ANALYSIS OF HYDROCARBONS (ALKANES) IN OIL MATRIX

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The European Food Safety Authority (EFSA) Scientific Opinion (2012) defined mineral oils as a complex mixture of hydrocarbons that constitute of mineral oil substituted hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH). MOSH contains straight or branched alkanes and alkylated cycloalkanes. While the MOAH, it contains aromatic hydrocarbons including alkyl-substituted.

Contamination of vegetable oils with the mineral oil occurred in 2008 when contamination of sunflower oil from Ukraine was detected from unknown origin. In 2009, contamination of walnut oil with food grade lubricant oil during refining process was reported in the European Union countries followed by identification of compounds eluted as mineral oil in grape seed oils in 2010.

The permitted levels of mineral oil in vegetable oils are still under discussion by the European Opinion of the Scientific Panel on Contaminants in the Food Chain (CONTAM). Furthermore, the exposure to MOAH and MOSH through food is potentially concerned due to migration of the mineral oil into dry food packed in recycled paperboard without barrier that can contribute significantly to the total dietary exposure.

In the palm oil industry, there are some reports and published papers on the method of analysis for lubricants in palm-based oleochemical products (Moh and Tang, 1999; 2000; 2001). The published methods are significantly for quality assurance purposes due to some problems to quantify the unresolved complex mixture (UCM) of hydrocarbons and the hump shape found in GC chromatogram was recognised as the presence of mineral oil contamination. Therefore, a quantitative method for determination of the UCM was developed and established based on the ISO method which was already adopted in the European Union countries.

Contamination of edible oil with thermal oil during processing may occur if precautionary steps are not taken. Moret and Conte (2008) reported that traces of lubricant, used in the maintenance of extraction plants could also be occasionally found in the vegetable oils. In Malaysia, the processing of palm and palm kernel oils into edible products involved a series of unit operations, which required heating. Deodorisation of edible oil at high temperature of about 240°C - 270°C is normally required for efficient separation and removal of volatile compounds. The temperature can be achieved either through direct electrical heating, or more commonly, by indirect heating with coils through which thermal heating fluid (THF) or high pressure steam is circulated (Rossell, 1993).

The mineral oil hydrocarbons mixtures are difficult to resolve into individual compounds for the analytical quantification. However, the quantification of total MOSH and MOAH and rough separation of paraffin and naphthene with MOSH is feasible with the current techniques available. The analysis of mineral oils has been intensively researched by scientist from the Suisse Authority Laboratory (Fiselier *et al.*, 2009).

In the developed method, the limit of detection (LOD) and limit of quantification (LOQ) in hexane were 0.005 $\mu g.\ ml^{-1}$ and 0. 010 $\mu g\ ml^{-1}$ respectively and the LOQ in palm oil was 0.020 $\mu g.\ g^{-1}$. The efficiency of the process, measured through the recoveries from spiked samples of palm oil was higher than 95%.

SCOPE

This test method describes a quantitative method of analysis for determination of mineral oil hydrocarbons (C10 - C56) in oil matrix by gas chromatographic flame ionisation detector (FID).

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METHOD

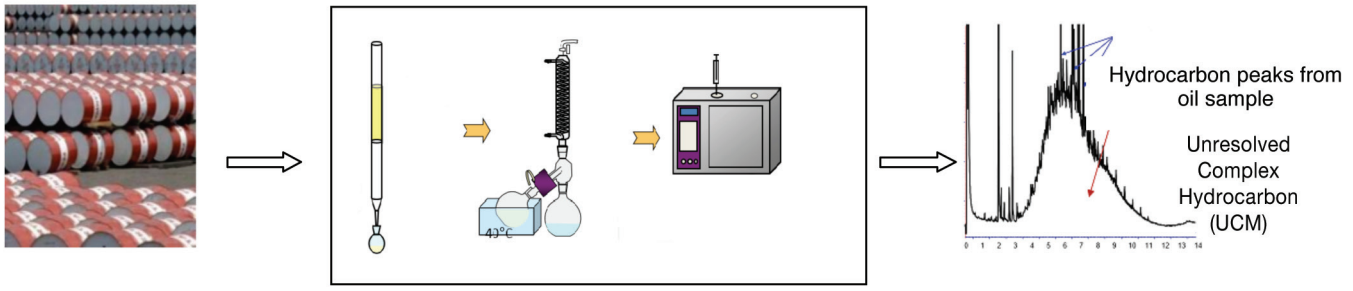


Figure 1. Method procedure for determination of hydrocarbons in palm oil products.

PRINCIPLE

Determination of mineral oil hydrocarbons in palm oil involved extraction process using column chromatography with silver nitrate impregnated silica gel (SNISG) to eliminate the fat matter. The chemical reaction of the double bonds in the fatty acids with silver ions formed a reversible complex compound and reduced the mobility of the fatty acids. Meanwhile, the mineral ions were not affected by the silver nitrate to elute MOH from the column chromatography. The column was eluted with hexane using a vacuum pump and the final extract was concentrated and analysed by gas chromatography (GC) with FID (*Figure 1*).

