

Application News

Detailed Hydrocarbon Analysis by GC-VUV Using ASTM D8369

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User Benefits

- ◆ GC-VUV enables detailed compositional analysis of gasoline in accordance with ASTM D8369.
- ◆ VUV Analyze™ facilitates peak deconvolution and quantitative calculations, simplifying data processing.

Introduction

The composition of fuels such as gasoline, diesel, and jet fuel critically influences physical properties including combustibility; therefore, detailed compositional information is of high importance. Gasoline typically comprises a complex mixture of over one hundred hydrocarbons, making qualitative identification of individual constituents highly time-consuming. ASTM D8369 defines procedures for the qualitative and quantitative determination of hydrocarbons and oxygenates (e.g., ethanol additives) in gasoline using a vacuum ultraviolet (VUV) detector.

In this application news, we present a compositional analysis of gasoline conducted on a Nexis GC-2030 system (Fig.1) in compliance with ASTM D8369. The VUV analysis software VUV Analyze was employed to perform peak deconvolution and quantitative calculations efficiently.

Compositional Analysis of Gasoline Using GC

Methods for qualitative and quantitative analysis of hydrocarbons and oxygenates in relatively low-boiling petroleum products such as gasoline are specified in standards including ASTM D8369, D6730, and D8071. Table 1 summarizes the characteristics of these methods.

ASTM D6730 employs the widely used flame ionization detector (FID) and performs separation over approximately three hours; this Detailed Hydrocarbon Analysis (DHA) approach has long been used. Identification in DHA relies on retention indices; tools such as PONAsolution™ can reduce manual identification effort and enable automated quantitation (see [Application News No. 01-00863-EN](#)).

In contrast, D8071 and D8369 utilize VUV detector. In these methods, both retention indices and absorbance spectra are used for identification, allowing spectral deconvolution of coeluting components. Consequently, analysis time can be shortened relative to FID-based methods. D8369, referred to as Verified Hydrocarbon Analysis (VHA™), is gaining attention as a modern approach for gasoline compositional analysis. Moreover, by changing columns, a single VUV detector can be applied to analyses under ASTM D8369, D8071, D8267 (jet fuel), and D8368 (diesel), enabling multiple fuel types to be analyzed on the same instrument.



Fig. 1 Nexis™ GC-2030 + VGA-101

VUV Absorbance Spectra

Conventional DHA per ASTM D6730 separates major components over roughly three hours, yet coelution still occurs for certain analytes. The VUV detector provides compound-specific spectral information in addition to retention time (see Fig. 2), thereby enabling deconvolution of coeluted components (illustrated in Fig. 3) and markedly reducing analysis time.

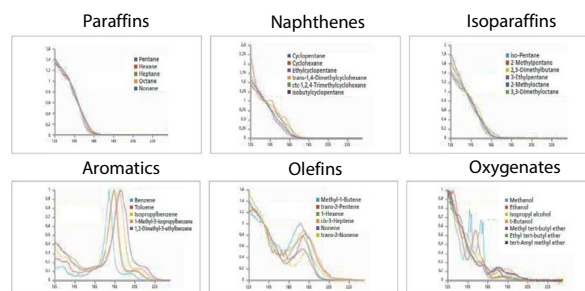


Fig. 2 VUV absorbance spectra for various compounds

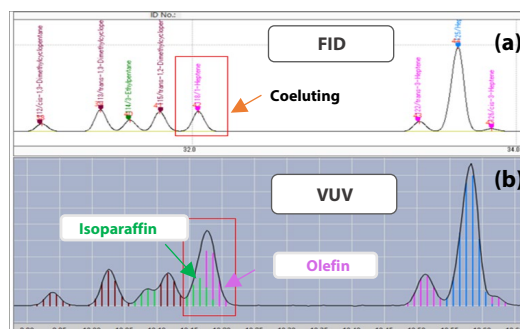


Fig. 3 Chromatograms of gasoline using FID(a) and VUV(b)

