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Interlaboratory Comparison on Dioxins i Food 2003

Final report

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Summary

In 2003, the fourth round of interlaboratory comparisons was conducted on the determination of the 2,3,7,8-chlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) as well as dioxin-like non-ortho and mono-ortho chlorinated biphenyls (PCBs) in three different food items. The objectives were to offer a quality assurance instrument for the participating laboratories, to assess the between laboratory reproducibility and to assess the readiness of expert laboratories world-wide to determine levels of dioxins and dioxin-like PCBs in regular foodstuffs.

The 2003 study was performed on sample homogenates of turkey meat, salmon filet and cheese. In addition, three standard solutions were provided containing known concentrations of a) PCDDs/ PCDFs, b) non-ortho PCBs and c) mono-ortho PCBs. Eighty-three (83) participating laboratories received the testing materials in February 2003 and results were returned from 77 laboratories in 24 different countries by the deadline in May. Most laboratories participated in all of the three food items. This report, made available as a pdf-file on the web in July, has been discussed among the participants at a consultation meeting during the Dioxin 2003 Symposium in Boston, USA.

This report presents all of the results reported from the participating laboratories for the 29 analytes assigned a toxic equivalency factor (TEF) by the WHO in 1998: all seventeen 2,3,7,8-substituted PCDDs and PCDFs, the non-ortho substituted PCBs #77, 81, 126 and 169, and the eight mono-ortho substituted PCBs #105, 114, 118, 123, 156, 157, 167, 189, in the three food items on a fresh weight and lipid weight basis. Assigned values for the analytes were determined by the participant consensus technique using simple statistics. Non-detected congeners were assigned a concentration corresponding to the reported detection limit. The consensus values for each analyte in the three food samples were determined as follows: The median of all reported concentrations for each analyte was calculated. All values above two times the median were then removed from the calculation. The consensus median and consensus mean plus standard deviation were calculated from the remaining data. Toxic equivalents (TEQs) were calculated from the consensus values of individual congeners using the toxic equivalency factors derived by WHO in 1998 (Appendix D). Z-scores were calculated for each laboratory's result of PCDD/PCDF TEQ using a deviation of ±20% of the consensus TEQs.

The consensus value for the standard solutions were calculated in the same manner except that values outside ± 50% of the median of all values were removed prior to final calculation of the consensus median and mean.

The consensus values for the lipid content were calculated by first excluding results deviating more than two standard deviations (± 2 SD1) from the mean of all values and then re-calculating the median, mean and standard deviation.

Two of the samples, turkey meat and salmon filet, had elevated contamination levels exceeding the maximum limit given for PCDD/PCDF TEQ within the European Union. The majority of the laboratories reported results with a satisfactory trueness (±20%) for these food samples. For the low contaminated cheese sample, the deviation from the consensus value is larger for most of the laboratories. However, at these low levels it is not reasonable to apply the same quality criteria as for samples contaminated close to established maximum levels.

The evaluation of the laboratories' report on the analytical methods used showed a high similarity of techniques used for the gas chromatographic separation and mass spectrometric determination of dioxins and dioxin-like PCBs. However, there is a great variation in the methods used for cleanup.

It might therefore be concluded that the performance of laboratories world-wide in determining dioxin-like compounds is generally good for food samples with elevated contamination levels. However, the analysis of background contaminated food samples provides difficulties for a number of laboratories, probably due to insufficient limits of detection or blank contamination.

Introduction

In order to ensure consumer protection and reduce human exposure to dioxins through food consumption, the Commission of the European Communities recently issued maximum levels for dioxins in foodstuffs as well as feeding stuffs. In addition, action levels will be introduced as a tool for competent authorities and operators to highlight those cases were it is appropriate to identify a source of contamination and to take measures for its reduction or elimination, i.e., when significant levels of dioxins above background level are found in foodstuffs and feedingstuffs. So far, these limit levels are set for dioxins only, not including the dioxin-like PCBs, given the very limited data available on the prevalence of the latter. A need was therefore identified to generate reliable data not only on the presence of dioxins, but especially of dioxin-like PCBs in a wide range of foodstuffs and feeding stuffs in order to obtain a reliable database. Accordingly, Member States are requested to perform frequent monitoring of the presence of dioxins and dioxin-like PCBs in food and feed.

