

Determination of polycyclic aromatic hydrocarbon compounds in edible oils by GC-MS

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Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) is a group of carcinogenic compounds consisting of fused aromatic rings, which is formed due to incomplete combustion of organic substances. The heavy PAHs containing more than four aromatic rings are chemically stable and very toxic. PAHs are lipophilic in nature and often found in edible oils, fats

and food stuffs. In 2005, the European Union Commission Regulation (EC, No 208/2005) set the maximum level of PAH (with benzo[a]pyrene as a marker) in oils and fats to be 2.0 mg/kg. In this study, PAH-selective SPE extraction coupled with GC-MS SIM mode method were used to determine the PAHs in edible oils.

Materials and Methods

Standards and Sample Preparation

Calibration standards were prepared at concentrations of 1, 2, 5, 10, 20, 50 and 100 ng/mL in methylene chloride. Chrysene-d12 was added as the internal standard at 100 ng/mL for quantitation.

Extraction of PAHs from edible oils (sunflower oil and canola oil) were carried out by passing diluted oil samples through molecularly imprinted polymer (MIP) solid phase

extraction (SPE) cartridge; SupelMIP™ SPE-PAHs (from Supelco Analytical) which is customized for effective extraction of PAHs. The elution solvent was evaporated by nitrogen blow, after which the sample was reconstituted. Internal standard compound, Chrysene-d12 was added to the oil sample before extraction [1]. The processed sample was then introduced to GC-MS for subsequent analysis.

Instrument & Analytical Conditions

A highly sensitive GC-MS method was developed by using Shimadzu GCMS-QP2010Plus with AOC-20i+s liquid auto-sampler (Fig. 1) with the analysis conditions as shown in Table 1.



Fig. 1 Shimadzu GCMS-QP2010 Plus with AOC-20i+s



For reference:
Shimadzu GCMS-QP2010 Ultra can be used for the same application.

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Table 1 GC-MS analysis conditions

Gas Chromatograph	
Injector temperature	300°C
Carrier gas	Helium
Injection mode	Splitless
Sampling time	1.00 min
Flow control mode	Linear velocity
Column flow	2 mL/min
Total flow	50 mL/min
High pressure injection	250 kPa for 2 min
Column	Rtx-5MS, 30 m length, 0.25 mm ID, 0.25 µm film thickness
Column oven temperature	60°C (hold for 0 min) Rate 25°C/min to 275°C (hold for 0 min) Rate 20°C/min to 280°C (hold for 5 min) Rate 10°C/min to 300°C (hold for 2 min)
Injection volume	4 µL
Mass Spectrometer	
Interface temperature	250°C
Ion source temperature	200°C
Solvent cut time	2 min
Acquisition mode	Selected Ion Monitoring (SIM)
Event time	0.2 sec
Compound	SIM Monitored ions (<i>m/z</i>)
Fluoranthene/Pyrene	202* , 200, 203
Benz[a]anthracene/Chrysene	226, 228* , 229
Benzo[b]fluoranthene/ Benzo[a]pyrene	250, 252*
Dibenz[a,h]anthracene	276, 278* , 279
Benzo[ghi]perylene/ Indeno[1,2,3-cd]pyrene	274, 276* , 277
Chrysene-d12 (Internal Standard)	236, 240* , 241

*The figures in bold are the quantitative ions

Results and Discussion

A GC-MS method was developed based on Selected Ion Monitoring (SIM) mode and employing the High Pressure Injection (HPI) technique for injecting of 4 µL sample to determine the presence of PAHs in edible oils. Seven-point calibration curves ranging from 1 ng/mL to 100 ng/mL were

established with Internal standard method. The linearity of the calibration curves for the PAHs are shown in Fig. 2. The signal intensity of the target ion and reference ions for each PAH for calibration standard with concentration of 1 ng/mL are displayed in Fig. 3.

