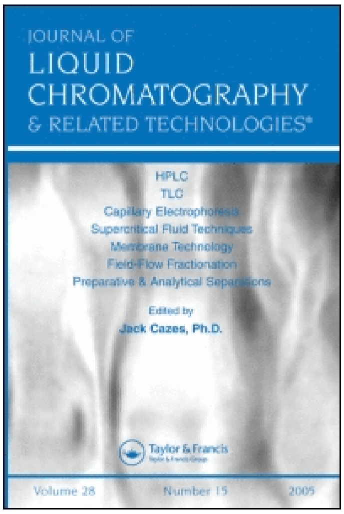

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Dhole, Vivek R. and Ghosal, G. K.(1995) 'Quality Assurance of Petrol by HPLC', Journal of Liquid Chromatography & Related Technologies, 18: 12, 2475 — 2488
To link to this Article: DOI: 10.1080/10826079508013976
URL: http://dx.doi.org/10.1080/10826079508013976

JOURNAL OF LIQUID CHROMATOGRAPHY, 18(12), 2475-2488 (1995)

QUALITY ASSURANCE OF PETROL BY HPLC

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ABSTRACT

A simple and rapid reverse phase HPLC method has been developed for the determination of adulteration in petrol (gasoline) with Kerosene. Methanolic solutions of petrol, Kerosene and their synthetic admixtures were analysed on HPLC using C_{18} ODS column and Acetonitrile : Water (8:2) as mobile phase, at the flow rate of 1 ml/min and UV-absorption detection at 285 nm. The UV detector at 285 nm gives specificity to detection, since the alkyl naphthalenes predominantly present in kerosene have strong, characteristic absorption around 285 nm. The amplitudes of the peaks corresponding to these naphthalenes (C-10 - C-12) increased with the added quantum of kerosene linearly. Average values with ± SD of intrachromatographic ratios generated for the peak heights of the naphthalenes Σ(C-10 to C-12) divided by peak height of solvent methanol were tabulated. These ratios could be used to get a linear curve if evaluated graphically against corresponding (P:K) composition for determining extent of adulteration with kerosene, even down to a level of 5% v/v in suspected petrol samples.

INTRODUCTION

Kerosene being a readily available, specially subsidised domestic cooking fuel has a substantially lower price than the commonly used automobile fuel, petrol (motor gasoline) in Indian-sub-continent and many other countries. The large price difference, between those of petrol and kerosene, has induced an expensive economic offence of the petrol adulteration with kerosene. Moreover, use of such adulterated petrol not only reduces the performance but it also causes serious damage to the automobile engines. Hence early detection and estimation of kerosene in adulterated petrol samples is highly important for the law enforcement agencies and also for ensuring the quality and performance of the fuel (petrol) before using in the motor vehicles. For this purpose the suspected petrol samples are often referred to the Forensic Science Laboratories and also to the quality control,testing laboratories of the petroleum oil companies/refineries.

Number of publications have dealt with the quality assurance/detection of adulteration in petrol/diesel by using various physico-chemical and analytical instrumental methods such as, distillation ranges (1-3), flash point (4), octane number (1,2), specific gravity (5), aniline point (5), thin-layer-chromatography (TLC) (6-9),gas-chromatography (GC) (10-12), UV -spectrophotometry (13), semimicro-chromatography (14), critical-micelle-concentration (CMC) (15), rapid-phase-titration-procedure (16), and high-performance-size exclusion chromatography (17) with varying degree of success.

To supplement detection of adulteration in petrol with kerosene usually done by us by monitoring, distillation ranges (1-3), specific gravity (5), aniline point (5), TLC (6-9) and gas-chromatography amongst the other parameters, the utility of reverse-phase HPLC with a UV absorption detector has been presented here.

EXPERIMENTAL

Materials :-

Number of authentic/standard petrol samples (n=10), belonging to different petroleum companies, viz., Esso, Hindustan Petroleum, Indian Oil Corporation (IOC) and Bharat Petroleum etc. and number of kerosene samples (n=10) were procured from different sources from the market. HPLC grade solvents acetonitrile, methanol and water and AR grade (spectra pure) naphthalene (I), 2-methyl naphthalene (II) and 2,6-dimethyl naphthalene (III) and standard Borosil pipettes, volumetric flasks were used.

