REMOVAL OF PCDD/FS AND DL-PCBS FROM FISH OILS BY VOLATILISATION PROCEDURES

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Introduction

Fish oils have the advantage to contain high concentrations of ω3 fatty acids: mainly eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), anti-oxydants and lipophilic vitamins. It has been shown that the intake of these compounds can reduce the risk of cardiovascular diseases[1], arterial thrombosis, autoimmune[2] and inflammatory problems[3,4].

Unfortunately, fish oils also contain contaminants like dioxins and PCBs.

The challenge is then to discard the dioxins and PCBs from the oils without affecting the nutritional quality of the oils.

Activated carbon has shown very good results to remove dioxins, furans and non-ortho PCBs. Nevertheless, the removal efficiency for mono-ortho PCB was less effective.[5,6]

Other techniques were tested: volatilisation procedures (packed column stripping and cross-flow stripping). Preliminary results showed a higher efficiency for dl-PCBs than for PCDD/Fs. Based on the complementarity of these techniques with activated carbon treatment for a total removal approach of those pollutants, further tests using a combination between activated carbon treatment with either the packed column stripping or cross-flow stripping were assessed.

Materials and methods

Fish oils

Neutralised and winterised fish oil with a significant content of dioxins and PCBs was obtained from a Scandinavian fish oil processor.

Treatments

Packed column stripping and cross-flow stripping are procedures at high temperature, low pressure and injection of a stripping agent (steam).

The differences are:
- The residence time: very short in packed column stripping and usually longer (variable) in deodorisation.
- The pressure: pressure drop in packed column stripping and constant in cross-flow stripping.
- The contact between oil and steam: countercurrent contact in packed column stripping and cross-flow contact in cross-flow stripping.

<u>The packed column stripping</u> tests were processed under different stripping temperatures, top pressures and percentages of steam injected. For each of the 5 stripping temperatures (180, 190, 200, 210, 220°C), 3 different conditions were applied:

1. P_{top}= 1.15 mbar; ΔP=0,7 mbar; %steam=1,1%
2. P_{top}= 2 mbar; ΔP=1,5 mbar; %steam=2%
3. P_{top}= 4 mbar; ΔP=2 mbar; %steam=4%

$P_{bottom} = P_{top} + \Delta P$ and $P_{average} = (P_{bottom} + P_{top})/2$

For example 3, P_{bottom}=4mbar+ 2mbar= 6mbar and $P_{average}$= (6mbar+4mbar)/2= 5mbar

<u>The cross-flow stripping</u> process consisted of 3 steps:

First, heating from ambient temperature to temperature of cross-flow stripping at 6 mbar and with a small steam injection. Secondly, cross-flow stripping for 60 minutes under the selected conditions (T, P and % steam). Third, cooling (from temperature of cross-flow stripping to ambient temperature) at 6 mbar and with a small steam injection.

The 5 cross-flow stripping temperatures were 180, 190, 200, 210, 220°C. At each temperature, 3 different pressure/steam conditions were applied:

1. P= 1,1 mbar, % steam= 1,1%
2. P= 2 mbar, % steam= 2%
3. P= 4 mbar, % steam= 4%

Since the selected techniques (activated carbon, packed column stripping and cross-flow stripping), used individually, don't fully remove all the dioxins, furans, non-ortho PCBs and mono-ortho PCBs, we also tested the combination of 2 techniques.

GC-HRMS

The GC-HRMS analyses were performed by the Center of Analysis of Residues in Traces, Université de Liège. The procedure has been described elsewhere[7]. Briefly, 2g of fish oil was loaded on an automated Power-Prep system (Fluid Management System, inc., Waltham, MA, USA). The sample was then processed through a set of disposable columns: a high capacity acid silica column, a small multi-layer silica column, a basic alumina column and a PX-21 carbon column. The final extract was concentrated to 10µL in nonane prior to GC-HRMS injection.

Results and discussion

One of the aims of the project was to find the best method to reduce dioxins, furans and dl-PCB in order to be in compliance with European legislation.

The norm set for fish oils by the European Commission for the maximum PCDD/Fs level for food (human consumption) is 2 pg WHO-TEQ/g fat and the norm for feed (animal feeding) is 6 pg WHO-TEQ/g fat.

