

REACTION BETWEEN CHLORINE AND A DIMETHYLAMINE CONTAINING POLYELECTROLYTE LEADING TO THE FORMATION OF N-NITROSO DIMETHYLAMINE.

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INTRODUCTION

Interest in the small organic molecule, N-Nitroso dimethylamine (NDMA), was rekindled early in 1990 with the discovery that groundwater in the Elmira area was contaminated with this material.

NDMA is known to cause liver and kidney cancers in animals. Based on this and other information, it has been estimated that an additional lifetime cancer risk of 1 in 11 000,000 in humans is posed by a concentration of 14 parts per trillion in drinking water⁽¹⁾. This concentration is the currently accepted drinking water guideline. Fourteen ppt is roughly equivalent to the addition of one drop of pure NDMA (about 25 mg) to 25 semi-tractor trailer loads of water (about 2500 m³).

NDMA has been known to industry for well over a century. In 1864, its formation during reaction of nitrous acid and trimethylamine was reported⁽²⁾. It was widely used in the 1940's and 50's in the manufacture of the rocket fuel, 1,1-dimethylhydrazine. NDMA is also well known in the rubber industry where it can occur during compounding and curing operations⁽³⁾. The structure is shown in Figure 1.

In addition to industrial sources, NDMA can also be formed in many other ways, NDMA forming reactions have been reported often in the scientific literature⁽⁴⁻¹⁰⁾. Our interest in the contribution of such reactions to environmental NDMA contamination arose from the discovery of the nitrosamine in the treated water supply of a small community that did not appear to be subject to direct industrial contamination. As the result of this study, carried out by a project team comprised of Pollutech Environmental, Health & Welfare Canada and Environment Canada, a new and potentially novel source of NDMA was discovered. This report describes the findings of the research team.

The treatment of the water in question involved the chlorination of raw river water, using sodium hypochlorite, followed by flocculation with alum and an organic polymer of the diallyl-dimethyl ammonium type. After flocculation, the clarified water was passed through a mixed bed filter prior to distribution. The chlorine residual was adjusted to about 0.5 ppm before distribution.

There were several possible routes by which NDMA may have occurred in treated drinking water. The most likely included:

- direct contamination by NDMA
- chemical reaction between the appropriate precursors
- artefactual production occurring during sample analysis
- bacterial or enzymatic action

Direct contamination and artefactual production could be ruled out, leaving bacterial action or chemical reaction as possibilities. The formation of NDMA in soil, water and sewage by bacterial action has been reported ^(11, 12), but chemical reaction was the most likely source in view of the number of possible precursors that were available.

The formation of NDMA from the reaction of precursors under a wide variety of conditions ranging from mild to brutal, has been well documented in the scientific literature. Most reactions require a source of nitrite and a secondary, tertiary or quaternary amine ^(9, 13). Generally a mildly acidic pH is required, but is not essential ^(9, 13).

In the present circumstances, several potential precursors were present. The raw river water was found to contain about 50 ppb nitrite and the presence of dimethylamine from agricultural runoff was suspected. Many herbicides such as 2,4-D are applied to fields as the dimethylamine salt.

The polyelectrolyte used in the water treatment was also a potential amine source. This material was of the poly (dialyl dimethyl ammonium) variety having the structure shown in Figure 2 ⁽¹⁴⁾.

FINDINGS

The first step in determining the source of the NDMA was to obtain samples of water at various points throughout the treatment process. Samples were collected and analysed for NDMA by isotope dilution using combined gas chromatography-mass spectrometry (GCMS) in selected ion monitoring mode. By this technique, we were able to detect 10 ppt.

The results of these analyses showed that while the inlet water was free of NDMA, the nitrosamine was present in the tank where the raw water was mixed with the treatment chemicals and at all points thereafter.

The results suggested a role of the treatment chemicals, therefore, the second step was to analyse the chemicals themselves for NDMA.

For use in the treatment system, the alum was prepared as a 12% solution, hypochlorite as a 1 % stock and the polymer as a 1.0 - 1.2% stock made up in treated water. Table 1 shows that the alum and chlorine stocks were essentially free of NDMA. The polymer stock, however, contained 74 ppt NDMA.

From these measurements alone we were not able to determine whether the contamination in the polymer stock was present as a contaminant in the original formulation or was formed by subsequent chemical reaction. Further measurements allowed the distinction to be made.

