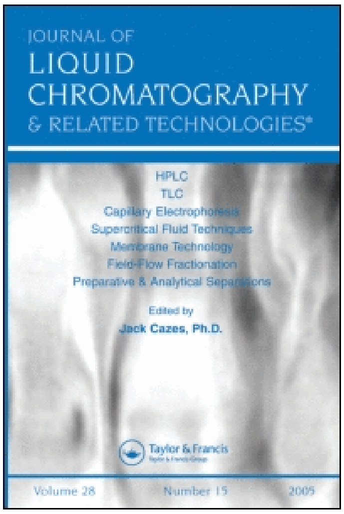

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Vivek R. Dhole[a]; G. K. Ghosal[b]
[a] Regional Forensic Science Laboratory, State of Maharashtra Ganeshkhind, Pune, India [b] Petro-Chemical Technology Department, Laxminarayan Institute of Technology, Nagpur, India

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DETECTION AND CHARACTERIZATION OF PETROLEUM BASED ACCELERANTS IN FIRE DEBRIS BY HPLC

VIVEK R. DHOLE[1]* AND G. K. GHOSAL[2]
[1]Regional Forensic Science Laboratory
State of Maharashtra
Ganeshkhind, Pune 411 007, India
[2]Petro-Chemical Technology Department
Laxminarayan Institute of Technology (LIT)
Amravati Road
Nagpur (M.S.), India

ABSTRACT

A reverse phase HPLC method has been developed for the detection and characterisation of fire accelerants, viz., petrol (gasoline), kerosene, diesel fuel and their residues, generally encountered in investigations of suspected arson cases. Methanolic solutions of these petroleum products and their residues were analysed on HPLC using C-18 reverse phase column. Mobile phase of Acetonitrile: Water (8:2) at the flow rate of 1 ml/min and UV absorption detection at 275 nm and 285 nm were used. The UV detector at 275 nm and 285 nm gives specificity to detection, as the alkyl naphthalenes (aromatics) predominantly present in these petroleum products/residues have strong, characteristic absorption around 275 and 285 nm. Characteristic patterns of chromatograms coupled with intrachromatographic peak height ratios, generated amongst the peaks of naphthalene, 2-methyl-naphthalene and 2,6-dimethyl-naphthalene identified in the

chromatograms of the petroleum products/residues in question, further adds to the specificity of analysis.

INTRODUCTION

Fire debris from suspected fire and arson cases, all over the world, prominently involve the petroleum products such as petrol (motor gasoline), kerosene and diesel fuel etc. as incendiary materials. A large number of homicidal/suicidal burning cases in the Indian sub-continent have a typical unfortunate, "bride burning" context, resulting due to "dowry disputes", also involve such petroleum-based fire accelerants. In such cases partially burnt/charred clothes, bed sheets, carpets coal, hay etc. from the victim, accused and scene of offence are often referred to Forensic Science Laboratories for the detection and characterisation of these petroleum products/residues. These partly burnt objects, mostly clothes etc., when received in the Laboratories, are generally already exposed to adverse environmental conditions, such as heat, air etc. thereby losing more volatile fractions of these petroleum products. However, higher boiling hydrocarbons remain trapped in the fabric of the clothes or burnt debris.

Earlier, we ourselves and several other workers have reported a variety of physico-chemical and instrumental methods, such as, normal (1) and derivative (2) Ultraviolet spectrophotometry, Infra-Red spectrophotometry (3-5), NMR (3), TLC (6-9), Gas Chromatography (10-15), GC-MS (16-18), Super-Critical-Fluid-Chromatography (19), Specific-Gravity (20), Aniline point (20) and Distillation range studies (21) etc. for the detection and identification of petroleum products and their residues with varying degree of success.

