

Supercritical Fluid Processing of Fish Oils: Extraction of Polychlorinated Biphenyls

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Polychlorinated biphenyls can be extracted from fish oils with supercritical carbon dioxide at quite modest temperature and pressure with little yield loss of the fish oils. The distribution coefficient, viz, the ratio of the concentration of polychlorinated biphenyls in the carbon dioxide and fish oil phases, respectively, was measured to be about 0.01 (wt basis). The selectivity of carbon dioxide for polychlorinated biphenyls was found to be very high, about 13 at a concentration of about 10 ppm.

Evidence has accumulated that suggests certain polyunsaturated fatty acids found in fish oils may have a therapeutic effect on the cardiovascular system (1-3), and increasing attention is being directed to the clinical study of fish oils in the human diet. Methods for purifying and concentrating the active polyunsaturated components are being developed and refined. For example, high performance liquid chromatography (HPLC) (4,5) and silver resin chromatography (6) are effective in resolving virtually pure ethyl esters of fish oil fatty acids at the laboratory level. High vacuum distillation can also concentrate the esters, but the high temperature levels required for distillation, even at very high vacuum, can result in degradative reaction of the highly unsaturated components, such as eicosapentaenoic and docosahexaenoic acids. Fish oil esters have also been concentrated to a very high degree by supercritical fluid fractionation (7-11), and using urea crystallized esters, concentrations of eicosapentaenoic acid as high as 96% have been obtained by supercritical fluid fractionation (11).

Objectionable components such as odor compounds, free fatty acids and polychlorinated biphenyls (PCB's) are present in fish oils. Processing methods exist for removing some of the components; for example, odor compounds can be volatilized quite easily, free fatty acids can be removed by caustic treatment, but only very high vacuum distillation can effect a separation of PCB's from the fish oil. As stated previously, however, the attendant high temperature levels required to remove PCB's can cause degradation of the highly unsaturated active components.

The separation of PCB's from cod liver oil using supercritical carbon dioxide at modest temperature levels where no degradative reaction of the unsaturated components would be anticipated was examined at this laboratory, and the results of initial feasibility experiments are reported; the primary thrust of the feasibility tests was the determination of distribution coefficients and the selectivity for PCB's in the carbon dioxide-PCB-fish oil ternary system.

EXPERIMENTAL

A flow-through extraction system (Superpressure, Inc., now Newport Scientific, Inc., Jessup, Maryland) shown schematically in Figure 1 was used for the tests. Descriptions of the operation of various flow-through systems

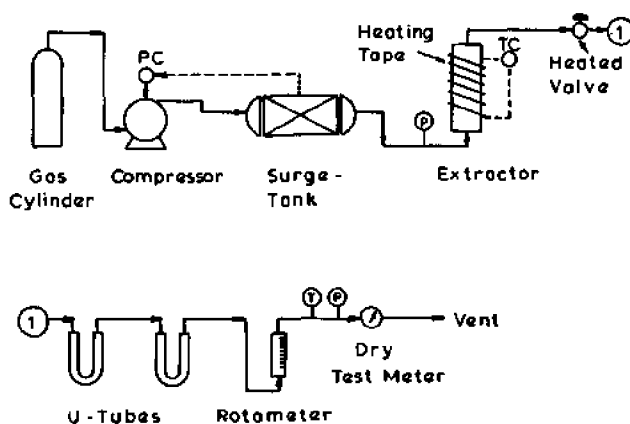


FIG. 1. Experimental apparatus, supercritical carbon dioxide extraction of PCB's from fish oil. TC, Temperature controller; PC, pressure controller; P, pressure gauge; T, thermocouple.

have been presented elsewhere (7-11), and only a brief summary of the operation is given here for its relevance to the discussion of the results. An amount of PCB-containing cod liver oil is charged to an extraction vessel and the vessel sealed and attached to the extraction system. Carbon dioxide at the desired temperature and pressure is supplied to the temperature-controlled extractor. As the carbon dioxide flows through the charge of fish oil, it extracts PCB's and some fish oil; the concentrations of PCB's and fish oil in the carbon dioxide and the ratio of PCB to fish oil are dependent upon operating pressure and temperature and the PCB concentration in the fish oil. After the stream leaves the extraction vessel, it is reduced to ambient pressure across an expansion/flow control valve. When the pressure is reduced, the dissolved PCB's and fish oil precipitate and collect in a cold trap maintained at dry ice temperature. The flow rate and volume of carbon dioxide are measured with a flow meter and dry test meter, respectively.

A number of extraction pressure levels were tested to obtain various individual fractions, and PCB determination in the fractions was carried out by a combination of gas chromatography (GC) (using electron capture detection) and chlorine analysis. PCB's are a complex mixture of many chlorinated biphenyl components which are fractionated during the extraction, and total chlorine analysis allowed an estimate of the maximum PCB concentration in each fraction to be made. The gravimetric analysis of the extracts and the chemical analysis of PCB's allowed total material and PCB balances to be made. Distribution coefficients and selectivity values were calculated from the concentration values and material balances as presented.