Table 1 shows that mixtures of polymer stock with alum or alum with chlorine stock did not

lead to NDMA formation. A mixture of polymer with hypochlorite, however, contained ppb levels of NDMA. The addition of alum to polymer-hypochlorite mixtures appeared to enhance NDMA formation, but this was not confirmed.

The results of these initial trials indicated that the reaction of sodium hypochlorite at a concentration of about 0.5% (5000 ppm) with a 0.6% solution of the polymer led to the formation of NDMA. A rough estimate suggests that NDMA was formed under these reaction conditions in about 0.04 to 0.3% yield or put another way; one in every 300 to 3000 dimethyl amine groups in the polymer was converted to NDMA.

It was important at this point to confirm that the formed material was indeed NDMA. This was of particular concern in view of the simplicity of the mass spectrum of NDMA and the resulting possibility that the single ion monitoring GCMS system may have been fooled by molecules or fragments with the same molecular weight.

For structural confirmation, extracts of reaction mixtures were examined by GCMS in full scan mode. For this work a Hewlett-Packard 5985 GC/MS system was used. Figure 3 illustrates the mass-spectra obtained from mixtures of authentic NDMA with the DB-NDMA analogue, and from the material formed during the polymer-hypochlorite reaction. Both spectra contain the ions 80, 55 and 46 from the d_6 NDMA analogue used in the assay, in addition to the dominant ions arising from NDMA, having masses of 74 and 42. The spectra are virtually identical, confirming the presence of NDMA in the reaction mixture.

The reactions described above were carried out using stock solutions of chemicals prepared on-site for the water treatment process using local tap water for dilution. To further explore the condition under which such reactions may occur, a series of laboratory simulations were carried out.

The results of Trial 1, shown in Table 2, show the formation of NDMA arising from a one hour reaction of polymer and hypochlorite in pure laboratory water. The presence of NDMA in this mixture indicates that the reaction occurs quickly and does not require precursors which may be present in tap or river water. Nitrite was not added to the reaction mixture and none was detectable in the laboratory water used.

Reaction of the components of Trial 1 for 20 hours did not lead to an increase in NDMA concentration. In fact, only about one half of the amount generated in the one hour reaction was detected. We have not yet established whether some of the nitrosamine formed in the one hour reaction was subsequently destroyed by the chlorine or if the decrease in NDMA concentration was the result of analytical variability.

In view of previous reports of the artefactual formation of NDMA during the methylene chloride extraction of chlorinated water containing precursor amines (5, 15), a sample of the reaction mixture from Trial 2 was de-chlorinated with sodium thiosulphate prior to extraction. The results, shown as Trial 3 in Table 2, show only a 20% decrease in NDMA concentrations compared to Trial 2. This result indicates that the bulk of the NDMA formed was not generated artefactually by this mechanism.

Trial 4 in Table 2 explored the reaction of a high concentration of polymer (5000 ppm) with low concentrations of chlorine (1.5 ppm) such as many occur above the sludge blanket during the

settling process. The results show that low levels of NDMA may be formed, under these conditions.

We attempted to determine the NDMA content of actual sludge from the treatment process, however, in these experiments we were not able to recover the deuterated NDMA standard which was added to the samples prior to extraction. As a result, any NDMA that may have been present would not be recovered by this extraction procedure. We, therefore, were not able to confirm the formation of NDMA in the sludge blanket under actual plant conditions.

Trial 5 in Table 2 simulated the reaction of low concentrations of both polymer and hypochlorite (0.5 ppm polymer and 1.5 ppm total chlorine) such would occur under conditions of ideal mixing in the treatment process. The results show that no detectable levels of NDMA were found under these conditions after a 20 hour reaction at room temperature.

DISCUSSION

Our results indicate that the reaction between hypochlorite and poly (diallyl-dimethyl ammonium chloride) leading to the formation of NDMA requires a high concentration of the polymer and is promoted by high concentrations of chlorine. NDMA does not appear to be formed when the reactants are present at the concentrations normally used in water treatment (about 1 ppm of each).

The reaction is likely instantaneous and concentrations of NDMA do not appear to increase with time beyond one hour. This may indicate that some destruction of NDMA occurs during long incubation in the presence of hypochlorite or that the reaction involves a small subset of active sites in the polymer.

In our experiments, we compared freshly prepared batches of polymer with aged (several weeks) preparations and while more NDMA may have been formed from aged preparations, the contaminant was also formed from fresh material diluted in pure laboratory water.

