

## THE ARSENIC CONTENT IN SOME NORWEGIAN FISH PRODUCTS

BY

E. EGAAS and O.R. BRÆKKAN  
Institute of Vitamin Research  
Directorate of Fisheries, Bergen

### ABSTRACT

Arsenic has been analyzed in 43 samples of fresh, frozen, smoked and canned fish products by a method based on freeze drying, dry digestion, isolation of the element by hydride generation and atomic absorption spectrophotometer measurement. The content varied between 0.15 and 18.7 mg As per kg wet weight. Based on dry weight, the highest values were found among the meat samples of crustaceans (19.0 to 58.6 mg per kg), cod milt (43.2 mg per kg) and smoked fillets of cod (25.3 mg per kg) and Greenland halibut (20.9 mg per kg). The samples of whale meat and cod roe caviar gave the lowest values of arsenic, both 0.53 mg per kg dry weight. An excretion experiment on arsenic in shrimp meat (prawn meat) showed that 99.4% of the arsenic in the diet was digested. After 3 days, 99.6% had been excreted in the urine. This reaffirms that arsenic in shrimp is present in a form that does not accumulate in the tissues as opposed to arsenic trioxide.

### INTRODUCTION

Arsenic has been extensively studied because of the toxicity of arsenous compounds and the use of arseno-organic compounds in medicine and insecticides (FROST, 1967). In a report from a Commission on Arsenical Poisoning in Sweden (BANG, 1919), the attention was focused on the varied and often quite considerable urinary excretion of arsenic in normal persons. Its dietary origin was established, and fish was found to be the main source. While fruits, vegetables, cereals and meat rarely exceed contents of 0.25 mg As per kg (WESTÖÖ and RYDÄLV, 1972), marine products usually contain 1 to 20 and may exceed 100 mg As per kg wet weight (UNDERWOOD, 1971).

The quick and nearly complete excretion in the urine of arsenic from sea food was demonstrated in 1935 by COULSON et al. with feeding experiments on rats. WESTÖÖ and RYDÄLV (1972) came to the same conclusion in an excretion experiment on humans. Arsenic was considered to be presented as non-toxic organic compounds, as opposed to the poisonous

trioxide and hydride. Some organic compounds (arsanilic acid and others) have been reported to influence favourably growth and health, and are used as feed additives for domestic animals (OVERBY and FREDRICKSON, 1963). In many countries, the arsenic content in food is restricted by law or regulation; levels between 2 and 5 mg As per kg wet weight being common. Some countries, among them USA and the U.K., have given exceptions for fish and fish products.

This paper reports contents of arsenic in some Norwegian fish products obtained from the local fish market and from retail shops. The samples were also analyzed for their selenium content and the results are reported in the previous paper (EGAAS and BRÆKKAN, 1977. Shrimp meat (prawn meat), which showed the highest content of arsenic, was tested in an excretion experiment on rats, and the results are given in an appendix.

#### MATERIALS AND METHODS

Fresh, frozen, smoked and canned products were obtained from the local fish market and from retail shops. Canned products were partly obtained from the Norwegian Quality Control Institute for Canned Fish Products, to ensure representative average samples. All samples were ground, freeze dried and homogenized. Dry matter was determined in connection with the freeze drying. The samples were stored in tightly closed plastic bottles until analyzed.

Two replicates of 0.2 to 0.5 g of the freeze dried samples were weighed into crucibles. 3 ml of a suspension of  $MgO + Mg(NO_3)_2$  were added as ashing aid (UTHE et al., 1974). After 4 hours of evaporation at 70 to 100°C, the samples were ashed for 8 hours at 550°C. The ash was dissolved in 25 ml 6N HCl, and further dilution was made prior to the AAS measuring. Arsenic was isolated from the acidified solution by the hydride generation technique, using pellets of  $NaBH_4$  as reducing agent, argon as carrier gas and hydrogen as fuel (FERNANDEZ, 1973) and measured on a Perkin-Elmer 403 Atomic Absorption Spectrophotometer equipped with an electrodeless discharge lamp.