HPLC would be a powerful complementary technique for the detection and characterisation of petroleum products/residues. Petroleum oil analysis employing liquid chromatography has primarily involved gel permeation and straight phase systems (22-25). Application of reverse-phase liquid chromatography for separation of polyaromatics present in petroleum oils utilising fluorescence detector has been demonstrated (26-29). Methanol extracts were chromatographed on a reverse phase column followed by fluorescene spectroscopic identification of some major peaks (30). The methanol extractables from the API (American Petroleum Institute) fuel oil No.2 standard included two and three fused ring aromatics (naphthalene, 2-methyl-naphthalene and fluorene were identified). A reverse phase liquid chromatographic oil spill identification technique employing dual UV detection (λ = 210 and 254 nm) was developed using water/methanol gradient for fuel oils and crude oils (31). In the present work a study was undertaken to separate and identify the aromatics/Polycyclic Aromatic Hydrocarbons (PAH) in the methanolic solutions of the most commonly used petroleum products, viz., petrol (motor gasoline), kerosene, diesel fuel and their residues in fire/ arson/burning cases by reverse phase liquid chromatography employing UV detection at specifically chosen wavelengths (λ = 275 and 285 nm.). Pattern recognition of chromatograms at these wavelengths was also useful for the detection and characterisation of these petroleum products.

EXPERIMENTAL

Materials :-

In the present work different standard petrol and diesel samples belonging to different petroleum companies, viz., Hindustan Petroleum, Esso, Indian Oil Corporation, and Bharat Petroleum and different kerosene samples were procured from the market. HPLC grade Acetonitrile, Methanol and Water and AR grade Diethyl ether, Naphthalene, 2-Methyl-naphthalene and 2, 6-Dimethyl-naphthalene; Quick fit standard glass distillation assembly; cloth pieces (30 cms x 30 cms) of varied textile natures were utilised.

Equipment:-

The HPLC system consisted of Thermoseparation products Co. HPLC unit, RP-C-18 column (Lichrospher 100-RP-18, 5 µm, 250 mm Length x 4 mm I.D.) variable wavelength UV detector fitted with Datajet ch-1 integrator.

Chromatographic conditions:-

Mobile phase of Isocratic solvent system comprising of Acetonitrile : Water (80: 20) was used. A flow rate of 1 ml/min at ambient temperature (30° C) was employed throughout the experiment. Detection wavelengths were chosen at 275 nm and 285 nm on the UV absorption detector. Integrator conditions were kept at, Attenuation = 4, Chart speed = 1 cm/min, Threshold = 1.0 and peak width = 0.04.

Preparation of the samples/standards:-

About 30 sq. cms pieces of cloth samples of varied textile natures such as cotton, synthetic (nylon) and terricot etc. were sprayed with different samples of petrol, kerosene and diesel separately. Subsequently they were partially or severely burnt at ambient conditions resulting in either semicharred or charred cloth materials and then extinguished, simulating such materials as received in actual fire/arson cases. These cloth materials were suitably cut into small pieces and directly extracted with 30 ml (3 x 10 ml) portions of diethyl ether. The cloth pieces for which a clear/colourless ether extract could not be achieved were subjected to steam distillation in a quick-fit glass assembly to collect first 15 ml of distillate followed by extraction with diethyl ether. The ether extract was filtered and evaporated at room temperature to dryness and the residue was dissolved in 3 ml of methanol with vigorous shaking for about 5 minutes and then the methanolic solution was filtered through Whatman-41 filter paper. The clear filtrate thus obtained was utilised for HPLC analysis.

1.0 ml each of fresh petrol, kerosene and diesel fuels (liquids) were separately diluted exactly 100 times with methanol.

25 ml of fresh petrol (gasoline) was evaporated at ambient temperature to 0.5 ml, thus obtaining 2% v/v of residue. This residue was diluted 20 times with methanol.

10 μg/ml of naphthalene (I) and 20 μg/ml each of 2-methyl-naphthalene (II) and 2,6 dimethyl-naphthalene (III) were separately prepared in methanol.

Method:-

10 µl each of the methanolic solutions of fresh petrol, kerosene and diesel fuel samples; evaporated petrol; and also the residues of petrol, kerosene and diesel (prepared from the simulation burning experiment) and standard/reference markers of naphthalenes (I), (II) and (III) prepared as described above were separately injected on HPLC, employing the "Chromatographic conditions" as described above.

RESULTS AND DISCUSSION

Typically characteristic individual patterns of chromatograms were observed for petrol, kerosene and diesel samples, their residues and evaporated petrol samples at 275 and 285 nm wavelengths separately, representative chromatograms are shown in Figures 1 to 4 respectively. Standard reference markers of Naphthalene (I), 2-Methyl-naphthalene (II) and 2,6-Dimethyl-naphthalene (III) were identified as the major/prominent peaks (constituents) at Retention Time (RT) of 4.9, 6.2 and 8.0 ± 0.1 respectively in the chromatograms for the residues of petrol, kerosene and diesel, evaporated petrol and even in the fresh kerosene and diesel fuel samples both at 275 and 285 nm (Figures 1 to 4). Identification of other minor

FIGURE - 1(a)* : HPLC chromatogram of fresh petrol (1% v/v in methanol) at 275 nm UV-detection.

