ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) IN OIL MATRIX

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Polycyclic aromatic hydrocarbons (PAH) are a group of chemicals which compose of two or more fused aromatic rings (*Figure 1*). PAH are ubiquitous in environment. PAH are also commonly used as intermediate in the production of plastics and plasticiser, dyes and pesticides. The increasing demand for manufactured goods from fossil fuels that contained compounds may also contribute PAH to the environment. Furthermore, human activities such as open burning, manufacturing of charcoal, incineration, fumes from vehicles, cigarettes smoking and cooking techniques also contributed to PAH contamination in the environment. PAH are toxic compounds and reduced exposure to these chemicals is proposed due to their toxicity effects and risk to human health. Major sources of exposure to PAH contamination are through contaminated foods and polluted air. Foods can be contaminated with PAH that are present in the air (deposition), soil (transfer) or water (via deposition and transfer), or during improper preparation, processing and cooking of the foods. Processing of food such as drying and smoking at high temperature, grilling, roasting and frying also contributed towards PAH contamination in foods (Guillen, 1997; Philips, 1999). PAH are chemically stable compounds formed in different food matrices. Some of PAH that deposited on the surface of crops might undergo degradation while others might react with components of food matrices during prolong storage (Howard and Fazio, 1980). Mineral oil-based lubricant used in the maintenance of extraction plants could also be the potential source of PAH in vegetable oil (Moret and Conte, 2000).

SCOPE

This test method describes a quantitative method of analysis for determination of PAH namely chrysene, benzo(a)anthracene, benzo(b)fluoranthene and benzo(a)pyrene (PAH4) in oil matrix by high performance liquid chromatography (HPLC) with fluorescence detection (FLD).

METHODOLOGY

PAH in palm oil were determined by on-line coupling of donor-acceptor complex chromatography (DACC) column to an analytical and HPLC with fluorescence detection. The oil samples were eluted over the DACC column which would act as an electron acceptor. The DACC column retained PAH compounds by π-π interaction and the oil components were eluted as waste. The PAH compounds were then transferred on-line to analytical reversed phase column for separation and detected at different wavelengths of 260 nm and 440 nm for excitation and emission respectively. The retention time of individual PAH was used to identify the individual compound. The levels of PAH in oil sample were calculated by external calibration of standards solutions.

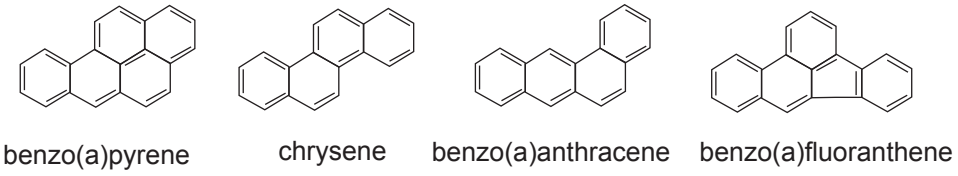

Figure 1. Chemical structures of PAH4.

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BENEFIT

The developed method can be used for simultaneous detection and quantification of sum of PAH4 in vegetable oils as regulated by the European Union. The level for sum of PAH4 is below 10.0 μg kg^{-1} and the level of individually benzo(a)pyrene is below 2.0 μg kg^{-1} respectively.

RESULTS AND DISCUSSIONS

Method validation was carried out based on single laboratory method validation requirements. *Table 1* shows the spiking levels used for recovery studies. Linear calibration curves for four compounds of PAH was successfully established with R^2, ranging from 0.9993 - 0.9998 (*Figure 3*). The limit of detection (LOD) was 0.01 ug kg^{-1} and limit of quantification (LOQ) was 0.1 ug kg^{-1}. The recovery was higher 90% (*Table 2*). The retention time of PAH4 was used to identify the individual compound (*Figure 2*). The levels of PAH4 in oil samples were calculated based on external calibration curve. Cross-check study on the performance of method of analysis showed that the results from MPOB laboratory were comparable to the European Union Reference Laboratory (*Table 3*).

CONCLUSION

The method can be easily applied for routine analysis of PAH4 in palm oil product. The HPLC instrument used for the analysis can be easily maintained and optimised to meet the required conditions.

INDICATIVE COST

The cost for analysis is RM 350 per sample per element, including sample preparation and analysis. Additional RM 100 per element is charged to the sample for multi element analysis. The cost is subjected to change without prior notice.

TABLE 1. SPIKING LEVELS OF STANDARD SOLUTION OF PAH4 IN AN APPROXIMATELY 1.0 g OIL SAMPLES

PAH	Std. conc. (μg ml^{-1})	Level 1 (μg kg^{-1})	Level 2 (μg kg^{-1})	Level 3 (μg kg^{-1})	Level 4 (μg kg^{-1})	Level 5 (μg kg^{-1})
Benzo(a)anthracene	4.02	1.99	3.99	10.05	20.10	40.20
Chrysene	3.64	1.80	3.61	9.10	18.20	36.40
Benzo(b)flouranthene	4.12	2.04	4.09	10.30	20.60	41.20
Benzo(a)pyrene	4.84	2.40	4.80	12.10	24.20	48.40
Total	-	8.20	16.49	41.55	83.1	166.2

