ISOPRENOID HYDROCARBONS AS FINGERPRINTS FOR IDENTIFICATION OF SPILL OILS IN INDONESIAN MARINE ENVIRONMENT

by

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ABSTRACT

Along with the increasing transport of crude oils to the refinery sites, many accidents of oil spills have been occurred in Indonesian waters. Such spills might be purely an accident but some others are suspected to be deliberately spilled. Nevertheless, both cases need an identification system to trace back the spill source and eventually the spill data can be brought to the court as an evident.

Previously, the identification system was conducted through a pattern recognition of n-paraffin hydrocarbons of crude oil samples which are very distinguished from their gas chromatographic (GC) pattern of n-C_{17}*, Pristane, n-*C_{18}*, Phytane, and other n-paraffin's down to n-*C_{30}*. Unfortunately, some crude oils have similar pattern that matching of two chromatograms could give an ambiguity result.*

Pattern recognition of isoprenoid hydrocarbons have been developed to characterized crude oils that potentially pollute the Indonesian waters. Differing from the n-paraffin that each hydrocarbon peak can be determined definitely, the developed method does not need to identify each of the isoprenoid hydrocarbons, instead pattern of their chromatographic separation are sufficiently distinguished. GC isoprenoid pattern recognition is made from the isoprenoid peaks that emerge between n-C_{17} *and n-*C_{18}*. It two crude oils having similar pattern of n-paraffin's show very distinct pattern of iso-paraffin's. The method thus can be used as complimentary step in matching the GC pattern of crude oil samples.*

Although in some cases GC isoprenoid peaks are not completely separated, this would not be disadvantages since their retention time and area can be measured and integrated definitely, respectively. Nevertheless, the separation of iso-paraffin peaks can be easily conducted using a recent GC method namely a comprehensive two dimensional gas chromatography (GCxGC), a method which is recommended to be implemented further in this research.

Key words: fingerprints, pattern recognition, n-paraffin.

I. INTRODUCTION

Crude oils are recovered, transported and transferred in large quantities through the world. The pollution of the marine, coastal and harbor environments by crude oils and its products continues to be an issue around the world. In an archipelago country such as Indonesia, Indonesian coasts and waters are continually affected by crude oil pollution. The pollution might arise by natural seepage from the sea floor, but typically it occurs as a result of an accident, such as a well, shipping or bunkering incident, or by deliberate discharge from the bilges of vessels.

Bilge discharges are subject to the MARPOL Regulations. A discharge that is in compliance with these regulations should not lead to pollution of the shoreline and pollute the sea water. Discharges that contain high concentration of oily material are illegal and the perpetrator might be sought. Responsibility is sometimes declared without recourse to evidential proof, but evidence of culpability is generally required. Legal proceedings may follow and the desire for successful court prosecutions has been a strong driver to improve the efficacy of means to identify the culprit.

In order to trace back the spill oils, we have attempted to develop a method of fingerprinting of crude oils. Previously we have tried to use n-paraffin pattern of crude oils*(1,2,3)*. The fingerprinting methods used in that experiment were gas chromatography and infrared spectrometry methods. Although infrared method also gave positive results, the infrared spectra pattern was often influenced by light fraction of hydrocarbons. Many of light hydrocarbon groups disappeared in the infrared spectrum causing ambiguous results when matching between fresh and weathered crude oils.

Gas chromatography (GC) method has been used mostly in the petroleum laboratories. The powerful of GC in separating thousands of hydrocarbons in crude oil and its products is undisputable. Unlike spectroscopic methods that rely on the chemical groups of compounds, GC separates a mixture to an individual compound. In case of crude oils and their products, the separation of hydrocarbon mixture is based on the boiling point of the hydrocarbon compounds. It is, therefore, we can choose or analyze the chromatogram according to the boiling range of hydrocarbons, which are indicated by their retention time in the chromatogram. We can neglect, for example, the light fraction of hydrocarbons for the purpose of fingerprinting of weathered crude oils.

GC can be considered as "back horse" method in characterizing and fingerprinting crude oil and its products(4). More over, unlike with the spectroscopy instruments, such as infrared spectrophotometer, most petroleum and environmental laboratories possess the GC instruments. Another method such as Gas chromatography-Mass Spectroscopy (GC-MS) method is undoubtedly a powerful method for fingerprinting of crude oils and its products(5)**.** The only disadvantages of GC-MS method is, beside of its price, it needs skilled technicians and careful maintenance of the instrument. In addition, only very few laboratories in Indonesia possess GC-MS instrument.