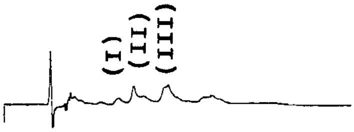

FIGURE-1(b)* : HPLC Chromatogram of fresh petrol (1% v/v in methanol) at 285 nm UV-detection.

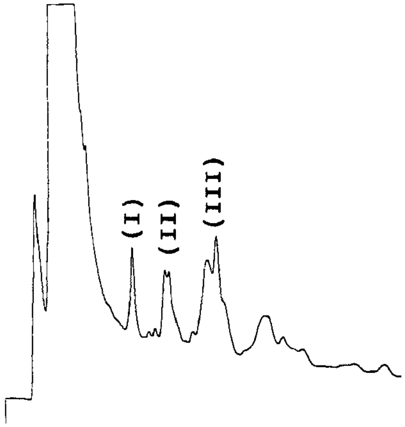

FIGURE -1(c)* : HPLC Chromatogram of petrol residues, from experimental partly burnt clothes , in methanol solvent at 275 nm UV- detection.

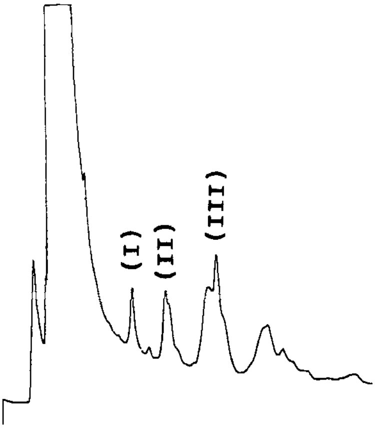

FIGURE-1 (d)* : HPLC Chromatogram of petrol residues, from experimental partly burnt clothes, in methanol solvent at 285 nm UV- detection.

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* FIGURES 1 to 4 :- Quantity of injection = 10 µl each. Symbols (I), (II) and (III) marked in the chromatograms represent the peaks for Naphthalene, 2-methyl-naphthalene and 2,6 -Dimethyl-naphthalene respectively. Chromatographic conditions are described in the text.

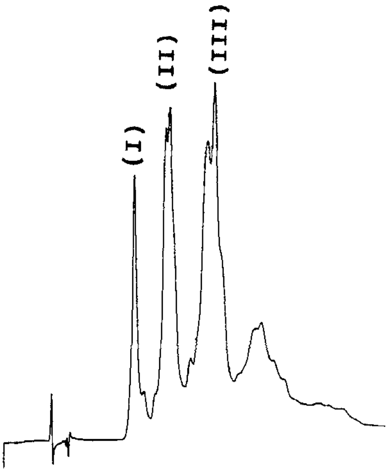

FIGURE-2 (a)* : HPLC Chromatogram of Kerosene (1% v/v in methanol) at 275 nm UV- detection.

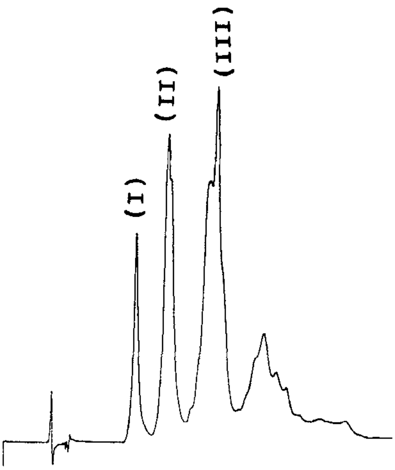

FIGURE - 2(b)* : HPLC Chromatogram of Kerosene (1% v/v in methanol) at 285 nm UV- detection.

