Organohalogen Compounds, Volume 60, Pages 53-56 (2003)

SELECTIVE ACCELERATED SOLVENT EXTRACTION OF PCBSs FROM FOOD AND FEED SAMPLES

Sune Sporring and Erland Björklund

Department of Analytical Chemistry, Lund University, P.O. Box 124, SE-22100 Lund, Sweden

Introduction

After the Belgian dioxin-poisoning crisis in 1999, there has been an increased public awareness of food quality. In Belgium feedingstuffs were contaminated with dioxins and there was a great demand for fast extraction and analysis of a large number of samples. It was discovered that all the contaminated samples also had a high content of PCBs with a congener pattern similar to Aroclor 1260 and PCBs were therefore used as an indicator for dioxin contamination.[1] Traditional PCB analysis consists of 3 steps: extraction, cleanup and separation. Extraction and cleanup have traditionally been the most work and time demanding steps. The available extraction methods which efficiently extract the PCBs are also known to co-extract interfering compounds including fat. Accelerated Solvent Extraction (ASE^{TM}) has shown its potential by performing simultaneous extraction and cleanup of food and feedingstuffs. All previous publications have utilized the ASE 200 system,[2,3,4] with a maximum extraction cell size of 33 ml, which limits the amount of sample that can be handled. In this work the development of an on-line extraction method is described for the new ASE 300. This instrument has the advantage that cell sizes up to 100 ml can be used. Previously it has been shown that H_2SO_4:Silica (40:60 w/w) is the best fat retainer for food and feedingstuffs and this was also used in this study. Advantages of this fat retainer are the price and the effectiveness in removing fat and other matrix component giving very clean extracts.[3]

Methods and Materials

All solvents used were pesticide grade and were supplied by Fluka as were silica and Na_2SO_4. All extractions were carried out on a ASE 300^{TM} (Dionex, Sunnyvale, CA). PCB analysis were performed with an Agilent 6890N GC equipped with a dual-column system and two ECDs similar to Rahman *et al.*[5]. PCB standards were prepared from a Standard Reference Material (NIST 2262) and used for calibration and spiking. Lard fat, consisting of triglycerides, was supplied by the former Swedish Meat Research Institute (Kävlinge, Sweden). Naturally contaminated fish meal was delivered by State Official Laboratory (ROLT, Turvuren, Belguim). Fat was determined gravimetrically. PCB spiked lard fat and fish meal extracts were analysed using dual column GC-ECD.

Results and Discussion

The starting point for the investigation was to study the fat retaining capability of sulphuric acid impregnated silica under different extraction conditions using pure lard fat as matrix in the 34 ml cells. In all cases 0.5 g of lard fat was used in four different combinations; 0.5 g fat combined with either 5.0 g retainer, 6.7 g retainer, 10.0 g retainer or 20.0 g retainer. For the packing of the cell, see figure 1.

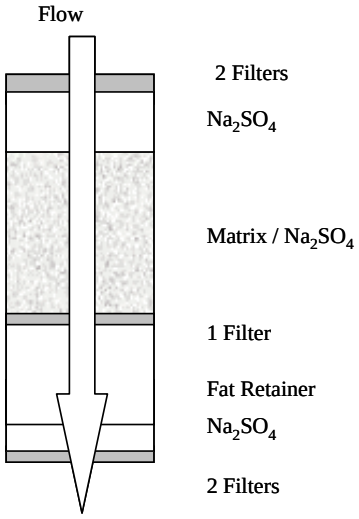

Figure 1. Packing of the extraction cell

This resulted in fat to fat retainer (FFR) ratios of 0.100, 0.075, 0.050 and 0.025. All combinations were tested at two temperatures (50 and 100 °C) with three different solvent types (*n*-pentane, *n*-hexane and *n*-heptane). Each experiment was performed in triplicate. After the extraction the extracts were evaporated under a gentle stream of N_2 and the residues were gravimetrically determined. The results are presented in figure 2.