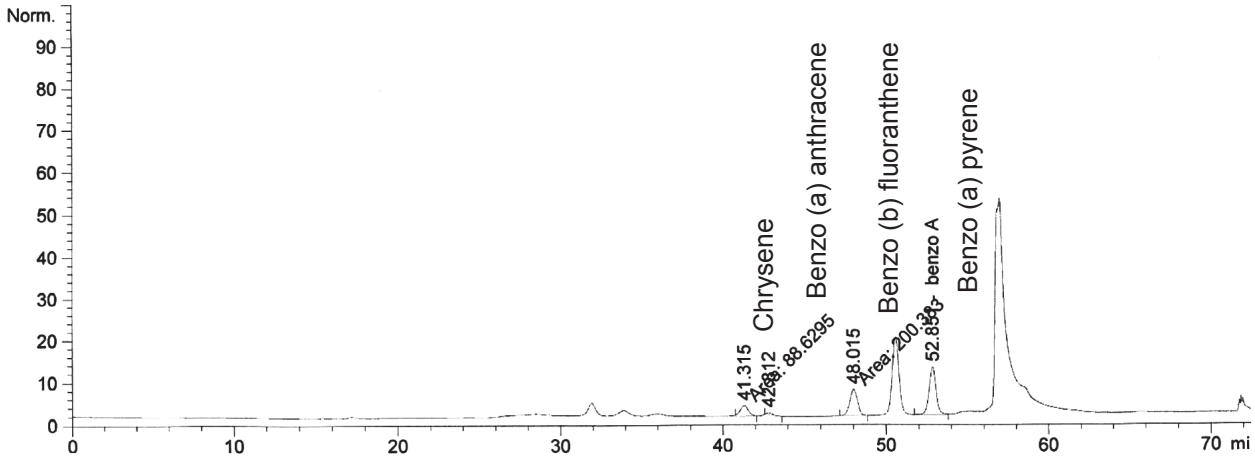

Figure 2. HPLC chromatogram for PAH4 detected at different retention times.

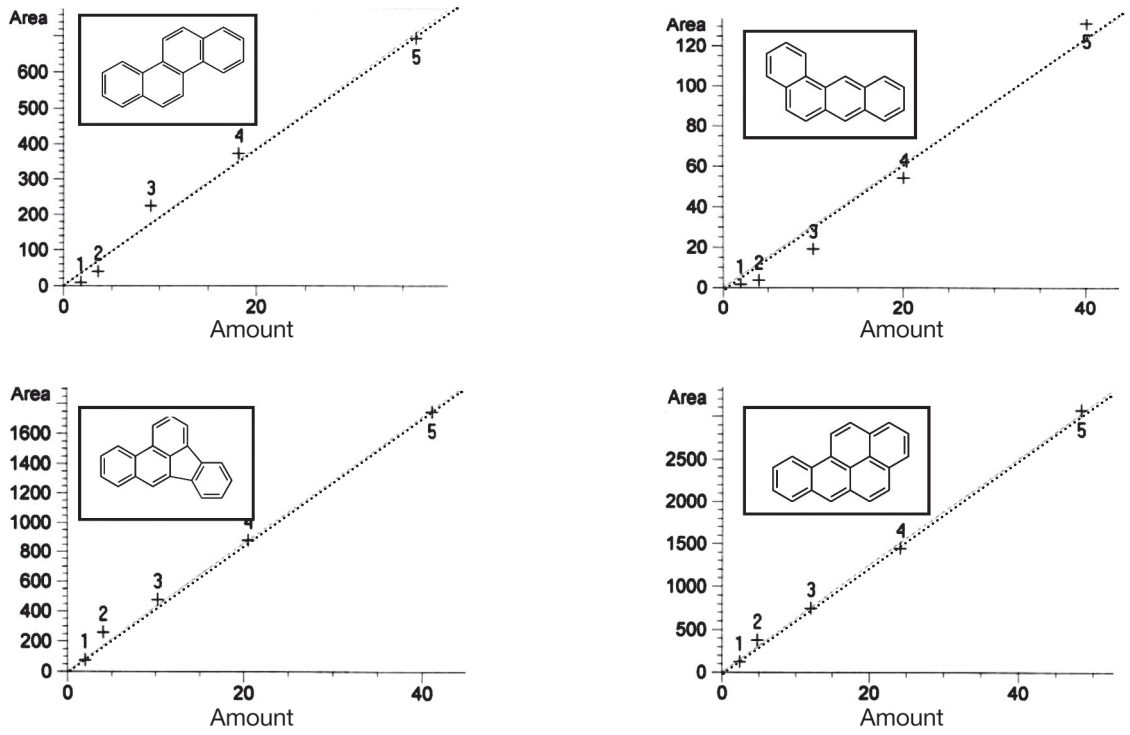

Figure 3. Matrix-matched calibration curve for individual PAH.

RECOVERY STUDIES

TABLE 2. PERCENTAGE RECOVERY FROM SPIKED SAMPLES

Level	Standard concentration (ppb)	Spiking volume / weight (µl)	Sample concentration (ppb)	% Recovery
1	8.20	0.5/1g	9.20	112.0
2	16.49	1.0/1g	16.25	98.5

CROSS-CHECK ANALYSIS

TABLE 3. CROSS-CHECK RESULTS FOR CONTAMINATED SAMPLES RECEIVED FROM NORTHERN AREA

Laboratory	PAH4 (ppb)	B(a)P (ppb)
Greece	14.35	3.73
Dr A Verwey	14.00	3.00
MPOB	14.19	3.04
MPOB	5.39	0.93
MPOB	4.06	0.13
MPOB	6.65	1.32

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