Table 1 Comparison of ASTM D8369, D8071 and D6730

	D8369	D8071	D6730
Report Items	PIONA group	PIONA group	PIONA group
Detector	Individual compounds VUV	select compounds (EtOH, BTX etc.) VUV	Individual compounds FID
Analysis Time (min)	49	35	ca. 180
Qualification	Retention Indices + VUV spectra	Retention Indices + VUV spectra	Retention Indices
Quantification	Corrected Percentage Peak Area Method	Corrected Percentage Peak Area Method	Corrected Percentage Peak Area Method

■ Deconvolution

VUV Analyze can deconvolute the absorbance spectrum of a coeluted peak into up to five constituent compound spectra. An example is presented in Fig. 4. First, the green spectrum (1) represents the acquired absorbance spectrum at a given retention time. Upon deconvolution, spectral library matching and retention index information identified 2,3,3-trimethylpentane and toluene as contributors (2). The combination of the two library spectra (3) closely reproduces the acquired spectrum (1), and the small residual (4) indicates successful deconvolution.

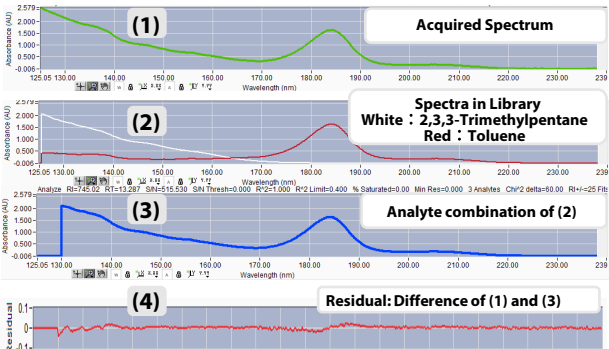


Fig.4 Example of deconvolution for gasoline

■ Analysis Procedure for ASTM D8369

ASTM D8369 prescribes initial measurement of an alkane mixture (VUV-RT) used as the retention index reference. Subsequently, a system validation standard (VUV1) and a QC sample (VUV-CS) are measured.

VUV Analyze includes dedicated analysis methods that, when the respective data files are loaded in sequence, automatically perform qualitative identification, quantitation, and pass/fail evaluation. Only after the QC sample passes may routine sample analyses proceed.

■ System Configuration and Analysis Conditions

The instrument configuration and analysis conditions used in this study are summarized in Table 2 and 3. A column oven low-temperature control device (CRG) was employed to improve separation of low-boiling components. Software comprised LabSolutions™ for GC control, VUVision™ for VUV detector control, and VUV Analyze for spectral analysis.

Table 2 System configuration

GC Model	: Nexis GC-2030 / AOC-30i
Injection Port	: SPL
Inlet Liner	: Topaz 4.0 mm ID Precision inlet Liner w/Wool
Column	: SH-1 (60 m × 0.25 mm I.D. × 0.25 μm) (P/N : 221-75719-60)
Detector	: VUV (VGA-101)
Options	: CRG-2030 (N ₂)
Software	: Labsolutions VUVision VUV Analyze

Table 3 Analysis conditions

Injection Temperature	: 250℃
Flow Control Mode	: Column Flow (He)
Column Flow	: 2.0 mL/min
Purge Flow	: 3.0 mL/min
Injection Volume	: 1.0 μL
Split ratio	: 300
Column Oven Temp. Program	: 5℃(4 min) → 18℃/min → 50℃(14 min) → 5.5℃/min → 200℃(1 min)
Transfer Line Temperature	: 275℃
Flow Cell Temperature	: 275℃
Makeup Gas Pressure	: 0.60 psi
Acquisition Frequency	: 5.0 Hz

■ Analysis of VUV-RT

A VUV-RT mixture containing n-alkanes from C4 to C15 was measured. The acquired data were processed in VUV Analyze to identify the alkanes and generate a retention index (RI) file containing retention indices and retention times. Future analyses used this RI file for retention index-based identification.

