D.	N.D.	N.D.
16180	ThermoSorb/A	Shell Core Finish Area	N.D.	N.D.	N.D.	N.D.
16182	ThermoSorb/A	Pep-set Mold Production	N.D.	N.D.	N.D.	N.D.
16184	ThermoSorb/A	Center of Mold Room	N.D.	N.D.	N.D.	N.D.

* N.D. - None detected - detection limit for dimethylamine = 0.5 μg/m^3

** DMA = Dimethylamine
TMA = Trimethylamine
DEA = Diethylamine
TEA = Triethylamine

FOUNDRY C

This plant has been in operation since 1932, however, the original plant was built 20 years earlier. The facility consists of six separate structures located in the same general area but on separate sites. Newer facilities are presently under construction. This plant employs 273 workers who produce about 600 tons of castings per month. This foundry is quite modern, using very sophisticated housekeeping and environmental controls. The amine sand core production process is not used at this facility. Other core making processes, such as the hot shell core and Pep-Set process, are used. These processes are located in three separate sites. The two metal casting areas are located in separate buildings, one of these areas was almost completely automated and had an excellent ventilation system.

SAMPLING STRATEGY

Air Samples

Five sample sites were selected for area air sampling for both N-nitroso compounds and precursor amines. The areas selected were, the Pep-Set operation where no bake sand molds are produced. The hot shell mold room where high temperatures are used to fuse sand into molds, the green sand molding area, the metal pouring deck where the castings are made and the sand shake out area where the metal is separated from the molds. These areas were selected for sampling because they represent a cross section of the operations of this foundry. Two battery operated pumps, one equipped with a ThermoSorb/N air sampling cartridge and the other with a ThermoSorb/A air sampling cartridge were placed side by side at each sampling site. These pumps were then operated for 3 hours with air sampling rates of from 1.5 to 2 L/min.

During our initial plant tour we did not observe any sources of either amines or N-nitroso compounds. We did, however, observe several combustion processes which could contribute oxides of nitrogen to the plant's atmosphere.

Air samples were examined to determine if the atmosphere in the sampled area contained any amines which could give rise to N-nitroso compounds.

RESULTS AND DISCUSSION

With the exception of the metal pouring deck area, where 0.1 $\mu g/m^3$ of N-nitrosodimethylamine was found, no other N-nitroso compounds or amines were found in this plant's atmosphere (Table 68). The remainder of the negative findings are not surprising since this plant does not use amines in any of its manufacturing areas. We conclude from these findings that there is no significant worker exposure to N-nitroso compounds in this plant and that there are no amine precursors to these chemicals in the plant's atmosphere (Table 69).

Table 68

Nitrosamine Results - Air Samples

Foundry C

Sample No.	Collection Method	Sample Location	N-nitroso Compounds Detected
1	ThermoSorb/N	Pep Set Operation	N.D.
2	ThermoSorb/N	Hot Shell Mold Room	N.D.
3	ThermoSorb/N	Outside Control	N.D.
4	ThermoSorb/N	Green Sand Molding	N.D.
5	ThermoSorb/N	Metal Pouring Deck	0.1 $\mu g/m^3$** NDMA
6	ThermoSorb/N	Sand Shake Out Area	N.D.*

* N.D. - None detected - detection limit 0.1 $\mu g/m^3$ NDMA

** 0.1 $\mu g/m^3$ NDMA (N-nitrosodimethylamine) this level is too low for other confirmation methods.

Table 69

Amine Results - Air Samples

Foundry C

Sample No.	Collection Method	Sample Location	Amines Detected*			
			DMA	TMA	DEA	TEA
16187	ThermoSorb/A	Sand Shake Out Area	N.D.**	N.D.	N.D.	N.D.
16189	ThermoSorb/A	Metal Pouring Deck	N.D.	N.D.	N.D.	N.D.
16191	ThermoSorb/A	Green Sand Molding	N.D.	N.D.	N.D.	N.D.
16193	ThermoSorb/A	Pep-set Operation	N.D.	N.D.	N.D.	N.D.
16195	ThermoSorb/A	Hot Shell Mold Room	N.D.	N.D.	N.D.	N.D.