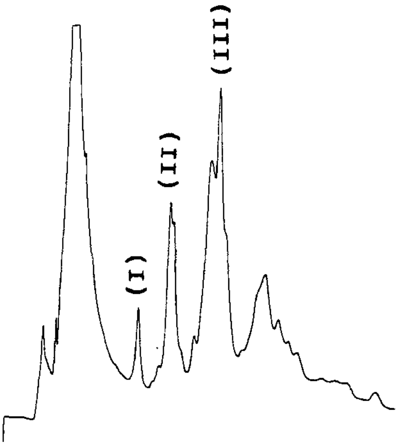

FIGURE - 2 (c)* : HPLC Chromatogram of Kerosene residues from experimental partly burnt clothes, in methanol solvent at 275 nm UV- detection.

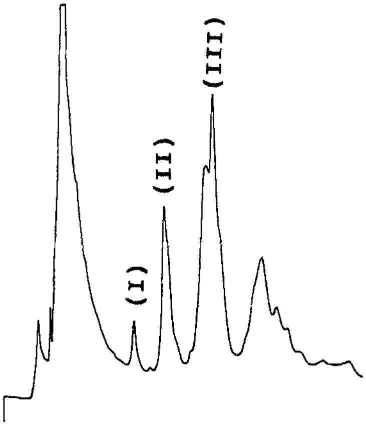

FIGURE - 2 (d)* : HPLC Chromatogram of Kerosene residues from experimental partly burnt clothes , in methanol solvent at 285 nm UV- detection.

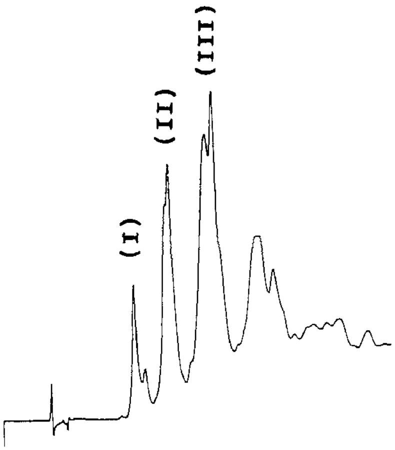

FIGURE - 3 (a)* : HPLC Chromatogram of diesel fuel (1% v/v in methanol) at 275 nm UV- detection.

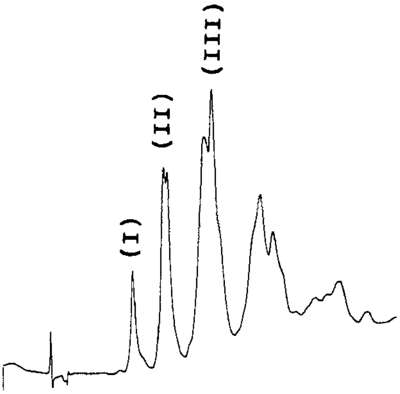

FIGURE - 3 (b)* : HPLC Chromatogram of diesel fuel (1% v/v in methanol) at 285 nm UV- detection.

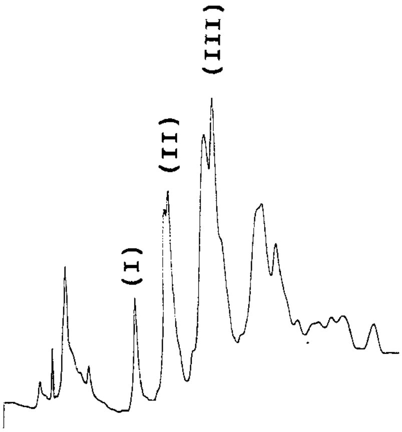

FIGURE - 3 (c)* : HPLC Chromatogram of diesel residues from experimental partly burnt clothes, in methanol solvent at 275 nm UV- detection.

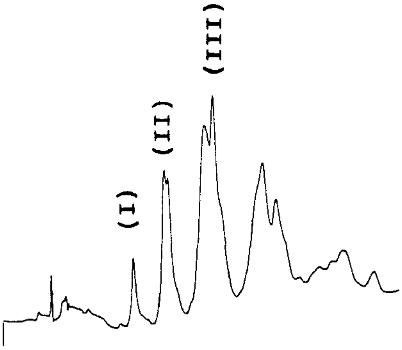

FIGURE - 3 (d)* : HPLC Chromatogram of diesel residues from experimental partly burnt clothes, in methanol solvent at 285 nm UV- detection.

