

UNHAIRING METHOD IDENTIFIED AS SOURCE OF N-NITROSODIMETHYLAMINE IN TANNERY ATMOSPHERE*

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Introduction

Volatile nitrosamines are low-molecular-weight compounds formed by the reaction of a secondary, tertiary, or quaternary amine with a nitrosating agent such as nitrous acid, nitrite, or various nitrogen oxides (1). They are of concern because they have been shown to be carcinogenic to laboratory animals even at very low concentrations (2, 3). There is considerable literature concerned with the presence of nitrosamines in foods (4, 5). Airborne nitrosamines have also been reported in a variety of industrial environments (6) as well as urban air (7).

In 1978, during the Air Pollution Control Association's annual meeting, a contractor for the National Institute for Occupational Health and Safety (NIOSH) reported finding a volatile nitrosamine, N-nitrosodimethylamine (NDMA) in the air of a tannery (8). While no incidence of human cancer has been attributed to nitrosamines to date, the finding of this compound caused representatives of the tanning industry to request that our laboratory (ERRC) investigate the NIOSH finding and to determine the source of the nitrosamine. The results of this study are reported in this paper.

Materials and Methods

AIR SAMPLING. Air samples were obtained by drawing a volume of 60 liters of air through a 1.5-cm diameter glass collector containing 15 g of Tenax GC**. Tenax GC is a porous polymer of 2,6 diphenyl-p-phenylene oxide reported to have strong affinity for NDMA (9). A battery-operated Bendix air pump (Model BDX 55-HD), operating at approximately 1 liter/min, was used to take air samples from various locations throughout several tanneries. It became apparent that the highest concentrations of NDMA were located in the beamhouse, so most of the samples were taken from that area.

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† Agricultural Research Service, U.S. Department of Agriculture.

** Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

AQUEOUS AND SOLID SAMPLES. Aqueous samples were taken throughout the beamhouse and from the combined effluent streams. In two instances solid samples were scraped from surfaces of equipment and floors in various sections of the tannery. A section of a wooden beam from one location was also taken for analysis.

PREPARATION OF SAMPLES FOR NDMA ANALYSIS. The exposed Tenax GC was extracted by passing 80 ml of redistilled diethyl ether through the collector column. The ether was concentrated in a Kuderna Danish flask to a volume of 1.0 ml. Aqueous samples were distilled from a 1 N NaOH solution and the distillate extracted with three 100-ml portions of methylene chloride (DCM). The extract was dried over sodium sulfate and concentrated as in the Tenax extraction. Solid samples were extracted with DCM, the DCM distilled from 1 N NaOH and the aqueous distillate extracted with three 70-ml portions of DCM. The combined DCM was washed first with 50 ml of 6 N HCl and then with 50 ml of 5 N NaOH. The DCM extract was then dried with sodium sulfate and concentrated as before.

HEAD SPACE SAMPLING. In separate experiments, solid samples of floor scrapings from the loft of one tannery and a block of wood from a beam in another tannery were placed in a closed vessel. Three 1-liter air samples were taken from the vessel over a period of 24 hr and passed through Tenax GC. Samples for NDMA analysis were handled as described above.

NDMA ANALYSIS. Analysis of the nitrosamine was performed on a Varian-Aerograph Model 2700 gas chromatograph interfaced with a Thermal Energy Analyzer (TEA) as a detector (10). A 6- μ l sample was injected into a stainless steel column 275 cm x 3 mm packed with 15 percent carbowax 20 M-TPA on 60-80 mesh Gas Chrom P. The column was programmed from 130°C to 190°C at 4°/min with an argon carrier flow of 35 ml/min. The injector port temperature was 190°C. The TEA operating conditions were: catalytic pyrolyzer at 450°C, cold trap at -115°C, and a vacuum of 2 - mm Hg.

CONFIRMATION. NDMA was confirmed, in selected samples, by use of a Varian-Aerograph Model 2700 gas chromatograph, equipped with a glass column 6 ft x 1/4 in. (od) packed with 15 percent Carbowax 20 M-TPA, connected to a Varian MAT 311 A mass spectrometer. Further details can be found in a paper by Pensabene et al. (11).