* Amines - DMA - Dimethylamine
TMA Trimethylamine
DEA - Diethylamine
TEA - Triethylamine

** N.D. - none detected - detection limit 0.5 $\mu g/m^3$ for dimethylamine

FOUNDRY D

The plant was built in 1920 and presently has four separate buildings occupying about three acres. The largest of these buildings, the main production area, has about 100,000 square feet. This plant has 155 employees, 11 are in management and it produces 300-500 tons of castings per month. The mold and core production facilities are located in separate areas within the main production building. The plant produces a large variety of castings using green sand moldings, hot shell sand cores and the no-bake Isocure cores. They do not use amines to manufacture their sand cores.

SAMPLING STRATEGY

Air Samples

Five sample sites were selected for area air sampling for both N-nitroso compounds and amines. The areas selected were the coremaking room, the no-bake core production, the green sand mold room, the metal casting area and the sand shake out area. These areas were selected because they represented a cross section of this foundry's general activities. Two MSA Model C battery operated pumps, one equipped with a ThermoSorb/Nair sampling cartridge and the other with a ThermoSorb/A air sampling cartridge were placed side-by-side at each sampling site. These pumps were then operated for three hours with air sampling rates of from 1.5 to 2 L/min.

During the initial plant tour no sources for either amines or N-nitroso compounds were observed. However, several combustion processes were observed which would contribute oxides of nitrogen to the plant's atmosphere. The amine air samples were collected to determine if the atmosphere in the sampled areas contained any amine precursors which could give rise to N-nitroso compounds. Amines that can give rise to N-nitroso compounds include secondary amines such as, dimethylamine, diethylamine and morpholine.

Bulk Samples

Composite sand samples were also collected from the waste sand within the core manufacturing area in order to determine if amines were present in the sand-binder mix.

RESULTS AND DISCUSSION

No N-nitroso compounds or amines were found in this plant's atmosphere (Table 70). The composite sand sample did not contain any amines at a detection limit of 0.5 μg/g for dimethylamine. These findings were not unexpected since the plant does not use amines in its sand core production process. The amine air samples were examined for the presence of dimethylamine (DMA), trimethylamine (TMA), diethylamine (DEA) and triethylamine (TEA) (Table 71). Other amines such as N-ethyldimethylamine (EDMA) and morpholine, had they been present in the sampled air, would also have been collected and detected by the sampling and analytical methods.

Table 70

Nitrosamine Results - Air Samples

Foundry D

Sample #	Collection Method	Sample Location	N-nitroso Compound Detected
1	ThermoSorb/N	Core Making Room	ND*
2	ThermoSorb/N	No Bake Core Production	ND
3	ThermoSorb/N	Green Sand Mold Area	ND
4	ThermoSorb/N	Sand Shake Out Area	ND
5	ThermoSorb/N	Mold Pouring Area	ND

* ND - None detected, detection limit - 0.1 μg/m^3 for N-nitrosodimethylamine

Table 71

Amine Results - Air Samples

Foundry D

Sample #	Collection Method	Sample Location	Amine Detected*			
			DMA	TMA	DEA	TEA
1	ThermoSorb/A	Core Room	ND**	ND	ND	ND
2	ThermoSorb/A	No Bake Core Production	ND	ND	ND	ND
3	ThermoSorb/A	Green Sand Mold Area	ND	ND	ND	ND
4	ThermoSorb/A	Sand Shake Out Area	ND	ND	ND	ND
5	ThermoSorb/A	Mold Pouring Area	ND	ND	ND	ND

*Amines Detected - DMA - Dimethylamine
TMA - Trimethylamine
DEA - Diethylamine
TEA - Triethylamine

**None Detected - detection limit 0.5 μg/m^3 for dimethylamine

FOUNDRY E

This plant was surveyed for N-nitroso compounds during October 17, 1978 by NIOSH and OSHA personnel. The plant has 340 employees and it produces grey steel castings. Castings are made at this facility using sand shell cores, green sand molds and the Ashland amine sand cores. It is the Ashland sand core making process that is of interest in this plant. This process uses potentialy nitrosatable amines. The areas surveyed in this plant include the core making room, a room 60' x 100', and the employees lunch room.