#### RESULTS AND DISCUSSION

Altogether 43 products representing common sea food and fish products in retail sale and some canned products mainly for export were analyzed for arsenic. The results are given in Table 1 and 2, where the contents are calculated based on dry and wet weight. The products showed a total variation between 0.15 and 18.7 mg As per kg wet weight. This is in close agreement with the conclusions UNDERWOOD (1971) arrived at

Table 1. The concentration of arsenic in some fish products.

Sample of	Dry matter, %	Arsenic	
		Dry weight mg/kg	Wet weight mg/kg
<b>Cod (<i>Gadus morrhua</i>)</b>			
Frozen fillet .....	23.0	5.78	1.33
Smoked .....	23.5	25.3	5.95
Breaded-fillet .....	42.0	8.12	3.41
«Lutefisk» .....	14.4	1.37	0.20
<b>Coalfish (<i>Gadus virens</i>)</b>			
Frozen fillet .....	19.9	3.05	0.61
Breaded-fillet .....	35.5	1.60	0.56
Fish cakes .....	20.7	10.7	2.22
<b>Halibut (<i>Hippoglossus hippoglossus</i>)</b>			
Fillet .....	21.0	5.68	1.19
<b>Greenland Halibut (<i>Hippoglossus reinhardtius</i>) Smoked .....</b>			
	37.6	20.9	7.84
<b>Plaice (<i>Pleuronecta platessa</i>)</b>			
Fillet .....	18.0	7.66	1.38
<b>Herring (<i>Clupea harengus</i>)</b>			
Salt-cured .....	59.6	5.34	3.18
<b>Mackerel (<i>Scomber scombrus</i>)</b>			
Smoked .....	47.5	7.07	3.36
<b>Salmon (<i>Salmo salar</i>)</b>			
Smoked .....	38.7	6.68	2.59
<b>Deep sea prawn (<i>Pandalus borealis</i>)</b>			
Meat .....	31.9	58.6	18.7
<b>Lobster (<i>Homarus vulgaris</i>)</b>			
Meat .....	21.3	19.0	4.40
Roe .....	32.1	11.5	3.68
Whale meat .....	29.3	0.53	0.15

in reviewing the literature on arsenic contents in food. As established earlier, shellfish showed the highest contents in the present material, with values between 4.5 and 18.7 mg per kg wet weight (19.0 to 58.6 mg per kg dry weight). Other samples with high contents were cod milt with a content of 6.22 mg per kg wet weight (43.2 mg per kg dry weight) and smoked

Table 2. The concentration of arsenic in some canned and preserved fish products.

Sample of	Dry matter, %	Arsenic	
		Dry weight mg/kg	Wet weight mg/kg
<b>Cod</b>			
Pressed cod roe.....	32.2	2.14	0.69
Cod milt .....	14.4	43.2	6.22
Smoked cod roe and liver .....	56.7	2.74	1.56
Roe/liver paste .....	51.8	7.43	3.85
Cod liver paste .....	58.2	5.85	3.41
Cod roe caviar .....	70.0	0.53	0.37
<b>Coalfish</b>			
Smoked fillet in soya-sauce .....	51.4	1.05	0.54
Fish balls in bouillon .....	16.8	2.56	0.43
” ” ” ” .....	14.9	1.26	0.19
<b>Haddock</b>			
Fishpudding .....	19.8	4.58	0.91
<b>Mackerel</b>			
Fillet in onion sauce .....	46.1	5.18	2.39
” ” chili sauce .....	41.8	3.59	1.50
” ” orignon sauce .....	42.5	3.59	1.53
” ” estragon sauce.....	37.2	3.84	1.43
” ” curry sauce .....	45.3	3.00	1.36
” ” mustard sauce .....	43.7	2.76	1.21
” ” worchester sauce.....	41.9	2.76	1.16
” ” dill sauce .....	43.8	5.34	2.34
” ” tomato sauce .....	52.4	5.55	2.91
” ” norwegian oil .....	49.6	2.76	1.37
<b>Herring</b>			
Kippered .....	46.3	1.88	0.87
Semi-preserved .....	53.0	2.53	1.34
<b>Brisling(sprat)</b>			
Smoked in oil .....	89.9	4.73	4.25
«Anchovies» (semi-preserved) .....	51.0	4.22	2.15
<b>Crab</b>			
Natural crab .....	21.7	47.9	10.4
Crab paste .....	21.7	54.4	11.8

fillets of cod and Greenland halibut with respectively 6 and 7.8 mg per kg wet weight (25.3 and 20.9 per kg dry weight). The lowest values of arsenic was found in whale meat and «lutefisk», 0.15 and 0.20 mg per kg wet weight (0.53 and 1.37 mg per kg dry weight).