This report describes our works regarding with the use of GC method for fingerprinting of crude oils that might pollute the Indonesian marine environment. Detail description of the works may be read in an unpublished report*(6)***.**

II. EXPERIMENTAL

Gas Chromatography Analysis

Crude oil samples are prepared by dissolving in n-hexane to separate between malthenes containing hydrocarbons that dissolve in n-hexane and asphalthenes containing polar substances that precipitate. The n-hexane aliquots are then subjected to gas chromatography analysis using instrumental conditions as follows:

Instrument : GC HP 5890 series II
Injector : Split-splitless, split ratio 50 : 0.5
Detector : FID
Column : Capillary Column 30 m x 0.32 mm x 0.25 um DB-5 non-polar station ary phase
Injector temperature : 280 ^{o}C
Detector temperature: 300 oC
Column temperature : Initial Temperature : 35 ^{o}C
: Initial Time : 5 menit
: Program Rate :10 ^{o}C/min
: Hold Temperature : 300 ^{o}C
: Hold Time : 45 min
: Pressure : 8.8 psi
Carrier gas : Helium

Chromatografic Evaluation of n-Paraffin and Iso-paraffin peaks

Chromatograms of the crude oil samples show very distinct peaks of n-paraffin hydrocarbons and iso-paraffin hydrocarbons. The chromatograms are evaluated according to n-paraffin peaks beginning from nC_{17} to $n\text{-}C_{25}$, including Pristane, in which each of n-paraffin peak area and Pristane peak area are normalized to phytane peak area. This normalization technique will give ten numbers of fingerprints of n-paraffins.

The iso-paraffin peaks are chosen that emerge between $n\text{-}C_{17}$ and $n\text{-}C_{18}$. These peaks are not normalized to certain peaks, instead they are evaluated according to their peak area.

The ten numbers of n-paraffin fingerprints and iso-paraffin fingerprints of each crude oil are compared or matched using pattern recognition methods as follows:

- Numeric comparison using relative standard deviation, RSD (Figure 1)
- Numeric comparison using correlation coefficient, r (Figure 2)
- Graphical comparison through x-y scattered and radar graphic.

As shown in Figure 1, each fingerprint number of n-paraffin peaks of a suspect crude oil sample is compared or matched to the related peaks of data base crude oils. The comparison criterion (K1, named as a statistic RSD) is determined statistically from the RSD of the analysis. If the calculated RSD of the two peaks being compared is less or equal to the statistic RSD, the value of comparison (P) is set to be 1, otherwise P is zero. The summation of the values of comparison P indicates the probability of matching. The summation of P of 10 (defined as K2) is assumed to be the most probable match.

Comparison between two series of numbers can also be performed by calculating the value of the correlation coefficient, r. If the value of r is between 0.9 - 1, the two series of number is assumed to be correlated or matched. Otherwise the two series of numbers is non-matched (see Figure 2).

Graphical representation of the series of numbers is simply made using common method such as Microsoft Excell. Two graphical modes are used in this experiment, i.e. x-y scattered and radar graphic.

III. RESULTS AND DISCUSSION

Chromatographic analysis of crude oil samples gave a chromatogram representing separation of hundreds of hydrocarbons as depicted in Figure 3. The n-paraffin hydrocarbons can be distinguished from other hydrocarbons by their very distinct peaks which are very tall and regular. The position of n-C_{17}, Pristane, n-C_{18}, and Phytane hydrocarbons can be easily recognized by their split peaks.

