DSP systems
The missing link in your laboratory!

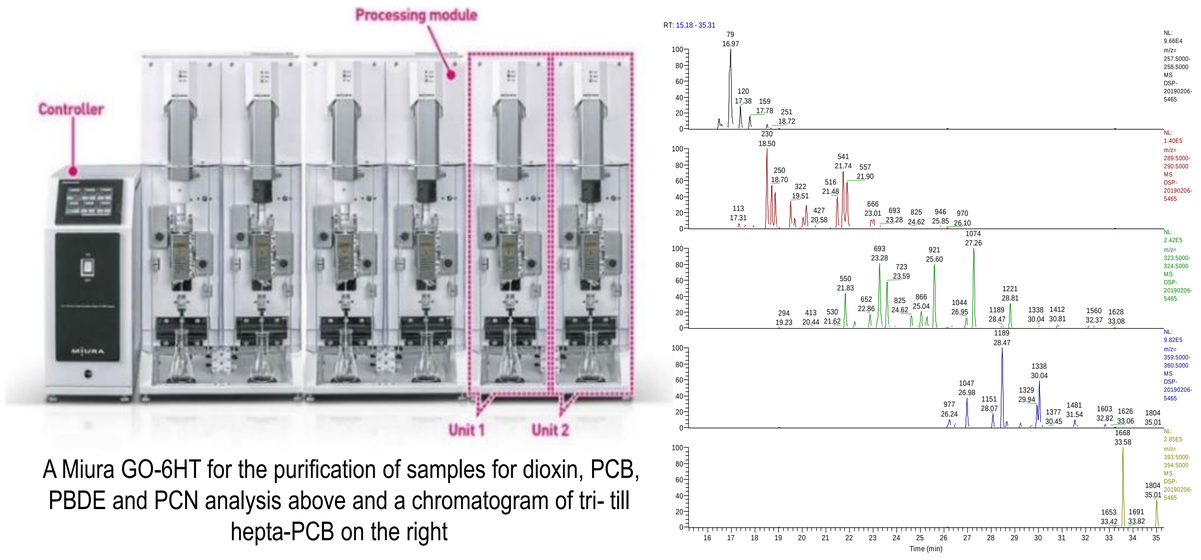
www.dspsystems.eu

Sustainable chemistry for POPs analysis by using the next generation automated purification system

Guillaume ten Dam[1], Hiroyuki Fujita[2], Jeroen Markesteijn[3], Chris van Wakeren[1] and Wim Traag[1]
[1] DSP-Systems, Ede The Netherlands | [2] Miura, Matsuyama Japan | [3] NofaLab, Schiedam The Netherlands

Introduction

The detection of polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like polychlorinated biphenyls (non-ortho, mono-ortho substituted CBs) as well as marker PCBs in food, feed and environmental samples have been subject of intensive research. Concentrations in biological samples are very low, in general in the low pg/g range while in environmental samples the concentrations are higher. In order to achieve low limits of quantitation and unambiguous identification, highly sensitive and specific methods are required.
A new technology for automated sample clean-up was introduced in 2015 for the European market in which dioxins and non-ortho PCBs are often analysed in a single measurement and mono-ortho PCBs and marker PCBs in a second. The method uses a minimal amount of solvent (without dichloromethane) and results in two fractions of around 1.5ml. In this study the performance of this technology is demonstrated as well its use for other contaminants.



A Miura GO-6HT for the purification of samples for dioxin, PCB, PBDE and PCN analysis above and a chromatogram of tri- till hepta-PCB on the right