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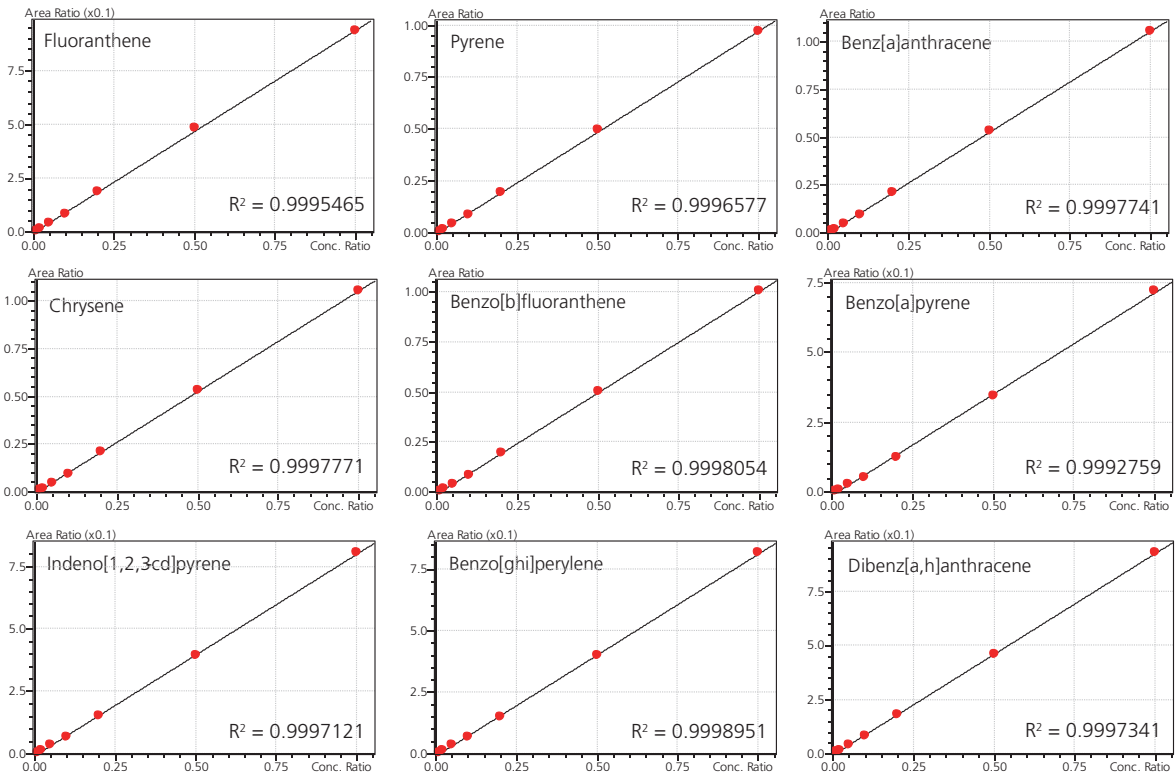


Fig. 2 Internal standard calibration curves of 9 PAHs (1~100 ng/mL)

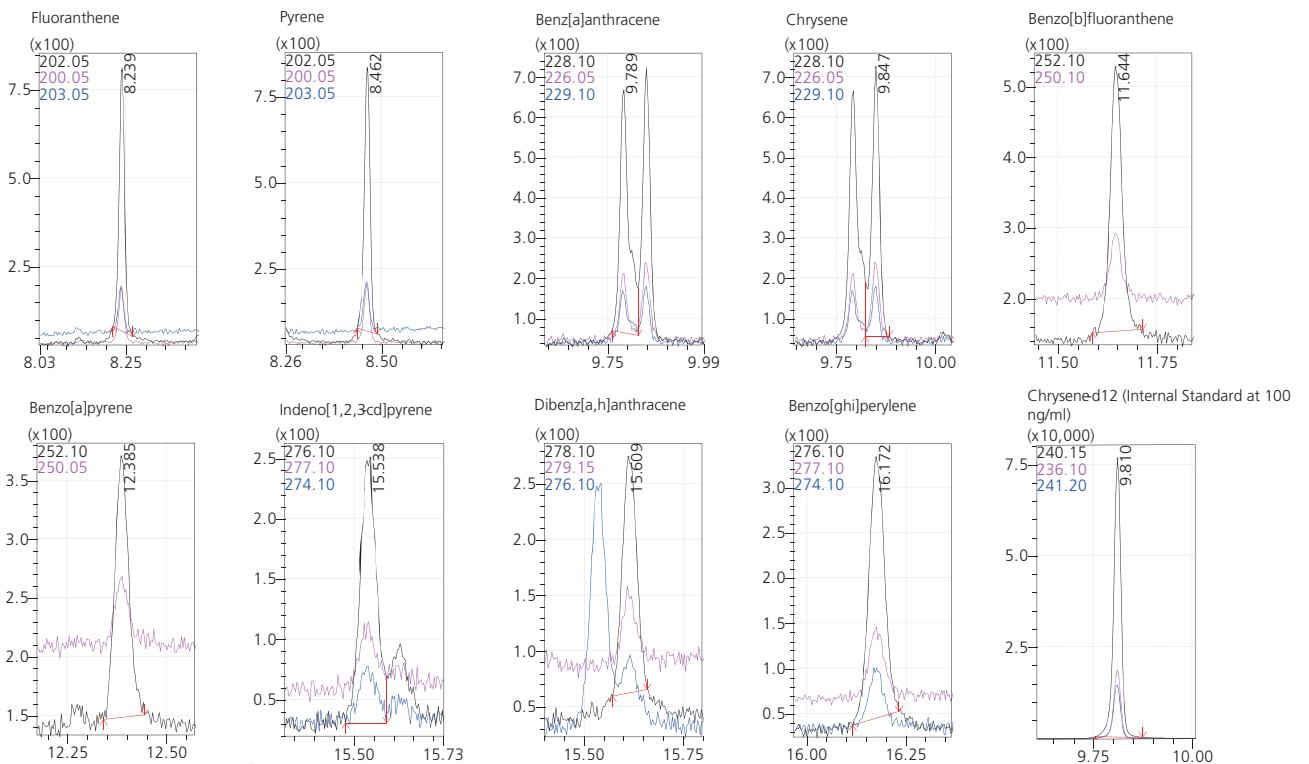


Fig. 3 Calibration standard of PAHs of 1 ng/mL

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Fig. 4 shows the Total Ion Chromatograms (TICs) and the Mass Chromatograms (MCs) obtained from SIM mode for the PAHs standard mixture (100 ng/ml) and the edible oil samples. PAHs were detected in both oil samples

(sunflower oil and canola oil) and the result are summarized in Table 2. An example of the quantitation result for Indeno[1,2,3-cd]pyrene (Peak 7) in sunflower oil is displayed in Fig. 5.