In an analysis of several elements in 85 samples of fish species and

fish by products, JULSHAMN et al. found contents of arsenic varying between 0.3 and 19 mg per kg wet weight, corresponding well with the present results.

Arsenic contents seem to vary greatly within different samples of the same kind of fish. One example of this is seen in Table 1 where the two fillets of coalfish showed less arsenic than the composite product of coalfish fish cakes. The present study did not aim at a comparison of biological distribution of arsenic, but at providing some values for dietary evaluation.

LUNDE (1972) studied the origin of arsenic in fish and his results indicate that several arseno-organic compounds are present in fish tissues and may have been synthesized in marine organisms from inorganic arsenic.

The high content of arsenic in many sea foods suggests the need for a simple test on the quick excretion by animals of the arsenic ingested with these products. An example of such a test is given as an appendix to this paper.

#### APPENDIX

##### *A TEST ON THE EXCRETION WITH THE URINE OF NATURALLY OCCURRING ARSENIC IN SHRIMP MEAT FED TO RATS*

The sample of meat of deep sea prawn, designated shrimp meat in the trade, had the highest content of arsenic, 18.7 mg per kg wet weight, and it was found of interest to try this product in an excretion experiment on rats, corresponding to the study of COULSON et al. (1935). The shrimp meat was freeze dried, homogenized and mixed into the normal stock diet in amounts sufficient to give a concentration of 38.5 mg As per kg diet. The feeding was restricted to 12 g per day, which was accepted by the rats. This corresponds to an intake of 462 mg As per rat. Five male rats of Wistar/Møll derivation of an average weight of 150 g were housed in metabolic cages permitting collection of urine and faeces, and were fed for one week the stock diet containing 0.05 mg As per kg. Urine and faeces were collected during the last two days. The rats were then given one meal of the shrimp meat diet, followed by the stock diet for the next seven days. Urine was collected and pooled each day. Faeces was collected each day and pooled the last day of the experiment. The urine samples were evaporated to dryness under an infrared lamp after addition of 3g  $Mg(NO_3)_2$  per 15 ml. The dry samples were ashed for 2 hours at 550°C. Determination of arsenic was otherwise performed as described under MATERIALS AND METHODS.

The rats digested 99.4% of the arsenic given in the diet. Of the digested arsenic, 91% was excreted in the urine during the first 24 hours. After three days, 99.6% had been excreted (Fig. 1).

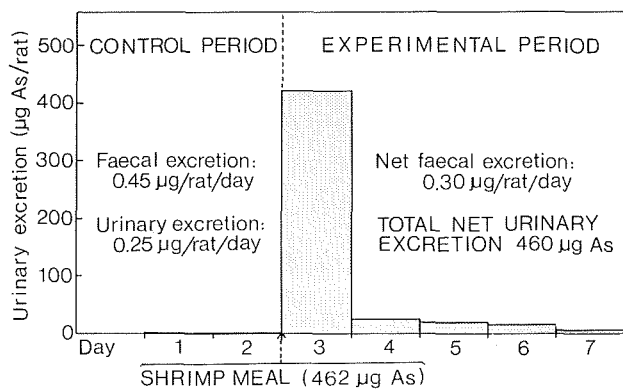


Fig. 1. A graphical presentation of the excretion in urine of arsenic naturally occurring in shrimp meat fed to rats.

From two similar excretion experiments on shrimp made by COULSON et al., (1935) the average digested arsenic was 97.4% and the average excreted in the urine within three days was 97.2% of the digested arsenic. A further experiment at our institute on canned crab (JULSHAMN, private communication) support the conclusion that naturally occurring arsenic is rapidly excreted with the urine. In contrast,  $As_2O_3$  accumulates in the tissues (COULSON et al., 1935, MORGAREIDGE, 1963.)

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