

LEVELS OF POLYCHLORINATED DIBENZOFURANS AND DIBENZO-p-DIOXINS IN CRUDE
AND PROCESSED FISH OILS IN RELATION TO ORIGIN AND CLEANING METHOD

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ABSTRACT

The levels of polychlorinated dibenzofurans (PCDF) and dibenzo-p-dioxins (PCDD) in crude and processed fish oils were determined. Significantly lower concentrations were found in crude oils from the South Pacific compared to the North Atlantic. Different methods were studied to remove PCDF/PCDD. Only molecular distillation was able to reduce the levels below 1 ppt 2,3,7,8-TCDD-equivalents (Nordic model).

INTRODUCTION

Recent studies concerning the main intake routes of PCDF/PCDD for humans concluded that uptake by food is probably the most important source for the levels found in human breast milk, blood and adipose tissue [1]. Marine organisms on top of the food chain and with a high fat content have a high bio-concentration factor and considerable levels of PCDF/PCDD can be found in fish [2,3] as well as fish oils [4,5]. Fish oils are used as raw materials for margarine and edible fat production and as additives in the food industry. In addition, the direct intake of medical fish oils has found an increasing popularity due to their high content of non-saturated fatty acids which have a prophylactic effect against cardio-vascular diseases. The aim of the presented work was to determine the general level of PCDF/PCDD in crude and processed fish oil produced by the Norwegian fish oil industry. The removal of PCDF/PCDD by different cleaning techniques was also studied. Furthermore, the levels in fish oils from the North Atlantic were compared with those from the South Pacific where environmental pollution looks to be a less serious problem compared to the Northern hemisphere due to fewer industrialized areas.

EXPERIMENTAL

Samples of crude and processed fish oils were collected from large homogenized batches in clean new glass bottles of 100 ml volume which were heated for 6 hours at 450 °C. A polypropylene screw cap was used. Blank values equivalent to the detection limits were found in 100 ml toluene stored for 1 week in the bottles and concentrated to 100 µl prior to the analysis.

10 g of the oil was mixed with the tenfold amount of sodium sulphate in a household mixer with an insert made from polypropylene and a solution of ¹³C-marked 2,3,7,8-chlorine-substituted congeners (1-4 pg/g sample for each isomer) in hexane was added consisting of 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD. The clean-up and quantification method is described in detail elsewhere [2] and, therefore, only a brief summary is given below:

1. Sample clean-up using the procedure by Smith and Stalling with some modifications.
2. Final clean-up using a combination of two Pasteur pipettes, one filled with sulfuric acid coated silica and one with aluminum oxide.
3. Separation by HRGC on SP 2330 and quantification by electron impact (2,3,7,8-TCDD, in a few cases also by high resolution techniques) or negative ion chemical ionization mass spectrometry.

RESULTS AND DISCUSSION

As can be seen from Table I the levels in crude fish oils and oils processed according to the standard procedure described below from the North Atlantic (about 63 to 75° N and east for Greenland) are comparable with those earlier reported by Rappe [4] and Fürst [5]. A few samples of sardine oils and not further specified fish oils from the South Pacific west of Chile had concentrations which were about one order of magnitude lower. This is a further indication that the Southern hemisphere is less polluted by persistent organochlorines in general. However, the variations in the levels can also partly be caused by the different marine species used for production. The following standard processes are often used for refining the oils:

- Elimination of free fatty acids by washing with water at 75 °C.
- Centrifugation and vacuum drying to remove water.
- Precipitation of high molecular compounds by cold filtration at 0° C.