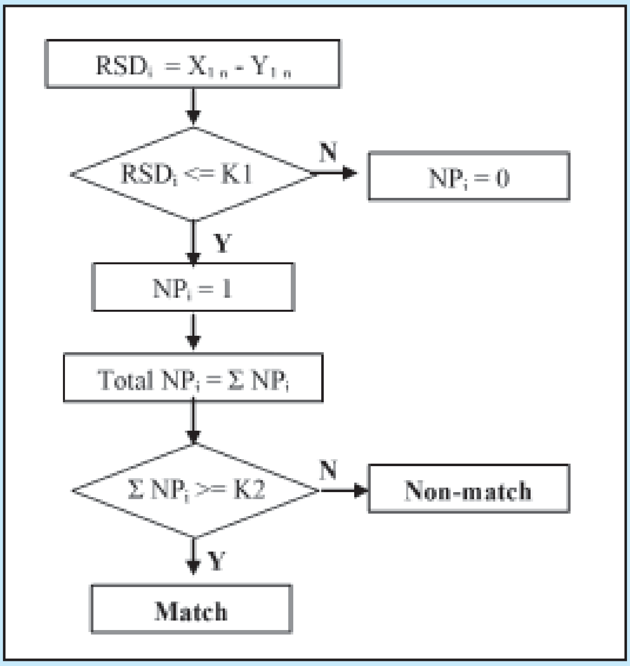

Figure 1
Numeric comparison using relative standard deviation, RSD

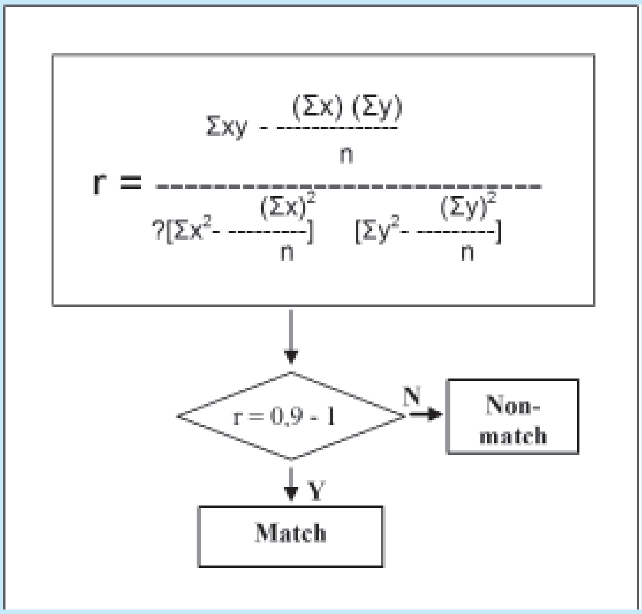

Figure 2
Numeric comparison using correlation coefficient, r

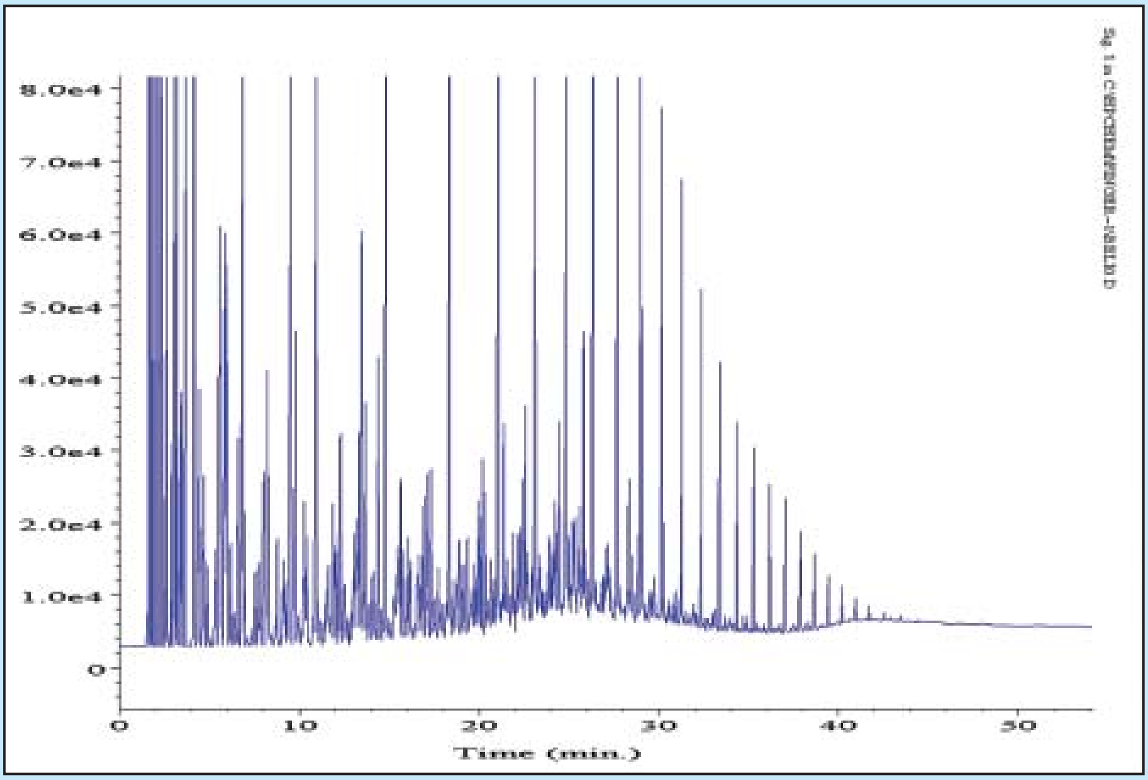

Figure 3
Gas chromatogram of crude oil

These hydrocarbons are identified being two split peaks that are located close each other. The first split peak is n-C_{17} and Pristane and the second one is n-C_{18} and Phytane (see Figure 4).

The position of n-C_{17} and Pristane as well as n-C_{18} and Phytane can be easily recognized by their split peaks

As shown in Figure 3 and Figure 4, the n-paraffin pattern is easily recognized by the regularity of their peaks either the height or the retention time. The logarithmic of the retention time versus the corresponding carbon number of the n-paraffin is linear. This n-paraffin pattern is therefore useful for distinguishing among crude oil samples. Figure 5 shows hydrocarbon peaks of two crude oils having very distinct pattern of n-paraffins.

The pattern recognition method in this research is modeled by rationing the peak area of each n-paraffin peak beginning from n-C_{17} to n-C-$_{25}$ and area of Pristane peak to the area of Phytane peak. These ratios result in a ten series of n-paraffin identity numbers of crude oil samples. This identity can be assumed to be a fingerprint of a crude oil in regard with the n-paraffin pattern. The identity of crude oils can be compared or matched using a computer program by calculating the difference of each number of identities. Table 1 shows an example of identity number of different crude oil samples.