There is a large demand for chemical laboratories that are able to monitor these contaminants at low levels in food and feed. Such analyses require high quality laboratory standards using highly selective and sensitive analytical techniques and validated procedures, accreditation by recognised bodies and successful participation in interlaboratory comparisons or proficiency testing. Requirements and quality criteria regarding the methods of analysis to be used for the official control of dioxins and the determination of dioxin-like PCBs in foodstuffs are, for example, layed down in a Directive of the European Commission. According to this Directive, "Successful participation in interlaboratory studies that assess laboratory proficiency is the best way to prove the competence in specific analyses... Therefore, the continuous particpation in interlaboratory studies for the determination of dioxins and dioxin-like PCBs in the relevant feed/food matrices is mandatory". Among the requirements to be met is that confirmatory methods based on HRGC/HRMS, show a trueness of ±20% at elevated dioxin levels, e.g., 50% of the maximum level, i.e., the TEQ value measured should agree with the assigned TEQ for a sample within 20%.

This study is the fourth round of a world-wide interlaboratory comparison study on dioxin-like compounds in food and has been organised by the Department of Analytical Chemistry, Division of Environmental Medicine, Norwegian Institute of Public Health in Oslo, Norway.

The exercise took place from February 2003, when the samples were shipped to the laboratories for analysis, to beginning of May 2003, when the last reports on the results were received. The draft report was available to the participants on the web (http://www.fhi.no) in July and has been discussed during a consultation meeting at the Dioxin 2003 Symposium in August in Boston, USA.

The main objective of this exercise was to assess the between laboratory reproducibility of dioxin-like compounds analyses in frequently consumed foods. It also serves as a QA/QC instrument for each participating laboratory to contribute to its proficiency. A further objective has been to assess the world-wide readiness and capacity of dioxin analyses of food. All of the participants from previous rounds of this series of "Interlaboratory Comparisons on Dioxin in Foods" were invited to participate. In addition, several other laboratories announced their participation. There was no limit to the total number of participating laboratories. The 77 laboratories that submitted results, and thereby contributed to the actual study results, are presented in Table 1.

Table 1. Participants that reported results in the Fourth Round of Interlaboratory Comparison on Dioxins in Food 2003.

AgriQuality New Zealand Limited
Ultra-Trace Laboratory
Lower Hutt, Wellington,
New Zealand

Alta Analytical Perspective
Wilmington, NC, USA

ARC Seibersdorf Research GmbH, Environmental & Life Sciences / Chemical Analytics
Seibersdorf, Austria

ARPA Piemonte, Dipartimento di Alessandria
Polo Microinquinanti
Alessandria, Italy

ARPAT - Agenzia Regionale per la Protezione Ambientale,
Dipartimento di Firenze
Firenze, Italy

AXYS Analytical Services Ltd.
Sidney, British Columbia, Canada

Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit
Oberschleißheim, Germany

Bayerisches Landesamt für Umweltschutz
Augsburg, Germany

Canadian Food Inspection Agency - CFIA
Calgary Laboratory
Calgary, Alberta, Canada

CARSO
Lyon, France

CART
University of Liège
Liège, Belgium

Central Science Laboratory
York, UK

CHELAB s.r.l.
Resana (TV), Italy

Chemisches Landes- und Staatliches Veterinär-untersuchungsamt
Münster, Germany

Chemisches und Veterinäruntersuchungsamt (CVUA)
Freiburg
Freiburg, Germany

Cheng-Shiu Institute of Technology
Kaohsiung County, Taiwan, ROC

Consorzio Interuniversitario Nazionale la Chimica per l'Ambiente
Marghera (Venezia), Italy

Department of Environmental and Occupational Health, National Cheng Kung University, College of Medicin
Tainan, Taiwan, R.O.C.

