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Application Data Sheet

No.190

System Gas Chromatograph

Analysis of PIONA composition in finished motor gasoline by GC-VUV

An analytical method was established in this paper for determination of the contents of all hydrocarbon components and specific hydrocarbon groups of paraffins, isoparaffins, olefins, naphthenes and aromatic hydrocarbons (PIONA) in finished motor gasoline by GC-VUV. The analysis results showed the method could complete the analysis of all hydrocarbon components in finished motor gasoline within 33 min. Various groups of hydrocarbons were identified by their specific VUV absorption spectra in the VUVision software platform and the coeluting species were effectively separated by the time interval deconvolution (TID) method in the full automatic data processing software VUVAnalyze and the results were valid and reliable. The relative standard deviation in 5 replicate tests was less than 1%, indicating good repeatability.

Key words: gas chromatograph, VUV detector, gasoline, PIONA, ASTM D8071

The hydrocarbon composition data of gasoline fraction distillates are indispensable and essential data for petroleum refining and processing engineering and are important indicators for evaluating the quality and suitability of gasoline products. Gasoline can be divided into straight run gasoline, reformed gasoline, catalytically cracked gasoline, gasoline alkylate, etherified gasoline, and finished motor gasoline according to its process type. Understanding the chemical composition of the gasoline fraction is an important basis for determining processing solutions for petroleum products. The gasoline fraction is a complex mixture of hydrocarbons.

Theoretical calculation suggests the major hydrocarbon components of this fraction can be composed of several hundred unique hydrocarbon species. It is difficult to separate and analyze these compounds accurately. Capillary gas chromatography (GC) in conjunction with retention index (RI) for detailed hydrocarbon analysis (DHA) of monomer hydrocarbons in gasoline has been specified in ASTM D5134, ASTM D6729, ASTM D6730, ASTM D6733 and SH/T0714, an equivalent Chinese industrial standard in China, and extensively used for process control analysis.

However, the PIONA components are so complex that their separation on a chromatographic column inevitably suffers from some coeluting species, resulting in errors in qualitative analysis. It is difficult to carry out qualitative analysis of the coeluting species simply by a comparison of their retention times with those of standard components. Moreover, the method has stringent requirements on the chromatographic column for separation and requires long analysis time (approx. 2 hours for an analysis), giving rise to increased quantitative error in final calculation results and decreased throughput.

An analytical method was proposed in this paper for the analysis of PIONA composition in gasoline by Shimadzu gas chromatograph GC-2030 and VUV detector VGA 101. Thise method has significantly lowered the requirements for chromatographic separation, reduced the time needed for the analysis, and increased the accuracy of final calculation results. Quantitative accuracy is improved by taking advantage of the components' unique spectral fingerprint and retention time for qualitative analysis and making use of the deconvolution function of professional software for the analysis of coeluting species.

Analyzer Information

System Configuration:
Nexis GC-2030 with VUV detector: VGA-101

Sample Information:
Gasoline

Methods met:
ASTM D8071

Conditions of analysis:

Column: SH-Rtx-1(30 m×0.25 mm×0.25 μm)	Injector temperature: 250 ℃
Column temperature program: 35 ℃ (10 min)_7 ℃/min_200 ℃	Transfer line temperature: 275 ℃
Column pressure: 78.8 kPa	Flow cell temperature: 275 ℃
Column flow: 1 mL/min	Make-up gas pressure: 0.35 psi
Injection mode: split (split ratio 300:1)	Spectral acquisition range: 125-430 nm
Injection volume: 1 μL	Spectral acquisition frequency: 4 Hz