Two series of the identity numbers can be defined as being match if the relative standard deviation (RSD) of each number is less or equal than a criterion (K1) as described in the methodology of this research. The matched numbers are then assigned having a matching value (P) of one, otherwise zero. If the summing up of the matching values is equal to fifteen (K2 criterion), the two crude oil samples are classified to be definitely match, otherwise non-match. The criterion value of K2 may be set to be less than ten depending on the weathering level experienced by the crude oil samples.

In addition to the comparison method mentioned above, the matching of two series of number can also be performed using correlation coefficient of the series. As an example, two series of number of crude A and crude B shown in Table 1 has a correlation coefficient of 0.55, while those of crude A and crude F the correlation coefficient is 0.91. When correlation coefficient is greater than 0.9, such as correlation coefficient between crude A and crude F, the numeric interpretation will still in doubt. In fact, crude A and crude F are different. The correlation coefficient having value of 0.9 to 1.0 is considered that the

Table 1
Identity number of crude oils

Peak No.	Hydrocarbons	Crude oil samples									
		A	B	C	D	E	F	G	H	I	J
1	Prystane	3,01	0,87	3,14	5,35	6,73	3,27	2,47	2,46	1,21	3,01
2	n-C$_{17}$	6,76	1,92	8,26	2,45	2,75	4,32	1,79	5,59	1,23	6,76
3	n-C$_{18}$	5,37	1,54	8,48	2,53	3,18	3,08	0,27	5,41	1,19	5,37
4	n-C$_{19}$	4,39	3,93	8,53	2,49	3,35	2,43	0,36	5,4	1,14	4,39
5	n-C$_{20}$	3,59	1,39	9,04	2,67	3,74	2	0,25	5,69	1,15	3,59
6	n-C$_{21}$	2,76	2,96	9,35	2,68	3,99	1,41	0,1	5,83	0,99	2,76
7	n-C$_{22}$	2,19	0,68	9,56	2,44	4,36	1,09	0,09	5,97	0,86	2,19
8	n-C$_{23}$	1,89	0,15	10,06	2,47	4,86	0,85	0,08	6,42	0,82	1,89
9	n-C$_{24}$	1,58	0,23	9,74	2,23	5,23	0,65	0,08	6,32	0,77	1,58
10	n-C$_{25}$	1,5	0,22	11,32	2,43	6,04	0,54	0,2	7,49	0,68	1,5

