DIOXINS GO QUECHERS – A NEW APPROACH IN THE ANALYSIS OF WELL-KNOWN CONTAMINANTS

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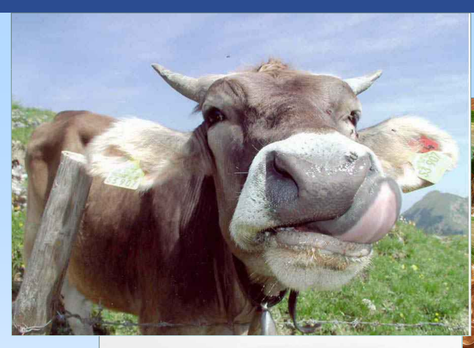
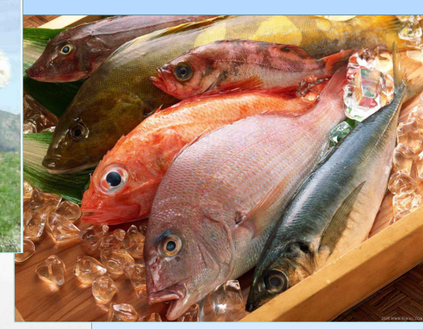
Introduction

PCDD/PCDFs are formed during combustion and as by-products of industrial processes. These compounds are highly resistant to breakdown processes, and consequently persist in the environment, followed by uptake into the food chain. The major part of human exposure to dioxins results from the consumption of food of animal origin including meat, fish, eggs and milk products. Maximum levels for dioxins and dioxin-like PCBs in these foods have been set by the Commission Regulation 1881/2006/EC, the methods of sampling and performance criteria for methods of analysis by the Directive 2002/69/EC.





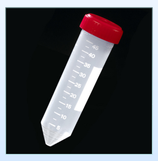
Conventional analytical methods for the analysis of PCDD/PCDFs in food (e.g. EPA 1613) contain laborious and time-consuming extraction processes, several clean-up steps followed by HRGC-HRMS analysis. The general duration of sample analysis is estimated between four to five days to meet the requirements regarding low limits of quantification, high recovery rates and analytical precision. Some steps in the sample preparation can be accelerated by pressurized liquid extraction or automated sample preparation systems implying extra costs for expensive equipment.

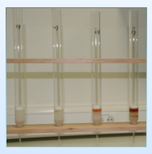
The aim of this study was to combine the flexibility and velocity of the well-known QuEChERS methodology for the analysis of pesticides with efficient primary and secondary clean-up steps generating a sample extract qualified for HRMS analysis without the need of cost-intensive extra devices.

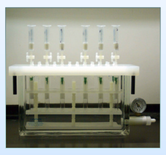
Experimental

Sample preparation scheme

Homogenized sample → ACN/DSPE extraction → Primary destructive cleanup → Secondary Al_2O_3 + AC cleanup → HRGC-HRMS (DFS, Thermo Fisher)







- Repetitive extraction of meat, fat and dairy samples in a matrix-solid phase dispersion (MSPD) process with acetonitrile
- No necessity for drying of humid samples
- First cleanup: fast destructive column cleanup with customized acidic/basic silica layers
- Second cleanup: cartridge cleanup with aluminum oxide and/or carbon black (without solvent change)
- The final extract was applied to HRGC-HRMS analysis (DFS, Thermo Fisher)

Results

- Total runtime of confirmatory PCDD/PCDF analyses possible within 48 hours

- The method was validated according to DIN EN 32645 and met the requirements of EC legislation regarding:
  - Accuracy
  - Precision
  - Recovery rates

- LOQs for 2,3,7,8-TCDD/-TCDF were in the range of 0,02 ppt.

Tab. 1: Validation data of PCDD/PCDFs obtained in a blank vegetable oil

Parameter	LOQ [ng/kg]	Recovery of corr. C^{13} ISTD [%]	CV [%]
2378-labelled PCDD congeners			
2378-TetraCDD	0,02	70	3,4
12378-PentaCDD	0,03	75	4,2
123478-HexaCDD	0,05	67	3,7
123678-HexaCDD	0,05	65	5,2
123789-HexaCDD	0,06	68	4,7
1234678-HeptaCDD	0,29	65	2,9
12346789-OctaCDD	0,78	71	4,1
2378-labelled PCDF congeners			
2378-TetraCDF	0,02	65	2,4
12378-PentaCDF	0,03	87	2,8
23478-PentaCDF	0,04	72	3,3
123478-HexaCDF	0,04	87	4,2
123678-HexaCDF	0,05	86	2,7
123789-HexaCDF	0,05	76	3,7
234678-HexaCDF	0,06	88	4,3
1234678-HeptaCDF	0,23	85	3,5
1234789-HeptaCDF	0,27	80	4,5
12346789-OctaCDF	0,67	75	3,4

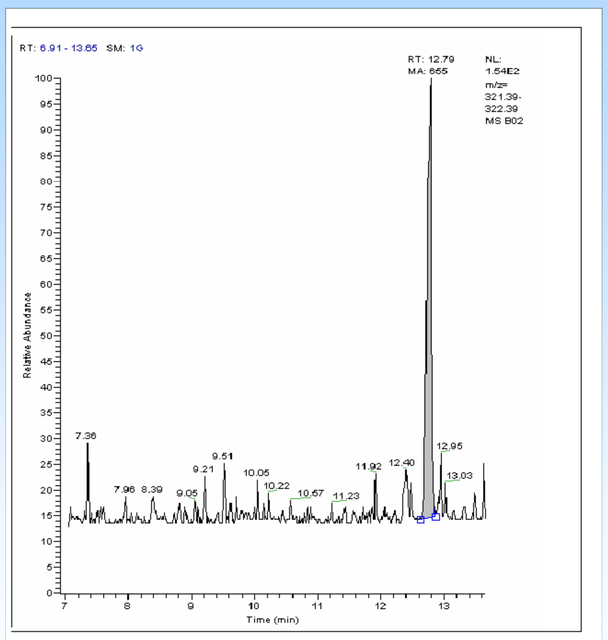


Fig.1: Olive oil sample containing 0,03 ppt 2,3,7,8-TCDD

Conclusions

- Conventional analytical methods for the analysis of PCDD/PCDFs in food often need
  - Laborious and time-consuming sample preparation processes
  - Expensive extra devices
- In this study a sensitive, robust and fast alternative analytical method was developed, meeting the requirements of EC legislation
- The total runtime of a confirmatory analysis can be run within 48 hours