Dioxin Analysis Unit, Australian Government Analytical Laboratory
Sydney, Australia

District Public Health Institute Ostrava, National Reference Laboratory for POPs Analysis
Frydek-Mistek, Czech Republic

Dr. Wessling Laboratorien GmbH
Altenberge, Germany

Eco-Center
Bolzano, Italy

Environmental Laboratory
Institut Químic de Sarrià - IQS
Barcelona, Spain

ERGO Forschungsgesellschaft mbH
Hamburg, Germany

Federal Environment Agency Austria
Vienna, Austria

Food GmbH
Jena, Germany

GfA Gesellschaft für Arbeitsplatz- und Umweltanalytik mbH
Münster-Roxel, Germany

GMLAB, Department of Chemistry, National Tsing Hua University, Taiwan, ROC
Hsinchu, Taiwan, ROC

Hong Kong Government Laboratory
Dr. W.C. Sham
Kowloon, Hong Kong

Hong Kong Government Laboratory
Dr. W.C. Chung
Kowloon, Hong Kong

Health Canada
Ottawa, Canada

Higiene e inspeccion de los alimentos
Universidad de Zaragoza
Zaragoza, Spain

INETI - Instituto Nacional de Engenharia e Tecnologia Industrial, DTIQ-LAQAS
Lisboa, Portugal

Institut Fresenius, Chemische und Biologische Laboratorien AG
Bayreuth, Germany

Institut für Energie- und Umwelttechnik IUTA e.V.
Duisburg, Germany

Institute of Food Safety and Nutrition, Danish Veterinary and Food Administration
Søborg, Denmark

Istituto zooprofilattico sperimentale dell'abruzzo del molise "G. Caporale"
Teramo, Italy

Istituto Superiore di Sanità
Roma, Italy

Japan Food Research Laboratories
Tama-City, Tokyo, Japan

Korea Food and Drug Administration, Dep. of food evaluation, pesticide residue
Seoul, Korea

LABERCA
Nantes, France

Laboratoire de Rouen
Rouen, France

Landesamt für Umweltschutz Sachsen-Anhalt, Standort Wittenberg, Dioxinlabor
Wittenberg, Germany

Landesamt für Verbraucherschutz und Landwirtschaft, Laborbereich
Potsdam, Deutschland

Landwirtschaftliche Untersuchungs- und Forschungsanstalt, LUFA
Rostock, Germany

LEM S.A.
Illkirch, France

LUFA-ITL GmbH
Kiel, Germany

Marchwood Scientific Services
Marchwood, Southampton, UK

Mass Spectrometry and Dioxin Analysis Lab, NCSR "Demokritos"
Athens, Greece

Micropollutants Technology
Thionville, France

MikroChem GmbH
Cölbe, Germany

MPU GmbH
Berlin, Germany

National Institute of Environmental Analysis/EPA
Chung Li City, Taoyuan County, Taiwan, R.O.C.

National Institute of Nutrition and Seafood Research
Bergen, Norway

National Public Health Institute – KTL
Kuopio, Finland

National Reference Centre for Dioxins and Related Compounds
Institute of Preventive and Clinical Medicine
Bratislava, Slovakia

Norwegian Institute of Public Health
Oslo, Norway

Norwegian Instiute for Air Research - NILU
Kjeller, Norway

Oekometric GmbH
Bayreuth, Germany

Research and Productivity Council
Fredericton, New Brunswick, Canada

RIKILT
Wageningen, The Netherlands

RIVM/Laboratory for Analytical Chemistry (LAC)
Bilthoven, The Netherlands

Scientific Analysis Laboratories Ltd
Manchester, UK

SGS Belgium NV
Institute for Applied Chromatography
Melsele, Belgium

Shimadzu Techno-Research Inc.
Kyoto City, Japan

Tauw Laboratories bv
Deventer, The Netherlands

TNO Environment, Energy and Process Innovation
Apeldoorn, Netherlands

Triangle Laboratories, Inc.
Durham, NC, USA

UEG - Institut für Umweltanalytik und Geotechnik
Wetzlar, Germany

Umeå University, Environmental Chemistry
Umeå, Sweden

Unilever
Bedfordshire, UK

US Environmental Protection Agency, Environmental Chemistry Laboratory
Stennis Space Center, MS, USA

USDA ARS, Biosciences Research Laboratory
Fargo, ND, USA

Vito
Mol, Belgium

VTT Technical Research Centre of Finland, VTT Processes
Espoo, Finland

Wellington Laboratories Inc.
Guelph, Ontario, Canada

Worthies Engineering Consultants Corp.
Taiwan, Taiwan, R.O.C.