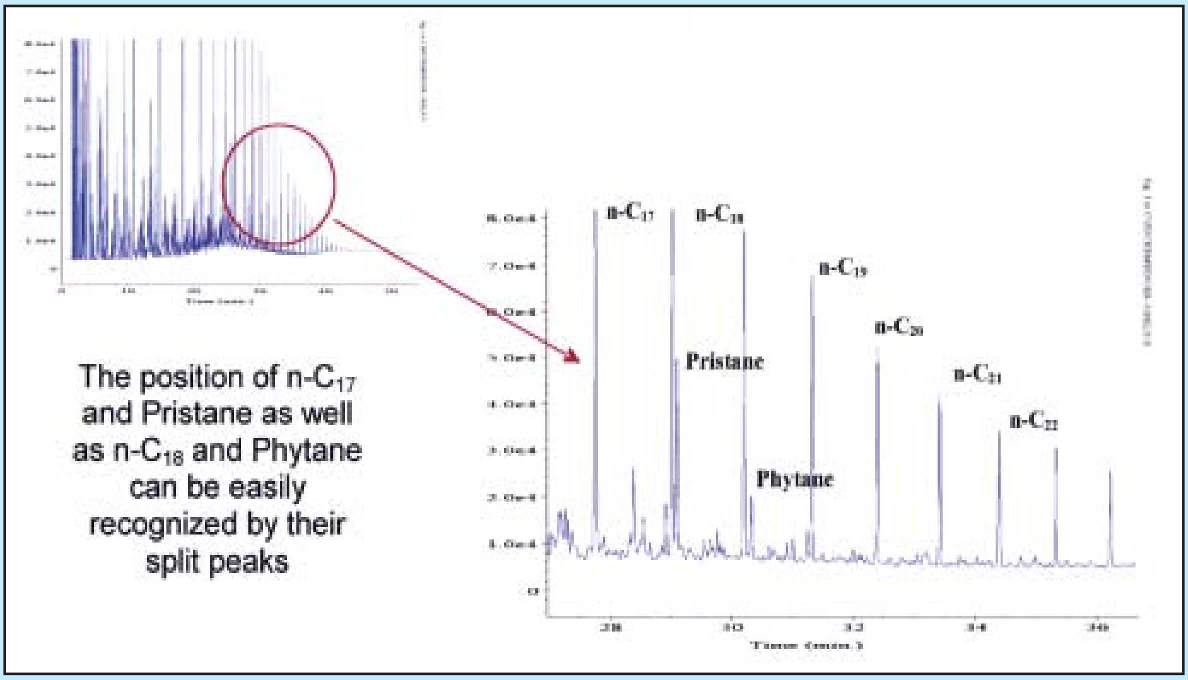

Figure 4
Location of n-C$_{17}$, Pristane, n-C$_{18}$, and Phytane peaks in the gas chromatogram of crude oil