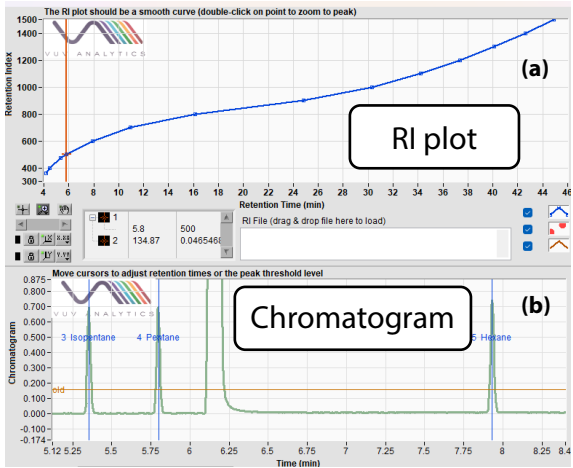


Fig. 5 Data processing of VUV-RT using VUV Analyze
:RI plot(a), chromatogram(b)

■ Analysis of VUV1 and VUV-CS

VUV1 and VUV-CS were measured to perform system validation testing and QC verification. Makeup gas pressure was adjusted so that the benzene response for VUV1 fell within the target range of 2.25–2.75. Mass percentage values for each PIONA component and the relative sensitivity (C14/C5; tetradecane/pentane) were confirmed to be within acceptable ranges. The VUV-CS QC sample, prepared as a standard gasoline, yielded quantitation values for all compounds within specification. Loading the measurement files into VUV Analyze produced a comprehensive report that allowed immediate review of all items (see Fig. 6).

Overall Status: <u>Pass</u>			
--- Category Mass % ---			
Pass?	Category	Target	Meas.
<u>Pass</u>	Paraffin	31.3270	30.3306
<u>Pass</u>	Isoparaffin	6.9440	7.2214
⋮			
C14/C5 (3.7945 / 1.0475) = 3.6223 (Allowed Range = 3.3346 to 4.9813) <u>Pass</u>			
--- benzene Response ---			
Pass?	Measured	Expected	Min
<u>Pass</u>	2.53	2.50	2.25

Fig. 6 Report for VUV1

■ Comparison of Quantification Results

To assess quantitative accuracy, a certified component standard (Tokyo Chemical Industry Co., Ltd., S0429) was analyzed. For all measured compounds, the difference between the measured value and the certified value was within 0.5 vol%, demonstrating equivalence with the conventional ASTM D6730 method (FID detection). Table 4 summarizes the measured results for the certified standard.

Table 4 Comparison of results between ASTM D8369 and D6730 (vol%)

Compound	a. Conc. of certificate	b. ASTM D8369	a - b	c. ASTM D6730	a - c
Benzene	0.5	0.569	0.069	0.552	0.052
Toluene	16.2	15.741	0.459	16.529	0.329
Xylene	10.7	10.213	0.487	10.755	0.055
MeOH	1.5	1.316	0.184	1.414	0.086
EtOH	5.3	5.314	0.014	5.194	0.106
MTBE	5.2	5.417	0.217	5.268	0.068
ETBE	5.2	5.581	0.381	5.187	0.013

■ Measurement of Gasoline Sample

Following completion of system validation testing, the gasoline sample was analyzed. VUV Analyze facilitates automated deconvolution by leveraging the retention index and absorbance spectral library. Quantitative results were reviewed in a two-dimensional table by carbon number and compound class (PIONA), and in individual component concentration reports (example shown in Fig. 7). In the chromatogram view (Fig. 8), peaks are color-coded by compound class, enabling visual identification of coeluted peaks. The absorbance spectrum at each data point can be inspected and the residual (agreement with the library spectrum) is displayed for each assignment.

Mass % Table							
	Paraffin	Isoparaffin	Olefin	Naphthene	Aromatic	Oxy	Totals
C1							
C2							
C3							
C4	0.7920	0.6999	0.9230				2.4149
C5	5.0798	8.5899	5.7759	0.4162			19.8619
C6	4.0984	10.6544	4.8948	1.8384	0.6990	4.5211	26.7061
C7	1.5355	7.1436	2.9451	1.7433	3.6543		17.0218
C8	0.4107	4.9201	2.1493	1.2353	6.0062		14.7216
C9	0.2121	1.1181	0.1161	0.2738	11.0653		12.7853
C10	0.1451	0.4986	0.0175	0.1147	3.7604		4.5362
C11	0.0738	0.1283	0.0166	0.1226	1.3907		1.7320
C12	0.0224	0.0485	0.0045	0.0126	0.0920		0.1800
C13		0.0262			0.0140		0.0402
C14							
C15							
Totals	12.3697	33.8276	16.8428	5.7569	26.6820	4.5211	100.0000

