Levels of Polychlorinated Dibenzo(p)dioxins, Dibenzofurans and Dioxin-like PCBs in Milk, Milk Products and Eggs from West European Countries

Stephan Hamm[1], Rainer Grümping[1], Jürgen Schwietering[1]

[1]eurofins/GfA

Introduction

With the Council Regulation EC/2375/2001[1] the EU Commission set maximum levels for polychlorinated Dibenzo(p) dioxins (PCDDs) and polychlorinated Dibenzofurans (PCDFs) in various foodstuffs. These maximum levels have been entered into force on July 1, 2002. In this Regulation the Commission, moreover, announced to review section 5 of Annex I for the first time until end of 2004 in particular with the a view to the inclusion of dioxin-like PCBs in the levels to be set. It is true that the Commission did not keep this but the revision is expected for 2005 instead.

While for dioxin contents in foodstuffs a substantial database has been collected[2] meanwhile, dioxin-like PCBs for the determination of a total TEQ have only been increasingly included during the last two/three years. Following the lack of legal regulations especially routine controls of foodstuffs by producers, converters and trade have often only been made for dioxins in the past. Partly only indicator PCBs have been included in the analyses in order to exclude possible PCB contaminations[3] or to check the compliance with legal regulations[4]. In recent times this has changed because of the forthcoming inclusion also of dioxin-like PCBs (dl-PCBs) into the maximum levels.

For many years the GfA has routinely performed analyses in food and feed for dioxins and dioxin-like PCBs [e.g. 5, 6, 7] on behalf of producers, converters, trade or supervising authorities from most various EU member states. This paper presents mean values and ranges of dioxin, dl-PCB and total TEQ values from 138 milk / milk product and 45 egg samples which were analysed as part of routine controls. As these samples have been taken during the last two years, they reflect quite a current contamination level.

Methods and Materials

The 138 milk and milk product samples are composed of 107 milk, 17 cheese, 11 butter and 3 yoghurt samples. Just like the 45 egg samples, these specimen were taken from mid 2003 to the beginning of 2005. The customers who ordered these examinations mainly come from West European countries. In both cases the sample collectives developed randomly but nevertheless a certain degree of representativity can be attributed to them.

The fresh samples were freeze-dried (Christ, Beta 1-8 Freeze-dryer) and further homogenised by means of grinding. A fat extraction of about 20 g of the dried and grinded sample material was done by means of Accelerated Solvent Extraction (ASE) using an ASE 300 instrument of Dionex Corp., Sunnyvale, CA, USA. The fat fraction finally was determined gravimetrically after evaporation of the solvents.

All PCDD/F and PCB analyses were performed by HRGC/HRMS. Each analysis included the determination of the seventeen PCDD/F congeners with 2,3,7,8-chlorosubstitution and the 12 dioxin-like PCB congeners for which toxic equivalency factors (TEF) were established by a working group of the WHO[8]. Prior to the fat extraction an isotope-labelled dioxin and a PCB surrogate standard were added to the sample material in order to control the extraction efficiency. For 16 native PCDD/F and each PCB congener to be quantified, the corresponding $^{13}C_{12}$-labelled compound was added to the fat extract as internal standard prior to the defatting and the subsequent chromatographic clean-up. The recoveries of the internal standards through the fat separation and all clean-up steps were determined by means of further ^{13}C-labelled internal PCDD and PCB standards added to the PCDD/F and the PCB fraction before GC/MS analysis. All the ^{13}C-labelled standards were from Cambridge Isotope Labs, Endover, USA.

A Power-Prep workstation (Fluid Management Systems, FMS) for automated clean-up was mainly used the for milk,