N-Nitroso Compounds in the Ambient Air of Metal Factories Using Metal-Working Fluids

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N-nitroso compounds are undesired industrial and environmental pollutants. They represent a major class of important chemical mutagens, carcinogens, teratogens, and immunotoxic agents, which have been described as a serious hazard to human health (Fuchs et al. 1995; Fadlallah et al. 1996; 1994a; 1994b; 1990a; Desjardins et al. 1992; Preussmann and Stewart 1984). In 1976, attention was focused on the occurrence of nitrosamines in the air and particularly in the workplace (Bretschneider and Matz 1976). In later studies, several populations were shown to be potentially exposed to volatile and non-volatile N-nitrosamines at significantly higher than background levels (Fadlallah et al. 1990b; Preussmann and Eisenbrand 1984; Fajen et al. 1980; 1982). Metal-working fluids (MWFs) are used for lubricating and cooling the cutting and grinding surfaces of metals in metallurgical industries. The presence of nitrosamines in MWFs has drawn considerable attention in recent years. Millions of gallons of MWFs are used annually in industrialized countries. N-nitrosodiethanolamine (NDELA) has been found to be present in several brands of industrial MWFs (Fadlallah et al. 1996., Keefer et al. 1990., Spiegelhalder et al. 1990). Workers handling NDELA contaminated products can be exposed to NDELA by direct contact or by inhalation of oil mists, during most machine shop operations. The dilute MWFs are sprayed, splashed and vaporized into the air particularly during milling and grinding operations. Since NDELA has been found to be carcinogenic in experimental animals, there is a great concern, that the workers can be exposed to this compound, if they use MWFs contaminated with NDELA. NDELA has been found to induce liver tumors and neoplasm in a variety of other organs in rats (Lijinsky and Kovatch 1985; Berger et al. 1987). Lung tumors were found in mice (Hecht et al. 1989) and tumors in the nasal cavity and trachea in hamsters (Hilfrich et al. 1978) when these animals were treated with NDELA. 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 (Brownstein 1979). In 1984, the United States Environmental Protection Agency (USEPA) passed a rule prohibiting the use of nitrates in MWFs containing alkanolamines. 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 direct contact or by inhalation of oil mists because a limited survey is available on MWFs used in Canada, this study was performed to assess the magnitude of the problem of human exposure to these carcinogenic compounds. This study reports the detection and identification of NDELA in the ambient air of metal factories using gas liquid chromatography-mass spectrometry (GLC-MS). The volatile N-nitrosamines were detected and identified in the factory environment by gas liquid chromatography coupled with a thermal energy analyzer (GLC-TEA).

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MATERIALS AND METHODS

The air samples of MWFs employed in this study were obtained from the Institut de Recherche en Santé et en Sécurité du Travail du Québec (Research Institute of Occupational Health and Safety of Québéc) in Montreal, Quebec. They were analyzed as received from this institute. N-nitrosodieethylamine (NDELA), N-nitrosodisopropylamine (NDiPLA), N-nitrosodimethylamine (NDMA), N-nitrosodiesthylamine (NDEA), N-nitrosodibutylamine (NDBA), N-nitrosomorpholine (NMOR) and N-nitrosopyrrolidine (NPyR) were purchased from Sigma Chemical Co., St-Louis, Missouri, USA. N-nitrosopiperidine (NPIP), N-nitrosodipropylamine (NDPA) and ammonium sulfamate were obtained from Eastman Kodak Company, Rochester, New York, USA. Trifluoroacetic anhydride (TFAA) and all solvents ‘distilled in glass’ grade were obtained from Caledon Laboratories Ltd., Georgetown, Ontario, Canada. Sodium sulfate anhydrous was purchased from J.T. Baker Chemical Co., Phillipsburg, New Jersey, USA.

NDELA in the ambient air of metal factories was detected and identified by gas liquid chromatography-mass spectrometry (GLC-MS). Mass spectra were recorded using a Finnigan GLC-MS TSQ 700. The analyses were performed using electron impact (EI) ionisation mode. The ion m/z 326 was selected for the quantitation of NDELA using SIM mode. Operating conditions were as follows: a DB-5 (J & W Scientific, Folsom, California, USA) fused-silica capillary column (30m x 0.25 mm I.D.; 0.25 mm film thickness was used. Helium was used as a carrier gas at a flow rate of 1 mL/min. The injection mode was splitless. The injector and transfer line temperature was 230°C. The initial oven temperature was maintained at 30°C for 2 min. then programmed at 20°C/min. to a final temperature of 230°C held for 10 min. Source temperature was 100°C, electron energy 70eV, emission current 0.30 mA, scan range 50 to 550 amu.

The volatile N-nitrosamines were detected and identified in the environment of different factories by gas liquid chromatography coupled with a thermal energy analyzcr (GLC-TEA). A Hewlett-Packard Model 5730A gas chromatograph with an integrator (Spectra-Physics, Model SP4000) coupled with a TEA detector (Thermedics Inc. Model 502) was used for this work. Operating conditions were as follows: a 2 m x 2 mm i.d. coiled glass column was packed with 10% Carbowax + 2% KOH on 80-100 mesh Chromosorb W (Chromatographic Specialties, Ontario, Canada). The initial temperature of the oven was 130°C. then programmed at 4°C/min. to a final temperature of 210°C held for 5 min. The injector temperature was maintained at 200°C. The nitrogen carrier gas flow through the column was 15 mL/min. The detector furnace was operated at 550°C and the cold trap at -196°C while vacuum in the reaction chamber was maintained at 0.65 mm/Hg.

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. Ontario, Canada), (185 mm x 24 mm, collecting solution capacity 25 mL) and their volatile analogues (e.g. NDMA, NDEA, NDPA, NDBA, NPIP, NPyR and NMOR) with Thermosorb/N cartridges (Thermedics Detection, Chelmsford, MA).

For the impinger trap method, the ambient air was drawn with an air-sampling pump (Model HFS 113A, Gillian Instrument Corp. N.J. USA) at a flow rate of 2 L/min for about 3 hr through a glass impinger containing 15 mL of 1 N KOH solution. N-nitroso compounds were collected in 1 N KOH solution. The extraction of non-volatile N-nitroso compounds was carried out as follows: To 10 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.