Analysis of Volatile N-Nitroso Compounds in Drinking Water at the Part per Trillion Level

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INTRODUCTION

Currently, there is considerable concern that chemical carcinogens are present, although at relatively low levels, in drinking water. In a recent EPA report (1), over 64 different organic compounds were identified in drinking water taken from the New Orleans, Louisiana area. The discovery of secondary amino compounds, including herbicides at the μg/l concentration level, is cause for concern since they have the potential of being nitrosated by nitrite to give the corresponding N-nitrosamines.

We report on the analysis of volatile N-nitrosamines in water at the sub μg/l level (parts per trillion). Water supplies in the New Orleans and Boston areas were tested, and volatile nitrosamines were not found to be present.

EXPERIMENTAL

Procedure

Two different concentration and extraction procedures were used: one based on liquid-liquid extraction, and the other based on the adsorption of the organic fraction on carbon and its subsequent extraction with chloroform and alcohol. In both cases, final quantitative analysis and identification were carried out on a single column gas chromatograph equipped with a N-nitroso compound specific thermal energy analyzer (TEA). The TEA and the gc-TEA interface are described elsewhere (2, 3). The chromatographic column was prepared from 6.5 mm x 2 mm i. d. stainless steel tube packed with 15% FFAP (15 g FFAP on 100 g chromasorb W. acid washed, DMCS treated, 80-100 mesh) and conditioned overnight at 220°C with carrier gas flowing prior to use. The column was operated isothermally at 200°C, with carrier gas flow rate in the range 10-30 ml/min. Commercial grade argon was used as the carrier gas.

For the liquid-liquid extraction, 500 ml of water was extracted three times with 25 ml of dichloromethane. A second 500 ml of water was extracted in a similar manner, and the

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combined extracts dried over 100 g of sodium sulfate. The sodium sulfate was filtered on a vacuum filter, the vacuum line being trapped at -151°C to condense out the more volatile nitrosamines. The vacuum trappings were combined with the filtrate. The extract was then concentrated on a Kuderna Danish apparatus at 58°C to a final volume of 0.8 ml. At 10 µl sample of the concentrate was injected onto the gas chromatograph.

For the carbon adsorption technique, water was drawn through several cyclindrical columns packed with activated charcoal. Both a Mega sample (representing 300,000 gallons of water) and a 70-year sample (representing 25,000 liters of water) were used. The 70-year sample represents the average amount of water consumed during a normal human lifespan. The charcoal from the traps was dried and then extracted with chloroform, and then alcohol (1). Both the Mega and the 70-year extracts were adjusted volumetrically to represent a one million fold concentration.

Chemicals

Distilled AnalaR grade solvents were used throughout. For the recovery experiments a mixture containing seven N-nitroso compounds, dimethylnitrosamine (DMN), diethylnitrosamine (DEN), dipropylnitrosamine (DPN), dibutylnitrosamine (DBN), N-nitrosopiperdine (PIP), N-nitrosopyrrolidine (PYRN) and N-nitroso sarcosinate (SARCOSN) at approximately the 2 mg/kg concentration level (2 ppm weight basis) in dichloromethane was made up gravimetrically. The standard N-nitroso compounds were used as received, without further purification.

Source of Water Samples

Water from the Carrollton Water Plant (New Orleans, Louisiana), Jefferson Parish No. 1 Water Plant (Metairie, Louisiana) and the Jefferson Parish No. 2 Water Plant (Marerro, Louisiana) was analyzed using both procedures. In addition, commercial bottled water from New Orleans, Mississippi River water from New Orleans, and tap water from both Boston, Massachusetts and Waltham, Massachusetts were tested.

Results and Discussion

Using both analytical extraction procedures, solvent blanks gave no response on the gc-TEA. For the solvent-solvent extraction procedure, it was possible to test directly the effectiveness, reliability, and sensitivity of the method by analyzing triply distilled and deionized water, both before and after the addition of a mixture of seven N-nitroso compounds at the sub 0.01 µg/l concentration level.

The distilled and deionized water gave no response on the tc-TEA.