RESULTS AND DISCUSSION

Table 1 gives the gravimetric and chemical analysis results of the carbon dioxide extraction of PCB-containing

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TABLE 1

Experimental Conditions and Analytical Results of Supercritical Carbon Dioxide Extraction of PCB's from Fish Oil^a

Fraction #	Extraction pressure (psig)	Weight of fraction (g)	Volume of CO ₂ required to extract fraction (SL's) ^b	PCB concentration in fraction (ppm)
Charge	—	22.07	—	8.7
1	2500	0.51	400	99
2	3300	1.63	500	48
3	5000	5.80	250	5.6
4	5500	2.78	250	2.4
5	6500	10.38	500	1.4

^aExtraction temperature, 70°C.

^bSL, standard liter, 1 atm, 20°C.

fish oil and the combinations of experimental parameters used to collect the fractions; temperature was held constant at 70°C. Based upon visual observation of the amount of extract collected, the pressure level was increased in arbitrary steps from 2500 to 6500 psig during the course of the extraction. With reference to the information given in Table 1, several sequential fractions were extracted from a single charge (22.07 g), the first fraction (0.51 g) obtained at 2500 psig, the second (1.63 g) at 3300 psig, and so on.

The determination of distribution coefficients was the primary goal of these tests although a secondary goal was to demonstrate that the PCB concentration in the fish oil could be lowered significantly. It is readily seen from the data tabulated that a nominal 10 ppm PCB fish oil can be separated into a small PCB-rich fraction containing about 100 ppm and a large fraction containing about 1 ppm.

The distribution coefficient of a component that is extracted from one phase into another is defined generally as the ratio of concentrations of the component in the respective phases; by convention the component being extracted by the solvent is in the numerator. For the specific case of carbon dioxide, PCB's and fish oil, the distribution coefficient is defined as

$$DC = (x_{\text{PCB}})_{\text{CO}_2} / (x_{\text{PCB}})_{\text{fish oil}} \quad [1]$$

where DC is the distribution coefficient
 $(x_{\text{PCB}})_{\text{CO}_2}$ is the concentration of PCB's in the carbon dioxide phase
 $(x_{\text{PCB}})_{\text{fish oil}}$ is the concentration of PCB's in the fish oil in equilibrium with $(x_{\text{PCB}})_{\text{CO}_2}$; weight units are used in subsequent calculations

The calculational procedure for obtaining distribution coefficients from the gravimetric data and the measured PCB concentration values in Table 1 derives from an unsteady state material balance on PCB's extracted by the carbon dioxide that is passing through the charge of fish oil during the test. The material balance relates the concentrations, initial charge and solvent volume by the equation

$$DC = \ln \frac{x_i}{x_f} \div R \quad [2]$$

where DC is the distribution coefficient
 R is the solvent-to-charge ratio
 x_i is the initial PCB concentration in the charge of fish oil
 x_f is the final PCB concentration in the fish oil at the end of the extraction

In the derivation of Equation 2 it is assumed that equilibrium prevails during the extraction and that the distribution coefficient is not a function of PCB concentration. In laboratory experiments at low flow rates equilibrium is essentially achieved; concerning the second assumption, even if the distribution coefficient is a function of concentration, over small concentration changes little error is introduced in the calculation. Additionally, in Equation 2 the amount of material in the vessel is assumed to be constant. This latter assumption also introduces little error in most laboratory situations where small fractions are removed from a large charge; for example, and in reference to the information in Table 1, extraction of only 0.51 g (Fraction 1) from a 22.07-g charge permits an average charge value of 21.82 g to be used in the calculation with complete accuracy. (A continuously-changing amount of charge can be handled explicitly, as, for example, in the case where the oil is dissolved to its solubility limit in carbon dioxide at conditions of extraction, but this degree of refinement was not applied to the calculations.) Finally, because the solubility of carbon dioxide in the fish oil is very small at 70°C (even at 6000 psi), PCB concentrations on a carbon dioxide-free basis were used in the equation.

For the test that generated the data given in Table 1 it is possible to obtain distribution coefficients at a number of points in the extraction sequence (and the test was carried out with the generation of a number of sequentially-extracted fractions expressly for the purpose of maximizing the amount of information obtained). The material balance on total oil (by gravimetric measurement) and on PCB's (by gravimetric and chemical analysis) was found to yield better than 95% recovery, and thus, the concentration of PCB's in the fish oil remaining in the extractor at any point in the sequence can be quite accurately calculated. To determine an intermediate point distribution coefficient the final PCB concentration, x_f , is replaced in Equation 2 by the concentration in the fish oil that exists at the end of the extraction of a fraction, and the distribution coefficient that represents the equilibrium situation during the extraction of that fraction can be calculated. Table 2 gives the distribution coefficient values calculated from the analytical and experimental information in Table 1. (There is no distribution coefficient listed for the last fraction; the amount of 10.38 g was completely extracted with no remaining "charge" left in the vessel.)

