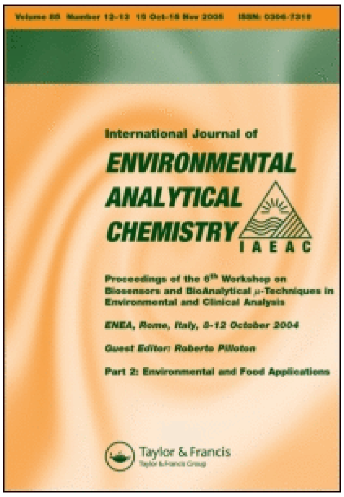

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DETERMINATION OF N-NITROSO COMPOUNDS IN THE ENVIRONMENT OF A METAL FACTORY USING METALWORKING FLUIDS

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By use of GLC-ECD and HPLC-TEA techniques for N-nitroso compounds, N-nitroso-diethanolamine (NDELA) has been found in concentrations of 1.4–6.0 $\mu g/m^3$ and 1.3–5.0 $\mu g/m^3$ respectively in all four air samples collected in the environment of a metalworking plant during metallurgical operations. NDELA was quantitated in air samples by GLC-ECD after converting it to its trifluoroacetyl derivative by reaction with the appropriate anhydride. NDELA was analyzed without derivatization in air samples using HPLC-TEA method. N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA) were also identified and later determined in two out of four air samples in concentrations of 0.08 $\mu g/m^3$ (for NDMA in both samples) and 0.14–0.16 $\mu g/m^3$ (for NDEA) using GLC-TEA procedure. The described method did not cause artifactual formation of N-nitrosomethyl-N-butylamine (NMBA) when methyl-N-butylamine was used as an internal marker of nitrosation during collection of NDELA in impinger traps.

KEY WORDS: N-nitroso compounds, GLC-ECD, HPLC-TEA, GLC-TEA.

INTRODUCTION

N-nitroso compounds are ubiquitous pollutants encountered in the environment, particularly in several chemical, agricultural and consumer products which characterize our modern society. They represent a major class of important chemical mutagens, carcinogens, and teratogens which have been described as a serious hazard to human health.[1]

Metalworking fluids (MWFs) are used for lubricating and cooling the cutting

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and grinding surfaces of metals in metalworking machines. The Canadian government had moved in 1979 to ban the importation, sale and advertisement of MWFs containing any nitrite when diethanolamine or triethanolamine is present.[2] In 1984, the Environmental Protection Agency (EPA) of the United States passed the rule of prohibiting the use of nitrites in MWFs containing alkanolamines.[3] This ban was inforced since technical triethanolamine contains about 20% diethanolamine, which has been found to be readily nitrosated to form N-nitrosodiethanolamine (NDELA). Analytical grade triethanolamine has also been found to generate NDELA, when nitrite is present concomitantly in MWFs. Before this legislation[2,3] alkanolamines were used as emulsifiers and nitrites as corrosion inhibitors in the formulation of MWFs.

NDELA has been found to be present at concentrations of 200–30 000 mg/kg,[4] 50–800 mg/kg,[5] 230–5530 mg/kg[6] and 0.04–593 mg/kg[7] in several brands of industrial MWFs. As substantial high levels of NDELA have been reported in the literature an attempt has been made in this investigation to determine the extent of workers' exposure to airborne NDELA. Human exposure to N-nitroso compounds shows a rather complex pattern, which is well documented by Preussmann.[8] Concern for the workers using MWFs has increased as a result of published reports that NDELA penetrates the skin of both rats[9] and humans[10,11] and that it is a more potent carcinogen than was previously surmised.[12] Despite the fact that NDELA is not sufficiently volatile to pose a problem as an air pollutant, sufficient exposure of workers can still occur by (i) dermal contact, either through splashing or by handling metal parts that have been soaked in the MWFs; (ii) inhalation or partly ingestion of an oil mist, which is sometimes formed around the machine, when the MWFs are used for cutting, drilling or grinding.

