

**GLOBAL™
ANALYSER
SOLUTIONS**

G·A·S



APPLICATION NOTE 206WA0814F

Fast DHA

Detailed Hydrocarbon Analyser

ASTM D5134 D6729
D6730 D6733
D7900
IP 601
Fast DHA
DHA Front End

G·A·S offers custom configured GC analysers for complex separations, data processing and reporting. We have over 35 years of experience in designing and building turnkey analysers for many application fields. Our analysers are designed to meet many accepted standard methods (like GPA, ASTM, UOP and ISO) in the Oil and Gas industry. The efficient hardware configurations are based on proven GC technology, resulting in robust instruments with an optimal return on investment.

The G·A·S DHA analyser offers detailed characterisation of petroleum streams like spark ignition engine fuels. Undiluted samples are injected on a high resolution capillary column, for the best possible separation of all individual components. Dedicated, fully automated software provides detailed reporting of the sample composition and calculation of several physical parameters. The G·A·S DHA analyser is the solution for all published ASTM, DIN, EN and IP methods.

GC instruments

DHA methods are based on obtaining as much as possible separation of individual components, using a single high resolution capillary column. Undiluted samples are injected using Split-Splitless or PTV injector with high split ratio, and FID is used for detection. The Thermo Trace 1300 GC is the optimal choice for this type of analysis, because the low thermal mass oven design offers superb retention time stability. This is of great importance for DHA, since component identification relies on retention time indices from a database.

iConnect module concept

The Trace 1300 GC offers the unique Instant Connect concept. Injector and detector modules can be replaced by the user in minutes, guaranteeing high uptime and low maintenance costs. See figure 2.

Columns and options

The columns for DHA are described by ASTM and other standardised methods. Restek Rtx-1, 50m*0.21mm is applied for ASTM D5134, while Rtx-DHA 100, 100m*0.25mm, is used for ASTM D6729. An optional tuning column is available for enhanced separation of oxygenated components (ASTM D6730/DHAX).

Depending on the complexity of the sample, the GC oven programming starts at 30 °C or at sub-ambient temperatures (cryogenic cooling option). The latter is especially needed in case of high olefin content and/or C1-C3 light petroleum compounds.

The typical analysis time for fast DHA is 80 minutes, and 140 minutes for the classical DHA method.



Figure 2. iConnect injector and detector technology



Figure 1. Trace 1310GC with AS 1310 autosampler



DHA calculation pack for Chromeleon V2.6								
Detailed Hydrocarbon Analysis								
Instrument	GC1	Sequence name	# Data G.A.S. FAST DHA pack (ASTM D6730)					
Instrument Method	DHA	Data Vault	ChromeleonLocal					
Processing Method	DHA - D6730 Calibration PIONA	Report Template	DHA Report D6730 V2.6					
Data File	DEHA-X	Seq. Line	8					
Injection Date	15/Aug/2014	Vial no.	116					
Injection Time	14:58	Inj Vol (uL)	0.2					
Calculation Type	Total	Peaks	159					
Physical property report								
Density @ 60/60 °F	0.7342	Notes:						
RVP @ 100 °F (psi)	4.75							
Research ON (RON)	65.8							
Motor ON (MON)	62.2							
MW (g/mol)	104.82	Gross Heat combustion @ 77 °F (25 °C)	Btu/lb KJ/Kg					
Bromine number	16.99	Nett Heat combustion @ 77 °F (25 °C)	19592 45570					
			18281 42522					
Composition report (mass %) Filter: PIONAX								
Carbon	n-Paraffins	iso-Paraffins	Olefins	Naphthenes	Aromatics	Oxygenates	Unknowns	Total
C1						0.23		0.23
C2						4.76		4.76
C3	0.03						0.02	0.05
C4	1.14	0.34					0.04	1.52
C5	3.49	2.75	1.37			1.84	1.21	10.65
C6	3.78	6.89	1.88	2.66	1.63	1.56		18.40
C7	2.58	7.72	1.36	5.15	3.02		0.05	19.88
C8	1.55	5.02	0.55	2.74	3.33		0.63	13.83
C9	1.18	5.91	1.13	0.59	1.87		0.18	10.86
C10	1.11	3.40	0.50	0.47	5.34			10.84
C11	1.18				1.52			2.69
C12	1.08				1.97			3.05
C12+	3.24						0.01	3.25
Total	20.36	32.03	6.79	11.62	18.68	3.40	2.14	100.00
Composition report (vol %) Filter: PIONAX								
Carbon	n-Paraffins	iso-Paraffins	Olefins	Naphthenes	Aromatics	Oxygenates	Unknowns	Total
C1						0.21		0.21
C2						4.38		4.38
C3	0.04						0.03	0.07
C4	1.43	0.44					0.05	1.93
C5	4.06	3.23	1.54			1.81	1.41	12.04
C6	4.19	7.63	2.03	2.54	1.35	1.53		19.27
C7	2.75	8.23	1.41	4.93	2.54		0.05	19.92
C8	1.61	5.18	0.56	2.57	2.80		0.66	13.37
C9	1.20	6.04	1.13	0.57	1.58		0.18	10.70
C10	1.11	3.40	0.48	0.41	4.50			9.92
C11	1.16				1.29			2.45
C12	1.05				1.57			2.62
C12+	3.11						0.01	3.12
Total	21.71	34.16	7.15	11.03	15.63	3.34	2.39	100.00