Typical Chromatograms and spectrograms

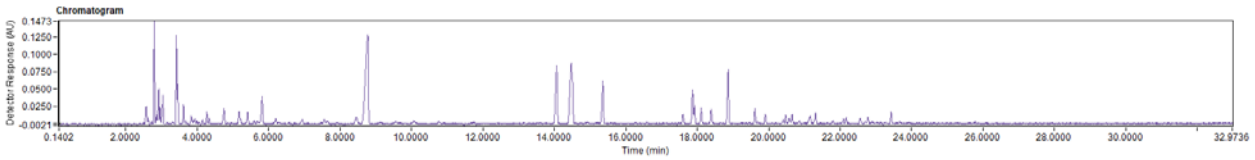

Fig. 1 A typical chromatogram of 95 octane number finished motor gasoline

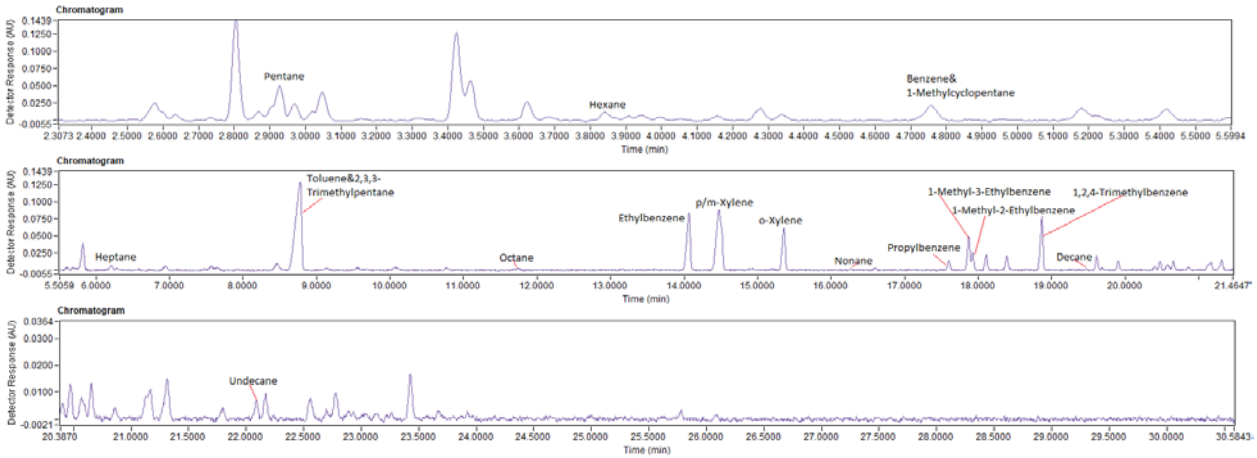

Fig. 2 Segmented chromatograms of 95 octane number finished motor gasoline

Fig. 3 was acquired from VUVAnalyze. The green region of the figure showed the original absorption spectrogram at a specific time and the blue region was its matched absorption spectrogram. As can be seen in the figure, benzene had good matching rates in these two absorption zones (125-160 nm and 175-205 nm). The TID chromatogram yielded by VUVision showed benzene and 1- methylcyclopentene were the coeluting species.

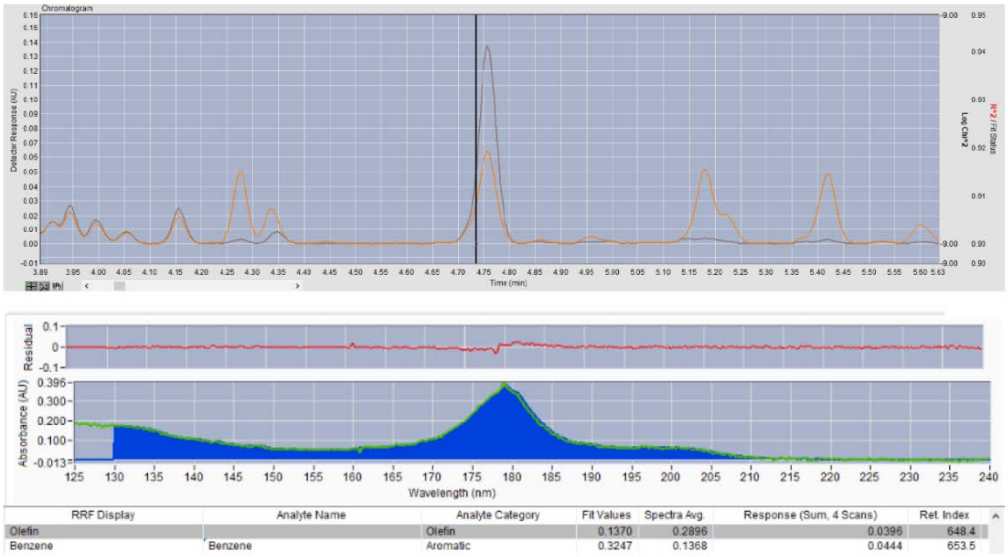

Fig. 3 Chromatograms and VUV spectrograms of the co-effluents benzene and the alkene