The objective of this study was to measure ambient air levels of nitrosamines in the vicinity of plant producing cutting, drilling, grinding or rolling operations. Since a limited survey is available on measurement of environmental N-nitroso compounds in the Canadian factory environment, this study was performed to assess the magnitude of the problem of human exposure to these carcinogenic compounds. This study reports the detection of NDELA in the ambient air of a metal factory using gas–liquid chromatography with electron capture detection (GLC-ECD) followed by its identification by high-performance liquid chromatography equipped with a thermal energy analyzer (HPLC-TEA). The volatile nitrosamines were detected and identified in the factory environment by gas–liquid chromatography coupled with a thermal energy analyzer (GLC-TEA).

MATERIALS AND METHODS*

The air samples were supplied by the Institut de Recherche en Santé et en Sécurité

**Caution:* Nitrosamines are potentially dangerous carcinogens. Care must be exercised when handling these materials. Consult IARC Scientific Publication No. 43—Laboratory Decontamination and Destruction of Carcinogens in Laboratory Wastes: Some Nitrosamines—International Agency for Research on Cancer, Lyon, France, 1982.

du Travail du Québec (IRSST) in Montreal. They were analyzed as received from IRSST.

Chemicals

The following N-nitroso compounds were used as standards throughout this study: N-nitrosodimethylamine (NDMA) was obtained from Aldrich Chemical Co., N-nitrosodiethylamine (NDEA), N-nitrosodipropylamine (NDPA), N-nitrosodibutylamine (NDBA), and N-nitrosopiperidine (NPIP) from Eastman Kodak Co., N-nitrosopyrrolidine (NPYR) and N-nitrosodiethanolamine (NDELA) from ICN Pharmaceuticals Inc., N-nitrosomorpholine (NMOR) from Ultra Scientific, Inc., and N-nitrosomethyl-N-butylamine (NMBA) from Sigma Chemical Co. All reagents were of analytical grade, and the solvents were "distilled-in-glass" type. Glass-distilled dichloromethane (methylene chloride-nitrosamine free) was obtained from Caledon Laboratories. The artifact free Thermosorb/N air sampling cartridges were purchased from Thermedics Inc.

Gas–Liquid Chromatography with Electron Capture Detection (GLC-ECD)

A Hewlett-Packard Model 5830A gas chromatograph (a keyboard-controlled instrument with a multifunction digital processor) equipped with a ^{63}Ni (555 megabecquerels) electron capture detector was used for these experiments. The following conditions were employed: a 1.8 m × 2-mm i.d. coiled glass column was packed with 3% OV-17 on 80/100 mesh Gas Chrom Q (Chromatographic Specialities). The oven temperature was maintained at 120 °C. Injector and detector temperatures were 240 °C and 300 °C respectively. The argon:methane (95:5) carrier gas flow rate was 40 ml/min.

High-Performance Liquid Chromatography Coupled with a Thermal Energy Analyzer (HPLC-TEA)

A Varian Model 8500 LC pump interfaced to a thermal energy analyzer (TEA) detector (Thermedics Inc., Model 502) was used for this study. The HPLC column (4.5 × 250 mm) was 5 μm Bondapak NH_2 (Waters). The mobile phase was iso-octane–dichloromethane–methanol (60:30:7 v/v). The flow rate was kept at 2.0 ml/min. The detector furnace was operated at 500 °C and the cold trap at -100 °C, while vacuum in the reaction chamber was maintained at 0.50 mm/Hg. The peaks were integrated with a Spectra-Physics Model SP 4000 integrator.

Gas–Liquid Chromatography with Thermal Energy Analyzer (GLC-TEA)

A Hewlett-Packard Model 5730A gas chromatograph with an integrator (Spectra-Physics, Model SP 4000) coupled with a TEA detector (Thermedics Inc., Model 502) was used for this work. Operating conditions were as follows: a 1.8-m × 2-mm i.d. coiled glass column was packed with 10% Carbowax +0.5% KOH on 80–100 mesh high performance Chromosorb W (Chromatographic Specialities). The oven temperature was maintained at 130 °C for 5 min, then programmed at 4 °/min to a final temperature of 180 °C held for 2 min. The injector temperature was maintained at 170 °C. The nitrogen carrier gas flow through the column was 20 ml/min. The detector furnace was operated at 450 °C and the cold trap at −196 °C, while vacuum in the reaction chamber was maintained at 0.65 mm/Hg.