Figure 3. G·A·S DHA Calculator report (Chromeleon)

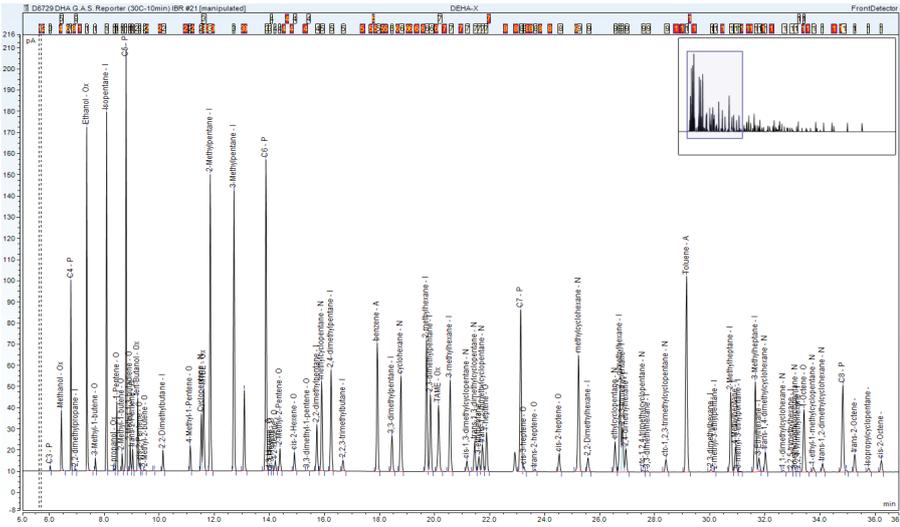


Figure 4. Zoomed DHA chromatogram

Index	Calculated	ID	Known Index	Name	ID	n	C	H	O	S	DBP	MBVI	MON	RON	Vapour Pressure	SG 15	Heat 1	Heat 2	Group	Order	
1				Methanol	31	1	4	1	2.8720	65.00	22.640	101.0	128.8	4.910	0.7965	6.562	8708.9218	0.00		P	1
2				Ethanol	33	2	6	1	0.8695	8.50	27.540	80.2	88.6	38.860	0.8274	19.369	2088.4663	0.00		I	2
3				propane	27	3	8	0	0.8727	47.70	42.000	100.0	100.0	277.500	0.5210	19.875	2058.627	0.00		P	3
4				isobutane	33	4	8	0	0.8742	-5.90	55.100	130.0	170.0	64.580	0.6013	19.341	2062.2871	0.00		I	4
5				butane	37	4	10	0	0.9057	-0.00	58.122	60.0	65.0	51.705	0.6940	19.657	2129.98	0.00		P	5
6				2,2-dimethylpropane	38	4	8	0	0.8742	1.00	55.100	130.0	153.0	48.880	0.6112	19.389	2070.2871	0.00		I	6
7				c2-butene	40	4	8	0	0.8742	3.70	55.100	130.0	153.0	45.750	0.6285	19.415	2072.2871	0.00		I	7
8				1,2-butadiene	41	2	6	1	1.8600	78.20	88.070	102.0	109.0	2.910	0.9877	11.536	1272.01	0.00		O	8
9				3-methyl-1-butene	42	4	8	0	0.8431	15.90	54.100	135.0	185.0	36.770	0.6576	19.567	2058.8223	0.00		I	9
10				cyclohexane	44	4	8	0	0.8742	12.80	55.100	100.0	100.0	34.000	0.6999	19.875	2097.2871	0.00		N	10
11				isopentane	45	5	10	0	0.8955	27.80	73.400	90.0	92.0	28.445	0.6747	19.304	2063.4863	0.00		I	11
12				1,4-pentadiene	45	5	8	0	0.8480	25.00	65.100	100.0	180.0	21.900	0.6963	19.533	2013.2227	0.00		O	12
13				2-butene	47	4	8	0	0.8431	27.00	54.100	100.0	200.0	41.500	0.6959	19.225	2034.8223	0.00		O	13
14				ethylcyclopropane	48	5	10	0	0.8739	35.92	70.100	100.0	100.0	40.000	0.6988	19.440	2071.7539	0.00		O	14
15				1-pentene	48	5	10	0	0.8739	30.00	70.100	100.0	110.0	19.100	0.6468	19.167	2048.7539	0.00		O	15
16				trans-2-pentene	53	5	10	0	0.8739	37.00	70.100	130.0	150.0	15.400	0.6254	19.119	2043.7539	0.00		O	16
17				hexylbenzol	54	4	10	1	1.1610	82.20	84.120	84.0	107.0	5.700	0.9100	14.005	1529.862	0.00		O	17
18				o1,2-pentene	55	5	10	0	0.8739	35.00	70.100	140.0	170.0	14.310	0.6683	19.027	2038.7539	0.00		O	18
19				1,3-pentadiene	56	6	12	0	0.8747	41.00	84.200	120.0	137.0	13.000	0.6684	19.028	2038.6078	0.00		O	19
20				3-methyl-2-butene	57	5	10	0	0.8480	40.80	65.100	100.0	180.0	13.200	0.6916	18.579	1965.2227	0.00		O	20
21				cyclopentadiene	60	5	6	0	0.8240	41.50	55.100	200.0	220.0	0.000	0.8241	18.181	1891.58	0.00		O	21
22				2,2-dimethylbutane	61	5	14	0	0.8963	49.70	86.175	93.4	91.8	9.860	0.6935	19.162	2065.8789	0.00		O	22
23				1,3-cyclohexadiene	62	6	8	0	0.8480	44.10	65.100	100.0	180.0	11.200	0.6994	18.806	1994.2227	0.00		O	23