Equipment :-

The HPLC system consisted of "Theromo-separation-products" (formerly "Spectra physics") company HPLC Unit, RP-C-18 column

(Lichrospher-100-RP-18, 5 μm, 250 mm length x 4 mm ID), variable wave-length UV absorption detector fitted with Datajet CH-1 integrator.

Chromatographic conditions :-

Mobile phase of isocratic solvent system, comprising of Acetonitrile : Water (8:2) was used. A flow rate of 1 ml/min. at ambient temperature (30°C) was maintained throughout the experiment. Detection wavelength was chosen at 285 nm on the UV absorption detector. Integrator conditions were kept at, Attenuation = 4, Chart-speed = 1 cm/min, Threshold = 1, Peakwidth = 0.04.

Standards/sample preparation :-

Number of authentic/standard petrol (P) and kerosene (K) samples (n=10 each) procured as described above were utilised to prepare ten different sets of synthetic admixtures in the range of (P), (9P + 1K), (8P + 2K) (7P + 3K), (6P + 4K), (5P + 5K), (4P + 6K) and (K) separately. Exactly 1% v/v solutions of all these synthetic admixtures were separately prepared with help of suitable standard volumetric flasks and pipetts by using methanol as a solvent. Exactly 1% v/v methanolic solution of suspected petrol sample if any from case work was also prepared.

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 as reference markers in methanol.

Method :-

Exactly 10 µl each of the 1% v/v methanolic solutions of fresh petrol, kerosene and their synthetic (P + K) admixtures, reference markers of naphthalenes (I), (II) and (III) and suspected petrol sample, if any, prepared as described above, were separately injected on HPLC unit employing the "Chromatographic conditions", as described above.

RESULTS AND DISCUSSION

Typically characteristic patterns of chromatograms were observed for petrol, kerosene and their synthetic admixtures. The representative chromatograms for (P), (9P + 1K)... to (4P + 6K) and (K) are shown in FIGURES 1 to 8 respectively. Peaks of the standard reference markers of naphthalene (I), 2-methyl-naphthalene (II) and 2, 6-dimethyl-naphthalene (III) were identified at Retention Times (RT) 4.9, 6.2 and 8.0 ± 0.1 min., respectively and solvent methanol (M) showed a small peak at RT = 1.8 ± 0.1 min. in these chromatograms (FIGURES 1 to 8).

Petrol (gasoline) samples chiefly consist of hydrocarbons of paraffinic, cycloparaffinic and aromatic series. Higher boiling

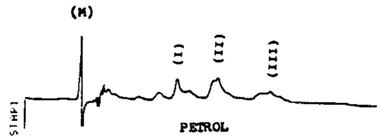

FIGURE - 1* : HPLC Chromatogram of Petrol (1% v/v in methanol).

FIGURE - 2* HPLC chromatogram of synthetic admixture of 9 Petrol + 1 Kerosene (1% v/v in methanol).

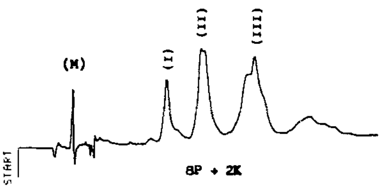

FIGURE - 3* : HPLC chromatogram of synthetic admixture of 8 petrol + 2 kerosene (1% v/v in methanol).

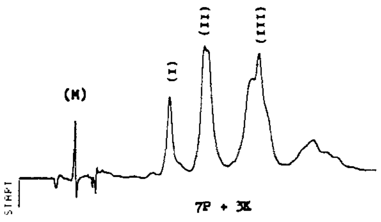

FIGURE - 4* : HPLC chromatogram of synthetic admixture of 7 Petrol + 3 Kerosene (1% v/v in methanol).

* FIGURES 1 to 8 : Quantity of injection = 10 µl each. Symbols (M) (I)(II) and (III) marked in the chromatograms represent the peaks for Methanol, Naphthalene, 2-Methyl-naphthalene and 2,6 - Dimethyl naphthalene respectively. Chromatographic conditions are described in the text.

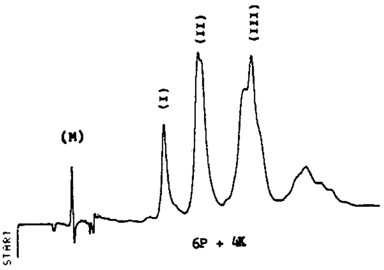

FIGURE - 5* : HPLC chromatogram of synthetic admixture of 6 Petrol + 4 Kerosene (1% v/v in methanol).

