PIONA Analysis using VUV

- ASTM D8071, prEN17734

- Identification by distinct UV spectra

- 5 ASTM/EN methods in one

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GAS offers custom configured GC analysers for many application fields for over 50 years. GAS analysers are designed to meet many standardised methods from GPA, ASTM, UOP, ISO, EN and others. The efficient configurations are based on proven GC technology, resulting in robust, highly productive instruments with an optimal return on investment.

ASTM Method D8071 and prEN17734 provide complete PIONA compound class characterisation as an alternative to ASTM D6839. Spectroscopy Detection (GC-VUV) from VUV Analytics offers relative simple instrumentation and automated analysis software with short runtimes and robust and reliable results.

The power of VUV spectra

Hydrocarbon analysis that previously required complex chromatographic separation can be simplified and shortened due to the ability to deconvolve overlapping spectral responses (figure 1). VUV absorbance spectra are typically highly structured and distinct for individual compounds, yet exhibit the intrinsic property of having similar features when measuring related compound classes, see figure 2. GC-VUV absorbance data is inherently three dimensional (time, absorbance, wavelength) and specific to the compound chemical structure.

Unmistakable spectral information

Due to the distinct spectra, the method is not dependent on very precise retention times (normally needed for DHA) or cutting times (column switching systems) , which often leads to error-prone results. VUV offers accurate individual compound speciation and bulk compound class characterisation (PIONA).
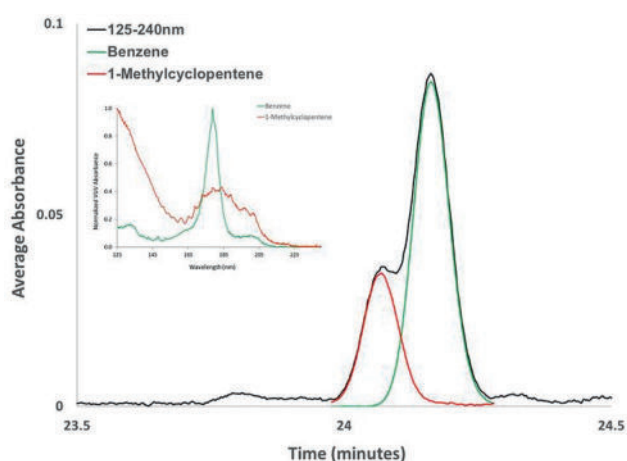
Straightforward instrument

GC-VUV uses easy instrumentation: Thermo Trace GC 1600 gas chromatograph, a single capillary column and VUV-VGA detector (figure 7). No traps, pre-column tuning or calibration requirements are needed. Method setup is easy, operational costs are low and time-consuming manual data review is no longer required.
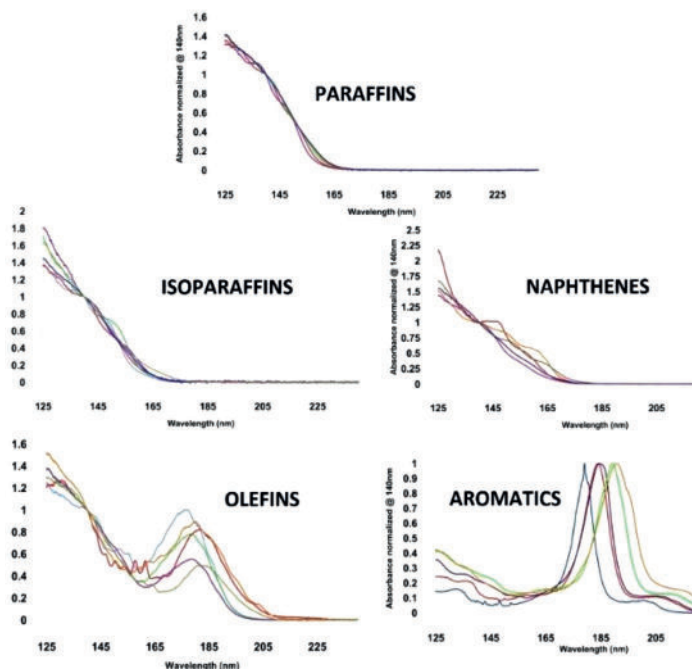

Figure 1
Example GC-VUV chromatogram of gasoline. Benzene and 1-methylcyclopentene are not well separated (black). Relative proportion of both components is displayed after deconvolution by VUV software (red/green).

Figure 2
Distinct spectra for PIONA component classes. VUV spectra are highly stable and independent of instrument settings. Reliable identification is also offered for paraffins and iso-paraffins, which apparently have small spectral differences.

Results

PIONA - ASTM D8071

ASTM D8071 provides compound class characterisation (PIONA) and individual compounds methanol, ethanol, isooctane, BTEX and naphthalenes. Excellent equivalence with existing methods D5443 & D6839 (Reformulyzer) is proven after completing an extensive Interlaboratory Study (ILS). D8071 also shows correlations equations for aromatics (D5769 & D1319), benzene (D3606 & D5769), olefins (D1319 & D6550), and ethanol (D5599), providing five ASTM methods in one. PIONA-VUV is fast: only 34 minutes runtime.