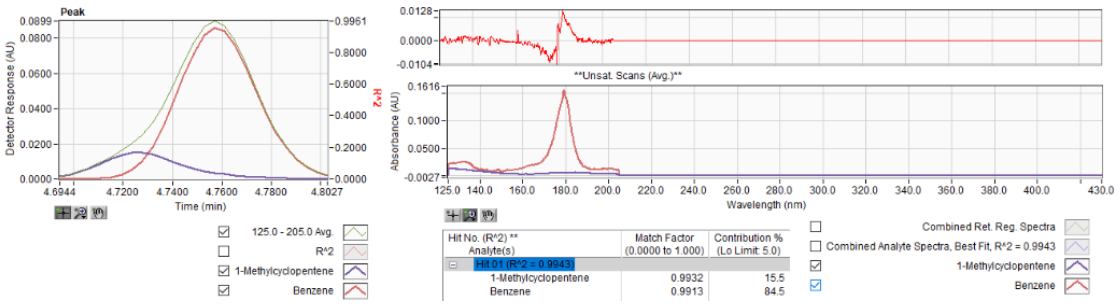

Fig. 4 TID chromatograms and VUV spectrograms of the coeluting compounds, benzene and 1- methylcyclopentene

Fig. 5 was acquired in VUVAnalyze, showing that toluene had good matching rates in these two absorption zones (125-160 nm and 175-205 nm). The TID chromatogram yielded by VUVision showed toluene and 2, 3, 3- trimethypentane were the coeluting species.

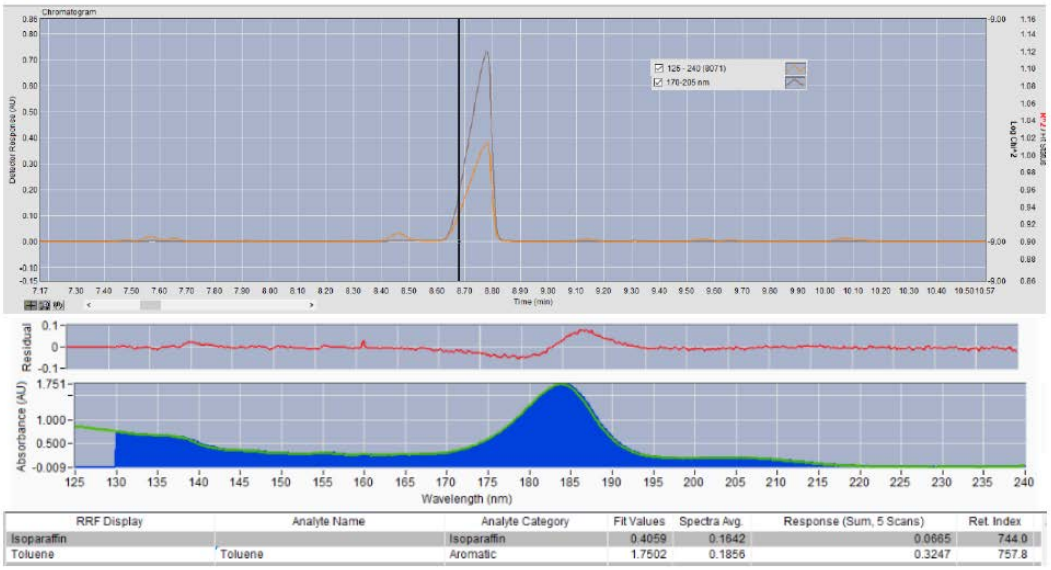

Fig. 5 TID Chromatograms and VUV spectrograms of the coeluting compounds, toluene and isoparaffins