Air Sampling

The air samples were collected by two methods. The sampling of non-volatile N-nitroso compounds (e.g. NDELA) was performed with impinger traps (Midget) (Supelco Ltd.), (185 mm × 24 mm, collecting solution capacity 25 ml) and their volatile analogs (e.g. NDMA, NDEA, NDPA, NDBA, NPIP, NPYR and NMOR) with Thermosorb/N cartridges (thermedics Inc.).

a) Impinger trap method

The ambient air was drawn with an air-sampling pump (Model HFS 113A, Gillian Instrument Corp.) at a flow rate of 2 l/min for about 3 h through a glass impinger containing 15 ml of 1 N KOH solution. N-nitroso compounds, if present, were collected in 1 N KOH solution. The extraction of non-volatile N-nitroso compounds was carried out as follows: To 15 ml of the sample in 1 N KOH solution were added 15 mg of ammonium sulfamate (nitrosation inhibitor). It was later extracted with 20 ml of ethyl acetate and the mixture was shaken mechanically on an Eberbach agitator for 10 min. After centrifuging at 600 g for 5 min, the organic layer was separated and filtered. The extraction procedure was repeated a second and third time. The organic phases were combined, dried over anhydrous sodium sulfate, filtered and evaporated to dryness under vacuum (15–25 mm/Hg) using a rotatory evaporator (Buchler Instruments Inc.) at 30 °C. The extract was then reconstituted with 0.5 ml of ethyl acetate and was divided into two aliquots—one was used for the analysis of NDELA by GLC-ECD after derivatization with trifluoroacetic anhydride (TFAA) and the other for identification of NDELA without derivatization by HPLC-TEA.

NDELA was derivatized after adding 50 μl of TFAA to the residue obtained after evaporation of the final sample extract to dryness at 30 °C under a slow stream of nitrogen. The mixture was vortexed for 30 s and then kept at room temperature (20 °C) for 2 h in the dark. It was again evaporated to dryness at 30 °C under a slow stream of nitrogen. The residue was then reconstituted with 50 μl of ethyl acetate and about 2 μl of this solution were injected into the gas chromatograph.

b) Thermosorb/N technique

A Thermosorb/N cartridge (20 mm long; 15 mm i.d.) containing a suitable sorbent and an amine trapping (complexing) agent, in addition to a nitrosating inhibitor was used. The air samples were collected by drawing air through the cartridges at a constant rate of 2 l/min for about 3 h using a pump (Model HFS 113A, Gillian

