COMPREHENSIVE GC × GC - MS ANALYSIS OF WASTE MOTOR OIL FROM MALAYSIA REVEALS *IN-SITU* PRODUCTION OF PAHs: A NEW POLLUTION SOURCE

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Introduction

Spillage and illegal dumping of waste crankcase oil or leakage of the same from vehicles onto road surfaces with the subsequent washout by street runoff seem to be a continous source of environmental pollution in an era of vehicular transport. To understand and examine this particular source, a detailed study on the chemical composition of the waste oil is needed. GC-MS is an effective technique in the separation of compounds, especially gas chromatography offers good separation and mass spectrometry offers compound identification; hence, it is widely used in environmental forensic studies[1]. However, crankcase oil is ladened with hydrocarbons such as (1) *n*-alkanes; (2) *iso*-alkanes; (3) steranes; (4) terpanes; (5) polynuclear aromatic hydrocarbons (PAHs); (6) aromatic steranes; and (7) specific polycyclic compounds[2]. In this kind of a situation selective detection of target compounds from overlapping co-contaminants is a challenging task. Multidimensional chromatographic techniques have been applied in the determination of polychlorinated biphenyls in complex environmental matrices[3-4]. Incorporating this principle in the comprehensive two dimensional GC × GC technique along with mass spectrometry has added ultra-high separation capability to environmental forensic studies[5-6]. This technology comes handy when separation of target substances from complicated matrices becomes problematic using ordinary GC-MS. We have applied GC × GC - MS technique in the analysis of some waste oil samples from Malaysia and the data were compared with that of GC-MS. Waste motor oil could be an important source of PAHs pollution in Malaysia as vehicular transport is heavy and environmental regulations do not restrict the release of motor oil to the environment strictly. Tropical climate with frequent storms enhance the release of contaminated motor oil to the environment. Application of GC × GC - MS technique under Shimadzu Corporation Analytical Laboratories has identified and confirmed the *in-situ* production of PAHs through pyrolytic processes in motor engine.

Materials and methods

Waste motor oil (crankcase oil) was sampled at 11 automobile repair shops in the district of Selangor, Malaysia. These were uncharacterized, uncategorized oil samples (MY-1,2,3,4,5,6,9,10,11,12,13) as oil was pooled over time in drums (storage tanks). On the other hand, two crankcase oil samples were collected directly from cars that came for repair (MY-7 & 8). One Castrol unused oil (MY-14) and one Yamaha unused oil (MY-15) were also sampled (control). The oil samples were dissolved in isooctane and analyzed directly in GC-MS and GC × GC - MS.

GC × GC - MS was performed on a gas chromatograph - quadrupole mass spectrometer GCMS-QP2010 Ultra (Shimadzu, Kyoto, Japan) and GC × GC modulator (Zoex Corp.). A DB®-1 (J&W Corp., methyl polysiloxane, 15 m × 0.25 mm I.D., 1.0 μm film thickness) and a Rtx®-WAX (Resteck Corp., 2.5 m x 0.1 mm I.D., df=0.1 μm) columns were connected through the GC × GC modulator as the first and second capillary columns, respectively. Results were processed using Zoex GC Image which is a special multipurpose GC × GC analysis software package. It is capable of directly reading GC × GC data obtained with GCMSsolution, converting it to a 2-dimensional image, and then analyzing it.