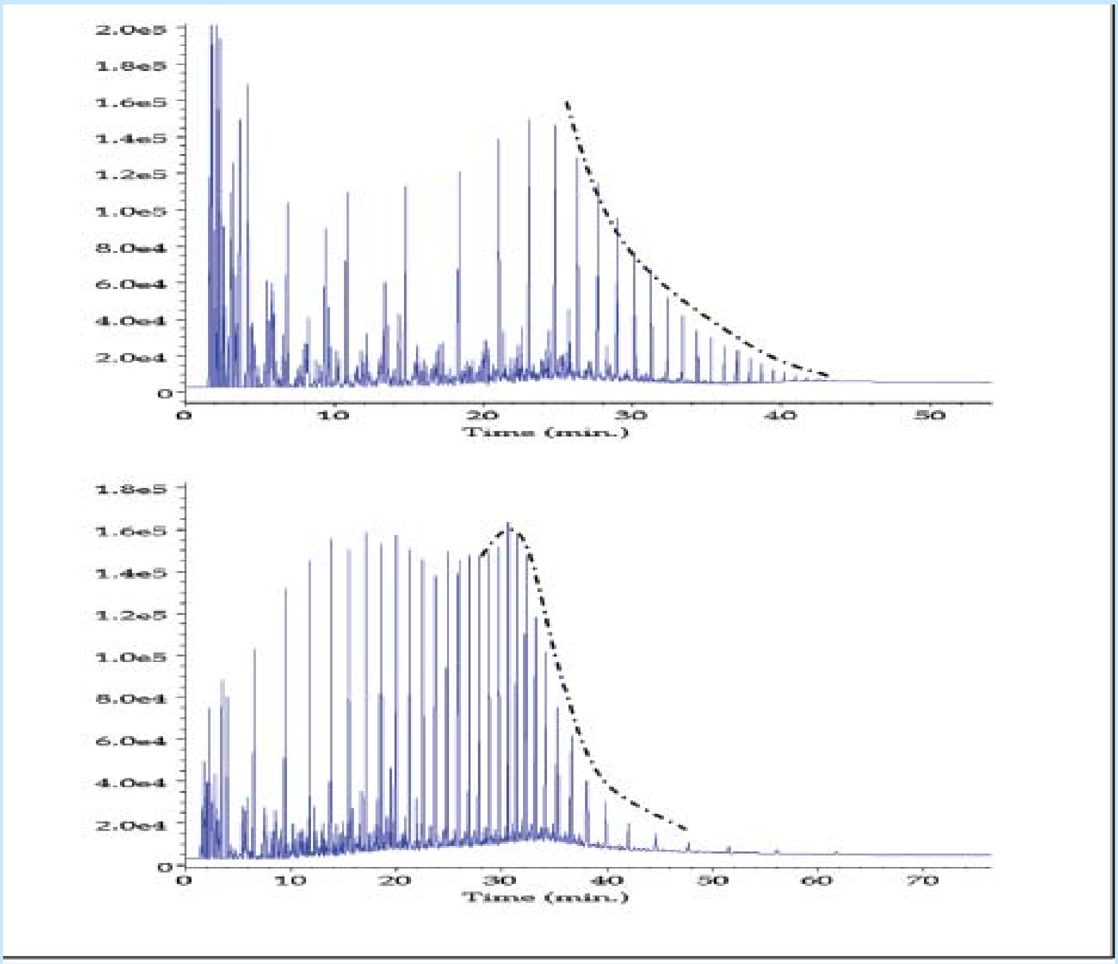

Figure 5
Two crude oil samples having different n-paraffin patern

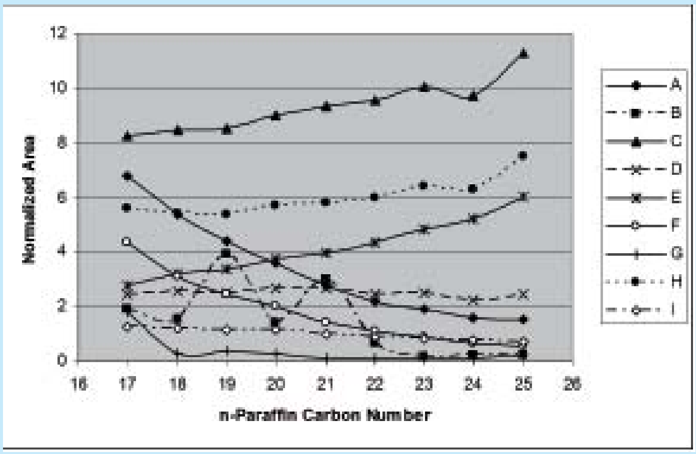

Figure 6
Graphical representation of n-paraffin pattern of crude oils

two series of numbers are correlated. It does not mean that the two series of number are the same. It is clear from Figure 6 that n-paraffin pattern of crude A and crude F are similar.

In order to have a more positive identification, the hydrocarbon patterns of such crude oils having similar n-paraffin pattern are further investigated. The hydrocarbon peaks located between n-paraffin peaks are iso-paraffins, which are commonly named as isoprenoid hydrocarbons (see Figure 7).