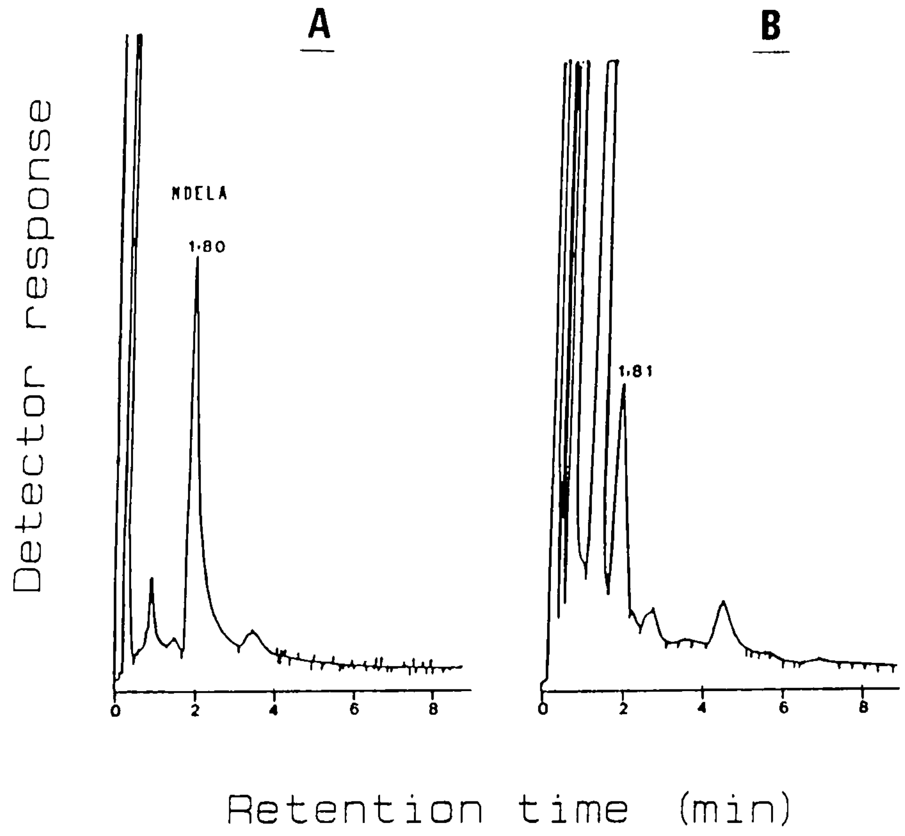

Figure 1 Chromatogram obtained from NDELA standard (A) and an air sample containing NDELA (B) derivatized with TFAA using GLC-ECD.

Instrument Corp.). After sampling, the sorbent was eluted with 2 ml of a mixture containing 25% methanol in 75% dichloromethane. A precise volume of about 5 μl were injected into the gas chromatograph coupled with TEA detector.

GLC-ECD, GLC-HPLC and GLC-TEA Analyses

For these analyses, a calibration factor of KF was calculated for each of the nitrosamines in the standard mixture based on duplicate injections. The concentration of the nitrosamines found in the extracts was calculated using the KF factor of the corresponding nitrosamine. The concentrations of the following N-nitrosamines were studied: NDELA, NDMA, NDEA, NDPA, NDBA, NPIP, NPYR and NMOR. A reagent blank was carried out in each batch of reagents.

RESULTS AND DISCUSSION

Figure 1 shows the chromatogram obtained by GLC-ECD analysis from NDELA standard (A) and an air sample containing NDELA (B) derivatized with TFAA. The identity of NDELA peak in the air sample was confirmed using nitrosamine-specific detector TEA coupled with HPLC (Figure 2). The non-identified N-nitrosamine peak in Figure 2 (B) is located at a retention time of 2.2 min.

The concentration of NDELA in different brands of MWFs as well as the airborne levels of NDELA, NDMA and NDEA in the plant surveyed are given in Table 1. The results showed that NDELA concentration in MWFs ranges from 36–97 μg/ml and its airborne levels in the samples vary from 1.4–6.0 $\mu g/m^3$ by GLC-ECD and 1.3–5.0 $\mu g/m^3$ by GLC-TEA. The higher levels obtained by GLC-ECD can be explained by the fact that ECD is not as specific as TEA detector to N-nitroso compounds.

NDMA and NDEA were the only volatile N-nitroso compounds, which could be found in samples C and D only (Table 1). Other volatile N-nitroso compounds (NDPA, NDBA, NPIP, NPYR and NMOR) could not be detected in any sample as their concentrations were below the detection limits of the described method. The data in Table 1 indicate, that there is no correlation between the NDELA concentration in MWFs and the levels of NDELA in the corresponding air samples.

Specificity Studies

In order to confirm the nature of the peaks measured by HPLC-TEA and GLC-TEA, a procedure based on diminution in the intensity, or the complete decomposition of the peaks of the substances by ultraviolet light[13] was used. The positive samples were subjected to photolysis by ultraviolet light at 366 nm for 60 mins. The peaks from positive samples completely disappeared after 60 mins, hence corroborating the theory that they represented N-nitroso compounds.

In order to confirm that no artifactual formation of N-nitrosamines occurred during air sampling and analysis procedure, methyl-N-butylamine was used as an internal marker of nitrosation. This compound was added to the impinger trap containing 1 N KOH, which was further analyzed after drawing ambient air using the described method. The analysis showed that no peak appeared at the retention time of NMBA under the experimental conditions used for HPLC-TEA. Thermosorb/N cartridges have not been found to be prone to artifactual formation of N-nitrosamines during air sampling and extraction procedure.[14] Therefore, it seems unlikely that the described methods give rise to artifactual formation of N-nitroso compounds.