The most interesting observation from the initial experiments were that a FFR of 0.050 gave almost 100 % fat removal. But by studying the results in details it could be seen that up to 18 mg of fat was extracted and it has previously been seen that even as little as a few mg of fat in the extracts can suppress the PCB recoveries when injected directly in the GC^2.
Ca 5 g of a naturally PCB contaminated fish meal were extracted at 100 °C with a FFR of 0.050, but the amount of co extracted fat was 25 mg and it was decided to choose a FFR of 0.025 for the reminding experiments. It also seemed that *n*-heptane gave slightly better fat removal and it is also know to be less toxic than e.g. *n*-hexane.

For the 100 ml cells a series of experiments were carried out using 3 g of lard fat combined with sulphuric acid impregnated silica, resulting in FFRs of 0.200, 0,150, 0.100, 0.075, 0.050 and 0.025. The extraction temperatures were 50 °C, 100 °C or 150 °C and each experiment was performed in triplicate and the results are presented in figure 3.

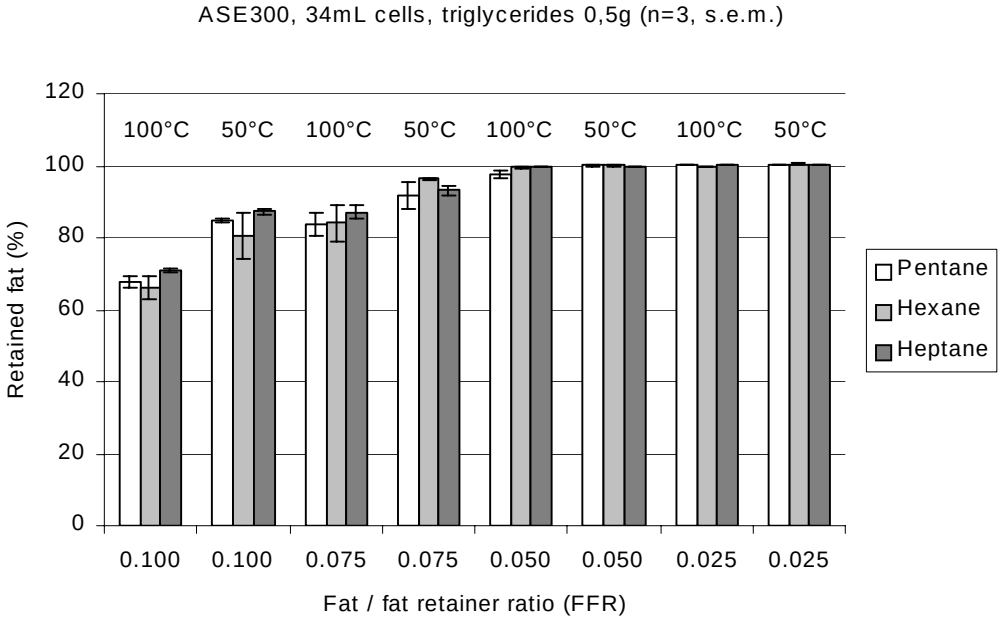

Figure 2. Amount of fat retained for sulfuric acid impregnated silica using different FFR ratios at two temperatures (50 and 100 °C) with three different solvent types (*n*-pentane, *n*-hexane and *n*-heptane). Each data point is an average of three measurements, error bars represents s.e.m.

For the 100 ml cells also the FFR of 0.025 was the best choice since higher FFR values led to too high levels of co-extracted fat (more than 2 mg).

Finally a few initial experiments were done where the extracts were analysed for the PCB content. For both the 34 ml and 100 ml cells the optimum conditions were: FFR: 0.025, solvent: n-heptane, temperature: 100 °C. For the fish meal extracted in the 34 ml cells, the average recovery of PCBs were in the range of 89-93 % when compared to certified values. Using 100 ml cells spiked triglycerides were extracted and also in this case quantitative recoveries with fat free extracts were obtained.

