

DETERMINATION OF POLYCHLORINATED BIPHENYL CONGENERS IN FOODSTUFFS AND ANIMAL FEED USING A TRIPLE QUADRUPOLE GC-MS/MS INSTRUMENT

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Introduction

Polychlorinated biphenyls (PCBs) are highly toxic Persistent Organic Pollutants (POPs) with properties that are detrimental to human health and have been linked to causing cancer, endocrine disruption and reproductive disorders. Until their ban in the late 20th Century, PCBs were widely manufactured for use in hundreds of industrial and commercial applications including electrical products and hydraulic equipment and as plasticizers in paints, plastics and, rubber products. Due to their lipophilic properties, PCB congeners that have been released into the environment can bio-accumulate in the tissues of small organisms and fish and thereby enter the Human food chain.

Current legislation in the United States [1] and the European Union (EU) [2] require the confirmation and quantitation of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyl congeners (dl-PCBs) in foodstuffs and animal feed by isotope dilution capillary gas chromatography – high resolution mass spectrometry (GC-HRMS). EU legislation also allows for the screening of these compounds in foodstuffs and animal feeds by other techniques, provided that specific, performance related criteria are met.

A study was undertaken to compare the quantitative performance of a gas chromatograph - triple quadrupole mass spectrometer (GC-MS/MS) system to that of a gas chromatograph - high resolution mass spectrometer (GC-HRMS) system for both dl-PCBs (#77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189) and non-dioxin like polychlorinated biphenyls (ndl-PCBs; #28, 52, 101, 138, 153 and 180). Eighty samples of four different foodstuffs and animal feeds - Cows' milk (n=11), Meat (n=19), Liver (n=5) and Animal Feed (n=45), were extracted and analyzed using GC-HRMS. The same sample vials were then transferred to the GC-MS/MS system and reanalyzed.

Materials and methods

Samples of foodstuff and animal feed were extracted and cleaned up with the final extracts prepared in Toluene. The extracts were analyzed by HR-GCMS using a Waters Autospec M472 at a resolution of R=10,000 and then transferred to an Agilent Technologies 7890A-7000B GC-MS/MS system where the dl- and ndl-PCBs and their ¹³C-labelled internal standards (ISTDs) were analyzed using multiple reaction monitoring (MRM) mode using two MS/MS transitions from two different pre-cursor ions for each analyte and its associated ISTD. The mass spectrometer was operated in electron impact (EI) ionization mode with electron energy set at -78 eV.

Results and discussion:

The agreement between the results (upperbound concentrations) obtained for the total of the 12 dl-PCB congeners on the GC-HRMS and the GC-MS/MS system for foodstuffs and animal feed samples at levels above 1 pg TEQ/g were within the range of $\pm 10\%$. The agreement between the results (upperbound concentrations) obtained for the sum of the 12 dl-PCB congeners on the GC-HRMS and the GC-MS/MS system for foodstuffs and animal feed samples at levels between 0.1 and 1 pg TEQ/g was within the range of $\pm 15\%$. Only those animal feed samples with total dl-PCB congener concentrations below 0.1pg TEQ /g gave some results with percentage differences greater than 15%. This is due to the lower limit of quantitation provided by the GC-HRMS system, but these levels are well below the current action limits and maximum residue limits set for dl-PCBs by EU legislation[3],[4].

The agreement between the sum of the results obtained for the 6 ndl-PCB congeners on the GC-HRMS and the GC-MS/MS system for foodstuffs and animal feed samples at levels between 0.5 and 10 ng/g was within the range of $\pm 10\%$. The GC-MS/MS system demonstrated the ability to determine ndl-PCB concentrations below 1 ng/g product. Some animal feed samples with total ndl-PCB congener concentrations below 0.5 ng/g gave results with percentage differences greater than +10%, but these concentration levels are likely to be well below the action limits set for ndl-PCBs in foodstuffs and animal feed samples by forthcoming EU legislation.

Acknowledgements:**References:**

1. EPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS.
2. Commission Regulation (EC) No 1883/2006 of 19 December 2006 Laying down methods of sampling and analysis for the official control of levels of dioxins and dioxin-like PCBs in certain foodstuffs.
3. Commission Regulation (EC) No 1881/2006 of 19 December 2006 Setting maximum levels for certain contaminants in foodstuffs.
4. Commission Regulation (EC) No 152/2009 Annexe V letter B of 27 January 2009 Laying down the methods of sampling and analysis for the official control of feed.