Peak areas of the isoprenoid hydrocarbons as depicted in Figure 7 are presented in Table 2. The peak areas are

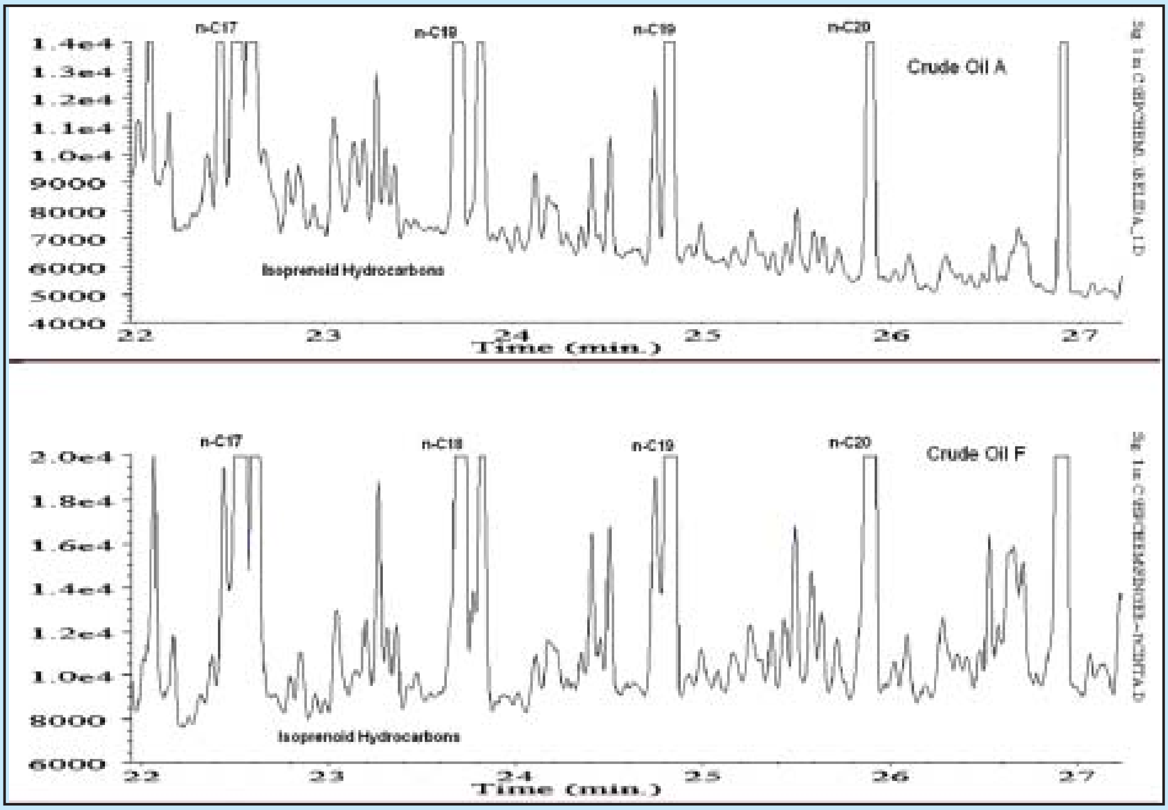

Figure 7
Chromatogram of isoprenoid hydrocarbons of crude oil samples

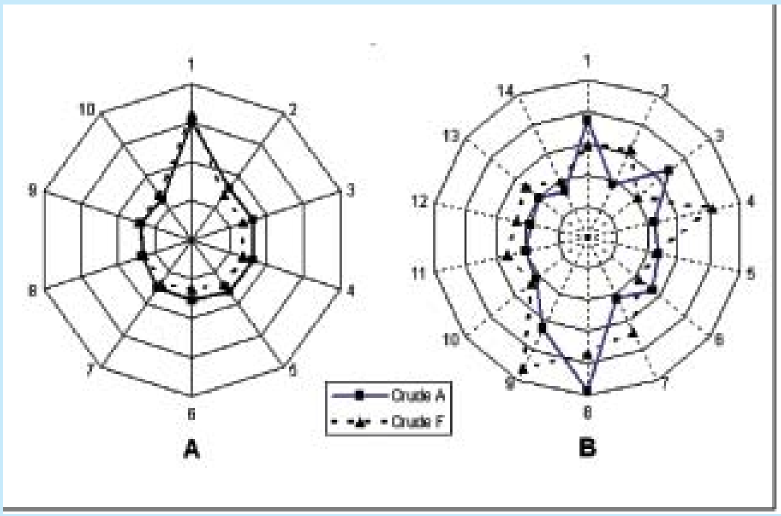

Figure 8
Radar graphic representation of hydrocarbon pattern of two different crude oil samples:
(A) n-paraffin pattern; (B) iso-paraffin pattern

measured for the isoprenoid peaks that located between n-C_{17} and n-C_{18}. The isoprenoid peaks consist of fourteen peaks that are much smaller than n-paraffin peaks. The isoprenoid peaks of crude A and crude F are very distinctive with regard to their relative height or area of the peaks (see dot curves in Figure 7). These peak areas of the isoprenoid hydrocarbons can thus be used as an additional fingerprint of the crude oil samples.