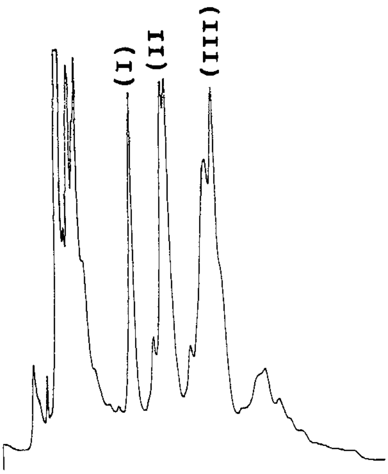

FIGURE - 4 (a)* : HPLC Chromatogram of evaporated - petrol (fresh petrol) evaporated at ambient temperature to obtain 2% v/v of residue and the residue was diluted 20 times with methanol) at 275 nm UV- detection.

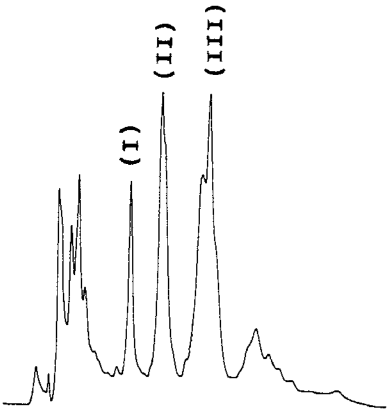

FIGURE - 4 (b)* : HPLC Chromatogram of evaporated - petrol (fresh petrol) evaporated at ambient temperature to obtain 2% v/v of residue and the residue was diluted 20 times with methanol) at 285 nm UV- detection.

peaks/constituents in the chromatograms of these petroleum products/residues could not be done because of the non-availability of other alkyl naphthalenes/ (PAH) etc. as reference markers.

It has been reported earlier by us and other workers also that, naphthalene, alkyl naphthalenes and other aromatics/(PAH) are richly/prominently present in the residues of petrol, kerosene and diesel fuels (from partly burnt objects), evaported petrol and also even in the fresh kerosene and diesel samples (1,2,6,7,11,16,17,22-24). The present work provides an additional proof in support of above findings.

Apart from characteristic individual pattern recognition of the chromatograms for these petroleum products/residues at 275 nm and 285 nm, it was further attempted to identify/characterise individual petroleum products and their residues with their chromatograms by generating the intrachromatographic ratios of the peak heights of major/prominent peaks pertaining to the naphthalenes (I), (II) and (III) in the following manner:-

(I) ÷ (II), (I) ÷ (III) and also (I) ÷ [(II)+(III)] at 285 nm UV-detection. These ratios were found to be individually characteristic for above mentioned petroleum products and their residues as shown in TABLE-1 and thus could be used for further characterisation/ identification/ confirmation of individual petroleum products and their residues. For finding out these ratios at 285 nm, peak heights were utilised rather than peak areas due to the incomplete separations of bands in 15-20 minutes elution range, utilising optimum chromatographic conditions.

It is revealed from the above Table-1 that the ± SD values of the ratios of peak heights amongst the

<u>Table</u> : 1. :- Average ($\overline{X}$) with (±) Standard Deviation (SD) values (n=6) of the intrachromatographic ratios of the peak heights of the peaks pertaining to the Naphthalene (I), 2-Methyl- Naphthalene (II) and 2,6-Dimethylnaphathalene (III), which are identified in the HPLC chromatograms of petrol, kerosene and diesel fuel and their residues at 285 nm UV-absorption detection.

Sr. No.	Sample	Average with ± SD values of peak height ratios :-		
		(I)÷(II)	(I)÷(III)	(I)÷[(II)+(III)]
1)	Petrol	1.0509 ± 0.0044	2.5000 ± 0.0048	0.7135 ± 0.0043
2)	Kerosene	0.6914 ± 0.0038	0.6266 ± 0.0037	0.3296 ± 0.0037
3)	Diesel	0.5207 ± 0.0034	0.3971 ± 0.0037	0.2250 ± 0.0036
4)	Petrol residues	0.8301 ± 0.0156	0.5001 ± 0.0153	0.3114 ± 0.0154
5)	Kerosene residues	0.2826 ± 0.0143	0.1725 ± 0.0144	0.1072 ± 0.0146
6)	Diesel residues	0.4412 ± 0.0133	0.3202 ± 0.0139	0.1853 ± 0.0138
7)	Evaporated petrol	0.6783 ± 0.0054	0.6850 ± 0.0051	0.3406 ± 0.0049