Results

The tannery initially cited by NIOSH as having NDMA was sampled. The levels of NDMA found in the samples, as compared to the results obtained earlier by NIOSH, are given in Table I. The analysis of these samples confirmed the presence of NDMA but at approximately 10-fold lower levels than in the NIOSH analyses. This result could be explained by the difference in operating conditions that existed during the two test periods. When the NIOSH samples were taken, the weather was cold and the building was closed to conserve heat. Our samples

TABLE I

N-NITROSODIMETHYLAMINE FOUND IN THE TANNERY
ATMOSPHERE BY USDA AND NIOSH

Location within tannery	NDMA ($\mu\text{g}/\text{m}^3$)	
	USDA	NIOSH
Hide house	— ^a	5.6
Soak	— ^a	13
Unhairing	3.2	27
Relime	7.3	13
Bate/pickle/tan	3.5	36
Split and shave	— ^a	28
Retan/color/fatliquor	3.2	47
Color set out	1.9	19
Paste dryer	0.7	11
Finishing	0.21	3.5
Control (outside air)	0.15	ND ^b

^a Not sampled.

^b ND—None detected; limit $<0.05 \mu\text{g}/\text{m}^3$.

were taken during the summer when the windows and doors were open throughout the tannery. This explanation is supported by an unpublished NIOSH contract report that a second sampling taken in June 1978 showed values of approximately one-tenth of those found in the previous samples taken in the cold weather.

NDMA was the only nitrosamine found in the beamhouse area, suggesting that dimethylamine, or a material containing dimethylamine, was the precursor. Dimethylamine sulfate (DMAS) was used in the chemical unhairing process in the tannery and was therefore considered the most likely source of the NDMA. Analysis of the DMAS itself revealed that it contained only a small amount of NDMA (<0.4 ppm), not enough to account for the amount present in the tannery atmosphere. Therefore, it was presumed the NDMA was formed by nitrosation of the DMAS in the beamhouse. As a result of our findings, it was decided to discontinue the use of DMAS in processing in order to determine what effect this would have on the atmospheric level of NDMA in the tannery.

To further support the hypothesis that DMAS was the source of the amine in the NDMA, additional air and aqueous samples were obtained from other tanneries. Samples were taken from three tanneries that use DMAS and from four other tanneries that do not. The tanneries manufactured a variety of products, including sole leather, side leather, and upholstery leather.

As shown in Table II, the air in the tanneries using DMAS contained levels of NDMA that were on the same order of magnitude as those found in the first tannery. In all cases, the NDMA levels were the highest in the beamhouse area.

TABLE II

N-NITROSODIMETHYLAMINE FOUND IN TANNERIES USING DMAS

Location within tannery	NDMA ($\mu\text{g}/\text{m}^3$)		
	Tannery A	Tannery B	Tannery C
Beamhouse	2.3	1.3	3.9
Relime	1.05	— ^a	3.6
Bate/pickle/tan	0.56	0.39	0.61
Retan/color/fatliquor	0.56	0.06	0.22
Finishing	— ^a	0.12	0.15
Control (outside air)	0.1	0.09	ND ^b

^a Not sampled.

^b ND—None detected; limit $<0.05 \mu\text{g}/\text{m}^3$.

The only indications of the presence of NDMA in the air of the tanneries not using DMAS were small amounts (0.03 to $0.35 \mu\text{g}/\text{m}^3$) in the beamhouse and one sample taken from outside the beamhouse area that showed a trace ($<0.05 \mu\text{g}/\text{m}^3$) of NDMA.

Aqueous samples were also taken from the tanneries that do, and from those that do not, use DMAS. None of the influent waters contained measurable amounts of NDMA. Effluent samples from unhairing, reliming, bating, and soaking, as well as composite effluent solutions, were tested. As shown in Table III, the effluents from the tanneries using DMAS showed levels of NDMA ranging from 0.26 to 1.7 ppb in every process except the soak. The soak samples had only a trace or none.

TABLE III

N-NITROSODIMETHYLAMINE IN AQUEOUS SAMPLES FROM TANNERIES USING DMAS

Aqueous sample	NDMA (ppb)		
	Tannery A	Tannery B	Tannery C
Influent	Tr	ND ^a	Tr
Relime	0.77	0.84	0.70
Unhair	1.3	— ^b	1.1
Bate	0.61	0.28	1.7
Soak	0.06	— ^b	ND
Composite effluent	0.93	0.26	1.3

^a ND—None detected; limit <0.05 ppb.

^b Not sampled.

Using the same procedures, only traces of NDMA were found in the effluent samples from the tanneries not using DMAS. The only exception was the effluent from one of these tanneries that contained 1.4 ppb of NDMA. It is unlikely that this anomaly is associated with the tanning process.

The original tannery was sampled for NDMA levels in the atmosphere four more times, and the results are given in Table IV. The first two samplings were made 1 week before and 2 weeks after discontinuing DMAS in the unhairing process. It was expected that the second of these experiments would show a major decrease in the NDMA level. Actually, however, only a 50 percent reduction was observed. Air samples taken in this tannery 2 months and 6 months later showed further small reductions in the airborne levels of nitrosamine, but they were still not completely eliminated. Finally, however, samplings taken from the tannery one year after the use of DMAS was discontinued showed NDMA levels in the same low range as those tanneries not using DMAS.