Results and discussion

The hydrocarbon families in motor lubricating oils are best studied using combined gas chromatography-mass spectrometry in full scan mode. Various homologous series of hydrocarbons were characterized at known fragment ions. The hydrocarbon series that provide the best information are: (1) *n*-alkanes; (2) *iso*-alkanes; (3) steranes; (4) terpanes; (5) polynuclear aromatic hydrocarbons (PAHs); (6) aromatic steranes; and (7) specific polycyclic compounds. Used waste lubricating and unused motor lubricating oils are highly depleted in the paraffinic hydrocarbons (*n*-alkane and *iso*-alkanes)[2]. In spite of that a lot of peaks were detected in a
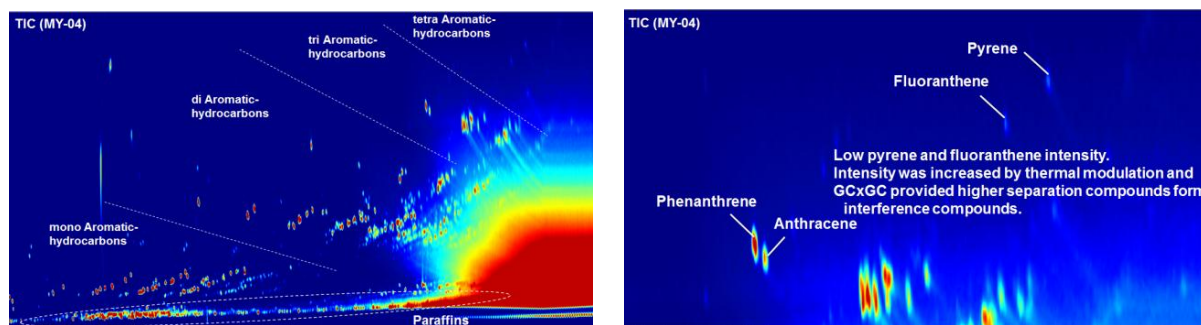

Figure 1. a) 2D Chromatogram of MY-04 used oil

b) Thermal modulation of MY-04 used oil

conventional GC-MS analysis which were overlapping in the total ion chromatogram. On the other hand with GC × GC - MS system incorporating high-polarity second column, it was possible to separate the paraffin from aromatic series, there by obtaining a blob distribution pattern reflecting the compound's structure. Polyaromatic hydrocarbons (PAHs), such as fluoranthene and pyrene, could be separated from oil matrix and their identification was easily performed using mass spectral similarity search (Fig. 1).

Used oil can be differentiated from unused lubricating oil, because it often has low molecular range hydrocarbons which are absent in the unused oil[2]. The area ratios of phenanthrene to anthracene and the area ratios of fluoranthene to pyrene were useful in evaluating and classifying oil sampels. However, while using regular GC-MS technique, anthracene was not detected and the area ratio of fluoranthene/pyrene was lower than
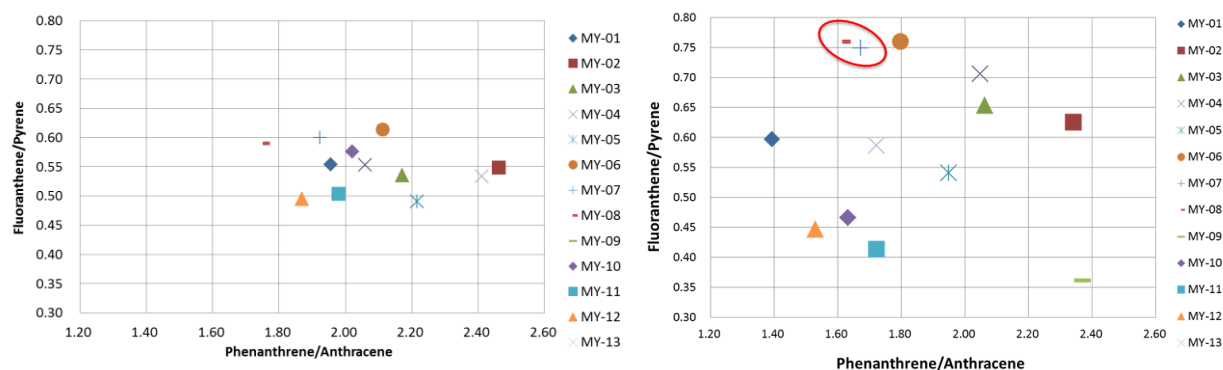

