CONCEPT LIFE SCIENCES

METHOD STATEMENT FOR THE DETERMINATION OF DIOXINS (PCDD/FS)

INTRODUCTION

The performance of this method is validated in accordance with internationally recognised procedures.
This procedure describes the determination of the 17 2,3,7,8 chlorinated dibenzo dioxins and dibenzo furans by isotope dilution high resolution gas chromatography-mass spectrometry. Methods are based on, US EPA Methods 23A and 1613 and BS EN 1948:2006 and are within the scope of Concept's UKAS accreditation.
Solid / Liquid Samples: The method is an in-house protocol based on US EPA Method 1613
M23 Stack Emission Samples: The method is an in-house protocol fulfilling the requirements of US EPA Method 23A
BS EN 1948 Stack Emission Samples: The method is an in-house protocol fulfilling the requirements of method BS/EN 1948:2006 parts 1-3.

PRINCIPLE

An aliquot of the sample is spiked with isotopically labelled internal standards and then the dioxins (and PCB) compounds are extracted into a solvent. These extracts are then concentrated by evaporation and then subjected to a number of clean up steps before analysis by High Resolution Gas Chromatography-High Resolution Mass Spectrometry (HRGC/HRMS). ^{13}C labelled internal standards are added to all test samples, spikes and blanks before analysis. The quantitative results are then corrected for the recovery of these standards.

SOLID SAMPLES

Including (but not restricted to): soil, ash, feedstuffs, stack emission, ambient air emission samples
0.05 to 30 g sample aliquots are taken (matrix dependent), spiked with labelled internal standards, then soxhlet extracted with appropriate organic solvent. The extract is concentrated and subjected to "Combination / Florisil Column" purification with optional additional clean up steps involving acid/base washing, carbon column chromatography etc. The purified extract is concentrated to 10-30 ul, spiked with labelled recovery standards and analysed by HRGC / HRMS.

LIQUID SAMPLES

0.2 to 1 l sample aliquots are taken, spiked with labelled internal standards and subjected to liquid-liquid extraction with organic solvents. The extract is concentrated and subjected to "Combination/Florisil Column" purification and further clean up measures if required. The

purified extract is concentrated to 10-30 ul, spiked with labelled recovery standards and analysed by HRGC / HRMS.

STATIONARY SOURCE EMISSIONS

The XAD resin / PUF and associated filter are spiked with labelled internal standards, then soxhlet extracted with an appropriate organic solvent.
Associated organic washings are concentrated to near dryness and mixed with the soxhlet raw extract.Associated aqueous washings are subjected to liquid-liquid extraction with organic solvent and combined with the soxhlet raw extract
The combined raw extract is concentrated and subjected to "Combination/Florisil Column" purification, with additional clean up steps as described earlier if required. The purified extract is concentrated to 10 - 30 ul, spiked with labelled recovery standards and analysed by HRGC / HRMS.

OTHER MATRICES

PCDD / F content of other matrices such as chemical products, (e.g., chlorophenol based preparations), biological / food / feed matrices with a high fat content e.g. human adipose and eggs, milk and blood may also be determined by this method, with suitable adjustments to the procedures for each respective matrix.

PERFORMANCE CHARACTERISTICS

SUBSTANCES DETERMINED

The 17 toxic 2,3,7,8 chlorinated dibenzo dioxins and dibenzo furans and optionally the total of all other tetra-hepta chlorinated congeners. Results are reported on a toxic equivalents basis.

RANGE OF APPLICATION

- Solid samples 0.2 to 900 ng / kg
- Aqueous samples 0.05 to 200 ng / l
- Emission Samples 0.005 to 20 ng per combined sample

LIMIT OF DETECTION

- Solid samples 0.2 ng / kg (0.2 ppt) for a 10 g sample
- Stack emission 3 - 5 pg in whole sample, 0.6 - 1.0 pg / m^3 for 5 m^3
- Ambient air sample 3 - 5 pg in whole sample, 3 - 5 fg / m^3 for 1000 m^3
- Aqueous samples 0.05 ng / l (5 pg / l), for 500 ml sample

Limits of detection can vary according to sample aliquot, internal standard recovery and matrix interference. The internal standard recovery and/or degree of interference can only be assessed on completion of the work. Therefore, the above figures are for guidance

ANALYTICAL QUALITY CONTROL

Analytical quality control is maintained by a number of measures:

- Multi-point calibration with authentic standards (with defined minimum performance characteristics)
- Analysis of reagent / method blanks within each analytical batch
- Ongoing quality assured by the use of labelled internal standards and sample by sample recovery calculation
- Participation in external proficiency testing and interlaboratory schemes such as FAPAS

REFERENCES

- Method 23A: Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) from Stationary Sources", US EPA, Revision 1, December 1996.
- Method 1613: "Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B", pubd. United States Environmental Protection Agency Office of Water Regulations and Standards, Industrial Technology Division, Office of Water, October 1994.
- BS/EN 1948:2006-1,2 and 3, 2006. 'Stationary source emissions-Determination of the mass concentration of PCDDs/PCDFs'.
- Method Implementation Document (MID 1948), "BS EN 1948 Parts 1-3: 2006, Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs. Part 1: Sampling of PCDDs/PCDFs, Part 2: Extraction and clean-up of PCDDs/PCDFs, Part 3: Identification and quantification of PCDDs/PCDFs" Environment Agency,
- Ambridge, P.F. et al , "Acceptance Criteria for analytical data on polychlorinated dibenzo- p -dioxins and polychlorinated dibenzofurans", Chemosphere , 21 (8): 999-1006, (1990).
- COMMISSION DIRECTIVE 2002/69/EC. of 26 July 2002, laying down the sampling methods and the methods of analysis for the official control of dioxins and the determination of dioxin-like PCBs in foodstuffs
- COMMISSION DIRECTIVE 2002/70/EC of 26 July 2002 establishing requirements for the determination of levels of dioxins and dioxin-like PCBs in feedingstuffs
- BS/ISO 18073:2004 Water quality - Determination of tetra to octa-chlorinated dioxins and furans - Method using isotope dilution HRGC/HRMS