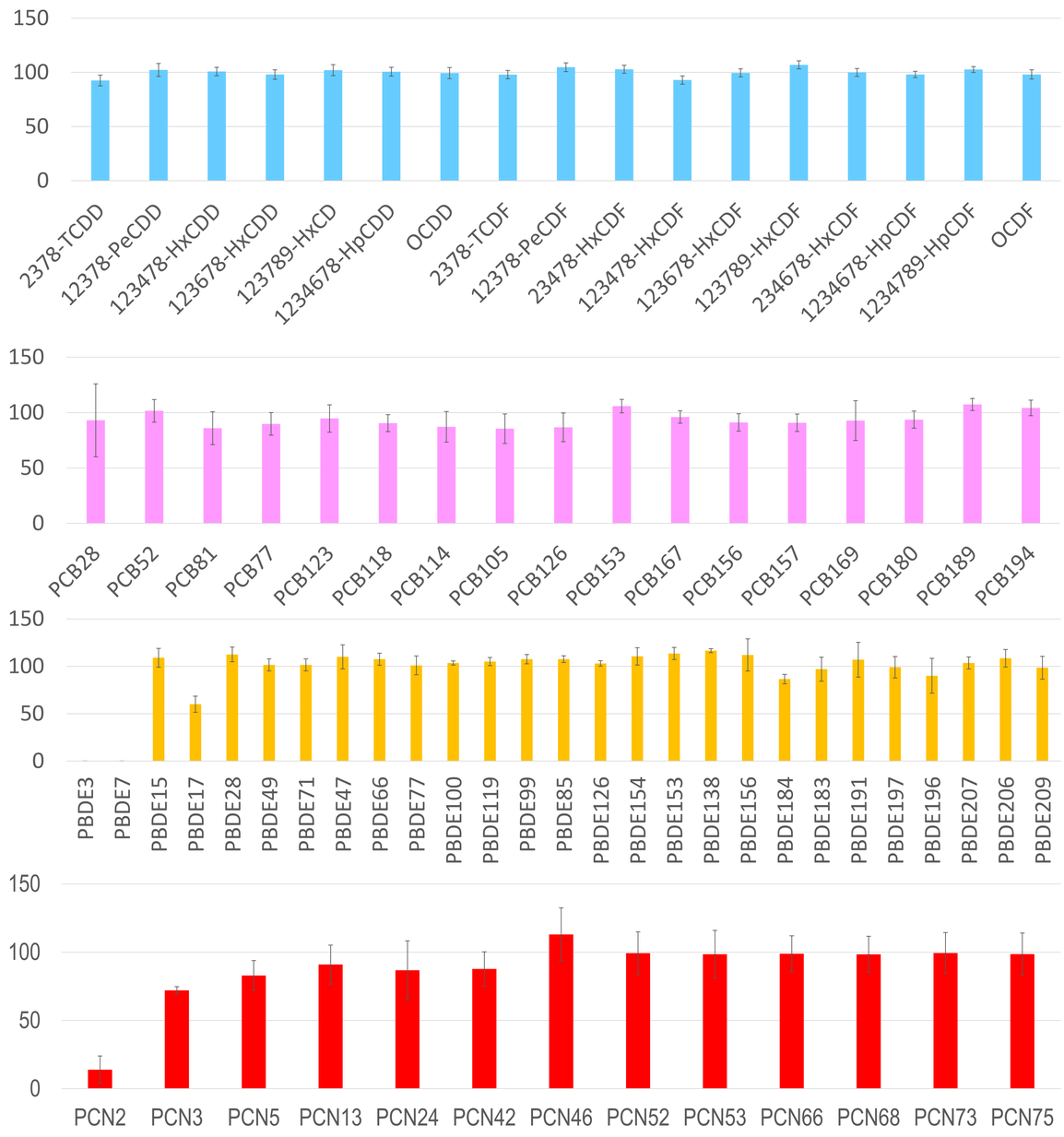
Standards

Native standards and ^{13}C internal standard from Cambridge Isotope Laboratories (Andover, MA) were used for the analyses of dioxins, PCBs, PBDEs and PCNs. Each sample was spiked with ^{13}C internal standards prior to purification and a relevant ^{13}C syringe standard after concentration of the purified extract.

Samples

A variety of samples were used for the studies. For dioxins and PCBs cod liver oil (EDF-5462 and EDF-5463) and fat from pork meat and egg was used. For PBDE fat from milk and for PCN fat from pig, palm free fatty acid distillate (PFAD) and fish oil.