Figure 5. Chromeleon internal database for ASTM 6729

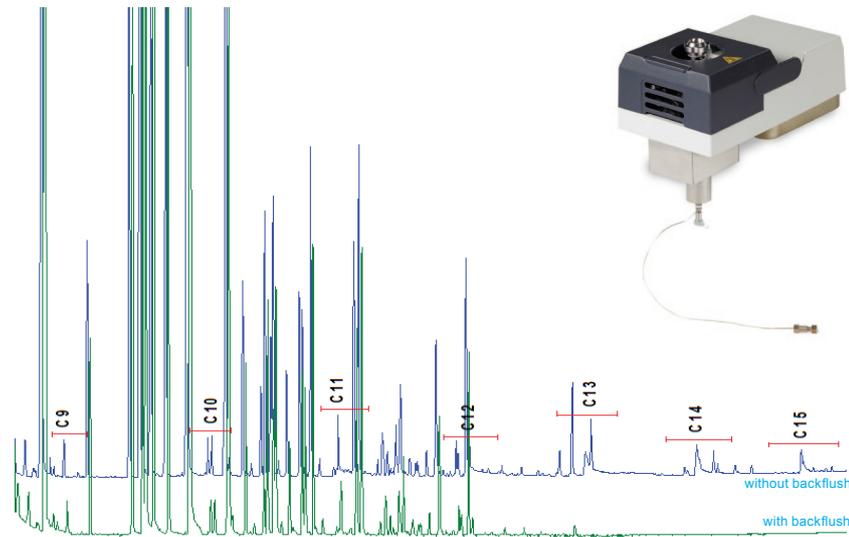


Figure 6. DHA Front End: backflush of C13+ using iConnect PTV BF module



G.A.S DHA Calculator software.

G.A.S offers DHA calculation software that is fully integrated in Chromeleon datasystem. The result is a very user-friendly and transparent system. Identification, calculation and reporting start automatically after each run, with the report shown in figure 3 as a result. The DHA Calculator software provides a solution for several published standard methods.

Identification and easy updating of the database

A calibration mixture containing n-alkanes is used to calculate the retention time indices of all components in the sample. The obtained indices are compared with known indices from the internal component database, see figure 5. The database with retention indices of 500 components is part of the software package. The graphical tuning of the database is an easy operation.

Results

The analysis results for each individual component are reported in mass% and volume% to the nearest 0.001 % for accurate results.

Calculation of group type and physical parameters

Besides reporting of all components, also hydrocarbon group type data is presented. These groups include normal, iso- and cyclic saturates, unsaturates, aromatic component and oxygenates (O-PIONA). Physical parameters like Specific Gravity, MON, RON, Vapour Pressure and Molar Weight are reported as well. See figure 3.

