

Determination of polycyclic aromatic hydrocarbons with LC-LC-GC-MS/MS

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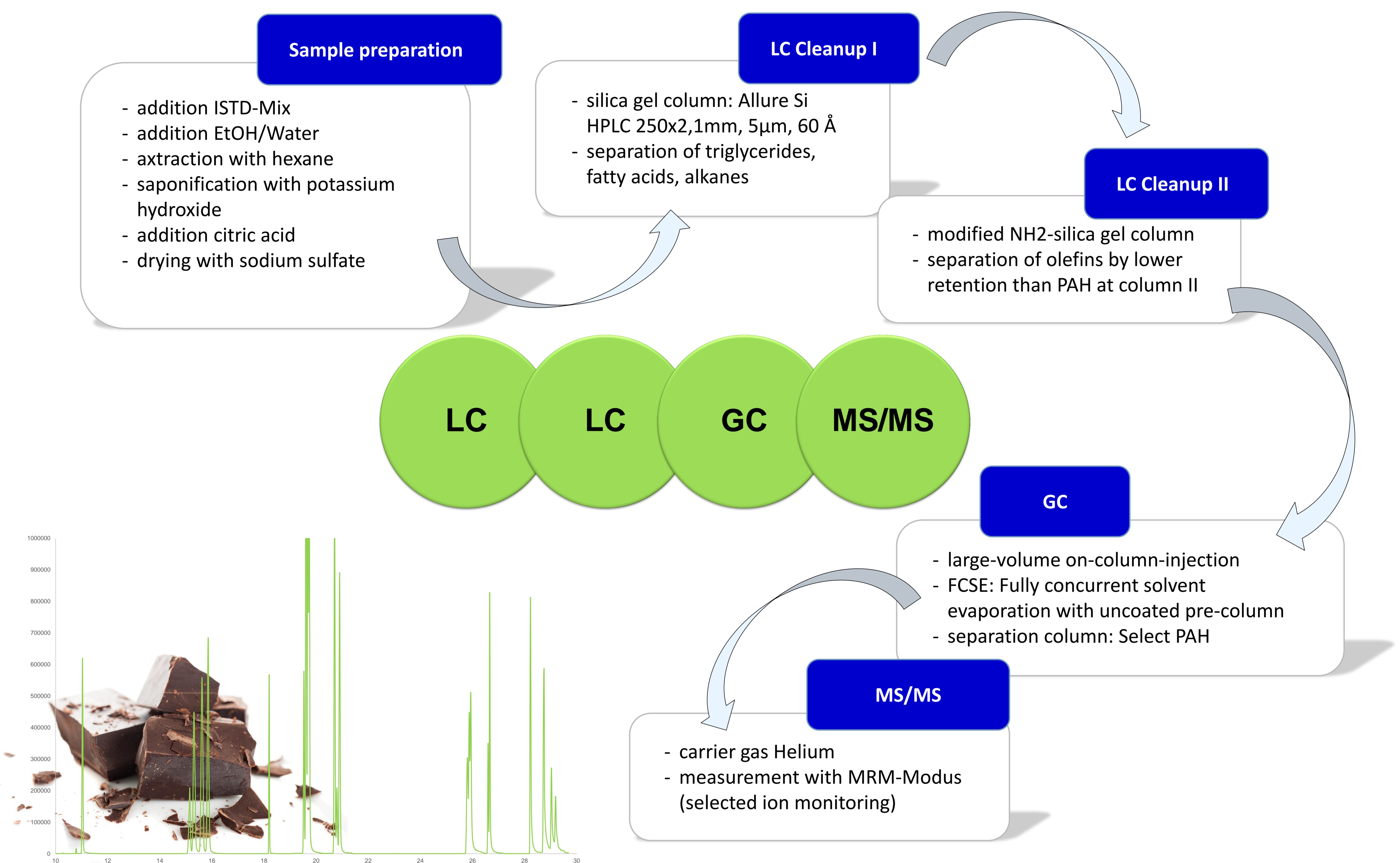
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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are found in many foods due to their ubiquitous presence. All manufacturing and treatment processes, in which foodstuffs are strongly heated or come into contact with combustion gases or fumes, can lead to higher PAH contents of the products. These include drying oilseeds or open-fired cereals, baking bread, roasting coffee, frying and smoking and grilling meat over an open fire. This substance group contains up to 250 different compounds. The acute toxicity of the PAH is low. The potential hazard is primarily due to the carcinogenic properties of some representatives of this substance group. In 2008, EFSA concluded in its opinion that the sum of four specific PAH compounds would best be an indicator for the content of PAHs in food. The PAH 4 includes benzo (a) anthracene, chrysene, benzo (b) fluoranthene and benzo (a) pyrene. Regulation (EC) No. 835/2011 lays down maximum amounts for benzo (a) pyrene and for PAK4 for the particular foodstuffs.



Analytics

The determination of polycyclic aromatic hydrocarbons in foodstuffs using LC-LC-GC-MS/MS requires only a simple and rapid sample preparation compared to the established methods (e.g., GPC purification). The preparation consists merely of an extraction and saponification step. The further cleanup is automated by coupling two HPLC columns. The sample extracts are purified by HPLC (removing triglycerides and biogenic interfering substances), fractionated and the fraction with the PAH is transferred into the gas chromatograph. Subsequent gas chromatographic separation is carried out with a special column for PAH (Select PAH), detection using a mass-selective detector (MS/MS)¹. The Chronos software also optimizes sample preparation by interlacing time. The LC cleanup does not start after the analysis of a previous sample has been completed, it starts the new sample while the analytic at the GC is still running. This significantly reduces waiting times for analytical systems.

Validation

The method presented here was tested for sensitivity, correctness, precision, linearity, and robustness. The quantification limit and detection limit were determined by means of a 10-point calibration with equidistant distances in the range of 0.04-0.4 µg/kg. To determine the precision, correctness and linearity, a 3-fold spiking was carried out on 3 concentration levels on the respective matrix (1, 2 and 5 µg/kg). Table 1 shows the determined performance characteristics of the method compared with the requirements according to Regulation (EC) No. 836/2011. All requirements of the EU Regulation are fulfilled.

Parameter	Validation data of the PAH 4 matrix: fats/oils	Validation data of the PAH 4 matrix: chocolate	Performance criteria according to VO (EG) Nr. 836/2011	Requirements fulfilled?
Repeatability	3,2 – 5,3%	3,8 – 5,9%	Horrat RSD _r < 2 (19%)	✓
Recovery	87 – 92%	89 – 93%	50 -120%	✓
Limit of detection (LOD)	0,03 µg/kg	0,03 µg/kg	≤ 0,3 µg/kg for every PAH	✓
Limit of quantification (LOQ)	0,1 µg/kg	0,1 µg/kg	≤ 0,9 µg/kg for every PAH	✓
Measurement uncertainty*	30-35%	30-40%	-	

*expanded measurement uncertainty, k=2

Reference:

¹ Nestola, M., Friedrich R., Bluhme P., *Anal. Chem.*, 2015, 87 (12), pp 6195–6203, "Universal Route to Polycyclic Aromatic Hydrocarbon Analysis in Foodstuff: Two-Dimensional Heart-Cut Liquid Chromatography-Gas-Chromatography-Mass Spectrometry"