A most novel aspect of the reaction is that it appears to proceed without any obvious external source of nitrite. We cannot rule out that nitrite is formed from the polymer during reaction with chlorine, but there was none detectable in the source water used in the experiments described in Table 2. Nitrite was, however, present at ppb concentrations in the raw river water and treated water used in earlier experiments. This may be one of the factors contributing to the higher levels of NDMA formed from these mixtures.

As the NDMA forming reaction proceeds most efficiently in the presence of high concentrations of polymer and hypochlorite, the identification of sites of potential concern in water treatment processes becomes a relatively easy matter. Such sites would generally be limited to the point at which the chemicals are added to the raw water or where the polymer sludge accumulates. The NDMA forming potential of any polymer/chlorine mix can easily be assessed by mixing equal amounts of 1 % stock solutions followed by analysis for NDMA. Should such potential exist, steps should be taken to ensure separation of the points of addition of chlorine and polymer and their adequate mixing with the raw water. Alternate polymers should also be considered.

Although we have found, no reports in the scientific literature describing a reaction of chlorine

and an organic polymer leading to NDMA, there are precedents for reactions between nitrite and amine precursors which are similar in structure to the polymer described in this report. In some cases it was suspected that chlorine played a role.

Kimoto and co-workers ⁽⁴⁾ studied tap water in the Philadelphia area and found that NDMA was formed when they added the precursor, dimethylamine (DMA), to the water. NDMA was not formed when a chemical, sodium thiosulphate, known to destroy chlorine, was added to the water before the DMA. The authors concluded that chlorine or some other oxidizing agent present in the water may promote the formation of nitrosamines in the presence of the appropriate precursor.

Kimoto and co-workers (1) studied the formation of NDMA when tap water was passed through resins (anion and cation exchange resins) used for water purification. They found that when purified water was passed through anion exchange resins, the amount of NDMA produced increased with the concentrations of chlorine added to the incoming water. The authors thought that the NDMA precursor was the quaternary ammonium ion of the exchange resin. It should also be noted, however, that despite the increased NDMA production with increasing chlorine, the amounts produced were less than that produced with city tap water. The authors concluded that something else other than chlorine in the tap water promoted the reaction.

Gough and co-workers ⁽⁶⁾ also reported the presence of NDMA in water treated with ion exchange resins. These workers established that the anion exchange resin led to the presence of NDMA. NDMA was also found in extracts of the resin itself, leading the authors to conclude that the material was not formed from a reaction between precursors in the water and free amines in the resin, but likely originated from the amines used to prepare the resins.

Angeles et al ⁽⁷⁾ also reported the formation of nitrosamines from ion exchange resins. These workers found that, in their experiments, both anion and cation exchange resins were necessary to form nitrosamines. In contrast to other studies they did not get a reaction with the anion exchange resin alone. The authors suggested that the formation of nitrosamines could be avoided by separating the anion and cation exchange resins or not using anion resins containing amine-based functional groups.

The International Agency for Research in Cancer (IARC) Monograph Series⁽¹⁾ cites several studies finding NDMA in water treated with ion exchange resins.

Fiddler et al ⁽⁹⁾ demonstrated that a range of tertiary and quaternary amines can form nitrosamines, including NDMA. The reaction conditions used by Fiddler may occur under actual water treatment situations and require only the precursors, nitrite and the amine, at a slightly acidic pH.

Abidi ⁽¹⁰⁾ reported that two dyes used as tracers in water monitoring can give rise to the formation of a related nitrosamine, N-diethylnitrosamine (NDEA), when exposed to nitrite in river water. Both dyes contained a tertiary amine group, (diethylamine) which was thought to react with nitrite in the water. Of particular interest in this study was that the NDEA forming reaction occurred when the dye and nitrate were present at extremely low concentrations (1 -20 ppb).

The observation that NDMA can be formed from tertiary and quaternary amines is of particular relevance to the present situation. The anion exchange resins and the polymer described in this report are both quaternary amines. Their structures are compared in Figure 4. The quaternary amine functional groups in the polymer are expected to be bound primarily in the cyclic structure shown in Figure 2. At the chain ends, however, non-cyclic amines may be present, as shown in Figure 4. These sites are expected to be the most susceptible to attack by chlorine. The presence of a limited number of chain end groups may also explain why a small amount of NDMA appears to be formed quickly, but the amounts do not increase with further incubation. An alternative explanation would be that the polymer preparations contain a small amount of un-reacted monomer or other reactive amine.