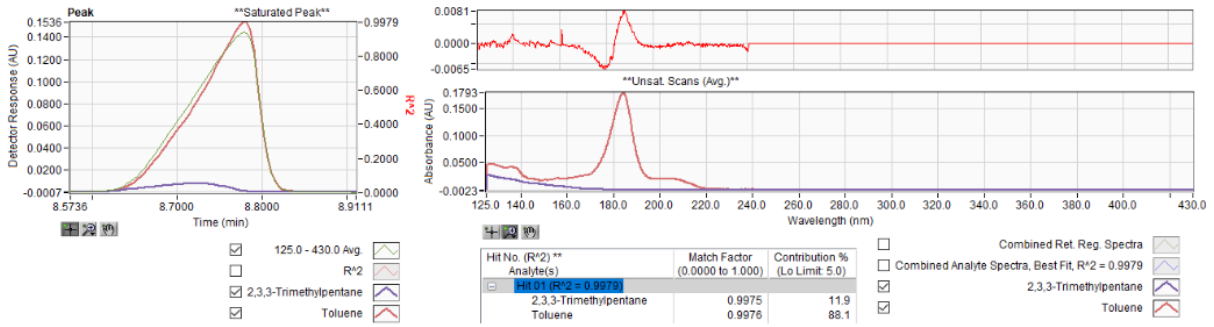

Fig. 6 TID chromatograms and VUV spectrograms of the coeluting species toluene and 2, 3, 3- trimethypentane

Overlaid spectra of constituent hydrocarbons

The method was developed on the basis of ASTM D8071 Standard Test Method for Determination of Hydrocarbon Group Types and Select Hydrocarbon and Oxygenate Compounds in Automotive Spark-Ignition Engine Fuel Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV) and in reference to the recommended D8071 spectrum database provided in VUV Analyze. It is suitable for determination of 6%-17% alkanes, 24%-70% branched alkanes, 0.1%-16% alkenes, 1%-14% cycloalkanes and 16%-58% aromatic hydrocarbons in finished motor gasoline. A sample of a commercially-available 95 octane number gasoline was subjected to analysis by the proposed method. The overlaid spectra of the hydrocarbon components (PIONAs) were as shown in the following Fig. 7- Fig. 11; and the mass fraction, volume fraction, and content of specified hydrocarbons and oxygen compounds were as shown in Fig. 12- Fig. 13.