SAMPLING STRATEGY

Air Samples

A total of 25 air samples and 9 bulk samples were collected for N-nitroso compound analysis. With the exception of the one sample collected in the lunch room, all of the samples were collected within the core production area. Eleven of the air samples were personal samples while the remaining 14 samples were area air samples. The air samples were collected using battery operated Bendix C-115 pumps equipped with either a ThermoSorb/N air sampling or an impinger containing 20 ml of 1N KOH. The air samples were collected by drawing air through the traps at a constant rate of from 1 to 4 L/min from 25 minutes to 7.5 hours. The total volume of air samples varied with each sample from 90 to 600 liters.

Bulk Samples

Nine bulk samples, consisting of four solid and five liquid samples, were collected for N-nitroso compound analysis. The solid samples were sand and iron oxides whereas the liquid consisted of resins and other sand binders. All nine of these materials were used in the sand core making processes.

RESULTS AND DISCUSSION

N-nitrosodimethylamine (NDMA) was found throughout the sand core production area except near a stack of hot sand cores which had just been removed from the tower oven (Table 72). The air in this area was found to contain 0.7 $\mu g/m^3$ of N-nitrosodiethylamine (NDEA), probably resulting from the trimethylamine gas used to help bind the sand cores. The highest level of NDEA, 1.4 $\mu g/m^3$ was found near the exhaust port of one of the thermal molds. All but one of the personal samples showed the presence of NDEA, with levels ranging from 0.1 $\mu g/m^3$ to 0.6 $\mu g/m^3$. Airborne NDMA concentration levels ranged from 0.1 $\mu g/m^3$ to 0.8 $\mu g/m^3$. The highest NDMA level, 0.8 $\mu g/m^3$ was found in the personal sample placed on the shell mold operator (Table 73). All of the personal air samplers were operated for 7 to 7.5 hours. The area air sampler using the ThermoSorb/N traps were operated 30 minutes, whereas the KOH traps were operated for 3 hours. NDEA appears in the KOH traps but not in the ThermoSorb/N air sample cartridges. However, ThermoSorb air samplers were not operating during the time that the triethylamine gas was being heavily used.

Table 72

Area Air Samples

Foundry E

Sample #	Collection Method	Sample Location	NDMA (μg/m^3)	NDEA (μg/m^3)
1	ThermoSorb/N	Back wall, behind molds	0.3	ND*
1'	KOH		0.3	
2	ThermoSorb/N	Above conveyor belt carrying molds	0.3	ND
2'	KOH		0.4	
3	ThermoSorb/N	Tower Oven	0.6	ND
3'	KOH		0.7	0.2
4	ThermoSorb/N	Chemical Storage Area	0.5	ND
4'	KOH		0.4	0.2
5	ThermoSorb/N	On air/gas dryer, near first Redford Mold	0.5	ND
5'	KOH		0.6	0.2
6	KOH	Lunch Room	0.6	ND
6'	ThermoSorb/N	Near stack of hot cores	ND	0.7
7	ThermoSorb/N	Above MC_1	0.5	1.4
7'	ThermoSorb/N	Above MC_3	0.5	ND

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*ND - None detected - detection limit for N-nitrosodiethylamine (NDEA) = 0.2 μg/m^3

Table 73

Personal Air Samples

Foundry E

Sample #	Collection Method	Worker Function	NDMA ($\mu g/m^3$)	NDEA ($\mu g/m^3$)
1	ThermoSorb/N	Isocure Operator	0.3	0.5
1'	KOH		0.3	0.2
2	ThermoSorb/N	Cleaning Isocure	0.4	0.6
2'	KOH		0.3	0.1
3	ThermoSorb/N	Shell Core Operator	0.8	0.3
3'	KOH		0.1	ND*
4	ThermoSorb/N	Stacking Cores	0.4	0.3
4'	KOH		0.2	0.1
5	ThermoSorb/N	Finishing Cores	0.5	0.5
5'	KOH		0.2	0.1

*ND - None detected - Detection limit for N-nitrosodiethylamine (NDEA) = 0.1 $\mu g/m^3$

Note: The higher levels of N-nitroso compounds were found in the ThermoSorb/N cartridges

Table 74

Bulk Sample Analysis

Foundry E

Sample #	Material Tested	Nitrosamines Found
1	Raw Sand	N.D.*
2	Mixed Sand	N.D.
3	Iron Oxide	N.D.
4	Zip slip-isocure	N.D.
5	Theme slik NF - shell mold process	N.D.
6	Triethylamine (TEA)	N.D.
7	Resin for Isocure	N.D.
8	Resin for Isocure	N.D.
9	Shell Mold Sand	N.D.