Figure 2. a) Identifying pyrogenic PAHs – GC-MS

b) More clarity in GC×GC-MS (e.g. MY-7&8)

that of the used oils (Fig. 2). The area ratios for thirteen used oil samples obtained from conventional GC-MS analysis did not clarify the differences among the samples. On the other hand, when the same samples were analysed using GC×GC-MS an ultra high resolution separation was obtained and the area ratios calculated based on this analysis distinctly differentiated used oils, unused oils and oils obtained directly from a car (vs pooled samples of various auromobiles over a period of time).
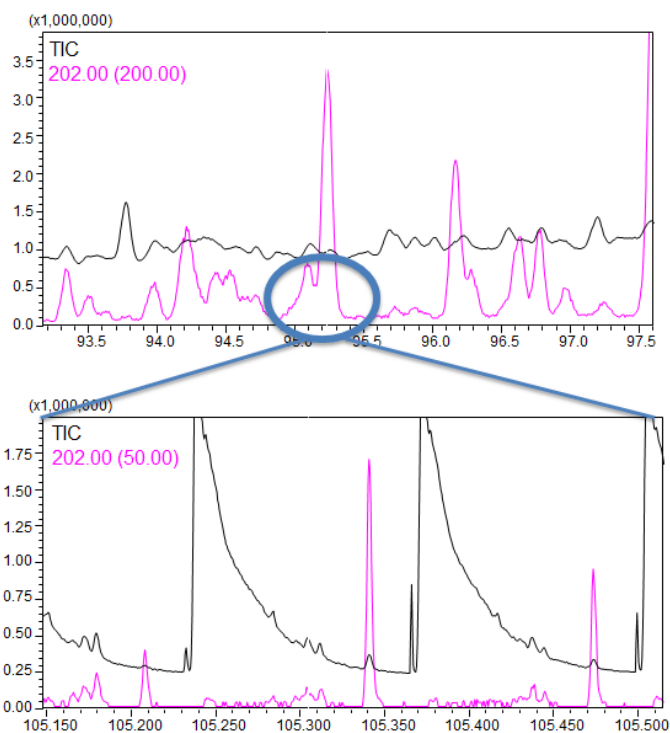
Figure 3. Upper: Phenanthrene identification was marred by alkyl PAHs in a conventional GC-MS system: Lower: GC×GC-MS analysis offered a clear solution to co-elution problems.
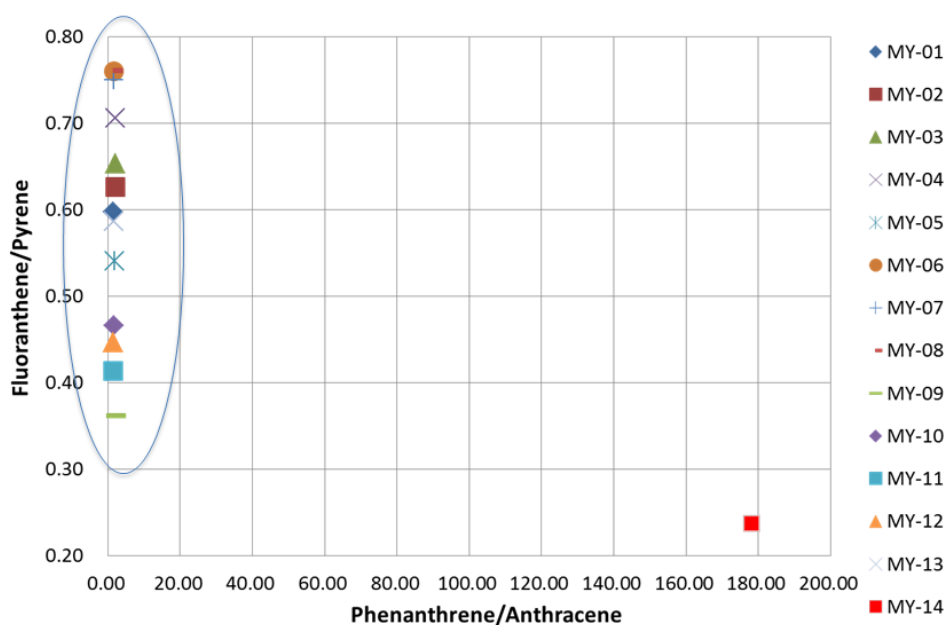

Figure 4. Fluoranthene/Pyrene:Phenanthrene/Anthracene ratios of used and unused crankcase oils revealing *in-situ* synthesis of PAHs during combustion. MY-14 is unused oil sample and the rest are used oil samples.