Generally, an increase in pressure will increase the distribution coefficient because of the increased solubility (extractability) of all the components. Referring to the data in Tables 1 and 2, it is seen that an increase in pressure from 2500 to 3300 psig increased the distribution coefficient from 0.008 to 0.015, but subsequent increases in pressure did not increase the distribution coefficient.

TABLE 2

Distribution Coefficients, Supercritical Carbon Dioxide Extraction of PCB's from Fish Oil

Fraction #	Distribution coefficient	Calculated solvent to feed ratio
1	0.008	125
2	0.015	66
3	0.014	71
4	0.014	71
5	—	—

This latter result could be due to a concentration effect on the distribution coefficient or to an increased deviation from equilibrium extraction during the course of the test as the PCB concentration decreases to very low levels in the residual fish oil. For this initial investigation, however, the overall important finding is that the distribution coefficient for extracting PCB's from fish oil with supercritical carbon dioxide at the test conditions is of the order of 0.01.

Distribution coefficients provide information for the design of an extraction process in which a PCB-contaminated fish oil is stripped of its PCB's by supercritical carbon dioxide in a countercurrent process. The inverse of the distribution coefficient gives an estimate of the solvent-to-feed ratio (12) (in a theoretical column of infinite height). A distribution coefficient of about 0.01 (an average of the values of 0.008 and 0.015 from Table 2) implies a solvent-to-feed ratio of 100 lb CO₂/lb fish oil; although a solvent-to-feed ratio of 100 is rather high for "conventional" industrial liquid-liquid extraction processes, that value is similar to the solvent-to-charge ratio used for decaffeinating coffee with carbon dioxide (13).

In parallel with distribution coefficients the selectivity of carbon dioxide for PCB's can be determined from the data in Tables 1 and 2. Selectivity, β , is defined as

$$\beta = (x_{\text{PCB}}/x_{\text{fish oil}})_{\text{ext}} \div (x_{\text{PCB}}/x_{\text{fish oil}})_{\text{equil}} \quad [3]$$

where β is the selectivity
 $(x_{\text{PCB}}/x_{\text{fish oil}})_{\text{ext}}$ is the ratio of PCB's to triglycerides in the extract phase
 $(x_{\text{PCB}}/x_{\text{fish oil}})_{\text{equil}}$ is the ratio of PCB's to triglycerides in the equilibrium solution

Using the average concentration of PCB's over the duration of the extraction of a fraction, the calculated selectivity values of carbon dioxide for PCB's are given in Table 3; the values decrease with increasing extraction

TABLE 3

Selectivity Values, Supercritical Carbon Dioxide Extraction of PCB's from Fish Oil

Fraction #	Selectivity
1	12.9
2	9.7
3	2.1
4	1.3
5	—

pressure as expected. Selectivity values as high as 13 are of great practical interest; in various industries such as chemicals, pharmaceuticals and petroleum, selectivity values as low as 2 are considered attractive (Vivian, J.E., private communication, 1986), and for heat-labile materials such as fish oils that might be difficult to purify by other techniques, 13 is, indeed, an attractive value.

It is frequently tempting to extrapolate the results of some initial laboratory feasibility tests to an industrial scale. These results on the extractions of PCB's from fish oils are quite interesting from technical considerations, but they should not yet be subjected to the extrapolation just mentioned. Each potential application of supercritical fluid extraction (or any other separations technology) should be subjected to a detailed economic viability evaluation, considering not only capital and operating costs but including also such factors as the current regulatory climate which can impact traditional processes, the competing process technologies, product performance specifications and the like.

Distribution coefficients are, of course, a necessary part of the information required to evaluate economic viability of the PCB extraction process, but other information on, for example, the fish oils' stability after carbon dioxide processing, must also be obtained. For example, evidence has been presented (8) suggesting that fish oils can be made "too pure" by carbon dioxide extraction; it was reported that fish oil that is extracted (or purified) with carbon dioxide can lose much of its unsaturation during storage and can polymerize. This results because natural antioxidants such as tocopherols and phospholipids that are present in crude fish oils are separated from the fish oils during extraction. Tocopherols present in the triglycerides exhibit a distribution coefficient and selectivity similar to those of PCB's (Krukoni, V.J., unpublished data), and thus, tocopherols are extracted preferentially from the fish oils by carbon dioxide. Furthermore, if the fish oil is subjected to a complete dissolution in carbon dioxide, phospholipids will be separated because they do not dissolve in carbon dioxide. The extraction of tocopherols and the simultaneous separation of phospholipids results in a highly purified fish oil fraction that exhibits low stability to autoxidation. Thus, many facets of fish oil extraction, not only the selectivity and distribution coefficients, but also factors such as stability and product performance, must be studied further; they are being examined at this and other laboratories.

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