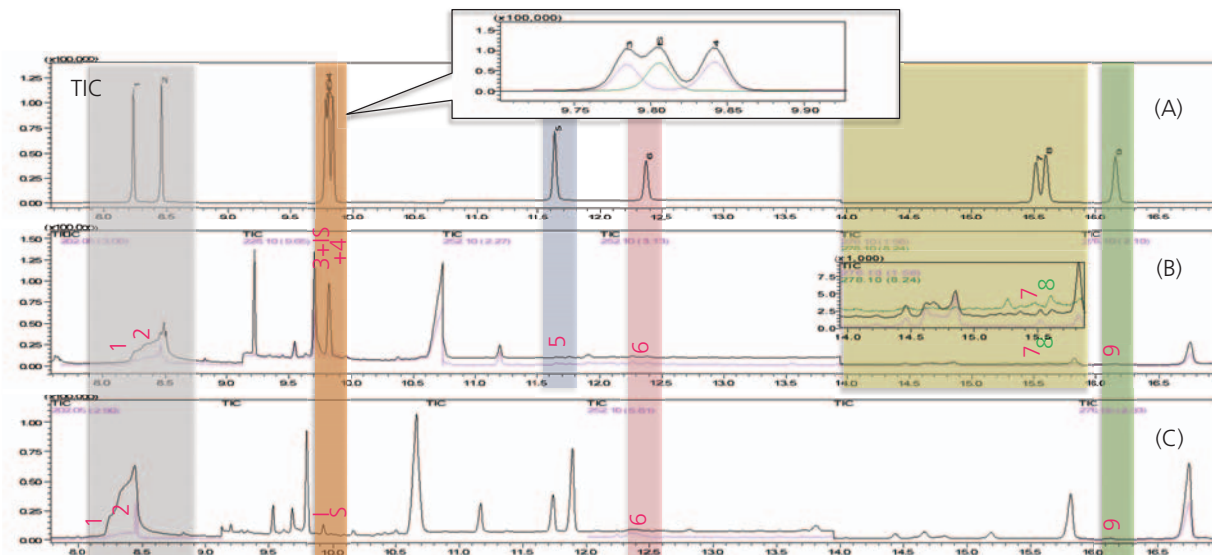
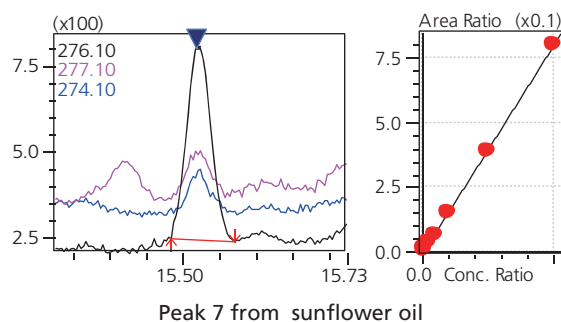


Fig. 4 TICs and MCs obtained from SIM mode of GC-MS
(A) Standard mixture of PAHs (100 ng/mL); (B) Sunflower oil and (C) Canola oil
Legend : TIC (—) and MCs (— & —)

Peak	Compound Name	Concentration ($\mu\text{g}/\text{kg}$)	
		Sunflower oil	Canola oil
1	Fluoranthene	0.3147	0.1834
2	Pyrene	0.9888	1.8457
3	Benz[a]anthracene	0.2253	ND*
4	Chrysene	0.3445	ND*
5	Benzo[b]fluoranthene	0.5140	ND*
6	Benzo[a]pyrene	0.7968	0.5460
7	Indeno[1,2,3-cd]pyrene	0.5511	ND*
8	Dibenz[a,h]anthracene	0.6291	ND*
9	Benzo[ghi]perylene	0.3673	0.3497



Type	m/z	Intensity	Set %	Act %
Target	276.10	548.00	100.00	100.00
Ref. Ion 1	277.10	23.77	23.77	22.08
Ref. Ion 2	274.10	21.20	21.20	19.34

Fig. 5 Quantitation result

Conclusion

A highly selective and sensitive method for determination of PAHs in edible oils was developed. The excellent selectivity of the analysis was due to the PAH-selective MIP-SPE extraction method coupled to SIM mode GC-MS method. Excellent linearity with correlation coefficient (R^2)

greater than 0.999 for all the nine PAHs ranging from 1 ng/mL to 100 ng/mL were obtained. In addition, with SIM mode method and HPI injection technique, good sensitivity for concentration of 1 ng/mL was achieved.

Reference

[1] Supelco Application Note 192, Extraction & Analysis of PAHs in Olive Oil Using SupelMIP SPE-PAH and GC-MS.



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