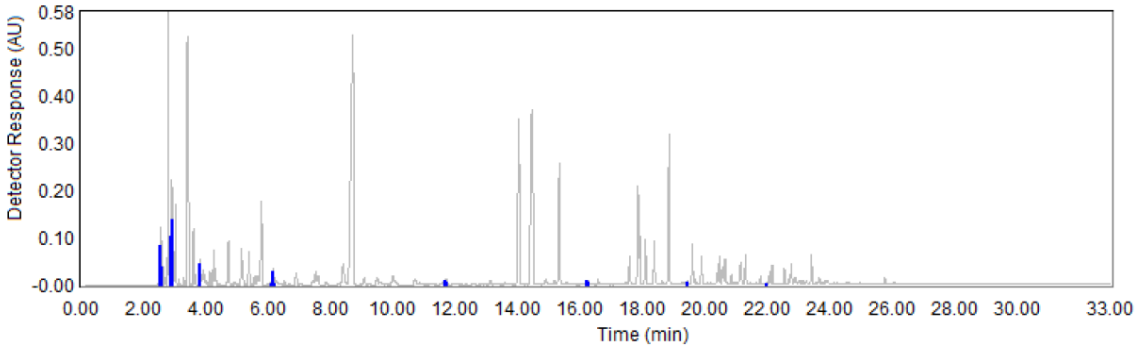

Fig. 7 Overlaid spectra of alkanes

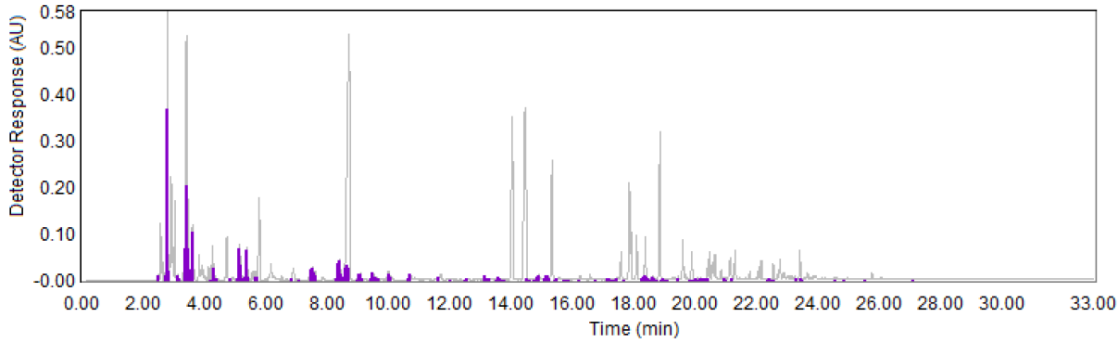

Fig. 8 Overlaid spectra of branched alkanes

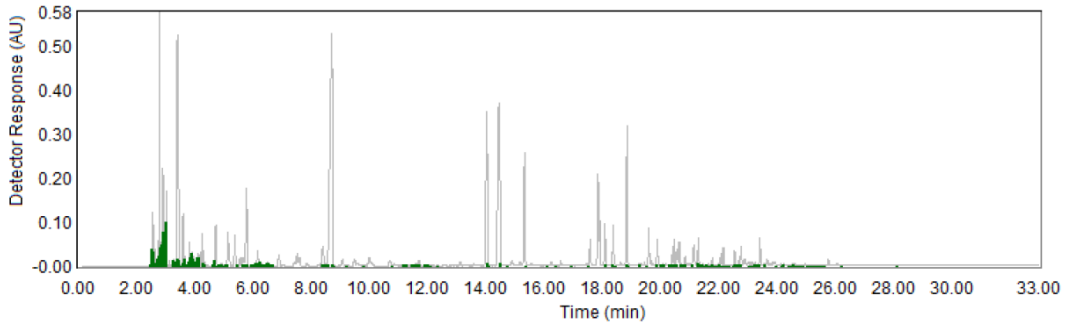

Fig. 9 Overlaid spectra of alkenes

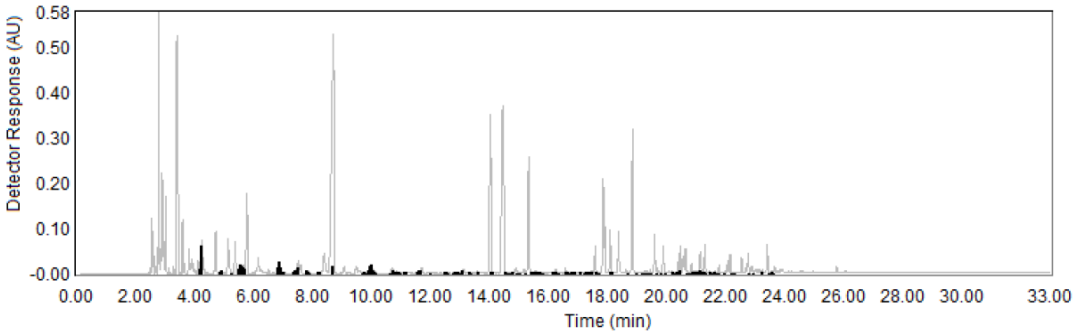

Fig. 10 Overlaid spectra of cycloalkanes

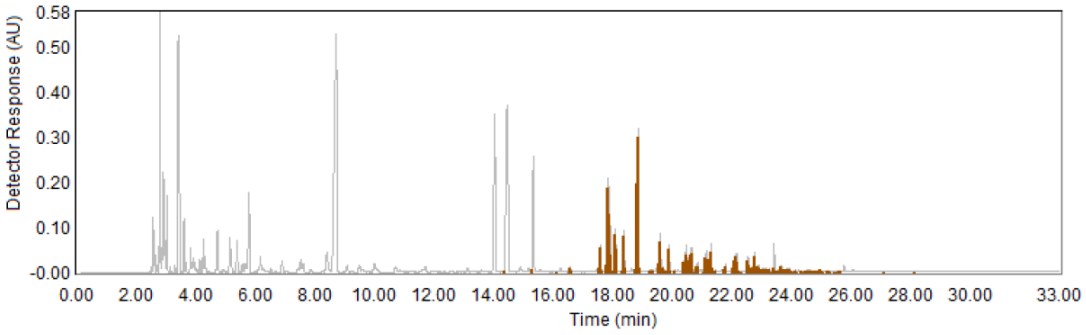

Fig. 11 Overlaid spectrua of aromatic hydrocarbons

Mass and volume fractions of the hydrocarbon components (PIONA)

Mass %

C. No.	P	I	O	N	A	Total
C1						
C2						
C3						
C4	1.263	0.174	1.209			2.646
C5	2.984	8.046	4.426			15.456
C6	0.831	6.912	2.437	1.574	0.670	12.425
C7	0.799	4.691	1.044	2.366	10.379	19.279
C8	0.282	10.503	0.390	2.180	13.944	27.300
C9	0.192	1.836	0.119	0.772	8.799	11.719
C10	0.105	0.756	0.478	0.470	4.595	6.404
C11	0.085	0.299	0.322	0.790	1.772	3.267
C12		0.135	0.088	0.045	0.352	0.621
C13		0.017	0.003		0.057	0.076
C14		0.006	0.006			0.011
C15						
C16						
C17						
C18						
C19						
Total	6.543	33.375	10.522	8.196	40.569	