peaks (I), (II) and (III) are quite low and thus indicate good precision of assay for all the petroleum products/residues from the present work. Further, it also indicates that amongst them ± SD values for residues of petroleum products from burnt debris are comparatively higher than the ± SD values for the corresponding fresh, original petroleum products and evaporated petrol sample (leaving a residue of 2% v/v). These higher values of ± SD for said petroleum residues in fire debris may be attributed to the variations in the degree of burning, relationship between these accelerants with various substrate materials and the effects of burning on them. However, even then better characterisation could be achieved by generating and considering all the three ratios as described above, viz., (I)÷(II); (I)÷(III) and (I)÷[(II) + (III)] at 285 nm detection (Table-1), along with the characteristic chromatographic pattern recognition of the individual petroleum products/residues, separately at both 275 nm and 285 nm wavelengths as shown in FIGURES 1 to 4.

Due to volatilisation and combustion composition of original fresh petrol is changed by depleting the petrol of its more volatile (low boiling) components and leaving it enriched in the high boiling point materials (such as alkyl naphthalenes and (PAH) etc.). The corresponding representative chromatograms reveal the amplitudes and, therefore, higher concentration/ enrichment of alkyl naphthalenes and (PAH) in the evaporated petrol (FIGURE-4) and petrol residues [(FIGURE-1 (c) (d)] samples than original fresh petrol [(FIGURE-1 (a) (b)]. These results are in agreement with the GC-MS work reported earlier (16,18).

Criterion for selection of wavelengths :-

Among the petroleum hydrocarbons, absorption of radiations in the ultraviolet region is mainly due to aromatics. Naphthalene and alkyl naphthalenes prevalent in the residues of petroleum products could be measured by their characteristic absorption at 225 ± 5 nm (1,2,35-37), 254 nm (31,35), 275 nm (2,35), 285 nm (2,35,37-39) and 319 nm (2,35,37). Amongst them wavelength at 319 nm was not chosen in the present study since it has significantly low absorptivities (log E values) for naphthalenes (C-10 to C-13) in the range of 1.2 to 2.5 (32,34,37) and, therefore, would affect the sensitivity of detection. Further, amongst the other wavelengths the absorption bands at 275 nm and 285 nm would provide both, characteristic as well as strong absorption for the naphthalenes (C-10 to C-13) and would be definately more specific than other wavelengths, e.g., 225 nm or even 254 nm (which shows absorption for all the compounds with monoaromatic/benzene- derivative structures also). Hence, for effectively separating the compounds of interest from the coeluting volatile impurities originating from the pyrolysis of substrate materials commonly encountered in the fire debris, UV-absorption measurements were done at specially chosen 275 and 285 nm wavelengths separately in the present work.

The absorptivities (log E values) at 285 nm of mono-nuclear aromatics, i.e., alkyl benzenes (C-8 to C-12) are less than 1.0 (37,40). However, the absorptivities are more than 2.5 for diphenyls (C-12 to C-13) and more than 3.5 for naphthalenes (C-10 to C-13) at 285 nm (37,40). Hence UV-absorption measurements at 285 nm would be most useful for the determination of total naphthalenes in the petroleum products. In fact, absorption at 285 nm is the basis of ASTM method D-1840 for the estimation of total naphthalenes in the jet fuels (38). Therefore, the ratios of peak heights amongst the naphthalenes (I), (II) and (III) were generated at 285 nm only (Table-1) in the present work.

The present method when applied to actual and simulated exhibits gave satisfactory results without intereference from commonly encountered impurities in such cases, such as, vegetable oils, body fats etc.. Other commonly encountered impurities would not show characteristic patterns of chromatograms as shown in FUGURES 1 to 4 along with characteristic peak height ratios as generated and shown in Table-1. The known negative blanks did not show characteristic peaks. At the same time, however, we acknowledge that much work remains to be done in this area before we clearly understand the relationship between various accelerants, substrate meterials and effects of fire or pyrolysis on them.

Thus the above HPLC method/approach is simple, rapid, sensitive and selective for the detection and characterisation of petroleum products/residues in day-to-day Forensic work. It could also be useful to the quality control/testing laboratories of the petroleum refineries and petro-chemicals/ (PAH) aromatic chemical industries etc.

ACKNOWLEDGEMENT

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