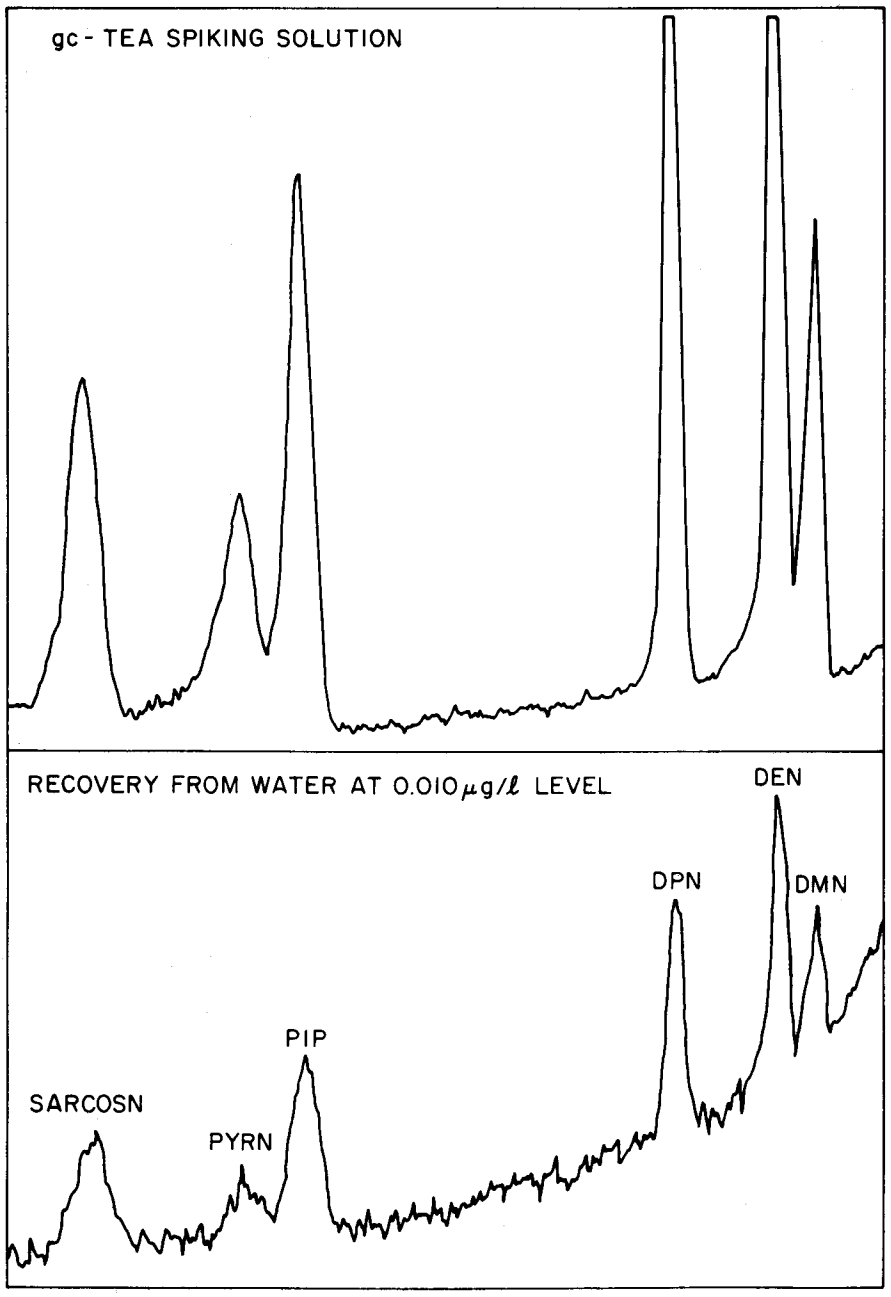
Figure 1A is a chromatogram of 10 µl of the mixture containing seven N-nitroso compounds that were added to the water. Figure 1B is the chromatogram of 10 µl of the final dichloromethane extract following concentration on the Kuderna Danish. From a comparison of the two chromatograms it is possible to calculate the efficiency of the extraction and analytical processes. Recovery efficiencies for the various N-nitroso compounds are tabulated in Table 1. At approximately 0.200 µg/l (200 ppt) concentration level the recovery efficiency is 30% for DMN, increasing to about 90% for the less volatile species. At a concentration of approximately 0.020 µg/l (20 ppt), similar recoveries were observed.

TABLE 1

RECOVERY EFFICIENCY OF N-NITROSO COMPOUNDS FROM WATER

Compound	Concn. µg/l (ppb)	Recovery Efficiency %	Concn. µg/l (ppb)	Recovery Efficiency %
Dimethyl nitrosamine	0.128	30	0.013	30
Diethyl nitrosamine	0.126	60	0.016	84
Dipropyl nitrosamine	0.190	70	0.020	84
Dibutyl nitrosamine	0.200	90	0.020	84
N-nitroso piperidine	0.206	88	0.021	84
N-nitroso pyrrolidine	0.174	50	0.017	-
N-nitroso sarcosinate	0.263	89	0.026	130

In every case, volatile gc-amenable N-nitroso compounds were not detected in the water samples. The chromatograph was also operated in the temperature program mode, with an initial oven temperature of 100°C, increasing at the rate of 5°C/min to 240°C, and then left for several hours; again, no trace of any N-nitroso compound was detected. For the liquid-liquid extraction procedure, this would indicate that volatile N-nitrosamines are definitely not present down to the 0.001 µg/l level (1 ppt). For the carbon extracts, assuming an efficiency of 100%, volatile N-nitrosamines were not detected at concentration levels down to 10 µg/l (0.01 ppt).


gc - TEA SPIKING SOLUTION
RECOVERY FROM WATER AT 0.010 μg/ℓ LEVEL
DEN
DPN
DMN
PIP
SARCOSN
PYRN

1A

1B

Conclusion

Volatile gc-amenable N-nitroso compounds have not been found to be present in drinking water, even at ultra trace levels. Since sensitive analytical procedures do not currently exist for detecting the non-volatile N-nitroso compounds, such as the N-nitrosotriazines, it should be clearly understood that these results refer only to the gas-chromatograph amenable N-nitroso compounds. Nothing is to be inferred as to the presence or absence of the more thermally labile N-nitroso compounds.

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