Design and practical implementation

Study design

As in the previous rounds of this interlaboratory comparison, the test material chosen represented naturally contaminated food samples. The analytes to be determined by each participating laboratory were all seventeen 2,3,7,8-substituted PCDDs and PCDFs, the four non-ortho substituted PCBs #77, 81, 126 and 169, and the eight mono-ortho substituted PCBs #105, 114, 118, 123, 156, 157, 167, 189. Analysis should be performed using the laboratory's own methods for sample preparation and instrumental analysis, their own standards and quantification procedures, and their own method for lipid determination.

It was recommended that laboratories determine as many as possible of all 2,3,7,8-substituted PCDDs/PCDFs and dioxin-like PCBs. The report should include the determined lipid percent for the test samples. Also the actual sample and lipid intake (g) for each determination should be reported. For each sample, laboratories should report one concentration on fresh and lipid weight basis for each congener which is detected (S/N ≥3) as well as the level of determination (LOD, S/N =3). Non-detected congeners (S/N <3) should be marked "N.D." in the Comments column of the Report form.

In addition, three standard solutions containing known concentrations of a) seventeen 2,3,7,8-substituted PCDDs/PCDFs, b) four non-ortho PCBs and c) eight mono-ortho PCBs were to be analysed using the laboratory's own quantification standards and methods. The results were to be reported on a separate form.

The test material consisted of German turkey meat contaminated from ball clay containing feed, salmon from the Baltic Sea and Dutch cheese. The laboratory could choose to participate in analysing one, two or all three of the food samples.

Collection, preparation, and distribution of samples

The test materials consisted of three non-fortified natural products. Contaminated turkey meat was obtained from the Chemical and Veterinary Control Agency, Freiburg, Germany, salmon from the Baltic Sea from the Swedish Food Control Authority, Uppsala, Sweden and cheese was purchased at a store in Oslo.

The highly contaminated turkey meat from Germany was mixed with background contaminated turkey meat purchased at a store in Oslo. Homogenisation of the mixture was performed in a continuously grinding and mixing apparatus. Homogeneity of the salmon filet was obtained by repeatedly grinding portions of the food item in a meat grinder and homogenising these portions in a mixer. Cheese was first chopped using a regular food processor and then repeatedly ground and mixed using a meat grinder and blender. Sub-samples of at least 100 g of turkey meat (T), 60 g of salmon filet (S) and 60 g of cheese (C) were placed into carefully cleaned screw-cap glass bottles and stored at –20 °C until shipment. The frozen samples were shipped to the participating laboratories marked as test material T, S and C.

Reporting and handling of data

Detailed instructions for participants and Excel report forms were sent out to the participants together with the samples in February 2003 (Appendix B). For each analyte in each sample, participants were requested to report a single value for the concentration or indicate non-detected congeners by "N.D.". In addition, detection limits had to be given for each analyte. Concentrations were to be reported both on lipid and on wet weight basis including the lipid content of the sample. Additionally, the concentrations of each analyte in the three standard solutions, determined by the laboratories' own quantification standards and methods, had to be reported.

Each participating laboratory was given a code number by the co-ordinators. Participants had access to their own code only and laboratory codes were not revealed to third parties.

On receipt by the co-ordinators, the raw data from the laboratories were entered into a database. The draft final report was generated and made available to all participants on the web in July 2003. The draft of the final report has been discussed at a consultation meeting at Dioxin2003 in August in Boston, USA.

Statistical analysis

Based on experiences from previous rounds, we have chosen the following approach for the calculation of

the consensus concentrations for each of the congeners:

Congener-by-congener medians were calculated from food sample data of all reporting laboratories using the detection limit as concentration for non-detected congeners (upperbound concentration). Outliers were defined as those values above two times the median of all values and were removed from the data set. The consensus values were defined as the median of the remaining data for each congener. In addition, the consensus mean and standard deviation (SD) were calculated from this data set for each congener. Those congener data which had been removed prior to consensus calculation are marked in the tables presenting the individual results.

