OPTIMISATION OF AN HRGC-HRMS METHOD FOR THE ANALYSIS OF PCDD/F'S IN SALMON AND SPINACH USING PTV AND/OR SPLITLESS INJECTION COUPLED WITH THIN FILM CAPILLARY GC.

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Introduction

The aim of this study was to optimise a GC-MS method, gaining the lowest possible detection limits to help monitor the constantly decreasing levels of PCDD/F's in the food chain. Fish represent a particularly difficult sample matrix, and also being bio-accumulative represent a 'good' source of PCDD/F's in the food chain.

Published levels[2] for UK salmon of 4.6 to 11ng/kg WHO TEQ show the need for a method with detection limits of the order 40 to 400 pg/kg WHO TEQ for reliable determination. However the ever decreasing legislative limits (as low as 0.5 ng/kg WHO TEQ) have further increased the need for fast reliable methods with extremely low detection limits.

Methods and Materials

All analysis was performed using an Agilent 6890 GC oven, fitted with both split/splitless and PTV injectors. The GC oven was directly interfaced to a Micromass AutoSpec Ultima^{NT} high-resolution mass spectrometer that was operated in the voltage selected ion recording mode at resolutions greater than 10,000 RP (10% valley definition).

A comparison was made of splitless injection and PTV injection on DB5-ms columns (J&W) of the following dimensions: - 60m, 250μm ID, 0.25 μm film; 40m, 180μm ID, 0.18 μm film and 20m, 180μm ID, 0.18 μm film.

Samples of fresh and farmed salmon, purchased from retail outlets in the Manchester area, as well as fresh spinach, extracted and cleaned up using methods based upon USEPA 1613[1] were then optimised further using the above GC columns. A comparison of results using PTV and splitless injection is presented, demonstrating reduced detection limits and analysis times using PTV and short, thin film columns.

Extraction and clean up

The samples were extracted and cleaned up using standard USEPA 1613 procedures.

Analytical

The mass spectrometer was operated in the voltage selected ion recording mode, at a resolution of 10,000 RP (10% valley) using acquisition systems for DB5-ms column analysis as recommended by USEPA 1613. The dwell times were reduced for some of the faster GC methods, to maintain the number of data points across a GC peak; to retain confidence in reported results.

Initially each GC column was optimised using both PTV injection and Splitless injection using the CS1 – CS5 calibration standards, with emphasis upon GC separation and absolute sensitivity, whilst also reducing the analysis time by the greatest amount possible.

The optimised injection conditions were then compared directly with those used for splitless injection, with a comparison of the detection limits obtained using 1ul splitless injections and larger volume solvent vent PTV injections using sample extracts.

Results and discussion

Initial analysis was carried out using splitless injection (1ul) and a standard J&W 60m DB5-ms capillary column. Using this standard method an LOD of 0.003 ng/kg WHO TEQ was determined, based upon standard analysis and a mass of sample extracted of 40g. Generally salmon samples give approximately 6-7% fat content, which when corrected for gives an LOD of 0.044 ng/kg (fat) WHO TEQ, a limit that easily meets the requirements for detected levels in the UK.

Analysis using a 40m DB5-ms 0.18 ID column mentioned above with similar GC parameters and splitless injection produced similar detection limits, but reduced the analysis time by nearly half.

Using optimised GC conditions and larger volume PTV injections, the 40m 0.18 column proved very reliable, allowing final detection limits based upon sample injections to be much lower than using standard splitless injections. The LOD's using 4ul injections were calculated to be <0.01 ng/kg WHO TEQ on a lipid adjusted basis.

Finally each optimised method was used to compare the levels determinable in salmon and spinach samples, with detection limits calculated on a sample to sample basis. Each sample injection met the detection limits quoted above with ease, and the samples displayed determinable levels falling within previously published[2] UK levels.

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References

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2. Robinson C. (2000), Dioxin 2000 abstract, Vol 47, page 378.