Figure 8 shows hydrocarbon pattern of two different crude oil samples. This figure indicates that even when the n-paraffin pattern of the crude oils shows similarity (Figure 8.A), their iso-paraffin pattern are quite different (Figure

8.B). The different pattern of iso-paraffin, therefore, can be used as complimentary data in case n-paraffin pattern of two crude oils is in doubt.

As depicted in Figure 7, the only disadvantage of iso-paraffin pattern is that the iso-paraffin hydrocarbons are not completely separated, unlike the separation of n-paraffin hydrocarbon. This condition is commonly occurs even when a high resolution capillary column is used for the separation of hydrocarbons in crude oil. The most probable reason is because of the separation depends only on the boiling points of the hydrocarbons. The difficulties in the separation are even worst if the crude oils have been experienced weathering. The complex hydrocarbons that can not be separated will result a hump or UCM, unresolved complex mixture, e.g. cyclic paraffins (naphthenes) and aromatics, which the GC column do not has the capacity to resolve. The use of two dimensional gas chromatography (gc x gc) showed that unresolved iso-paraffin, even UCM, can be completely separated[7-..] **.** This method will be applied in our research for including in the data base of fingerprinting of Indonesian crude oils.

IV. CONCLUSIONS AND RECOMMENDATIONS

After having several experiments, conclusions can be drawn as follows:

- Fingerprinting of Indonesian crude oils can be performed by matching the n-paraffin pattern of the crude oil samples starting from n-C_{17} as preliminary test.
- If the n-parafin pattern indicates similarity and give an ambigue or doubtfull results, then the matching of two crude oils can be further performed using iso-paraffin pattern.
- Matching of the hydrocarbon pattern of crude oils can be performed using standard deviation of each chromatography peak, coefficien correlation, or with the help of scaterred x-y or radar diagram.
- It is worhty to continue the work for collecting crude oil fingerprint data base by using two dimensional chromatography (gc x gc) method, since this method of gc × gc can resolve many of the saturated compounds and provide information previously unattainable with traditional gas chromatography or gas chromatography-mass spectrometry (GC-MS) methods.

REFERENCES

1. Mulyono, M and Murad, A, 1987, “Penyidikan Tumpahan Minyak Bumi dengan Metode Spectrofluorometri”, Proceeding pada Seminar Himpunan Kimia Indonesia, Surabaya.
2. Mulyono, M. and R. Desrina (1988) “Fingerprinting of Crude Oils by the Infrared Spectrophotometry Method”, Proc. 17th Annual Convention Indonesian Petroleum Association, vol. II, Jakarta, pp. 305-310.
3. Mulyono, M., (1989), “Fingerprinting Minyak Bumi”, Laporan Penelitian In-house 1988/1989, Buku 38, Pusat Penelitian dan Pengembangan Teknologi Minyak dan Gas Bumi “LEMIGAS”, Jakarta.
4. Bentz, A.P. (1976), “Oil Spill Identification”, Analytical Chemistry., 48, (6), 454A-472A.
5. Morison, R.D., 2000, Critical Review of Environmental Forensic Techniques: Part II, Environmental Forensics, 1, 175-195
6. Desrina, R., 2007, Inventarisasi dan Identifikasi (Fingerprinting) Minyak Bumi yang Berpotensi Mencemari Lingkungan Perairan Indonesia, Kegiatan No. 05.04.03.0040.1514 A , unpublished report, PPPTMGB “LEMIGAS”, Jakarta.
7. Frysinger, G. S., and Gaines, R. B. 2001. Separation and identification of petroleum biomarkers by comprehensive two-dimensional gas chromatography. J. Sep. Sci. 24:87–96.
8. Frysinger, G. S., Gaines, R. B., and Reddy, C. M. 2002. GC×GC: A new analytical tool for environmental forensics. Environ. Forens 3:27 –34.
9. Frysinger, G. S., Gaines, R. B., Xu, L., and Reddy, C. M. 2003. Resolving the unresolved complex mixture in petroleum-contaminated sediments. Environ. Sci. Technol. 37:1653–1662.