For the standard solutions, outliers were defined as those values outside ± 50% of the median of all reported values. Consensus median, mean and SD were calculated from the remaining data. The consensus of the lipid content was calculated as the mean after removal of values outside ± 2SD.

Not all laboratories determined all the 29 analytes and therefore the number of data used for the consensus between different congeners varies.

Toxic equivalents (TEQ) were calculated from the consensus values for three groups of analytes, PCDDs/PCDFs, non-ortho PCBs, and mono-ortho PCBs, using the toxic equivalency factors derived by WHO in 1998. As the detection limit was used for the concentration of non-detects, these TEQs represent upper bound concentrations.

Z-scores for PCDD/PCDF TEQs were calculated for each laboratory according to the following equation:

$$z = (x - X)/\sigma$$

where x = reported value; X = assigned value (consensus); σ = target value for standard deviation.

A σ target value of 20% of the consensus was used, i.e. z-scores between +1 and –1 reflect a deviation of ± 20% from the consensus value.

The final report and certificate

The draft of the final report was prepared by members of the co-ordination group in May and June 2003. Opportunity has been given to discuss the draft at the consultation meeting at the Dioxin 2003 Symposium in August in Boston, USA.

In the present report, the participants are presented in the tables and figures by their laboratory codes. Each laboratory has access to its own code only and the codes are not revealed to third parties. A certificate, stating the participant's code, will be sent to each participant contributing to the results together with the printed report in autumn 2003. Further copies of the report may then be ordered from the co-ordinators for a fee covering printing and mailing costs.

Co-ordination

The study was initiated and carried out by the Department of Analytical Chemistry, Division of Environmental Medicine, Norwegian Institute of Public Health, Oslo, Norway. Members of the co-ordination committee were:

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Georg Becher, PhD, Department Director and Professor
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Results

Results are presented in the chapters below. A participating laboratory will be able to compare its performance congener by congener with the other laboratories. Since variations in performances are based on several factors, it is recommended that each laboratory carefully evaluates the factors that, favourably or unfavourably, have contributed to its performance. A general reader of the report, who has no access to the laboratory codes, will be able to get a picture of the analytical performance of laboratories world-wide for determining dioxins in foods.

Presentation in the report

Seventy-seven laboratories from 24 different countries have submitted results. A summary of the results is presented in the chapters below, including the consensus statistics on fresh and lipid weight basis for concentrations and TEQ values of individual congeners, a summary of TEQ values for each food item, and the z-score plots for PCDD/PCDF TEQs based on a target deviation of ±20%. Further, the results of the lipid determinations are presented. Finally, individual results reported by the laboratories for concentrations for each congener are given for turkey meat, salmon filet and cheese.

Summarising comments on results

Analyte solution

For the three analyte solutions, 69-70 laboratories had reported concentrations for PCDDs/PCDFs, 54-57 laboratories for non-ortho PCBs, and 52-53 laboratories for mono-ortho PCBs. Even for the standard solutions with known concentrations, up to 6 values reported for a congener were outside ±50% the median of all values and had to be removed as outliers. The average relative standard deviation (RSD) for the 17 PCCD/PCDF congeners was 11% ranging from 8% for 1,2,3,4,7,8-HxCDF to 15% for OCDF. The average RSD for non-ortho PCBs and mono-ortho PCBs was 11 and 12%, respectively. The calculation of z-scores for the TEQs (target 13.6 pg/µl) of the PCDD/PCDF standard solution shows that still 10% of the laboratories report concentrations outside the range of ±20% of the target value. This may be regarded as a high number, as there are no interferences of sample matrix components in these determinations. The results should stimulate several of the laboratories to carefully check their calibration standards.

Turkey meat

For the turkey meat sample, 67 laboratories determined PCDDs/PCDFs. The dioxin contamination of the turkey meat originates from the use of ball clay as anti-caking additive in the animals' feed. The congener profile of PCDDs/PCDFs in ball clay has characteristic features with elevated concentrations of PCDDs compared to normal background exposure. This particular pattern resulted in few non-detected congeners for the PCDDs (2-17) compared to the number of non-detects for the PCDFs (16-52).