The European Commission recently published a Commission Regulation for the maximum level for the sum of dioxins, furans and dl PCBs[8,9]. This norm is 10 pg WHO TEQ/g oil for food and 24 pg WHO TEQ/g oil for feed.

As already mentioned, activated carbon is very efficient to reduce dioxins, furans and non-ortho PCBs but the removal efficiency for mono-ortho PCBs is lower. Therefore, we tested other techniques of purification in order to improve the removal of mono-ortho PCBs. These techniques are packed column stripping and cross-flow stripping.

Packed column stripping

Fifteen experiments were done under different stripping temperatures, pressures on the top of the column and percentages of steam injected. (Figure 1)

Figure 1 shows the results presented in pg WHO-TEQ/g fat. We separated the sum of PCDD/Fs, the sum of non-ortho PCBs and the sum of mono-ortho PCBs to compare the removal efficiency for the three groups of compounds.

Feedstock is the oil without any treatment.

The treatments 1, 4, 7, 10 and 13 were carried out at P_{top}= 1,15 mbar; ΔP=0,7mbar; %steam=1,1%

The treatments 2, 5, 8, 11 and 14 were carried out at P_{top}= 2 mbar; ΔP=1,5mbar; %steam=2%

The treatments 3, 6, 9, 12 and 15 were carried out at P_{top}= 4 mbar; ΔP=2mbar; %steam=4%

The dioxins and furans are the contaminants the most difficult to eliminate, the non-ortho and the mono-ortho PCBs are more easily reduced.

A higher stripping temperature gives a better elimination of the contaminants.

A lower ratio between average pressure on the column divided by the percentage of injected steam gives a better efficiency.

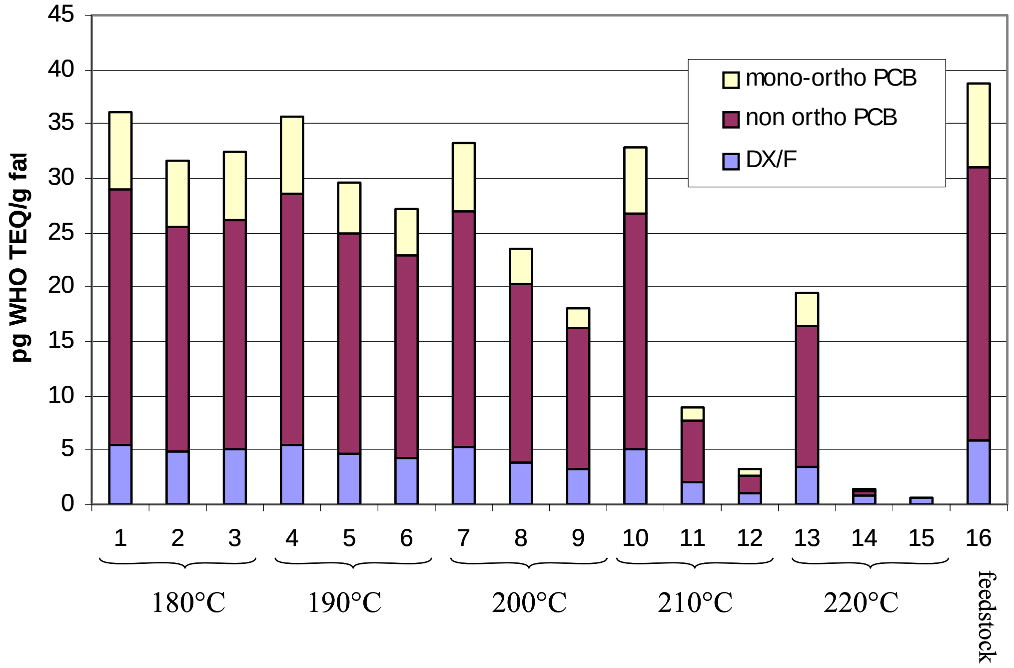

Figure 1: Results obtained for the PCDD/F, non-ortho and mono-ortho PCBs fractions with different packed column stripping treatments.