The principle of the analysis is summarised as follows:

- fractionation of the sample by liquid chromatography on silica gel and silica gel impregnated with $AgNO_3$ for processed and crude oil respectively;
- quantification with internal standard, C18; and
- GC/FID analysis on a short polar column.

BENEFIT

The developed method can be used for quantification of UCM of hydrocarbons (C10-C56) in palm oil.

RESULTS

Method validation was carried out based on single laboratory method validation. The LOD and LOQ in hexane solvent was 5.0 mg. kg^{-1} and 10.0 mg. kg^{-1} respectively. The LOQ in palm oil was 20 mg. kg^{-1}. The standard calibration was established with Regression Linear, R^2 of 0.9983 (*Figures 4* and *5*). The GC chromatograms of mineral oils detected at LOD and LOQ in hexane solvent are shown in *Figures 2* and *3*.

RECOVERIES STUDY

TABLE 1. RECOVERY OF MINERAL OIL HYDROCARBONS FROM SPIKED SAMPLES

Spiked concentration (ppm)	Recovery (%)
10	99
20	96
40	98

Table 1 shows good recoveries of mineral oils from spiked samples at three concentration levels obtained from the developed method and linear calibration curve was established with Regression Linear of $R^2 = 0.9983$. *Figure 6* shows the superimposed GC chromatogram of palm oil sample and spiked palm oil sample at 10 ug. kg^{-1}.

Calculation of Hydrocarbons (C10-C56) Content in Oil Matrix

The content of hydrocarbons in the UCM was calculated by determining the mass fraction of total hydrocarbons (W_{HC1}). The mass fraction was determined by integrating manually the total signal composed of UCM and the sharp peaks above the UCM from the point that baseline started to increase until the baseline at the retention time of n-octatetracontane (C_{48}). The mass fraction of hydrocarbons of natural origin (W_{HC2}) was obtained by re-integrating the chromatogram. The integration of the chromatogram was carried out by tracing manually the valley-to-valley baseline over the UCM profile for all the sharp peaks even the small ones. In the case of n-octadecane, C_{18} lied on the UCM peak, the area of the mass fraction of

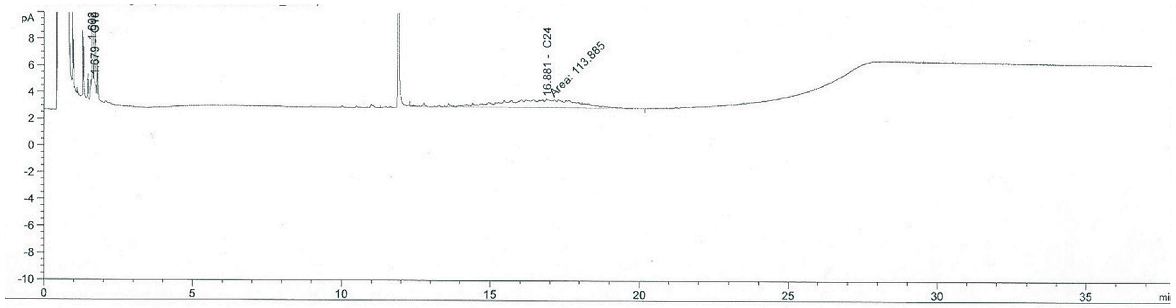


Figure 2. GC chromatogram for LOD at 5.0 ug ml^{-1} in hexane.

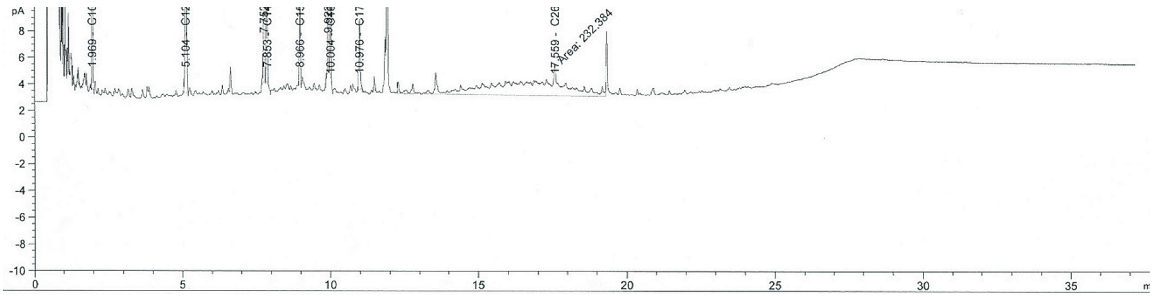


Figure 3. GC chromatogram for LOQ at 10 ug ml^{-1} in hexane.