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*ND - None detected- Detection limit for N-nitrosodiethylamine = 0.1 μg/g

SUMMARY OF IRON AND STEEL CASTING INDUSTRY

In total five foundries were included in this survey of the Iron and Steel Casting Industry for possible worker exposure to N-nitroso compounds. The primary reasons for surveying this industry were the discovery of airborne N-nitroso compounds in Foundry E and the possibility that the amine using sand core process could result in N-nitroso compounds in foundry environments. Three of these facilities (Foundries A, B, and E) used the amine catalyzed sand binding process in their sand core operation. With the exception of the finding of 0.1 $\mu g/m^3$ N-nitrosodimethylamine (NDMA) in one air sample collected in Foundry C, Foundry E was the only plant found to have N-nitroso compounds in its environment. The levels found in Foundry E's core making room and lunch room (the only areas sampled within the plant) ranged from 0.3 g/m^3 to 0.7 $\mu g/m^3$ for NDMA and from <0.2 $\mu g/m^3$ to 1.4 $\mu g/m^3$ for N-nitrosodiethylamine (NDEA).

Amine measurements were also obtained within Foundries A, B, C and D in both air samples and bulk samples of core making sand. At a detection limit of 0.5 g/m^3 for dimethylamine (DMA) no amines were found in the area air samples collected within these plants. In the bulk samples of sand, however, we identified 6 amines in the samples collected in Foundry A and 4 amines in the same sample from Foundry B (Table 75). Both of these foundries used an amine catalyzed sand core manufacturing process. However, during this survey Foundry B was not producing any sand cores. Foundry A was producing hot shell cores during the survey and at our request they briefly operated the amine catalyzed sand core equipment. Foundries C and D did not use amines in their sand core production process. Bulk samples from Foundry E were not examined for amines, however, they reported using triethylamine in their amine catalyzed sand core operation. The amine catalyzed sand core process was in operation during the survey at this plant.

The most likely source for the airborne N-nitroso compounds in Foundry E is the nitrosation of the amine catalyst by atmospheric oxides of nitrogen. The hot shell sand core process (located within the same room as the amine catalyzed sand core equipment in Foundries A, B, and E) uses high temperature gas burners to bind the sand. This process would produce oxides of nitrogen which could then act as a nitrosating agent. The hot shell sand core process was in operation in Foundry A during this survey. However, no N-nitroso compounds or amines were detected in the sand core room air sample. Without the nitrosatable amines N-nitroso compounds can not be formed.

The American Foundrymen's Society published in Control News, November 1, 1980 data from a "supplier" which showed that N-nitrosodimethylamine and N-nitrosodiethylamine were detected in the range of one part per billion (ppb) or less. The tests were conducted at the coremaking areas utilizing phenolic shell resin, phenolic hot box resin, phenolic urethane cold-box resin, mold curing and shakeout areas.

Further studies of N-nitroso compounds within this industry should focus on those plants that use the amine catalyzed sand core process and these studies should include the following:

- Environmental monitoring of N-nitroso compounds while the amine catalyzed sand core process is in normal operation.
- Measurement of airborne amines
- Measurement of atmospheric nitrogen oxide levels
- Measurement of airborne N-nitroso compounds within the metal pouring area when amine containing sand cores are being used.

Table 75

Summary of Amines Found in Foundry Sand

μg amine/g sand	Foundry A	Foundry B	Foundry C	Foundry D	Foundry E
1. Methylamine	2.6	N.D.*	N.D.	N.D.	N.S.**
2. Dimethylamine	1.2	N.D.	N.D.	N.D.	N.S.
3. Trimethylamine	3.8	2.0	N.D.	N.D.	N.S.
4. N-Ethyldimethylamine	14.2	19.0	N.D.	N.D.	N.S.
5. Triethylamine	0.2	0.4	N.D.	N.D.	N.S.
6. Morpholine	0.8	0.04	N.D.	N.D.	N.S.

