PAH in Oil and Tocopherols
- Analytical challenges to achieve the EC recommendation -

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Introduction

➢ In 2005 the European Commission (EC) define of a maximum level (MRL) for benzo(a)pyrene (BaP) in different foods. [1]

➢ At the same time a recommendation require data of 15 (so-called) heavier PAH (SCF PAH) up to October 2006 to prove BaP as a marker. [2]

➢ Latter one results in new challenges for the analytical part, because seven of the SCF PAH are not included in the analytical scope of the well known EPA PAH.

PAH in oil and tocopherols

➢ Oils and tocopherols (generating the vitamin E effect) are produced from oil seeds.

➢ Direct firing (seed drying process) and adsorption (from the environment) are responsible for PAH contamination of vegetable oils.

➢ Refining reduce amount of these contaminants in the oil. [3]

➢ Tocopherols are extracted from steam distillates as by-products by refining. [4]

➢ PAH are enriched in deodorization distillates.

➢ Depending on type of process, different PAH levels result in the tocopherols.

➢ Tocopherols are residues of the vegetable oil process thus the sample matrix is very complex.

➢ The analysis of vegetable oils require a simply application of gel-permeation chromatography (GPC) before mass spectrometry (GC-MS).

➢ The analysis of tocopherols proved to require a more complex clean up (see Fig. 1). [5]

Method

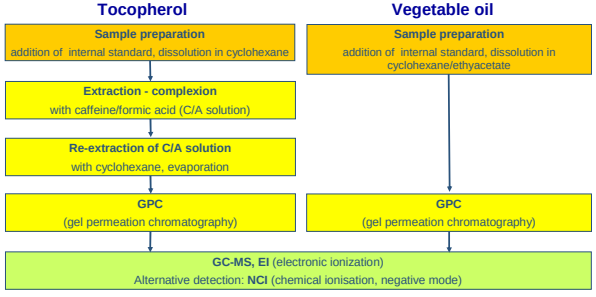

Fig. 1: Workflow of the analytical in-house method for the determination of PAH from oils and tocopherols

PAH in food – opinion and recommendation of the EC

→ The scientific committee in food *concluded that* ***benzo(a)pyrene (BAP)*** *may be used as a* ***marker*** *of occurrence and effect of the* ***carcinogenic PAH in food***, … Furthermore chemical analyses be **continued to collect data** on the whole PAH profile to **evaluate the contamination of food.** [6]

→ The collection of PAH data show a wide range of BaP (determined in 99.3% of all analysed 8861 samples) in different foods, for example see the data of some vegetable oil in Tab. 1 and Fig. 2. [7]

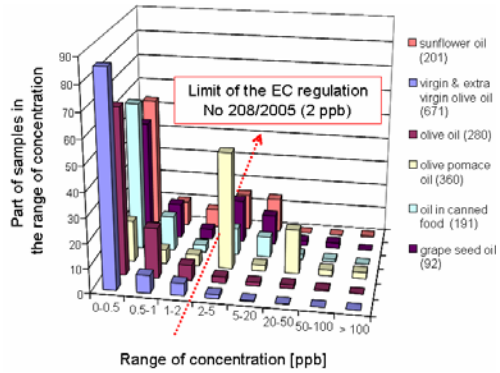

Fig. 2: Part of samples for the amount BaP of different oil samples (number of samples for the oil/pomace) [1,7]

Tab 1: Occurrence of BaP [µg/kg] in different oil samples (source [7])

food group	*number of samples*	mean	median	95th percentile	99th percentile
virgin & extra virgin olive oil	*671*	0.4	0.19	1.2	3.09
olive oil	*280*	1.7	0.25	2.53	33.73
olive pomace oil	*268*	17.7	9.57	70.45	134.96
oil in canned food	*191*	2.62	0.29	9.6	45.57
grape seed oil	*92*	4.2	0.58	16.86	59.17
sunfolwer oil	*201*	3.12	0.4	9.0	13.0

[1] COMMISSION REGULATION (EC) No 208/2005 of 4 February 2005 amending Regulation No 466/2001 as regards polycyclic hydrocarbons
[2] COMMISSION RECOMMENDATION of 4 February 2005 on the further investigations into the levels of polycyclic aromatic hydrocarbons in certain foods (C(2005) 256)
[3] Moret, S., Lanfranco, S. C. (2000) Journal of chromatography A, 882 (245-253)
[4] Tusan, M., Demirci, M. (2005) European Food Research Technology 220 (251-245)
[5] A. N. Sagredos, D. Sinha-Roy, Deutsche Lebensmittel-Rundschau 11 (1979) 350-352
[6] Opinion of the Scientific Committee on Food on the risks to human health of Polycyclic Aromatic Hydrocarbons in food, SC/CS/CNTN/PAH/29 Final, 4 December 2002
[7] Report of experts participating in Task 3.2.12, October 2004, COLLECTION OF OCCURRENCE DATA ON POLYCYCLIC AROMATIC HYDROCARBONS IN FOOD
[8] Collins, J. et al. (1998) Regul. Toxicol. Pharmacol., 28 (45-54)
[9] Jacob, J.; Greim, H. (Ed´s) Polycyclische aromatische Kohlenwasserstoffe (PAH), Forschungsberichte (DFG), Wiley-VCH, Weinheim (2004)

Discussion

→ To legally regulate the amount BaP is an easy and reliable way to exclude the highest contaminated samples (Tab. 1), but higher (more toxic) PAH are not acquired.

→ According to the commission the collection of the PAH [7] show the need to obtain more reliable data, especially for the higher and more carcinogenic PAH, to verify the reliability of BaP as a marker.

→ As a consequence the EC recommendation require values for the following SCF PAH [2]:

The following PAH (BjF excluded) are determinated by the presented method (Fig. 1), some are also detectable by NCI mode :

Benz(a)anthracene (0.1*)
Benz(b)fluoranthene (0.1)
Benz(k)fluoranthene (0.1)
Benz(ghi)perylene (0.01)
Benz(a)pyrene BaP (1)
Chrysene (0.01)
Dibenz(ah)anthracene (5)
Indeno(123cd)pyrene (0.1)

LOQ = 0.5 µg/kg (Method Fig. 1), included in the 16 US EPA PAHs

Cyclopenta(cd)pyrene (0.1)
Dibenzo(ae)pyrene (1)
Dibenzo(ah)pyrene (10)
Dibenzo(ai)pyrene (10)
Dibenzo(al)pyrene (10)
5-Methylchrysene
Benz(j)fluoranthene BjF (0.1)
(detectable as sum (Bb+j+kF)

LOQ = 1.0 µg/kg (Method Fig. 1)

*TEQ = toxicity equivalent, based on toxicity of BaP [8, 9]

Conclusion

➢ The collected PAH data confirm the presence of very different amounts of BaP in oil samples.

➢ While the MRL of the commission exclude the highest contaminated samples, more data of the heavier SCF PAH are necessary to prove the reliability of BaP as a marker.

➢ The presented method allows to detect PAH in oils and, using a more sophisticated clean up procedure, also in the very complex matrix of the tocopherols.

➢ The method allows also to detect the required PAH with low detection limits. The more toxic PAH need the detection of lower values thus lower detection limits are necessary.

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