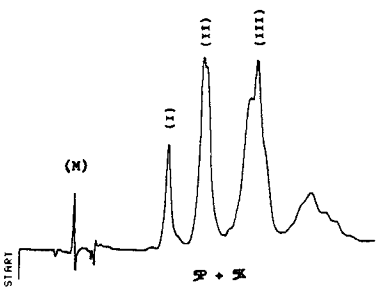

FIGURE - 6* : HPLC Chromatogram of synthetic admixture of 5 Petrol + 5 Kerosene (1% v/v in methanol).

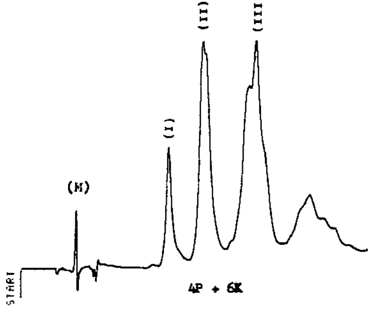

FIGURE - 7* : HPLC chromatogram of synthetic admixture of 4 Petrol + 6 Kerosene (1% v/v in methanol).

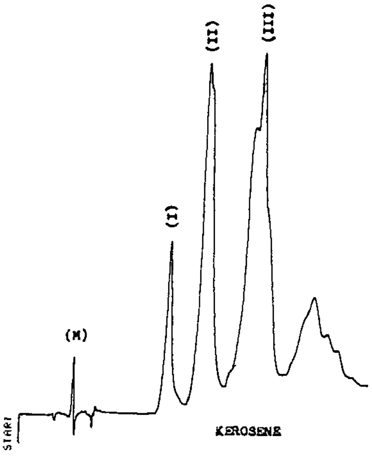

FIGURE - 8* : HPLC chromatogram of kerosene (1% v/v methanol).

petroleum products like kerosene or diesel also comprise of similar classes of hydrocarbons though with more complex molecules and higher carbon numbers of mixed nature (6-9, 13,18). Aromatics present in fresh (unevaporated) petrol are predominantly mononuclear (alkyl benzenes) with relatively low concentrations of dinuclear aromatics (alkyl naphthalenes) (13, 19-22). In contrast kerosenes are richer in dinuclear aromatics (alkyl naphthalenes) (13,22) with substantial proportions of mononuclear aromatics, diphenyls and traces of highly condensed aromatics (13,18). Thus the concentration of total naphthalenes/alkyl naphthalenes would be invariably high in kerosene and diesel than in fresh (unevaporated) petrol.

The above concept was experimentally confirmed by TLC results in our earlier work (6-9), and further by HPLC results in the present work, wherein the peak heights/amplitudes of the naphthalenes (I), (II) and (III) show an increasing trend in the chromatograms of the (P : K) synthetic admixtures as the percentage of kerosene goes on increasing from (P), (9P + 1K) ... to (4P + 6K) and (K) (FIGURES 1 to 8).

Criterion for the selection of wavelength :-

Among the petroleum hydrocarbons absorption of radiations in the ultraviolet region is mainly due to aromatics. Alkyl naphthalenes could be measured by their absorptions at 225 ± 5 nm (23-26), 275 nm (22-24) 285 (13,22-24, 27,28) and 319 nm (13,24). However, petrol (gasoline) generally shows high absorption upto 275 nm (due to predominance of alkyl benzenes) and thereafter shows a rapid tapering off (13), since the absorptivities (log E values) at 285 nm of mononuclear aromatics, i.e., alkyl benzenes (C-8 to C-12) are less than 1.0 (29). However, the absorptivities (log E) are more than 2.5 for diphenyls (C-12 and C-13) and are more than 3.5 for naphthalenes (C-10 to C-13) at 285 nm (29). Hence UV-absorption measurements at 285 nm would be most useful for the determination of total naphthalenes from kerosene in petrol. The criterion for selection of wavelength for UV detection in the present HPLC work is based on the concept discussed above. In fact absorption at 285 nm is the basis of ASTM method D-1840 for the determination of total naphthalenes in jet fuels (27). Normal UV-Spectrophotometric method for the detection of naphthalenes at 285 nm has been presented by other workers also (13). However, it was further established by other workers that the direct, normal UV-spectrophotometric detection of naphthalenes at 285 nm is inapplicable in petroleum (gasoline) sample because of the serious interference from monoaromatics (28). But the HPLC technique because of its powerful chromatographic separation facility if coupled with characteristic UV detection at 285 nm as suggested in the present work could be used as a better alternative approach than the ASTM (27) and other direct UV-spectrophotometric method (13) for determining total naphthalenes in petroleum products without interference from alkyl benzenes etc.

