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ANALYZING MULTI-CLASS PERSISTENT ORGANIC POLLUTANTS (OCPS, PCBS, PBDES, AND PAHS) IN FOOD MATRICES IN A SINGLE INJECTION BY APGC-MS/MS

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Introduction:
The application of gas chromatography coupled to mass spectrometry (GC-MS) is well established and documented for the analysis of ubiquitous environmental contaminants, such as persistent organic pollutants (POPs). Four classes of globally regulated POPs are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and organochlorine pesticides (OCPs).

Here we present the development and validation of a quantitative method for 141 multi-class POP compounds in a variety of foodstuffs to ensure continued monitoring and consumer safety in Quebec, Canada. Time-consuming and costly analyses are a major drain on food and environmental testing laboratories, where multi-analyte methods are preferred for efficient use of resources.

Sample preparation:
Milk, infant formula, beef, pork, chicken, and fish were analyzed for PCB, PBDE, OCP, and PAH compounds using the following generic extraction procedure. Homogenized sample (12 g) was placed in a 50-mL glass centrifuge tube and fortified with internal standard. A smaller sample portion (10 g) was weighed for foods with high fat content (e.g. beef). Water (5 mL) was added to the solid food samples and reconstituted powder milk formulae. Samples were vortexed and allowed to stand for 20 minutes. Ethyl acetate (10 mL) was added and samples were shaken vigorously for 1 minute. QuEChERS salts, magnesium sulphate (4 g), and sodium chloride (2 g) were added to the tubes and shaken vigorously for an additional minute.

Following centrifugation, the supernatant was removed, evaporated, and reconstituted in dichloromethane. It was then filtered through 0.45 μm PTFE filters in preparation for gel permeation chromatography (GPC). EnvirosepABC GPC pre column (60 x 21.2 mm) and column (350 x 21.2 mm) were used, with dichloromethane as eluent (5 mL.min-1). The resultant extract was transferred to a suitable tube for evaporation, where the GPC collection tube was rinsed three times with dichloromethane. These rinses were combined with the original extract and evaporated to 750 μL. The volume was then made up to 1 mL in hexane and silica gel cleanup was performed. Silica columns were prepared by adding silica (2 g) into a 1 cm wide borosilicate glass column with a glass wool frit. These columns were conditioned with 3:1 hexane: dichloromethane solution (12 mL), followed by hexane (8 mL). The samples were loaded and eluted using 3:1 hexane: dichloromethane solution (20 mL). These extracts were evaporated to <0.5 mL, and fortified once more with the internal standard. All samples were made up to 500 μL volume with isooctane, vortexed, and analyzed using the Xevo TQ-S with APGC.

Results and discussion:
The optimization of a single cleanup method for a variety of analytes has been shown to achieve satisfactory recoveries, while allowing Atmospheric Pressure Gas Chromatography (APGC) coupled with tandem quadrupole mass spectrometry to quantify analytes below the regulatory limit. The validated method using TQ-S with APGC was submitted and successfully accredited in accordance with international standard ISO 17025. For ease of discussion, the method's results for multi-class analytes will be demonstrated using pork meat in terms of excellent recoveries, repeatability, linearity, and LODs achieved.

Using the optimized generic sample preparation and cleanup method, the percentage recoveries ranged from 65% to 122% in pork matrix. Percentage relative standard deviations (%RSD) were found to be <20% for all analytes. This is an acceptable level for multi-residue analysis in complex matrices, showing low variance for all of the PBDEs, PCBs, PAHs, and OCPs when spiked at parts per trillion (ppt, equating to ng.kg-1) levels in the complex matrix. Good correlation was achieved (R2>0.99) over a satisfactory

working range of 2 to 25 μg.kg-1. This working range was deemed most appropriate, allowing for the accurate quantification for all analytes at legislated levels where applicable.

The developed method allowed for excellent repeatability for the multi-class components fortified at low levels in a variety of matrices. This is well demonstrated by the validation data to be shown, where excellent recoveries and method repeatability were achieved for all analytes fortified in pork meat (n= 9) at levels between 50 to 1000 ng.kg-1. Furthermore, excellent sensitivity and selectivity were determined, as shown in Figure 1 below for an example analyte from each compound class in pork matrix, spiked at 50 ng.kg-1 and compared against a pork sample blank.

Figure 1: Excellent sensitivity and selectivity determined for 50 fg on column for: A. PBDE #17 and #28; B. methyl-5-chrysene; C. PCB #126; and D. oxychlordane, in comparison to a blank extracted pork sample.

This validated and accredited method has been implemented by the MAPAQ for the routine analysis of a multitude of meats, fish, milk, and infant formula to ensure consumer safety in Quebec, Canada. When compared with traditional GC-EI-MS methods, increased sensitivity, less maintenance, and routine cleaning has been required using this method, further improving laboratory efficiency.