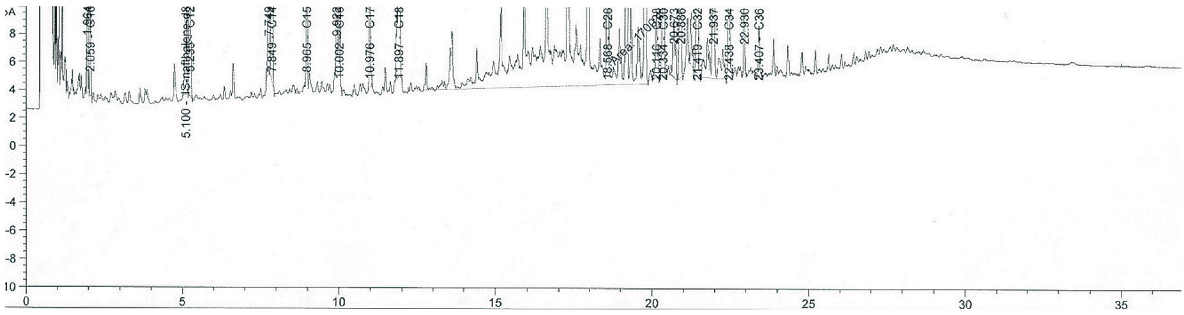


Figure 4. GC chromatogram for LOQ at 20.0 mg kg^{-1} in palm oil.

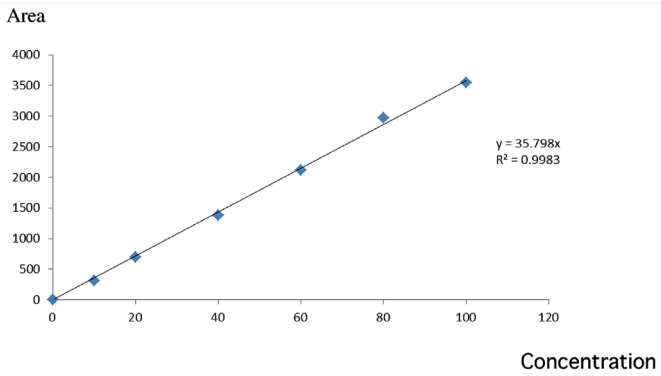
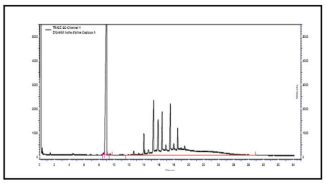


Figure 5. Standard calibration curve.

W_{HC} of the hydrocarbons content was calculated as follows:

$$W_{HC} = \frac{\Sigma A_i . m_{is} . 1000}{A_{is} . m}$$



where,

ΣA_i is the peak area of all peaks other than the internal standard peak (either the peaks above the UCM only for W_{HC2}, or the UCM + the peaks above the UCM for W_{HC1}).

A_{is} is the peak area of the internal standard peak.

m_{is} is the mass, milligram, of the internal standard in 1 ml solution.

m is the mass of the test portion, in grams.

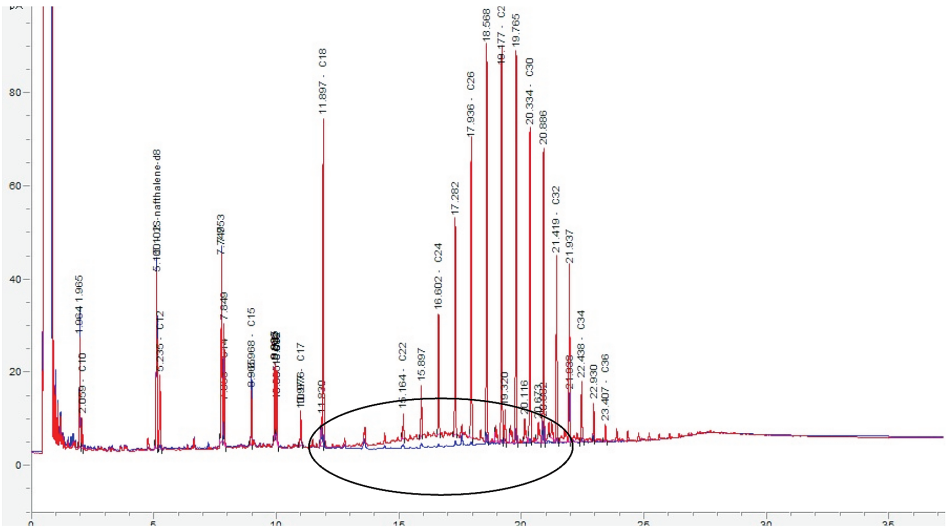
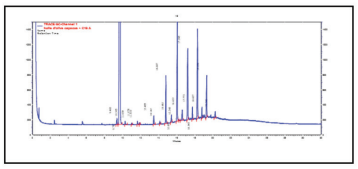


Figure 6. Superimposed GC chromatograms of palm oil sample and spiked sample at concentration level of 10 ug. kg^{-1}.

The content of hydrocarbons attributed to mineral origin ($W_{MO\text{-}C10\text{-}C56,}$ expressed as a mass fraction in milligrams per kilogram), was calculated as follows:

$$W_{MO} = W_{HC1} - W_{HC2}$$



CONCLUSION

MPOB has successfully developed a quantitative method for determination of hydrocarbons (C10-C56) in palm oil and the method can be applied for routine analysis.

INDICATIVE COST

The cost of analysis per sample is RM 500 and is subject to change.

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