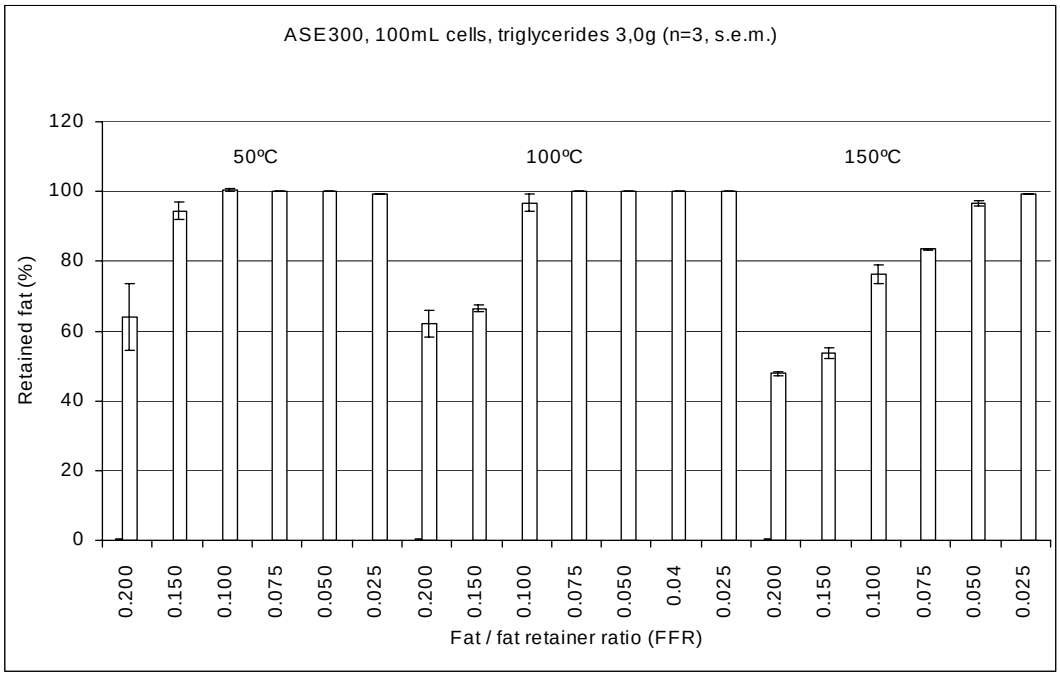

Figure 3. Amount of fat retained for sulfuric acid impregnated silica using different FFR ratios at three temperatures (50, 100 and 150 °C) with *n*-heptane as the extraction solvent. Each data point is an average of three measurements, error bars represents s.e.m.

Conclusion

When applying the developed selective ASE method, with on-line cleanup, in a routine laboratory it is possible to get an improved sample throughput. For low contaminated samples with a relatively high fat content especially the large cell size of 100 ml on the ASE 300 instrument is useful. In some cases even larger cell sizes would be preferable. The developed method will be tested on a number of certified reference materials to demonstrate its applicability to a broad range of food and feed matriced.

Acknowledgements

This work is part of the DIFFERENCE project, supported by the European Commission, project no. G6RD-CT-2001-00623.

References

1. Bernard A., Hermans C., Broeckaert F., De Poorter G., De Cock A. and Houins G. (1999) Nature 401, 231.
2. Müller A., Björklund E. and von Holst C. (2001) J. Chromatogr. A 925, 197
3. Björklund E., Müller A and von Holst C. (2001) Anal. Chem. 73, 4050
4. Gómez-Ariza J. L., Bujanlance M., Giráldez I., Velasco A. and Morales E. (2002) J. Chromatogr. A. 946, 209
5. Rahman M. S., Bøwadt S. and Larsen, B. (1993) J. High Res. Chrom. 16, 731