It has been noticed earlier that used crankcase oil carried pyrogenic and petrogenic signatures of PAHs[1]. Incorporation of unburned fuel (gasoline or diesel) in the car lead to petrogenic signatures while PAHs generated in the combustion chamber in the engine brought pyrogenic signatures to the crankcase oil. The PAHs profile for "fresh" crankcase oil displayed severe depletion of heavy molecular weight PAHs. Hence the ratio of heavy to light (H/L) molecular weight PAHs had been used to identify pyrogenicity[1]. In the same way, fluoranthene and pyrene were often associated during natural matrices analyses and were considered as typical pyrogenic products derived from high-temperature condensation of lower molecular weight aromatic compounds[7]. In fact, phenanthrene and anthracene are two structural isomers. Because of their different physico-chemical properties, they could behave differently in the environment and could lead to different values for their Phe/An ratio that would give useful information on the PAH origin[8]. Phenanthrene is more thermodynamically stable than anthracene, so, Phe/An ratio is observed to be very high in PAH petrogenic pollution, but lower in pyrolytic contamination cases. Similarly, fluoranthene versus pyrene ratios are used to derive the same conclusion. The current research revealed that conventional GC-MS technique might not reveal the concentrations accurately and hence blur the source identification, whereas, GC×GC-MS analysis will result in unambiquitous, accurate and sensitive determination of target compounds even in a complex mixture/matrix. Hence GC×GC-MS technique has identified *in-situ* production of PAHs in automobile combustion processes, thereby, revealing a new source of PAHs pollution to the environment.

Conclusion

In comparison to conventional GC-MS analysis GC×GC-MS analysis revealed higher separation power and accurate determination of target compounds in complex matrix, even without conventional cleanup methods. Thus a complex matrix such as waste motor oil (crankcase oil) with hundreds of hydrocarbons when injected directly in GC×GC-MS system was separated into several groups of compounds and allowed accurate determination of target compounds. Such an application in the present study revealed *in-situ* production of PAHs during automobile engine combustion process, thereby revealing a new pollution source of PAHs to the environment. Thus GC×GC-MS could be effectively used in finger printing and source identification in environmental forensic studies.

References:
1. Zakaria MP, Takada H, Tsutsumi S, Ohno K, Yamada J, Kouno E, Kumata H. (2002); *Environ. Sci. Technol.* 36, 1907-1918
2. Kaplan IR, Lu ST, Alimi HM, MacMurphy J. (2001); *Environ. Forensics* 2, 231-248
3. Kannan N, Schulz DE, Petrick G, Duinker JC. (1992); *Intern. J. Environ. Anal. Chem.* 47, 201-215
4. Kannan N, Petrick G, Schulz D, Duinker J, Boon J, van Arnhem,E, Jansen S. (1991); *Chemosphere*, 23, 1055-1076
5. Beens, J, Boelens H, Tijssen R, Blomberg J.(1998); *J. High Resol. Chromatogr.* 21, 47-54
6. Blomberg J, Schoenmakers PJ, Beens J, Tijssen R. (1997); *J. High Resol. Chromatogr.* 20, 539–544
7. Socloa HH, Garriguesb M, Ewald M. (2000); Mar. Pollut. Bull. 40(5), 387-396
8. Gschweng PM, Hites RA. (1981); *Geochim. Cosmochim. Acta.* 45, 2359–2367