Bull. Environm. Contam. Toxicol. 25, 106-112 (1980)

Detection of Volatile Nitrosamines in Waste Water from Chemical Plants by Combined Capillary Gas Chromatography-Mass Spectrometry+

G. Hartmetz and J. Slemrova

Institute of Hygiene, University Mainz, Hochhaus am Augustusplatz, D-6500 Mainz, FRG

Detection of carcinogenic nitrosamines in foodstuffs has been reported in a large number of publications (e.g., see WALKER et al. 1976), while searches for these compounds in drinking, surface or waste water have only seldom been reported.

In the drinking water in the regions of New Orleans and Baltimore, levels of volatile nitrosamines in the parts-per-trillion range have not been found (FINE et al. 1975). However, a dimethylnitrosamine content of 35-940 ng/L was found in the sea water of Curtis Bay and Stonehouse Cove in Baltimore. This contamination was traced to a nearby plant where dimethylnitrosamine was used as an intermediate in the synthesis of unsymetrical dimethylhydrazines (FINE et al. 1977).

In Germany examinations of single samples from the rivers Main and Neckar showed, with detection limits of 0.5 and 0.1 µg/L respectively, no indication of contamination with these substances (SANDER et al. 1974, DURE et al. 1975). In an examination of samples from 12 different points on the Rhine from Basle to the Dutch frontier, no traces of nitrosamines (detection limit 0.1 µg/L) could be found (HARTMETZ + SLEMROVA 1978).

The aim of the present work was to test the waste water and purification plant effluent from chemical factories engaged in the production and use of amines. Analyses were restricted to the following members of the homologous series of aliphatic symmetrical nitrosamines: dimethylnitrosamine (DMN), diethylnitrosamine (DEN), dipropylnitrosamine (DPN), and dibutylnitrosamine (DBN).

MATERIALS AND METHOD

In a first step 2.5 L of the water sample is concentrated by freezing to 500 mL (BAKER 1967) and transferred to a 2-L flask. The water is mixed with 200 g NaCl and the pH adjusted to 12. The extraction of nitrosamines then takes place in the apparatus described by LIKENS + NICKERSON (1964), modified for our purposes. The method is based on the principle of steam distillation and simultaneous extraction (Fig. 1).

+ With the support of the Deutsche Forschungsgemeinschaft.

0007-4861/80/0025-0106 $01.40

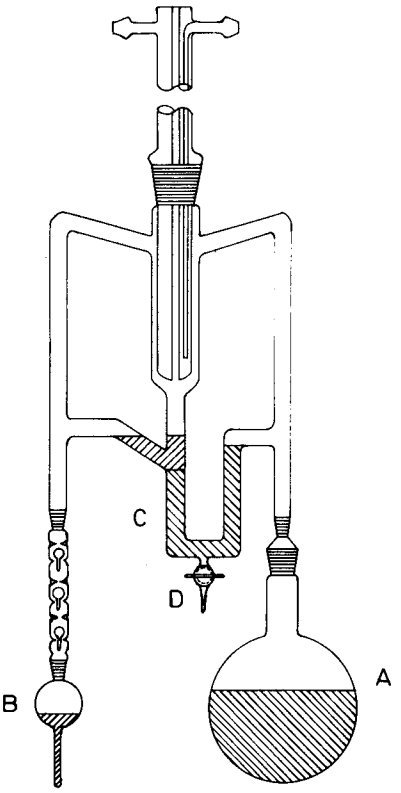

Fig 1 Apparatus for the Enrichment and Isolation of Volatile Nitrosamines.

The water sample in flask A and 20 mL of diethyl ether in flask B are brought to the boil. The nitrosamines and other steam volatile compounds contained in the water, as well as steam and ether, condense on the cooler which is maintained at -20 ^{o}C, and drop into the U-tube C. The ether overlies the water phase and runs, enriched with nitrosamines back into flask B, while the nitrosamine-depleted water flows back into flask A. At the end of the extraction (2 h) the ether remaining in the U-tube is decanted back into flask B. The extract is concentrated to 3-5 mL by distilling off the ether, mixed with 1 mL hexane, and finally concentrated to 1 mL under a stream of nitrogen. The recovery efficiencies of the method for water fortified with 1 ppb DMN, DEN, DPN and DBN each were 42, 70, 75 and 76 %, respectively.

Determination of the nitrosamines was carried out by combined gas chromatography-mass spectrometry. The gas chromatographic separation (Fig. 2) followed unsplit injection into a thin film glass capillary (liquid phase WG 11, length 50 m, i.d. 0.2 mm) in a Carlo Erba Model 2101 gas chromatograph (injection block after GROB + GROB 1972). Gas chromatographic conditions:

carrier gas He at a pressure of 2 bar, temperature programming 100 °C for 5 min, then 3 °C/min to 190 °C.