In either case, in view of the relative ease with which nitrosamines can be formed from amine based material under conditions which can occur in water and treatment plants, the use of alkyl amine based additives in these applications should perhaps be re-evaluated.

REFERENCES

- 1 W.H. Lederer, Regulatory chemicals of health and environmental concern Van Nostrand Reinhold Co; New York pp 207-209 (1985)
2. Cited in: P.A.S. Smith and R.N. Loeppky Nitrosative cleavage of tertiary amines J. Am. Chem. Soc. 89: 1147-1157 (1967)
3. K. Verscheusen, Hand book of Environmental data on organic chemicals Van Norstrand Reinhold Co., New York, pg 558 (1983)
4. W.I Kimoto, C.J. Dooley, J. Carre, and W. Fiddler. Nitrosamines in tap water after concentration by a carbonaceous adsorbent Water Res. 15: 1099 - 1106 (1981)
5. W.1. Kmoto, C.J. Dooley, J. Carre and W. Fiddler. Role of strong ion exchange resins in nitrosamine formation in water. Water Res. 14: 869-876 (1980)
6. T.A. Gough, K.S. Webb and M.F. McPhail. Volatile nitrosamines from ion-exchange resins Food Cosmet Toxicol. 15: 437-440 (1977)
7. R.M. Angeles, L.K. Keefer, P.P. Roller and S.J. Uhm. Chemical models for possible nftrosamine artefact formation in Environmental analyses. In: Environmental aspects of N-Nitroso compounds (E.A. Walker, Ed) IARC Scientific Publication 19,109-115 (1978)
8. N-Nitroso dimethylamine In IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans 17: 125 (1978)
9. W. Fiddler, J.W. Pensabene, R.C. Doerr and A.E. Wasserman. Formation of N-nitroso dimethylamine from naturally occurring quaternary ammonium compounds and tertiary amines. Nature 236: 307 (1972)
10. S.L. Abidi. Detection of diethylnitrosamine in nitrite-rich water following treatment with

rhodamine flow tracers. Water Res. 16: 197-204 (1982)

11. A. Ayanaba, W. Verstrete, and M. Alexander. Possible Microbial contribution to Nitrosamine formation in sewage and soil. J. National Cancer Inst. 50: 811-813 (1973)

12. C. Calmels, A. Oshima, and H. Bartsch. Nitrosamine formation by denitrifying and non-denitrifying bacteria: Implication of nitrite reductase and nitrate reductase in nitrosation catalysis. J.Gen Microbiol. 134: 221-226 (1988)

13. P.A.S. Smith and R.N. Loeppky. Nitrosative cleavage of tertiary amines J.Am. Chem. Soc. 89: 1147-1157 (1967)

14. Kirk-Othmer Concise. Encyclopedia of Chemical Technology, pp. 492-494. J. Wiley and Sons, New York (1 985)

15. J.B. Cohen and J.D. Backman. Measurement of environmental nitrosamines in Environmental aspects of N-nitroso compounds. (E.A. Walker Editor) IARC Scientific Publication 19, 257-372 (1978)

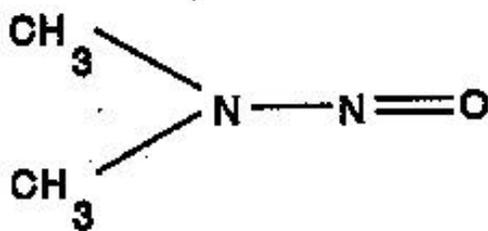
TABLE 1: NDMA CONCENTRATIONS IN INDIVIDUAL AND COMBINED WATER TREATMENT CHEMICALS

Solution	NDMA (ppt)
Alum stock (12% w/v)	< 10
Hypochlorite stock (1.0% w/v)	11
Polymer stock (1.2% w/v)	74
Alum and polymer (1:1)	45
Alum and chlorine (1:1)	< 10
Hypochlorite and polymer (1:1)	1300 - 7200
Hypochlorite and alum and polymer (1:1:1)	3000 - 12000

TABLE 2: LABORATORY SIMULATION OF REACTION CONDITIONS

Conditions	NDMA
0.5% polymer 0.5% hypochlorite 1 hour reaction	310
0.5% polymer 0.5% hypochlorite 20 hour reaction	150
as in 2, residual chlorine destroyed before extraction	120
0.5% polymer 1.5 ppm hypochlorite 20 hour reaction	56
0.5 ppm polymer 1.5 ppm hypochlorite	< 10

FIGURE 1



N-Nitrosodimethylamine (NDM)

FIGURE 2.