Custom calculations

Custom calculations like n-C4/i-C4 ratio are added on request.

Database filters

Database filters are available to exclude component groups in specific sample streams (PNA, PIONA, PIONAX) for reliable identification.

ASTM D7900: DHA Front End + Simdist MERGE

DHA front-end analysis according to ASTM D7900 is available using the optional iConnect PTV backflush module, for C₁-C₉ detailed analysis in crude oil. C₁₃ and higher boiling components are backflushed, see figure 6. The Simdist data can be merged with ASTM D7169 data for full characterisation of crude oil.

Specifications

Standard methods: ASTM D5134, D6729, D6730, D6733, D7900, IP601, IP PM DL, Fast DHA, DHA Front End.

HARDWARE

Configuration: 1-channel instrument based on Thermo Trace 1300 GC with iConnect SSL and FID,

Triplus RSH or AS/AI-1310 liquid autosamplers

Optional: iConnect PTV module with backflush for DHA-front end analysis.

Cryogenic oven cooling (CO₂ or LN₂)

Hydrogen safety system in case of Hydrogen carrier gas

Application:

Detailed analysis of petroleum products in the range of gasoline to middle distillates. Separation of as many as possible components using a long high resolution capillary column with optional pre-column for polarity tuning. Dedicated DHA software for analysis of the individual component concentrations; grouping on carbon number; grouping on component type (O-PIONA); and calculation of the various physical properties of the sample. Software merge of DHA and Simdist data in case of DHA in crudes.

Sample requirements: Undiluted sample injection.

Analysis Time: Typical 80 minutes for Fast DHA using H₂ carrier gas; 140 minutes in case of the classical method

Calibration standards: G.A.S supplies all needed calibration standards and reference samples

SOFTWARE

G.A.S DHA Calculator: integrated calculation module in Chromeleon.

Reporting of:

- individual components (mass% and volume%)
- O-PIONA group type data (mass% and volume%)
- physical properties: Specific Gravity, True Boiling Point, MON, RON, Reid Vapour Pressure, RVP, Bromine number, Gross heat combustion (Btu/lb), Nett heat combustion (Btu/lb), Molecular Weight
- Gross + Nett heat combustion (Btu/lb and KJ/kg)
- custom calculations on request
- database filters for selective identification (PNA, PIONA, PIONAX)
- DHA/Simdist merge according to ASTM D7900



Figure 7. Calibration standards and reference samples

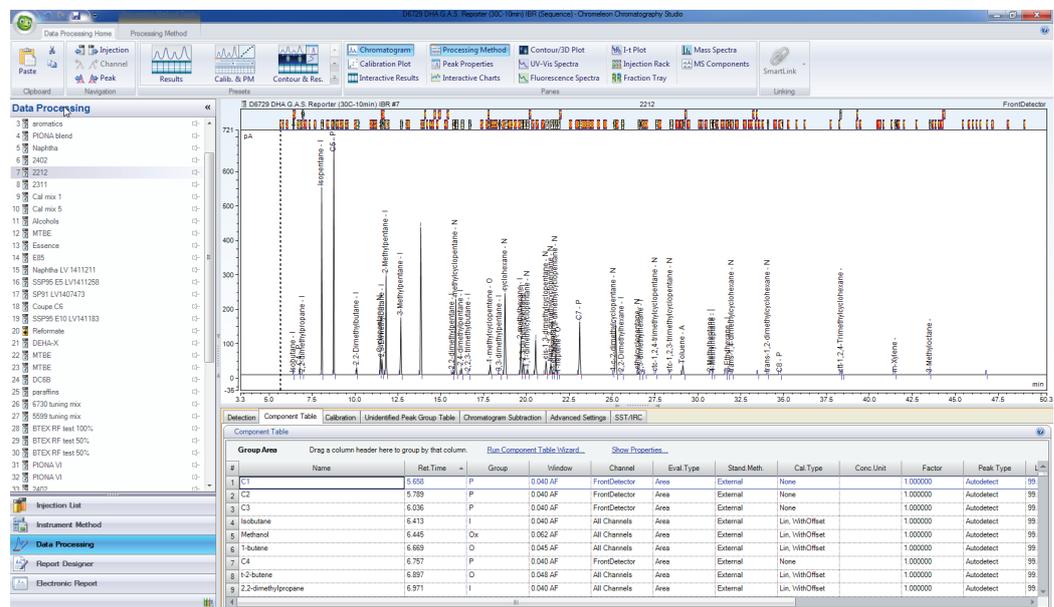


Figure 8. Chromeleon datasytem - DHA workflow



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