The open coupling to the mass spectrometer (HENNEBERG et al. 1975) consisted of a Pt/Ir capillary (50 cm long, 0.3 mm i.d.). The mass spectrometer was a Varian CH 7. The carrier gas was He at a pressure of 2 bar, the temperature of the injection block was 200 °C, that of the capillary column 110-150 °C, and that of the coupling 120 °C. Ionisation in the mass spectrometer took place at an electron energy of 70 eV and electron emission of 300 µA.

Qualitative detection in complex water extracts depends on the fulfilment of several criteria. For the mass fragmentographic recording in the GC-MS combination the substance-specific molecular ions and a few fragments were chosen (DMN - m/e 74; DEN - m/e 102; DPN - m/e 130, 113; DBN - m/e 158, 141). The peaks appearing as nitrosamines in the mass fragmentograms were rerun with appropriate reference substances at two different column temperatures. Some extracts were irradiated with UV light; their signal was eliminated by photolytic destruction. Fig 3 shwos the mass fragmentogram of an extract of a purification plant effluent (A), the same extract with the addition of 0.2 ng (DMN (B), and after irradiation with UV light at 360 nm (C).

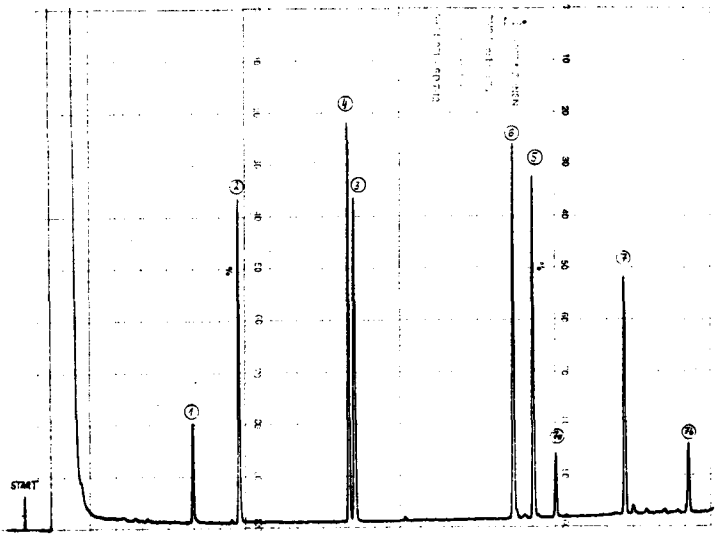

Fig. 2 Gas Chromatographic Separation of a Nitrosamine Mixture in a Thin Film Capillary.
(1) DMN, (2) DEN, (3) methylbutylnitrosamine, (4) DPN, (5) nitrosopiperidine, (6) DBN, (7) dipentylnitrosamine, (7a,b) isomers of dipentylnitrosamine

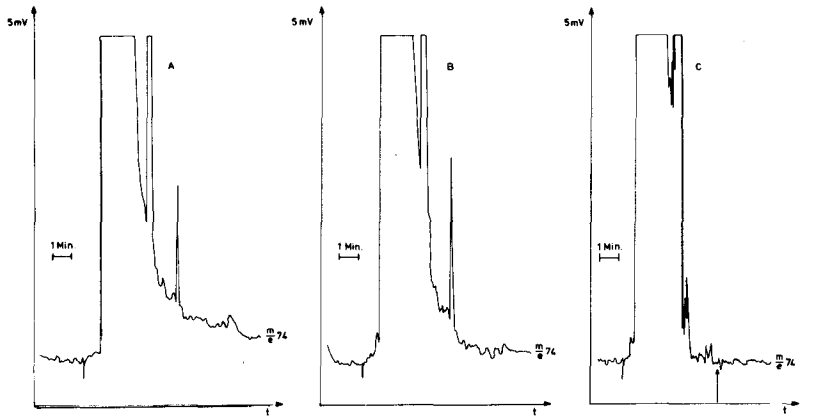

Fig. 3 Mass Fragmentograms of an Extract of a Purification Plant Effluent.

Mass fragmentographic quantitation requires the use of an internal standard. Although the variation coefficient of repeated gas chromatographic analyses is about 3 %, unreproducible adsorption effects in the GC-MS interface cause unavoidably greater scatter (coefficient of variation 40 %).

In the extracts examined we could usually find only DMN and DEN; in only one sample we found DPN in addition. Because DPN is nearest to DMN and DEN in gas chromatographic behaviour, we used this nitrosamine as internal standard. The calibration curve drawn through the peak height was linear between 0.5 and 16 ng DMN or DEN (the calibration mixture contained in each case 5 ng DPN). The variation coefficient of single estimations was improved to 8 % by the use of the internal standard. Fig. 4 shows the mass fragmentogram of a DPN fortified water extract.