Intra-chromatographic ratios :-

A close look at the chromatograms for synthetic admixtures from (P), (9P + 1K) ... to (4P + 6K) and (K) (FIGURES 1 to 8) reveals an increasing trend of peak heights, as described above, especially for the peaks corresponding to naphthalenes (I), (II) and (III) at RT = 4.9, 6.2 and 8.0 ± 0.1 min. respectively. However, the peak height for solvent methanol (M) at RT = 1.8 ± 0.1 min. is almost the same in all these chromatograms (FIGURES 1 to 8) since the quantity of injection is exactly same, i.e., 10 ul each for all the (P : K) synthetic admixtures. It was also observed that the peak height for solvent methanol is directly proportional to the quantity of injection. Apart from characteristic chromatographic pattern recognition for different (P:K) compositions (FIGURES 1 to 8) it was further attempted to determine intrachromatographic peak height ratios in the following manner, i.e., $\Sigma((I) + (II) + (III))$ divided by (M). For finding out these ratios, peak heights were utilised rather than peak areas due to the incomplete separation of bands in the 15 min. elution range, utilising optimum chromatographic conditions. Average values with ± SD of these peak height ratios for various (P:K) synthetic admixtures derived from ten different sets are shown in TABLE 1.

TABLE 1 :-

Average (X) with ± SD values (n = 10) of the intrachromatographic ratios of the peak heights for ((Naphthalene (I) + 2 methyl-naphthalene (II) + 2,6-Dimethyl-naphthalene (III)) ÷ Methanol (M), identified in the HPLC chromatograms of various (P:K) synthetic admixtures.

Sr. No.	(P : K) Composition	Average with ± SD* values of peak height ratios. ((I)+(II)+(III)) ÷ (M)	% CV.@
1.	Petrol (P)	1.2632 ± 0.0551	4.362
2.	(9P + 1K)	2.5790 ± 0.0665	2.578
3.	(8P + 2K)	3.7894 ± 0.0731	1.929
4.	(7P + 3K)	5.2631 ± 0.0818	1.554
5.	(6P + 4K)	6.6316 ± 0.0867	1.307
6.	(5P + 5K)	7.8947 ± 0.0848	1.074
7.	(4P + 6K)	9.1578 ± 0.0918	1.002
8.	Kerosene (K)	14.1052 ± 0.0935	0.663

* SD = Standard Deviation @ C.V. = Coefficient of Variation.

Since % C.V. is less than even 5% for all the (P : K) compositions, the results from the present HPLC work (TABLE-1) indicate good precision of assay. The average values of the peak height ratios from TABLE -1 if plotted against corresponding (P : K) composition, i.e., (P), (9P + 1K) ... to (4P + 6K) and (K) etc. give a straight line curve which could be utilised for determining the percentage of kerosene in the suspected petrol sample by finding out the peak height ratio from its HPLC chromatogram and then with the help of straight line curve graph derived from TABLE-1 as described above one can easily find out the extent of adulteration in the suspected petrol sample.

Thus the proposed HPLC method/approach could be routinely used as a simple, rapid, sensitive (even down to a level of 5% v/v) and reliable complementary method for the determination of adulteration in petrol with kerosene in Forensic Science Laboratories. It could also be used by the quality control/testing laboratories of the petroleum refineries and petrochemical / (PAH) etc. industries in day-to-day work.

ACKNOWLEDGEMENT

The authors are thankful to Mr. S.O. Baisane, Director, Forensic Science Laboratories, State of Maharashtra, Bombay for the encouragement in this work. The authors are also grateful to M/s Chromline Equipment Co., Bombay for providing HPLC instrumental facility for this work.

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Received: August 5, 1994
Accepted: March 8, 1995