Fig. 7 Two-dimensional table by carbon number and compound class (PIONA) for gasoline sample

■ Conclusion

A detailed compositional analysis of gasoline in accordance with ASTM D8369 was conducted. The use of a VUV detector allowed spectral deconvolution of coeluting peaks, reducing analysis time from approximately three hours (typical for FID-based DHA) to approximately 50 minutes. Measurement of a certified standard confirmed that quantitative results were equivalent to those obtained by ASTM D6730. Additionally, employing dedicated methods in the VUV Analyze software enabled streamlined system checks and automated qualitative and quantitative computations. The incorporation of absorbance spectra into qualitative identification reduces the risk of misidentification because each compound class exhibits characteristic spectral features.

<Related Applications>

1. Detailed Hydrocarbon Analysis by Nexis GC-2030 Using ASTM D6730, [Application News No. 01-00863-EN](#)
2. Analysis of PIONA composition in finished motor gasoline by GC-VUV- [Application Data Sheet No.190](#)

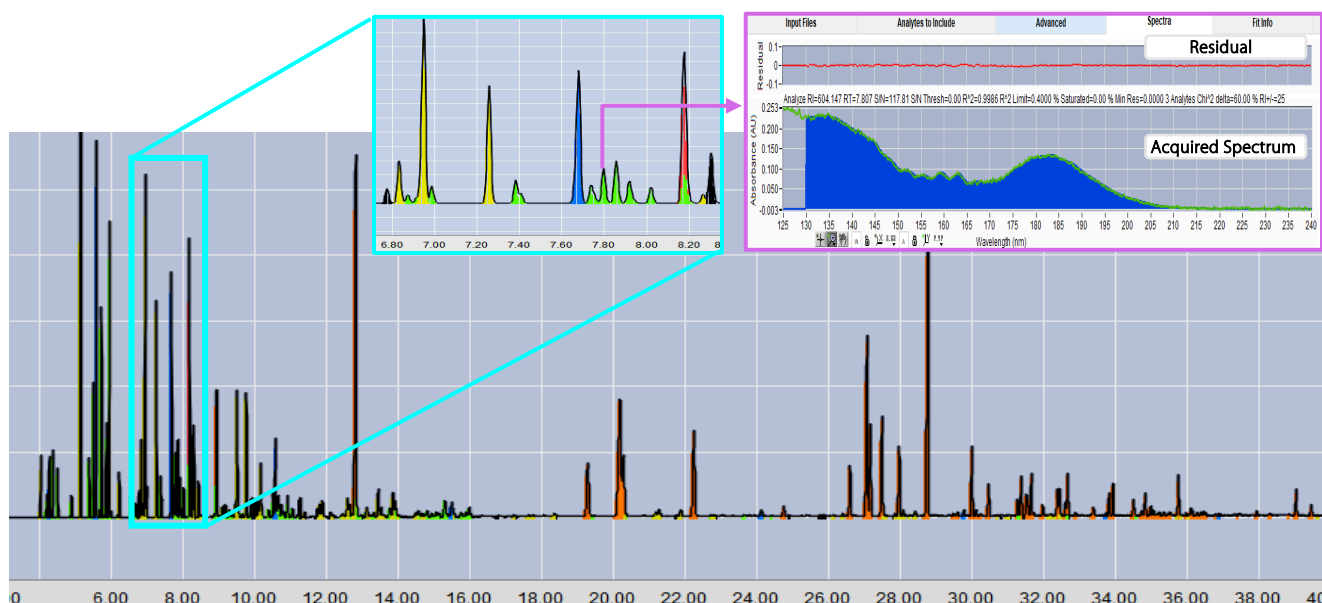


Fig. 8 Chromatogram and VUV absorbance spectra for gasoline sample

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➤ **VGA-100/ VGA-101**
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