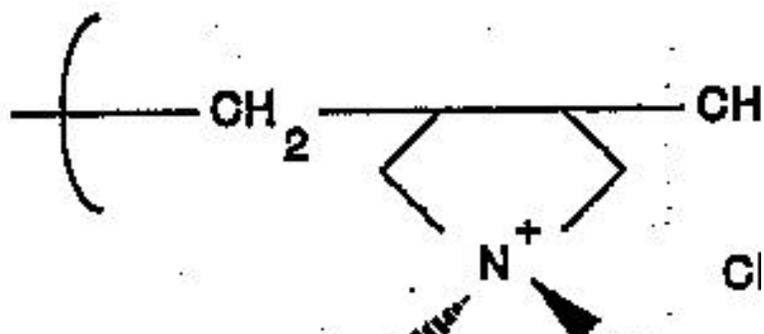
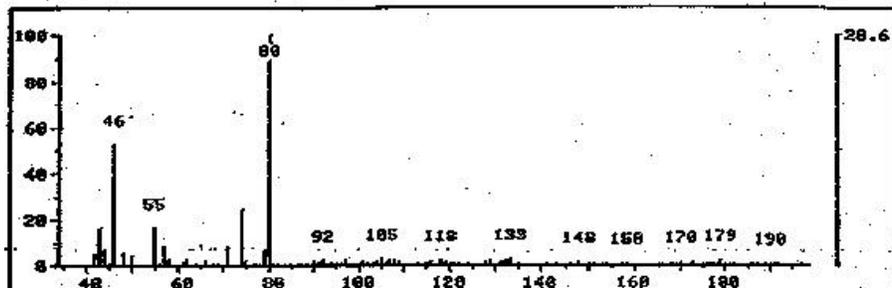


FIGURE 3

COMPARISON OF TOTAL ION PROFILE AND MASS SPECTRUM OF AUTHENTIC NDMA WITH THAT FORMED DURING REACTION OF POLYMER AND CHLORINE

A: AUTHENTIC NDMA WITH d_6 - NDMA STANDARD



B: CHEMICAL FORMED DURING REACTION OF POLYMER AND CHLORINE

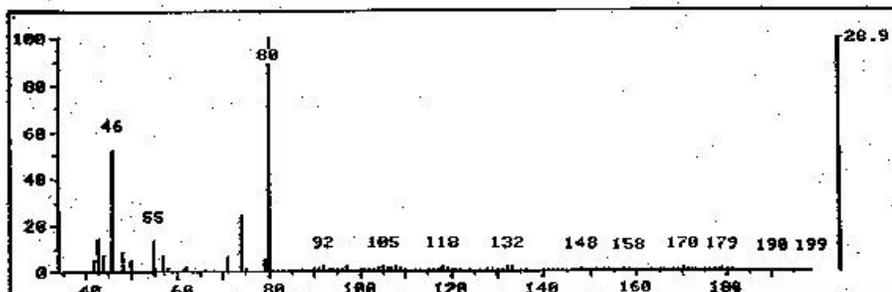
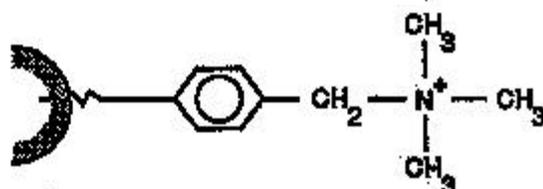
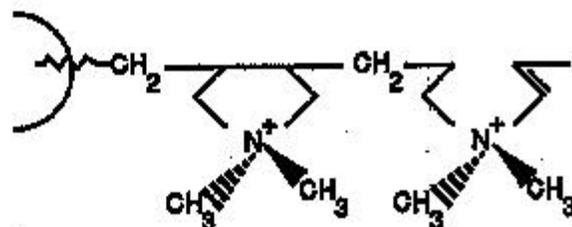


FIGURE 4

Typical Anion Exchange Resin Structure



Suggested Polymer Chain End Structure



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