The PCDD/PCDF consensus TEQ on fresh weight basis was 0.25 ppt with a RSD of 14% corresponding to 6.6 pg TEQ/g lipid (RSD 19%). The contamination therefore exceeds by 230% the maximum limit of 2 pg PCDD/PCDF TEQ/g lipid being enforced in the European Union.

Values for dioxin-like PCBs were reported by 48 to 55 laboratories. The consensus values were quite low resulting in far more non-detects compared to the salmon. Especially CB-123 and CB-189 have low abundance. The mean RSD was 40%.

The total TEQ consensus for turkey meat was 0.27 ppt (fresh weight) and 7.2 ppt (lipid weight). Two of the congeners, 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, are the dominating contributors to total TEQ (85%), while PCBs contribute only 7%. This pattern with a dominance of PCDDs contribu ting to the total TEQ is typical for food produced from animals fed specific ball clay containing feed.

For the turkey meat, 73% of the laboratories had z-scores for PCDD/PCDF results on fresh weight basis within ±1 and 94% had z-scores between +2 and –2. The consensus for the lipid content was 3.7% with a RSD of 26%.

Salmon filet

Seventy-six (76) laboratories had determined PCDDs/PCDFs in salmon filet. The content of PCDDs/ PCDFs was relatively high (5.7 pg TEQ/g fw.) exceeding the maximum level of 4 pg TEQ/g fw. allowed in the European Union. As a result, the frequency of non-detected congeners is generally low and only high for the least abundant congeners, e.g., 43 and 51 laboratories reported ND for 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8,9-HpCDF, respectively. Between 1 and 23 values reported

for different congeners had to be removed as outliers before consensus calculations. The RSD for the results on fresh weight basis was between 20% for the most abundant congeners, 2,3,7,8-TCDF, and 62% for the least abundant congeners, 1,2,3,4,7,8,9-HpCDF. The corresponding RSD of the calculated TEQ for PCDDs/PCDFs, however, was as low as 12% and 87% of the laboratories reported values of ±20% of the consensus value (z-score ±1).

Dioxin-like PCBs were determined by 57 to 63 laboratories. Also the PCB concentrations were high in this sample (10.4 pg PCB-TEQ/g fw.). The RSDs are similar to that of the PCDDs/PCDFs ranging from 21 to 58% for the different congeners with an average RSD of 32%.

The total TEQ consensus value for salmon filet was 16 ppt on fresh weight and 167 ppt on lipid weight basis. The contribution of the three groups of analytes to the total TEQ on fresh weight basis was 35%, 49% and 16% for PCDDs/PCDFs, non-ortho PCBs and mono-ortho PCBs, respectively. CB-126 alone constitutes 47% of the total TEQ. This confirms that dioxin-like PCBs make a dominating contribution to the total TEQ in marine fish.

The mean consensus of the reported lipid content was 9.5% with a RSD of 7.8%.

Cheese

For this sample, PCDDs/PCDFs were reported by 70 laboratories. As expected, the content of PCDDs/PCDFs was low representing background contamination. The PCDD/PCDF consensus TEQ was 0.09 ppt with a RSD of 20% and 0.37 ppt with a RSD of 21% on fresh weight basis and on lipid weight basis, respectively. When including dioxin-like PCBs, the RSD of total TEQ dropped to 13% and 15%, respectively.

PCBs were reported by 50 to 57 laboratories. The RSD for the consensus values on fresh weight basis for the different PCB congeners ranged from 23% to 63% with a mean of 36%.

The total TEQ based on the consensus concentrations was 0.21 ppt on fresh weight (RSD13%) and 0.9 ppt on lipid weight basis (RSD15%), and PCDDs/PCDFs, non-ortho and mono-ortho PCBs contributed 42%, 46%, 12% to this total TEQ, respectively.

For 22 laboratories (30%), the calculated z-scores for PCDD/PCDF TEQs were between ±1, while for 42 laboratories (60%) the z-scores were within ±2.

