

Estimate of the Volatile Nitrosamine Content of Japanese Food

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Many N-nitrosamines are well documented to be carcinogens (MAGEE & BARNES 1956) and a class of volatile nitrosamines (NNA) have been detected in the environment (FINE et al. 1979) and in foods (MAKI et al. 1977, 1978; IYENGAR et al. 1976). NNA are formed readily from precursor amines and nitrite in acidic media. Various kinds of foods contain amines (KAWAMURA et al. 1971) and nitrite is permitted for use in cured meats.

We previously reported a trace analytical method (MAKI et al. 1978) for NNA in foods based on Thermal Energy Analyzer-Gas chromatography (TEA-GC).

A survey has been performed to determine the levels of the NNA in a wide range of normal and typical Japanese foods.

This paper deals with a summary of the results from 370 samples investigated, and estimation of the average daily intake of NNA from these foods.

MATERIALS AND METHODS

Samples: 370 samples were collected from the retailers in Tokyo area from 1976 through 1980, and stored at -20° until analysis.

Analysis: Volatile N-nitrosamines were analyzed by TEA-GC after extraction of NNA in the edible materials with dichloromethane. Each sample was examined for N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-propylamine, N-nitrosodi-isopropylamine, N-nitrosomethylbutylamine, N-nitrosodi-n-butylamine, N-nitrosodi-isobutylamine, N-nitrosomorpholine, N-nitrosopiperidine. The contents were expressed as μg per kg of wet weight.

RESULTS AND DISCUSSION

The number of 370 samples of food have been selected on the basis of the average consumption in Japan and analyzed for NNA by TEA-GC. The results of these investigations are shown in Table 1.

TABLE 1. Occurrence of volatile NNA in foodstuffs

Commodity	No. of samples examined	No. of samples containing NNA ($\mu\text{g/kg}$)			
		<0.1	0.1~1	1~10	>10
Cured meats	81	9	72	0	0
Canned fish & meat containing vegetable	29	26	2	1	0
Precooked frozen food	12	8	2	2	0
Dried fish	18	0	2	7	9
Broiled dried fish	9	0	1	1	7
Fish smoked & flavoured	14	1	3	6	4
Shiokara (soused cuttlefish)	5	0	2	3	0
Katsubushi (dried bonito)	3	0	0	3	0
Dairy products	23	23	0	0	0
Egg & chicken	24	13	5	6	0
Food seasoning & spice	12	10	1	1	0
Margarine	31	18	2	11	0
Mayonnaise	5	5	0	0	0
Beer	56	2	30	24	0
Sake	17	17	0	0	0
Tsukemono (pickled vegetables)	9	9	0	0	0
Miso & shōyu (soy sauce)	20	20	0	0	0
Rice	2	2	0	0	0
Total	370				

Eighty-one samples of cured meat which are permitted the use of nitrite as a preservative were examined and the contents of NDMA in all of the samples were less than 1 μg per kg in spite of the presence of nitrite ranging from 1 to 10 mg per kg. Ascorbic acid and sorbate are also used in the process for the production and the pH values of these samples were in the neutral region, and these may prevent the formation of NNA (MIRVISH et al. 1972, TANAKA et al. 1978).

Forty-one samples of canned fish and meat containing vegetable and precooked frozen foods were examined and NDMA was found in 7 samples in the range of 0.2 to 12 μg per kg. NDEA also occurred on four occasions (0.9-5.2 μg per kg) in canned and precooked frozen food, respectively. These results suggested that high levels of nitrate in various vegetables caused formation of no appreciable amount of NNA.

Twenty-four out of the 27 samples of dried fish did contain NDMA which range from 4 to 38 μg per kg. Furthermore, it was found that when the dried materials were broiled by treatment with coal-gas, NDMA contents increased approximately 30-fold before the treatment, but no increase was observed in electric oven. This effect may be attributed to the participation of nitrogen oxides formed in the combustion of coal-gas.

Fish products of smoked, flavoured, Shiokara (soured cuttlefish) and Katsuobushi (dried bonito) in 21 out of 22 samples also contained NDMA in concentration ranging from 0.5 to 13 μg per kg. The NDMA levels are comparable to those of dried materials.

Nitrosatable amines and precursors are natural constituents of animal feeds. Forty-seven samples of dairy products, egg and chicken were examined for NNA, and NDMA found in 11 of 24 samples of egg and chicken in the range of 0.5 to 2.9 μg per kg, but no NNA were detected in any of the dairy products.

Seasoning food, spice margarine and mayonnaise were examined in 48 samples, NDMA was present in 2 of 9 samples of seasoning foods in concentration ranging from 1.0 to 5.1 μg per kg. Margarine also contained NDMA in 13 out of 31 samples ranging from 0.1 to 2.9 μg per kg, but no mayonnaise and spice were contaminated with any detectable amounts of NNA in all of the samples.

All common varieties of beers contained NDMA in the range of trace to 4.2 μg per kg, but none of the Japanese alcohol Sake contained any detectable amounts of NNA.

Tsukemono (pickled vegetables), Miso and Shōyu (soy sauce), typical Japanese food had low levels

TABLE 2. Estimated daily intake of NNA from Japanese food

Commodity	# Consumption (g/day/person)	average (μ g/kg)	intake (ng/day)
Cured meats	12	0.5	6
Dried fish	54	13.5	* 729
Broiled dried fish	54	30	1620
Canned & Fish products	5	5	25
Dairy products, egg & chicken	76	0.7	53
Food seasoning	6	0.2	1.2
Oil & fats	18	0.9	16.5
Beer	30	1.6	48
Sake	19	0	0
Tsukemono, Miso & Shōyu	27	0.3	8
Rice	234	0	0
Total			1779 *(888)

Cited from the literature (MINISTRY OF HEALTH & WELFARE)

of NNA ; all Tsukemono less than 0.1 μ g per kg, but the possible high levels of nitrite or nitrate may induce in vivo formation of NNA. Out of 20 samples of Miso and Shōyu, nine samples contained NDMA in the range of 0.1 to 0.8 μ g per kg, however, none of any other NNA were detectable in all of these samples.

None of the rice samples contained any detectable amounts of NNA.

No NNA were detectable except NDMA and NDEA in any of these investigated foods.

The intake of these NNA can be calculated from the average intake of the appropriate foods (Table 2. MINISTRY OF HEALTH AND WELFARE 1979).

It is concluded that the likely intake of NDMA per person from the Japanese diet is approximately 1.8 μ g for NDMA.

It was reported that the average UK-food is approximately 1 μg per week per person, though, these low figures can be explained from the apparent absent of data on beer in this survey (GOUGH et al. 1978). Also, in West germany, the average daily of intake is estimated to be 1.1 μg of NDMA for per day per person (PREUSSMANN et al. 1979). The value of 1.8 μg of our data is in fairly good agreement with the data from both surveys.

Up to data, it was demonstrated that 1 mg per kg of NDMA contained in animal feed caused the minimum carcinogenic dose on long-term oral administration to rats (ARAI et al. 1979). On the basis of these data, the value of 1.8 μg NDMA per person corresponds to approximately 1/1000 of the amount of carcinogenic dose (1 mg per kg) as above mentioned.

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