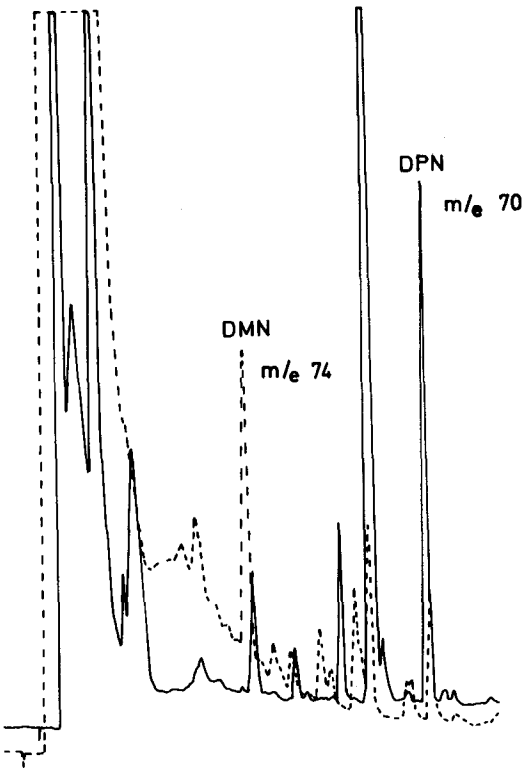

Fig. 4. Mass Fragmentogram of a DPN Fortified Water Extract.

RESULTS

We examined 7 samples of crude water from different production facilities and the purified waste water from a chemical-pharmaceutical plant. Table 1 gives the results for the crude waste water from 3 facilities. In the waste water of facility A DMN was detectable in all four samples, and in one sample DEN and DPN were also found. The waste water from facility B was contaminated with very low levels of DMN and DEN in only one case, and none of the compound could be found at facility C.

TABLE 1. Content of Volatile Nitrosamines in the Waste Water of Three Different Chemical Facilities

Facility	Sample	Concentration (ng/L)		
		DMN	DEN	DPN
A	1	4760	n.d.[1]	n.d.
	2	1700	n.d.	n.d.
	3	120	n.d.	n.d.
	4	500	100	1200
B	1	n.d.	n.d.	n.d.
	2	50	66	n.d.
C	1	n.d.	n.d.	n.d.

[1] Not detectable (detection limit 20 ng/L)

Table 2 shows the results of three analyses of the purification plant effluent from a chemical-pharmaceutical plant at four-weekly intervals, as well as one examination of the river water.

TABLE 2. Content of Volatile Nitrosamines in Purification Plant Effluent and Associated River

Sampling point	Concentration (ng/L)					
	DMN	DEN	DMN	DEN	DMN	DEN
1. 50 m before purification plant inflow	-[1]	-	-	-	n.d.[2]	n.d.
2. Purification plant effluent	5420	n.d.	510	23	9040	132
3. 50 m after purification plant inflow	-	-	-	-	2000	n.d.
4. 2000 m after purification plant inflow	-	-	-	-	n.d.	n.d.

[1] Not examined [2] Not detectable (detection limit 20 ng/L)

The concentrations in the purification works effluent varied considerably with time. In the river 50 m before the introduction of the effluent no nitrosamines could be found; 50 m downstream from the point of addition of the effluent we detected DMN at a concentration 1/5 of that in the effluent itself, while where the river joined the Rhine the nitrosamine concentration had fallen below the detection limit.

Our findings show that volatile nitrosamines are introduced into the surface water through the waste water of chemical plants. The nitrosamine concentrations in the waste waters examined are of the same order of magnitude as in various foodstuffs (WALKER et al. 1976). These concentrations are, however, so much reduced through dilution that at the mouth of a relatively small river at the Rhine (sampling point 4) no nitrosamines are detectable.

Acknowledgment. We thank K.-P. Bergmann for his careful MS measurements.

REFERENCES

BAKER, R.A.: Water Research 1, 97 (1967)

DURE, G., L.WEIL and K.E. QUENTIN: Z.Wasser- u. Abwasser-Forsch. 8, 20 (1975).

FINE, D.H., D.P.ROUNBEHLER, F.HUFFMAN, A.W.GARRISON, N.L.WOLFE and S.S.EPSTEIN: Bull.Environ.Contam.Toxicol. 14, 404 (1975).

FINE, D.H., D.P.ROUNBEHLER, A.ROUNBEHLER, A.SILVERGLEID, E.SAWICKI, K.KROST and G.A. DE MARRAIS: Environ.Sci. Technol. 11, 581 (1977).

GROB, K. and G.GROB: Chromatographia 5, 1 (1972).

HARTMETZ,G. and J.SLEMROVA: Symposium on Nitrat-Nitrit-Nitrosamine in Gewässern, Bochum, FRG, 9-10 Feb. 1978.

HENNEBERG, D., U.HENRICHS and G.SCHOMBURG: Chromatographia 8, 449 (1975).

LIKENS, S.T. and G.B.NICKERSON: Proc.Amer.Soc.Brewing Chemists 5, 5 (1964).

SANDER, J., E.SCHWEINSBERG, M.LADENSTEIN and F.SCHWEINSBERG: Zbl.Bakt.Hyg., I.Abt.Orig.A 227, 71 (1974).

WALKER, E.A., P.BOGOVSKI, L.GRICIUTE: Environmental N-Nitroso Compounds Analysis and Formation. IARC Scientific Publ.No.14 Lyon 1976