GLOBAL POPS TREATY AND QUALITY CRITERIA FOR INTERNATIONAL POPS MANAGEMENT

HUMAN POPS EXPOSURE – QUALITY CRITERIA FOR EVALUATION OF EXPOSURE PATHWAYS OF DIOXINS TO HUMANS

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), often simplified termed as "dioxins" belong to the group of persistent organic pollutants (POPs), which have been identified as a global problem to humans and the environment. At certain levels of exposure and body burden, dioxins can lead to severe perturbations of immune and endocrine functions and reproduction as well as to the development of malignant tumors. Based on new data on adverse effects of 2,3,7,8-TCDD on reproduction and neurobehaviour in rodents and monkeys, together with novel information on the molecular and cellular mechanisms of dioxin toxicity, the World Health Organization (WHO) revised in 1998 its former recommendation from 1990 and proposed a new tolerable daily intake value (TDI) for humans of 1-4 pg WHO-TEq/kg body weight[1]. Besides dioxins, this TDI value also includes 12 polychlorinated biphenyls (PCB) which show dioxin-like effects. Humans may become contaminated with dioxins through either accidental, occupational or background (environmental) exposure. While accidental and occupational dioxin exposure is normally limited to more or less small cohorts, background exposure effects all humans. An assessments of human dioxin intake taking into account all routes of exposure revealed that more than 90% of human dioxin intake derives from food. From this, about 90% comes from food of animal origin[2]. This demonstrates the specific importance of food for a risk assessment and risk management of human exposure to POPs and dioxins, in particular. PCDDs and PCDFs are found as complex mixtures in all kinds of food stuffs, mostly at levels as low as pg/kg or ng/kg product. Consequently, the determination of these low traces which often serve not only as a basis for an exposure estimation but also for administrative measures with considerable economic consequences requires a highly sophisticated analysis technique. Moreover, it seems mandatory to fix internationally harmonized minimum analytical requirements which have to be fulfilled as a prerequisite for a valid result.

Requirements for a reliable dioxin analysis

A reliable analysis of dioxins at ultra-trace levels in environmental, feed, food and human samples requires at least the following basic steps:

1. Representative sampling
2. Exhaustive extraction
3. Meticulous clean-up
4. Congener-specific separation
5. Sensitive analytical determination
6. Comprehensive quality control

The methods applied for this analysis must be described in a detailed protocol preferably according to ISO Standard 78/2 or similar requirements. Examples for such methods are **EPA Method 1613** for the determination of tetra- through octa-chlorinated dibenzo-p-dioxins and dibenzofurans in water, soil, sediment, sludge, tissue and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) or **Method EN-1948** for the determination of the mass concentration of PCDDs/PCDFs in stationary source emissions. EPA Method 1613 describes in great detail procedures for sample preparation, extraction and analysis and has in a way become the status of a "golden standard". Although one is permitted to modify the method in order to overcome interferences or to lower the costs, provided that all required performance criteria are met, it may restrict the analyst to a certain extent, if the application of only **one** method is stipulated.

In recognition of the fast advances that are occurring in analytical technology, a number of authorities do no longer demand to use only one standard or reference method but changed over to define minimum performance requirements which have to be fulfilled in order to demonstrate that a selected method is fit for purpose. Such requirements, which comprise analytical criteria as well as performance characteristics have recently been elaborated, for example, by expert groups for monitoring of pesticide and veterinary drug residues in the European Union[3,4]. As long as all criteria are fulfilled and their correspondence with the requirements is documented and can be demonstrated, the analyst may use any analytical method for a specific purpose. The advantage of this approach is that the mostly slow and long-lasting process of searching for the best method based on the results of inter-laboratory studies can be avoided. Instead, a more flexible and practical in-house validation can be performed. However, this validation has to follow strict guidelines and must at least consider the following performance characteristics:

1. Analytical limits
   - decision limit
   - detection capability
2. Accuracy
   - trueness
   - recovery
   - repeatability
   - reproducibility
3. Specificity
4. Applicability
   - analytes
   - matrices
   - concentration range
   - ruggedness

After showing that a method is fit for purpose, a continuous control of the method performance is necessary. Therefore, the application of a suitable quality assurance (QA) and quality control (QC) scheme is mandatory. With respect to the time-depending performance, this can be done, for example, by applying the well known Shewart control charts.

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Successful participation in proficiency tests is a complementary important and indispensable tool to prove evidence of method and laboratory performance. These tests must be performed for each matrix which has to be analyzed, because a successful participation in proficiency tests for soil or sewage samples does not necessarily also prove the competence of a laboratory in the field of feed, food or human samples with their lower contamination levels. This was especially shown in the Belgian dioxin crisis in 1999 with its urgent need to analyze thousands of feed and food samples. A number of certificates verifying that products were almost "free" of dioxins were more or less worthless due to the inadequate methods which were applied for the analytical determination.

Whereas soil or sewage sludge samples may eventually be analyzed with low resolution mass spectrometry, high resolution gas chromatography/high resolution mass spectrometry (HRGC/ HRMS) at a resolution of R=10,000 is mandatory for a reliable analysis of feed, food and human specimens at normal background levels. For the control of proposed tolerances for dioxins in food in the EU, a limit of determination of 0.1 pg WHO-TEQ/g fat (as upper bound determination limit) for products of land animal origin and of 0.1 pg WHO-TEQ/g product (as upper bound determination limit) for fish and fish products is under discussion. Upper bound concentrations are calculated assuming that all values of the different congeners less than the limit of determination are equal to the limit of determination. Together with additional requirements, these criteria should ensure that only qualified laboratories take part in food supervision and control activities of food producers.

Finally, laboratories performing dioxin analyses should be in compliance with internationally recognized quality control schemes, such as the OECD principles of good laboratory practice (GLP) or EN 45000 or combinations thereof and accredited for this purpose by an independent accreditation body.

References

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3. European Commission (1999), Guidance document on residue analytical methods, VI B II.1 8064/VI/97-rev.4, 15.12.98
4. European Commission (1999), Commission Decision laying down analytical methods to be used for detecting certain substances and residues thereof in live animals and animal products according to Council Directive 96/23/EC (Draft final version of revision of Commission Decision 93/256/EC)