CONCLUSIONS

GLC-ECD and HPLC-TEA procedures for the determination of airborne levels of NDELA in a metalworking plant was developed. GLC-ECD procedure gave higher values for air levels of NDELA in comparison to HPLC-TEA due to the non-specificity of ECD to N-nitroso compounds. NDMA and NDEA were also detected and later quantitated in two out of four ambient air samples of the same

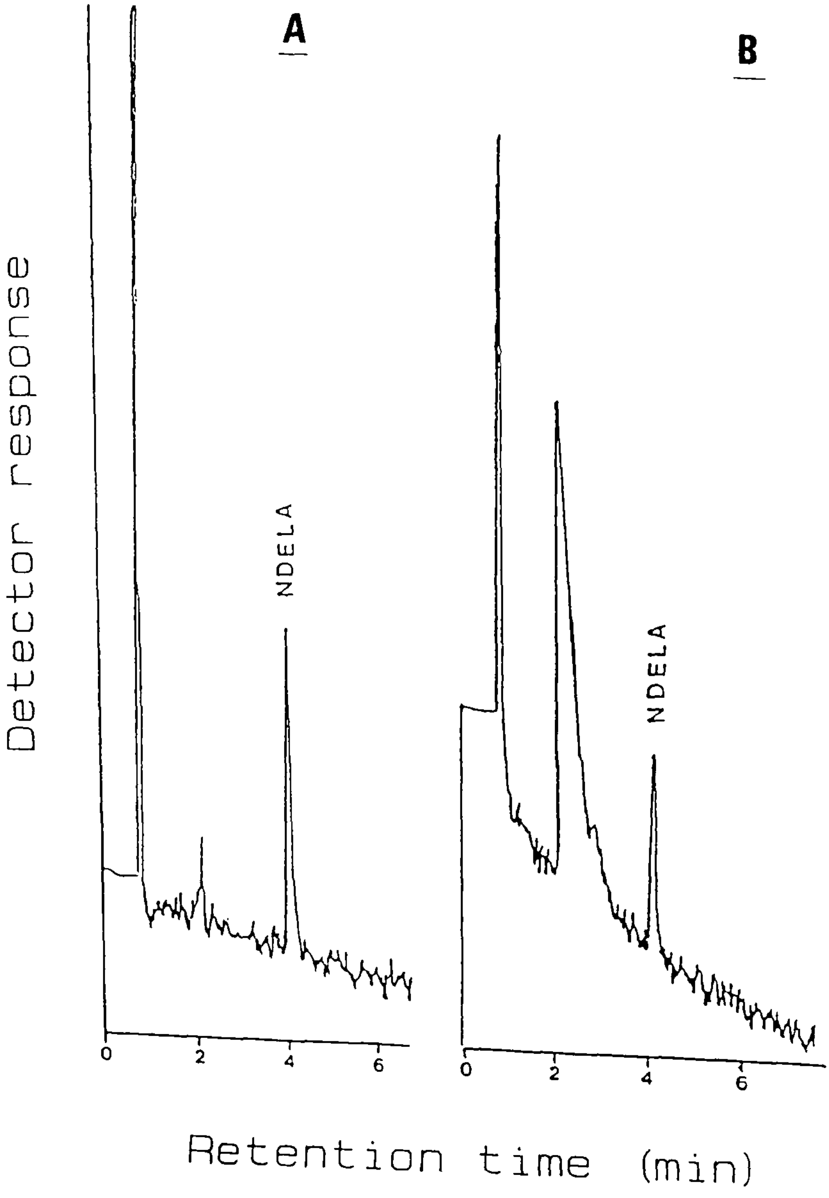

Figure 2 Chromatogram obtained from NDELA standard (A) and an air sample containing NDELA (B) using HPLC-TEA.

plant using GLC-TEA. NDPA, NDBA, NPIP, NPYR and NMOR could not be detected in any of the four samples examined in this study. The identification of N-nitroso compounds in the air samples by TEA was confirmed by ultraviolet photolysis at 366 nm.

Table 1 NDELA concentration in MWFs as well as airborne levels of NDELA, NDMA and NDEA in the surveyed plant

Sample	*NDELA concentration in MWFs* ($\mu g/ml$)	*Airborne levels* ($\mu g/m^3$)			
		NDELA		*NDMA*	*NDEA*
		GLC-ECD	*HPLC-TEA*	*GLC-TEA*	
A	68	6.0	5.0	ND	ND
B	36	4.9	3.8	ND	ND
C	97	2.4	2.1	0.08	0.14
D	45	1.4	1.3	0.08	0.16

ND = Not detectable.

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