Cross-flow stripping

The cross-flow stripping tests were done under different temperatures (from 180°C to 220°C), different pressures (from 1,1 mbar to 4 mbar) and different percentage of steam injected (from 1,1% to 4%). (Figure 2)
The treatments 1, 4, 7, 10 and 13 were carried out at P= 1,1 mbar; %steam=1,1%
The treatments 2, 5, 8, 11 and 14 were carried out at P= 2 mbar; %steam=2%
The treatments 3, 6, 9, 12 and 15 were carried out at P= 4 mbar; %steam=4%
Figure 2 shows that the best reduction is observed for the mono-ortho PCBs, the reduction of dioxins, furans and non-ortho PCBs is less efficient.
At 190°C, pressure of 1,1 mbar and a percentage of steam injected of 1,1%, the reduction of dioxins and furans is 53%, the reduction of non-ortho PCB is 50% and the reduction of mono-ortho PCB is 64%.

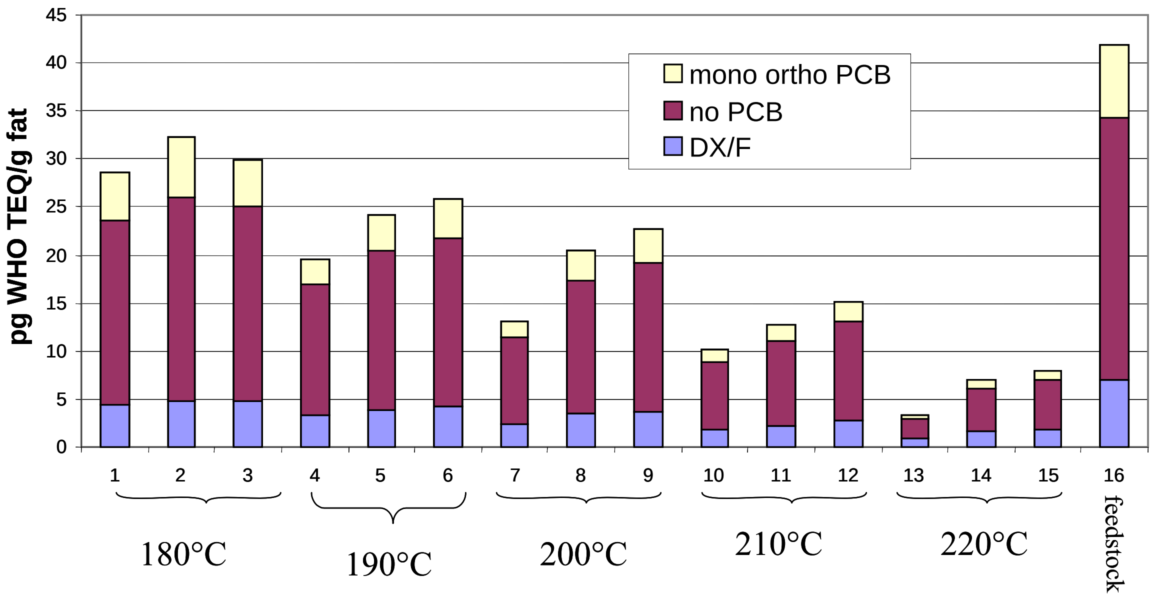

Figure 2: Results obtained for the PCDD/F, non-ortho and mono-ortho PCBs fractions with different cross-flow stripping treatments.

Combination of techniques
We decided to combine cross-flow stripping (instead of packed column stripping) with activated carbon because this technique is preferable in an industrial process.
The results obtained show that:
-There is a removal of 99% of dioxins and furans with 0.1% of activated carbon, 100% with 0,25 and 0,5% of activated carbon whatever the cross-flow stripping parameters
- More than 76% (depending of the cross-flow stripping parameters) of non-ortho PCBs are removed with 0.1% of activated carbon, more than 95% with 0,25 and 0,5% of activated carbon
- Between 36 and 60% (depending of the cross-flow stripping parameters) of mono-ortho PCBs are removed with 0.1% of activated carbon, and between 48 and 74% of reduction with 0,25 and 0,5% of activated carbon.
- No significant differences of percentages of reduction were observed if the activated carbon treatment was realised after cross-flow stripping or before cross-flow stripping treatment.

Acknowledgement
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