Volume %

C. No.	P	I	O	N	A	Total
C1						
C2						
C3						
C4	1.631	0.234	1.489			3.354
C5	3.562	9.705	5.039			18.305
C6	0.942	7.850	2.572	1.568	0.570	13.501
C7	0.874	5.126	1.075	2.333	8.947	18.355
C8	0.300	11.149	0.396	2.121	11.990	25.956
C9	0.200	1.906	0.121	0.738	7.543	10.508
C10	0.108	0.784	0.477	0.441	3.889	5.698
C11	0.086	0.293	0.321	0.729	1.504	2.934
C12		0.131	0.087	0.041	0.300	0.559
C13		0.016	0.003		0.049	0.068
C14		0.005	0.005			0.010
C15						
C16						
C17						
C18						
C19						
Total	7.703	37.198	11.584	7.971	34.791	

Fig. 12 Mass and volume fractions of PIONAs

Report Item	Category	Retention Time (min)	Mass %	Volume %
Methanol	Alcohol	-	-	-
Ethanol	Alcohol	2.769	0.795	0.753
Benzene	Aromatic	4.710	0.670	0.570
iso-octane	Isoparaffin	5.769	3.821	4.127
Toluene	Aromatic	8.690	10.379	8.947
Ethylbenzene	Aromatic	14.011	4.307	3.713
Naphthalene	Aromatic	23.390	0.331	0.241
Methylnaphthalenes	Aromatic	-	0.121	0.090
Xylenes	Aromatic	-	9.601	8.248

Fig. 13 Mass and volume fractions of specified hydrocarbons and oxygen compounds

Repeatability

1 uL of 95 octane number finished motor gasoline was directly injected for repeatability test. The RSD of 5 replicate injections was less than 1%, indicating good repeatability. For detailed results, refer to Table 1 and Table 2.

Table 1 Repeatability - mass fraction

	P	I	O	N	A
Mass fraction %	6.543	33.3751	10.522	8.1963	40.5688
	6.6444	33.7779	10.0381	8.1723	40.6605
	6.6811	33.715	10.0254	8.2656	40.6142
	6.5333	33.5703	10.2871	8.4836	40.4582
	6.6127	33.7445	10.0267	8.3573	40.6228
RSD/(n=5,%)	0.0572	0.1487	0.1980	0.1141	0.0697

Table 2 Repeatability - volume fraction

	P	I	O	N	A
Volume fraction %	7.703	37.1983	11.5839	7.9711	34.791
	7.8095	37.6159	11.1159	7.9659	34.8242
	7.8465	37.5471	11.0901	8.0554	34.7998
	7.6899	37.4039	11.3548	8.2399	34.6795
	7.7741	37.5855	11.1025	8.1362	34.7999
RSD/(n=5,%)	0.0603	0.1541	0.1938	0.1039	0.0509

Conclusion

An analytical method was established in this paper for determination of the contents of all hydrocarbon components and specific hydrocarbons groups of paraffins, isoparaffins, olefins, naphthenes and aromatic hydrocarbons (PIONA) in finished motor gasoline by GC-VUV. Analysis results with the method and the procedures in ASTM D8071 shown the proposed method can complete the analysis of all hydrocarbon components in 33 min. The method when used in combination with the specific VUV absorption spectra of hydrocarbons of various groups in VUVision and VUVAnalyze's TID function can effectively separate the coeluting species without the use of pre-column for preliminary separation of benzene and 1-methylcyclopentene or the use of an adsorption trap. The qualitative analysis is based on the analytes' characteristic VUV absorption spectra and retention time resulting in reliable and valid results. Considering the volatility of finished motor gasoline exposed in air, the repeatability of the method was assessed by 3 replicate tests and the RSD of the results was less than 1%, indicating good repeatability. The proposed method can be used for the assay of the contents of all hydrocarbon components and specific hydrocarbons groups of paraffins, isoparaffins, olefins, naphthenes and aromatic hydrocarbons (PIONAs) in finished motor gasoline.

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