TABLE IV

CONCENTRATION OF N-NITROSODIMETHYLAMINE FOUND IN
TANNERY ATMOSPHERE BEFORE AND AFTER DMAS DISCONTINUED

Location within tannery	NDMA ($\mu\text{g}/\text{m}^3$)				
	1 wk before DMAS discontinued	Time after DMAS discontinued			
		2 wk	2 mo	6 mo	1 yr
Beamhouse	3.2	2.6	3.1	1.4	0.40
Bate/pickle/tan	3.5	1.8	1.5	1.3	0.47
Retan/color/fatliquor	3.8	1.2	0.86	1.8	0.37
Color set out	1.9	0.48	0.86	1.1	0.09
Finishing	0.31	ND*	0.21	0.26	0.16
Outdoor control	0.12	ND*	ND	0.16	0.10

* ND—None detected; limit $<0.05 \mu\text{g}/\text{m}^3$.

Discussion

The persistence of NDMA in the tannery atmosphere for such a long time after the use of DMAS was discontinued suggested that some additional source of it was present.

Since NDMA is an oily liquid with a boiling point of 164°C and a high vapor pressure, one possible explanation was that residual NDMA found in various porous materials within the tannery could continually bleed NDMA into the atmosphere. This possibility was tested by examining the NDMA content of a number of solid materials commonly found in the tannery. These included a portion of the wooden structure itself, scrapings from the floor and machinery in the

beamhouse area, and grease from a catwalk over the fatliquor/color/retan area. A portion of a wooden beam was sectioned and reduced to sawdust. Significant amounts of NDMA were extracted from all of these solid materials. The interior of the wooden beam contained 1200-1300 ppb NDMA, the scrapings contained from 76 to 119 ppb, and the grease had 17 ppb.

To further test the hypothesis that these materials could indeed be the source of airborne NDMA, the various solids were placed in a 12-liter flask and air was then drawn intermittently over these solids for a 24-hr period and then through a Tenax GC detector absorbant. When this headspace was analyzed for nitrosamines, concentrations of from 3.5 to 12 $\mu\text{g}/\text{m}^3$ of NDMA were found over the wooden beam or the grease samples. None was detected from the floor scrapings.

Conclusions

The results of this study show that the major source of amine for the formation of NDMA found in tanneries is the DMAS used in the unhairing process. While a low level of NDMA (less than 0.4 $\mu\text{g}/\text{m}^3$) was found in all tanneries tested, those which used DMAS had significantly higher levels, particularly in the beamhouse area. Discontinuation of DMAS usage over a 12-month period in a closely monitored tannery resulted in a better than 98 per cent reduction in the nitrosamine level from that initially reported by NIOSH. The final level after 12 months was similar to that found in tanneries not using DMAS.

The results of this study suggest that tanners should eliminate the use of DMAS in the unhairing process because of the potential health risks associated with the formation of NDMA from DMAS, unless some means can be used to effectively eliminate worker exposure to NDMA. Elimination of sources of nitrosation such as gas heaters or propane-burning fork lifts or the installation of highly efficient ventilation systems might prevent NDMA formation or remove it from the tannery atmosphere. These alternatives, however, are likely to be impractical, expensive, or both.

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Discussion

MR. PAUL FINNEGAN (Discussion Leader): Thank you very much, Dave, for an excellent paper. Somehow it's reassuring to know that not all of the Government agencies are attempting to put tanners out of business.

We would like to take questions from the floor.

DR. STANLEY SHUTTLEWORTH (Leather Industries Research Institute): It seems to me that there's a terrific witch hunt on this cancer business and there seems to be a gap between finding that a compound is carcinogenic by administration in large quantities to animals and the actual observed amount of cancer. I've been around tanneries for a very long time, and I think the record in the tanning industry for cancer is fantastically good. I can hardly think of anybody, apart from heavy smokers, who've developed cancer in the tanneries. And you did mention that there was no real proof of the connection between nitrosodimethylamine and actual cancer. Is that a general observation?

DR. BAILEY: Yes. There's not been an actual correlation made.

DR. SHUTTLEWORTH: Surely, there is no correlation of carcinogens and cancer in this industry.

DR. BAILEY: That's a very complicated situation in this country right now. That would be pretty tough to do.

DR. JOHN MOYNIHAN (*The Leather Manufacturer*): Dave, you said that you found some levels of nitrosamine in tanneries where they weren't using DMAS. Does NIOSH regard these levels as significant? What would be the probable cause of this?