* N.D. = None detected - 0.5 μg/g detection limit for dimethylamine

** N.S. = Not sampled

SUMMARY

The object of this study of "N-nitroso Compounds in the Factory Environment" was to determine if workers were being exposed to N-nitroso compounds within selected factories. To accomplish this goal, 55 on-site surveys were made in 40 separate manufacturing facilities. The facilities included in this survey represent seven categories of industrial activity:

- The Fish Processing Industry
- Manufacturers and Users of Synthetic Metalworking Fluids
- Dye Manufacturing
- Rubber Manufacturing
- Leather Manufacturing
- The Soap, Detergent and Surfactant Industry
- The Iron and Steel Casting Industry (Foundries)

The industries, or industrial activities surveyed in this study were not examined in depth. For example, only 8 of 1200 rubber manufacturing facilities and only 9 of over 300 leather tanneries were included in this survey. Due to the limited scope of the study, other industries which may have N-nitroso compounds within their environments were not included. Examples of these other industries are: explosive manufacturers, ore smelters and amine manufacturers. The specific manufacturing facilities that were selected for on-site visits were chosen as representatives of the surveyed industry. The industries that were included in this survey were selected on the basis of one or more of the following:

- Known or suspected use of N-nitroso compounds
- Known use of products likely to be contaminated with N-nitroso compounds.
- Use of chemicals which could give rise to N-nitroso compounds
- Epidemiological data indicating the possibility of worker exposure to an environmental carcinogen
- The results of this study as it proceeded

In order to assess the potential worker exposure to N-nitroso compounds, environmental samples consisting of air and bulk samples were collected and analyzed using a mobile laboratory equipped for N-nitroso compound analysis. The on-site survey consisted of examining the facility for areas or processes where these compounds could be present followed by sampling those suspected areas. In most instances, both air and bulk samples were collected for

analysis. The air samples were usually area samples, the results of which represented the atmosphere within a specific area of the plant. However, process air samples were sometimes collected to determine if a specific process or point source could be responsible for the presence of any N-nitroso compound. These two types of air samples differed in that the area air samples could not determine the exact source for the N-nitroso compounds. The personal sampling method was developed by Thermo Electron and was phased into the study when the rubber and leather industries were found to have relatively high levels of nitrosamines. It was important at this stage to evaluate the actual potential for worker exposure and this was not practical with KOH traps.

N-nitroso compounds were found in 25 of the 40 plants surveyed. The N-nitroso compounds found were: N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosopyrrolidine (NPYR), N-nitrosomorpholine (NMOR), N-nitrosodiethanaolamine (NDElA) and N-nitrosodiphenylamine (NDPhA). All six of these compounds were found in air samples (only trace quantities of NDElA were found in one air sample), all of these compounds except NDEA and NDPA were also found in some of the bulk (NMOR), N-nitrosodiethanaolamine (NDElA) and N-nitrosodiphenylamine (NDPhA). All six of these compounds were found in air samples (only trace quantities of NDElA were found in one air sample), all of these compounds except NDEA and NDPA were also found in some of the bulk samples. The highest levels of airborne nitrosamines was the finding of 250 $\mu g/m^3$ of NMOR in a rubber tire plant. The bulk sample with the highest level of these compounds was metalworking fluid which contained NDElA in amounts from non-detectable up to almost 5 mg/ml. NDPhA was found in bulk samples collected in a rubber chemical manufacturing facility which was producing NDPhA at the time of the site visit, thus it is not surprising that percent amounts of this compound were found in floor scrapings and process samples. The other N-nitroso compounds, NDEA and NDPA, were found in trace amounts in air samples taken in two manufacturing facilities.

N-nitroso compounds were found in the working environments in one or more of the plants surveyed from all seven industries. The following is a rationale of why each industry may have worker exposure to N-nitroso compounds:

- Fish Processing Industry

  The small amount of NDMA found in the air and bulk samples may be the result of naturally occurring dimethylamine reacting with either nitrite or atmospheric nitrogen oxides.

- Manufacuters and Users of Synthetic Metal Working Fluids

  NDElA is a known contaminant in metalworking fluids formulated with nitrite and ethanolamines. Therefore, those plants that use these products may have workers exposed to pre-formed NDElA.

- Dye Industry

  In the manufacturing of dyes, nitrite and amines are frequently used and depending upon the dye being manufactured and the plant's operation N-nitroso compounds may be produced as unwanted by-products.

- Leather Industry

  The predominant N-nitroso compound found in this industry was NDMA. Its presence in tanneries appears to be the result of airborne dimethylamine, from the use of dimethylamine sulfate in the hide unhairing process, forming NDMA on surfaces or in the gas phase with nitrogen oxides from combustion sources.