Being typical of cheese, a high lipid content was determined with a consensus mean of 23.4% and a RSD of 10%.

Summary of analytical procedures

Participants of this fourth round were ask to fill in a report form covering a short description of the analytical procedures and methods used. In Appendix C, an evaluation of the report forms is given.

The first part covers sample preparation and cleanup. Although it was recommended to use the whole sample for analysis, only about 40% of the laboratories did so. About another 40% used about half of the sample provided probably to allow for a replicate analysis in case the first trial failed. However, it has to be taken into account that a too low sample intake might lead to a large number of non-detects in low contaminated food samples. All laboratories added 13C-labelled internal standards, however, the number of standards used for the total of 29 analytes varies greatly. Ideally, one isotopically labelled standard should be used for each analyte.

Solvents for extraction of lipids and analytes were mostly mixtures of a non-polar solvent, e.g. n-hexane, and a more polar solvent, e.g dichloromethane or acetone. For cleanup of the extracts, modified silica was used most often. Surprisingly, only 70% of the laboratories used activated carbon for isolation of planar compounds.

The second part regarded gas chromatographic conditions and mass spectrometric detection. The cleaned up extract is usually reduced to 20μL of which 1-2 μL are injected using the splitless injection technique and an injector temperature of 280°C. The most commonly used capillary columns are of 60 m length with a stationary phase of 5%phenyl-dimethylpolysiloxane. About 20% of the laboratories used a second polar column to check for co-eluting components in the dioxin fraction.

Mass spectrometric detection was almost exclusively performed using high-resolution instruments, and quantification was performed using peak area ratios.

Conclusions

In this fourth round of interlaboratory comparison exercise two of the samples, turkey meat and salmon filet, had elevated contamination levels of dioxins and for salmon also of dioxin-like PCBs. In contrast, the cheese sample had a low background contamination for both dioxins and dioxin-like PCBs. However, due to high consumption, even low contaminated food items may contribute significantly to human exposure to dioxins and dioxin-like PCBs. It is, therefore, important that laboratories also show sufficient ability to determine the low levels present in background contaminated foodstuffs.

Using the median of all values and removing reported values above 2 times the median, seems to give a good estimate of the true value for low contaminated samples where a considerable number congeners are non detected.

For turkey and salmon, 87% and 73% of the laboratories, respectively, reported PCDD/PCDF TEQs on fresh weight basis within ±20% (z-score ±1) of the consensus values. For the low contaminated cheese sample, it is more difficult to obtain a trueness of ±20% which was obtained by 30% of the laboratories. It might therefore be concluded that the performance of laboratories world-wide in determining dioxin-like compounds is generally good for food samples with elevated contamination levels. However, the analysis of background contaminated food samples provides difficulties for a number of laboratories, probably due to insufficient limits of detection or blank contamination.

For all food items except fishery products, the maximum values in the European Union are given in pg/g fat. Also, comparison of the contamination level in different food items requires levels given on a lipid weight basis. Therefore good accuracy for the determination of the fat content is important. In this study, especially the RSD for the consensus mean of lipid content in turkey was high (26%). Thereby, the calculated RSD of the total TEQ for this matrix increased from 13% for the fresh weight based consensus value to 17% for the lipid weight based consensus value.

In this fourth round, the majority of laboratories also determined dioxin-like non-ortho and mono-ortho PCBs. The importance of determining these compounds in food is demonstrated by their large contribution to the total TEQ especially in food from the marine environment.

The majority of laboratories used similar techniques for the gas chromatographic separation and mass spectrometric determination of the analytes. In contrast, extraction and cleanup procedures show a great variation among laboratories.

Acknowledgements

The participating laboratories are acknowledged for their participation in this interlaboratory comparison and their interest in its overall objectives, thereby making it clear that they value good analytical performance. All the individual analysts are acknowledged for their contributions to the results.

We are grateful to Cambridge Isotope Laboratories, Inc. for providing the standard solutions for this interlaboratory study. Dr. Malisch, Chemical and Veterinary Control Agency (CVUA), Freiburg, Germany and Dr. Marie Aune, The National Food Administration, Uppsala, Sweden are thanked for providing the turkey and salmon material, respectively.