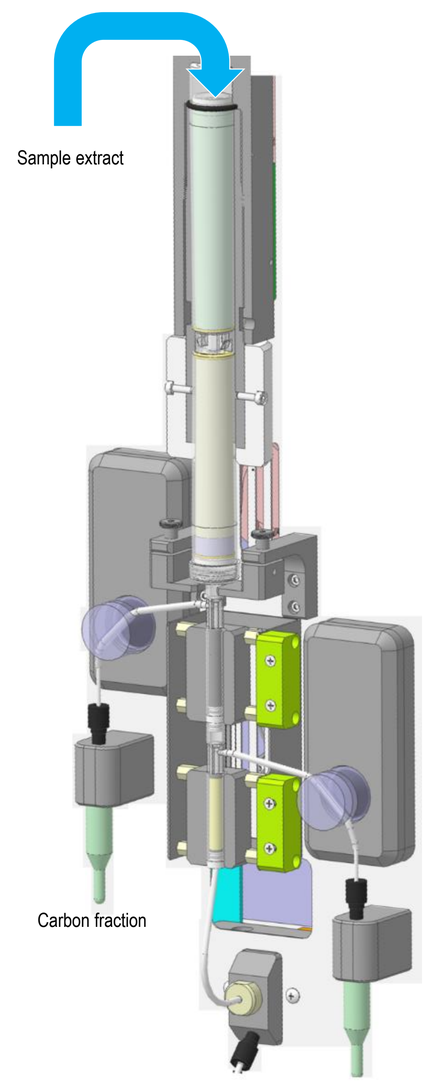
Results



Recovery of dioxin and PCBs in cod liver oil SRM and fat from pork meat and egg (Fujita et al., Dioxin2015), PBDE standards in milk fat (Fujita et al., Dioxin2017), PCN in several types of samples (DSP-Systems 2018:12)

Method

For each sample a set of four columns was used, in the following order: silica gel impregnated with silver nitrate (1st); silica gel impregnated with sulfuric acid (2nd); activated carbon (3rd) and alumina (4th). Each sample extract was transferred on top of the first column and after complete adsorption, which took in general less than five minutes, the set of columns was placed in the automated sample purification system (GO-6HT, Miura (Japan)). Before applying to the column-sets, the 1 – 4g sample were dissolved in 10ml hexane.
Next, the column set was eluted with 90 ml hexane (140 ml for PBDE) at a flowrate of 2.5 ml/min. During this step the temperature of the two purification columns was maintained at 60°C/140°F. This elevated temperature weakened the adsorption with silica gel and, as a result, the elution speed of dioxins and PCBs is increased. Also the chemical reaction rates (e.g. oxidation with sulfuric acid) with sample matrices is accelerated. PCDD/Fs and the four NO-PCBs are trapped on the activated carbon column while the MO- and NDL-PCBs are trapped on the alumina column. Both the alumina and the carbon column were eluted in backflush using a small amount of toluene resulting in two fractions, each of 1.5 ml. During these elution steps the temperature of the column sets was heated till 90°C/194°F.
After the purification the two fractions were evaporated using a centrifuge evaporator (Centrivap, Labconco (USA)) and reconstituted in 10µl nonane. Equivalent parts of each extract were transferred to a third vial to combine both fractions for the analysis of PCNs. All analysis were performed on a Gas Chromatograph High Resolution Mass Spectrometer (DFS, Thermo Scientific (Germany)) operated at 10.000 resolution.



Summary

The method was proven to generate highly purified extracts for the analysis of dioxins, PCBs, PBDE and PCNs while obtaining good recoveries for the majority of the congeners. Even when combining the two separate fractions the equivalent of 0,625 gram of fat could be injected interfering neither chromatography nor high resolution mass detection.
Some mono halogenated congeners showed low or no recovery. This was assumed to be caused by the strong absorption in the purification columns and further research was performed to improve recoveries for lower halogenated congeners.

In cooperation with

MIURA

Guillaume ten Dam
Food Valley BTA12
Darwinstraat 7a, 6718 XR Ede
The Netherlands
+31 683627499
Guillaume.ten.dam@dspsystems.eu

In cooperation with

NofaLab Laboratories
NofaGroup Quality in Control