

Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) and dioxin-like Polychlorinated Biphenyls (PCBs) in Cod Liver Oil by High-Resolution Gas Chromatography High-Resolution Mass Spectrometry (HRGC/HRMS)

R.K. Symons, D. Burniston, R. Jaber, E.J. Murby, N. Piro, M. Trout and A. Yates

Australian Government Analytical Laboratories

The general term "dioxin" refers collectively to a group of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) compounds. There are 75 different PCDDs and 135 different PCDFs. Each compound has a distinct number and configuration of chlorine atoms. These differences in chemical structure produce varying levels of toxicity among the PCDD/PCDF family. Dioxins are formed as unintentional by-products of industrial processes involving chlorine such as waste incineration, chemical and pesticide manufacturing, smelting and pulp and paper bleaching where elemental chlorine is still used in the process. The World Health Organisation (WHO) in its' assessment of dioxins has recently extended the dioxin list to include a number of 'dioxin-like' polychlorinated biphenyls (PCBs). PCBs were commercially produced and used in a number of industrial applications including insulating fluids or resins in transformers and capacitors, heat transfer fluids, hydraulic fluids, solvent extenders, flame retardants and dielectric fluids. The production of PCBs was banned in western countries in the late 1970's but they still persist widely in the environment. There are potentially 209 congeners likely to be present but in most studies only the toxicological significant congeners are measured.

The WHO has identified a number of dioxins (7), furans (10) and PCBs (12) that represent the highest risk to public health in terms of their toxicological properties at concentrations as low as parts per trillion (ppt) in food. Individual toxic equivalency factors (TEF) relative to 2,3,7,8-TCDD have been assigned to these 29 compounds and are shown in Table 1. These factors are used to calculate a total toxic equivalence (TEQ) from the concentrations of all compounds in a sample. For food samples this is expressed as pg WHO-TEQ/g fat using upperbound concentrations where it is assumed that the values for un-detected congeners are equal to the limit of determination.

Dioxins have been shown to be toxic at extremely low levels with the International Agency for Research on Cancer (IARC) announcing in 1997 that 2,3,7,8-tetrachlorodibenzo-p-dioxin was "carcinogenic to humans". These compounds are fat soluble, extremely persistent, bioaccumulate through the food chain and are ubiquitous. Approximately 95% of human exposure is believed to be through our diet with fatty food from animal origin being the predominant source. The risks of toxicity and a number environmental contamination incidents viz. the Belgium crisis have resulted in a heightened awareness of dioxins and associated compounds internationally.

The benefits of taking daily doses of cod liver oil have been extolled for centuries and this has led to it becoming one of the biggest selling supplements in Europe. The advantages of taking fish oils was recently discussed on "The Health Report" Radio National (ABC 2002). Some of the returns attributed to its' use include the relief of inflammatory pain associated with arthritic disease and increased blood flow leading to benefits to the heart and circulatory system.

The European Commission (EC) published regulations setting maximum levels for dioxins in foodstuffs that came into effect 1 July 2002. For the products falling into the following category Oils and fats – fish oil intended for human consumption a maximum limit was set at 2 pg WHO-PCDD/PCDF-TEQ/g fat. In a recommendation by the EC to further reduce human exposure to dioxins and dioxin-like PCBs, action levels for dioxins in foodstuffs were set requiring Member States to take further action if these levels were exceeded.

During August 2002, cod liver oil was purchased from a retail outlet in metropolitan Sydney. Replicate analyses of this sample were undertaken for PCDDs/PCDFs and dioxin-like PCBs using isotope dilution capillary gas chromatography-electron impact high-resolution mass spectrometry with monitoring of either M+, [M+2]+ or [M+4]+ ions. Sample extracts after lipid removal with sulfuric acid were chromatographically purified using a commercial automated clean-up procedure called PowerPrep[®] purchased from Fluid Management Systems. (Waltham, MA, USA). The analytical procedure is based upon standard United States Environmental Protection Agency methodologies.

To the best of our knowledge this is the first time fish oils intended for consumption by Australians have been assessed for their dioxin contamination.