DR. BAILEY: In answer to the first, I have to make it clear that, although I work for the Government, I am not connected with those agencies, and I can't answer for them. As I understand it, the monies that were available for continuing this particular line of work are not coming out of NIOSH this year. They are switching their emphasis to an epidemiological study of the tanning industry as one of a series of industries to be studied.

What levels? Nobody has set levels. The danger seems to be that when this kind of information becomes public and they can't set a measurable standard they say zero. As far as where the low levels are coming from that we found in the other tanneries, I have some suspicions that certain compounds, quaternary and tertiary amines, are possible sources of the dimethylamine group for the formation of dimethylnitrosamine. There are a number of these products used in the tannery, and these may be the source. We're going to be looking into these further.

MR. MOYNIHAN: And they all would be products used in the beamhouse?

DR. BAILEY: Yes.

DR. TOM THORSTENSEN (Thorstensen Laboratory): Dave, it occurred to me that even though you're not using dimethylamine sulfate in the unhairing system, dimethylamine is generated in unhairing systems during liming. Could this be a factor and could there be other closely related compounds that could give us trouble in the future even though we're not using these particular chemicals?

DR. BAILEY: In answer to the second part, yes. Other materials that you might use in the future could provide dimethylamine. In answer to the first part, I can only give you an indirect reason of why I think that it is not true. It is not the long limes. Long limes will not only produce dimethylamine, they should produce diethylamine, methylethylamine, and a variety of secondary amines. Where we looked in the air in a sole leather tannery where you encounter the long beam, we've found only dimethyl. So only dimethyl is being picked up and being made into nitrosamine. So, on an indirect basis, I say no, that's probably not a significant source.

DR. THORSTENSEN: Thank you.

MR. GEORGE STOCKMAN (Pfister & Vogel Tanning Company): The fact that you found 1200 to 3700 parts per billion in the wood from a beam, I think, is astounding. Were any measurements done on controls?

DR. BAILEY: In what respect? In terms of wood from another tannery?

MR. STOCKMAN: No. From a wood pile in the back yard or from a freshcut tree, or from a lumber yard or a similar "uncontaminated" source.

DR. BAILEY: No. We have not. That's something that should be done.

MR. CARL BONTEMPS (Rohm & Haas Company): David, in your final slide, you indicated that by stopping the use of dimethylamine sulfate you had a 95 percent reduction in the nitrosodimethylamine. You were comparing with the original NIOSH figures, but in your experiments and NIOSH's recheck at a later date, you had 1/10 the figures which is already 90 percent down. There was only another 5 percent in there. How do you relate that? And a second question, yesterday you indicated that exhaust from lift trucks was probably reacting in the tanneries with amines causing the nitrosodimethylamines. Could you comment on that, also?

DR. BAILEY: The basis for saying there was a 95 percent reduction is this: Going back to the original argument, the reason we saw a 90 percent decrease from April to August was simply because of the increased air circulation in the tannery. Under the closed conditions we found the high levels. That is not a matter of how much is being produced, it's a matter of how fast it's being blown out. We continued our testing throughout the year, the last testing being done in February when we were back at the closed condition again with less air circulation than we had in the summer months. That's the basis on which I claimed the 95 percent reduction.

In answer to the second question: as I originally stated, the formation of nitrosodimethylamine requires two components: a diamine, tertiary amine or quaternary amine and some nitrosating agent. Now, there is sufficient nitrosating capacity in the air of tanneries and separate studies have been done which show that we have both components in the tanneries. We suspect that the major source of nitrous oxide is from gas operated fork lift trucks; also any kind of open-flame heaters can be a source of nitrogen oxides.

MR. LOUIS TREVATHAN (Virginia Oak Tannery): You mentioned in your survey that one tannery showed no nitrosamines until you got to the effluent. Is it possible to form these NDMA's in the nitrification-denitrification cycle?

DR. BAILEY: The nitrification within the treatment area is a biological reaction, and the nitrates and nitrites in that solution might possibly be the cause, but unlikely in that case.

MR. FINNEGAN: Once again, thanks very much, Dave. Before we cut this off completely there's one question I have. Being from the Northeast tannery, I have been quite interested in this proposition. One of the things that we have done is to read the literature. We found that nitrosodimethylamines are destroyed when subjected to ultraviolet light. Going on the assumption that tannery workers won't drink the tannery liquors, the only danger would be from the air. If you drew all the air through a box that was completely full of ultraviolet radiation, would this in fact destroy or minimize to some safe level of nitrosodimethylamine?

DR. BAILEY: Yes, I'm sure it would. The question then is how do you engineer something like that? But it's certainly amenable to testing.

MR. FINNEGAN: Thank you very much, Dave.