PIONA - prEN17734 / EN 228

prEN17734 is used for the determination of saturated (paraffinic, iso-paraffinic and naphthenic), olefinic, aromatic and oxygenated hydrocarbons in automotive motor gasoline according to European fuel specifications such as EN 228. The test method is based on ASTM D8071 with modifications to the gas chromatographic oven temperature profile, and a larger number of oxygenates is analysed. See figure 6.
Figure 3,4 and 5 show ASTM D8071 reporting.

Volume %

C#	P	I	O	N	A	Oxy	Total
C1							
C2						10.24	10.24
C3			0.00				0.00
C4	1.45	0.09	0.05				1.59
C5	3.43	7.15	4.02	0.06			14.66
C6	2.16	8.07	2.37	1.67	0.67		14.94
C7	1.33	5.83	0.91	1.71	3.22		13.00
C8	0.61	18.46	0.64	1.70	4.84		26.26
C9	0.37	3.36	0.19	0.73	5.28		9.93
C10	0.20	1.01	1.02	0.70	2.27		5.21
C11	0.05	0.84	0.41	0.39	1.08		2.78
C12		0.23	0.28	0.01	0.36		0.89
C13		0.18	0.10		0.16		0.45
C14		0.06					0.06
C15		0.00					0.00
Total	9.62	45.29	10.00	6.96	17.88	10.24	100.00

Figure 3
PIONA report in volume %. Mass % and mole % are also available.

Report Name	Category	Retention Time (min)	Mass %	Volume %	Mole %	C#
Methanol						
Ethanol	Alcohol	2.77	11.04	10.24	21.12	2
iso-octane	Isoparaffin	6.09	7.31	7.73	5.64	8
Naphthalene	Aromatic	23.55	0.21	0.15	0.14	10
Methylnaphthalenes	Aromatic		0.25	0.18	0.15	11
Benzene	Aromatic	4.93	0.80	0.67	0.90	6
Toluene	Aromatic	9.03	3.82	3.22	3.65	7
Ethylbenzene	Aromatic	14.27	1.02	0.86	0.84	8
Xylenes	Aromatic		4.73	3.98	3.93	8

Figure 4
Example report of individual species like oxygenates, aromatics and iso-paraffins. Results in mass %, volume % and mole %.
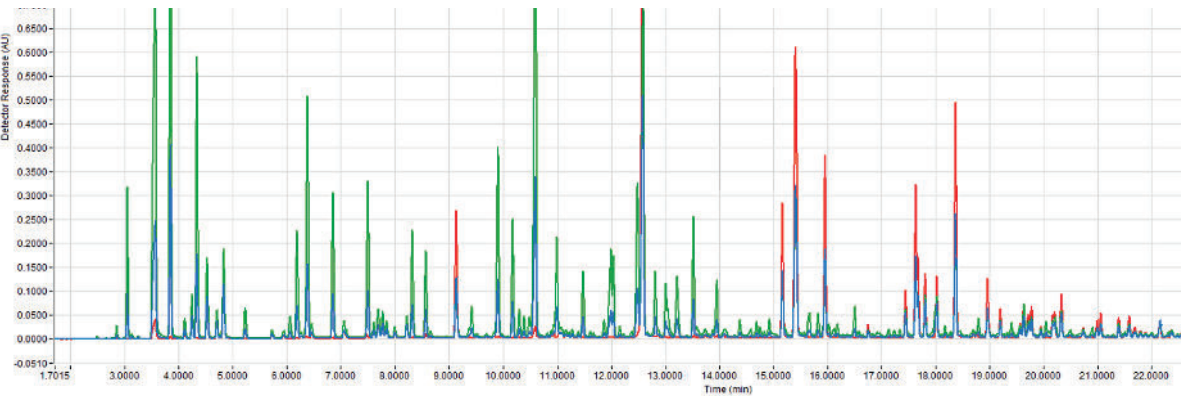

Figure 5
Example chromatogram by VUV-Analyze™ engine, showing spectral filters 170-200 nm (red, aromatics) and 125-160 nm (yellow, saturates). The blue graph represents the total signal. The runtime is 34 minutes.

ASTM D8071 - prEN17734

Standardised method:	ASTM D8071; prEN17734
Application:	Characterisation of PIONA+ (Paraffins, Iso-paraffins, Olefins, Naphthenes, Aromatics, Oxygenates) compounds in various hydrocarbon mixtures.
Analysis Time:	34 minutes
Column type:	Restek Rtx-1, 30m*0.25mm, df=0.25u
GC oven temperature program ASTM D8071:	35 °C (2 min) - 15 °C/min - 200 °C.
GC oven temperature program prEN17734:	5 °C (5 min) - 7.5 °C/min - 200 °C.

Property	Applicable Range (% (V/V))
Saturates	22 to 92
Olefins	0,5 to 42
Aromatics	2.7 to 63
Benzene	0,07 to 2,5
Toluene	0,4 to 31
Ethylbenzene	0,1 to 3,6
Xylenes	0,4 to 19
Methanol	0,06 to 15
Ethanol	0,04 to 25
MTBE	0,25 to 22
ETBE	0,25 to 23
TAME	0,25 to 22
TAEE	0,25 to 8.5
Oxygen	0,05 to 7,5 %(m/m)
Isopropanol	*
Isobutanol	*
tert-Butanol	*
Propanol	*
Acetone	*
tert-Pentanol	*
DIPE	*

Figure 7   VUV Analytics VGA-100 + Thermo Trace GC 1600

Figure 6   prEN17734 ranges of method applicability.
* range not set yet by ILS

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