- Rubber Industry

  Except for NDPhA which is used and manufactured by this industry, the N-nitroso compounds in the plant's environment seem to be associated with the heating and extrusion of formulated rubber. The major source for the predominant N-nitroso compound, NMOR, seems to be transnitrosation of morpholine via NDPhA.

- Soap, Detergent and Surfactant Industry

  The only N-nitroso compound found in this industry was a low level of NDMA (highest level = 0.8 $\mu g/m^3$). Airborne dimethylamine, used in the synthesis of some cationic surfactants, may have formed NDMA with ambient levels of nitrogen oxides.

- Iron and Steel Casting Industry (Foundries)

  Only one of the five plants surveyed was found to be contaminated with N-nitroso compounds. NDMA and NDEA were both found within this plant. An amine catalyzed sand core process was in operation at the time of the survey and triethylamine was reported being used. This amine, and dimethylamine from an unknown source, may have reacted with the nitrogen oxides being generated by the many combustion sources within the foundry to produce the discovered N-nitroso compounds.

Table 76 is a summary of air levels found in all the industries surveyed under the contract. The two industries of major concern were the rubber and leather. The removal of dimethylamine sulfate (DMAS) from the dehairing process in tanneries greatly reduced the N-nitrosodimethylamine levels. Nitrosamines were not found in tanneries that did not use DMAS.

The rubber industry required process substitution and engineering controls to reduce the airborne levels of nitrosamines. A better understanding of the potential of industrial generation of N-nitroso compounds was derived from the extensive work conducted in this industry.

The Rubber Manufacturers Association (RMA) conducted a detailed controlled study of nitrosamine formation under tire manufacturing conditions. The results of this study are available from the RMA in Washington, D.C.

Another by-product of this study was a two year skin painting study conducted by NIOSH under contract of commericially available cutting fluids. The concentration of N-nitroso compounds in each cutting fluid was documented throughout the study.

The results of this industry-wide study of nitrosamines in the industrial environment gives a clearer understanding of the mechanism and circumstances that could give rise to worker exposure. The industries that use nitrosatable amines should be encourage to examine their processes for potential nitrosamine formation. The scope of this study was limited but the results have demonstrated the potential for nitrosamine formation which should not be over looked by industries which utilize nitrosatable amines.

Table 76

SUMMARY OF AIR LEVELS IN INDUSTRIES SURVEYED FOR N-NITROSO COMPOUNDS

Industry	Number of Plants Surveyed	Plants with N-nitroso Compounds (air and/or bulk)	Primary N-nitroso Compounds Found	Number of Air Samples	Range µg/m³	Mean for Air Sampling µg/m³ (area, process and personal samples)	Possible worker Exposure by:
Fish Processing	2	2	NDMA	12	0.01 - 0.06 NDMA	0.03	----
Cutting Fluids	10	7	NDELA	22	<0.01 - 0.08 NDELA	0.01	skin
Dye*	3	1	NDMA>NDEA	21	<0.03 - 0.01 NDMA	0.03	----
					<0.03 - 0.06 NDEA	0.04	
Leather	9	6	NDMA>NMOR	156	<0.05 - 47 NDMA	3.4	Inhalation
					<0.05 - 2 NMOR	0.2	Skin
Rubber	8	7	NMOR>NDMA>NDPhA	77	0.02 - 250 NMOR	3.1	Inhalation
			NDEA>NDPYR	77	0.02 - 5.5 NDMA	0.6	
				12	0.01 - 1230 NDPhA	37.5	and
				2	0.13 - 1.4 NDEA	0.77	
				45	0.01 - 3.9 NDPYR	0.26	skin
Surfactant	3	1	NDMA	30	0.03 - 0.8 NDMA	0.2	Inhalation
Foundry	5	1	NDEA>NDMA	24	0.02 - 1.4 NDEA	0.26	Inhalation Skin
Total	40	25		499		3.3	

* Unidentified TEA Responsive compounds as high as 40 µg/cu m were found

NDMA - N-nitrosodimethylamine
NMOR - N-nitrosomorpholine
NDEA - N-nitrosodiethylamine
NDPhA - N-nitrosodiphenylamine
NDPYR - N-nitrosopyrrolidine
NDELA - N-nitrosodiethanolamine

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