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 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.

Figure 1. Trace 1310GC with AS 1310 autosampler

## 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.

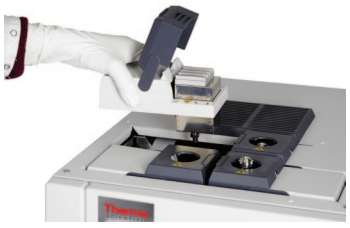

Figure 2. iConnect injector and detector technology

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 | | **Btu/lb** | **KJ/Kg** |
| **MW (g/mol)** | 104.82 | **Gross Heat combustion @ 77 °F (25 °C)** | 19592 | 45570 |
| **Bromine number** | 16.99 | **Nett Heat combustion @ 77 °F (25 °C)** | 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)

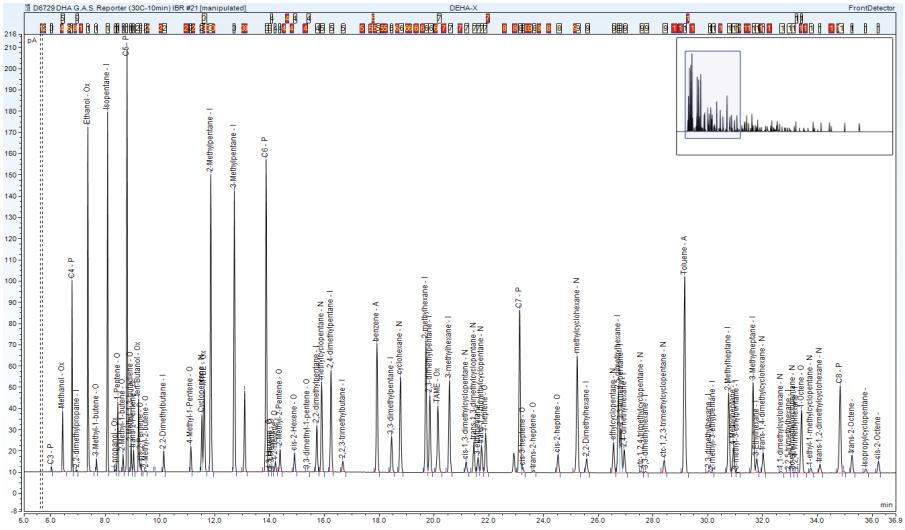

Figure 4. Zoomed DHA chromatogram

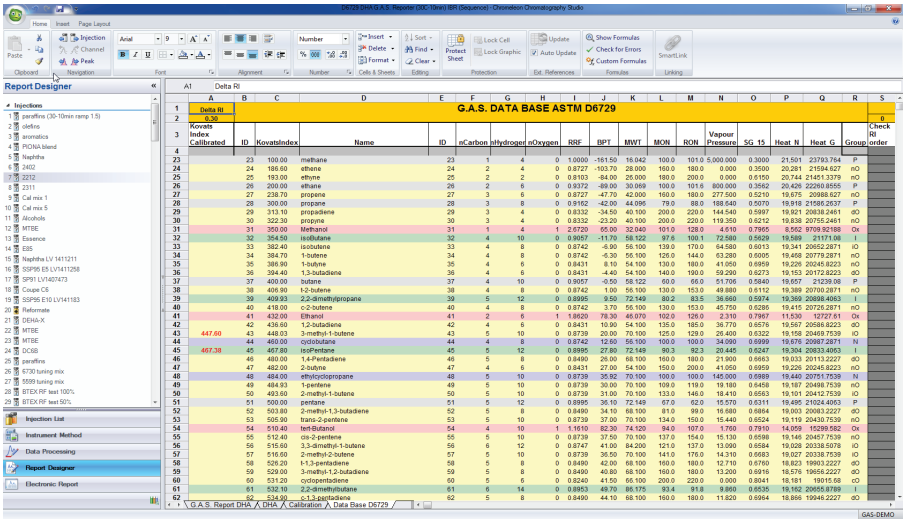

Figure 5. Chromeleon internal database for ASTM 6729

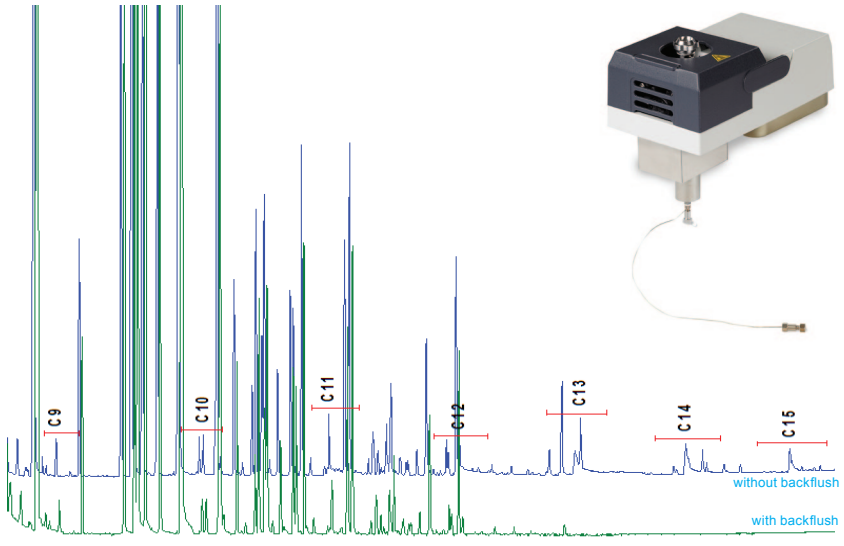


Figure 6. DHA Front End: backflush of C13+ using iConnect PTV BF module

## 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 $C_1$-$C_9$ detailed analysis in crude oil. $C_{13}$ 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 ($CO_2$ or $LN_2$)
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 $H_2$ carrier gas; 140 minutes in case of the classical method

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

Figure 7. 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

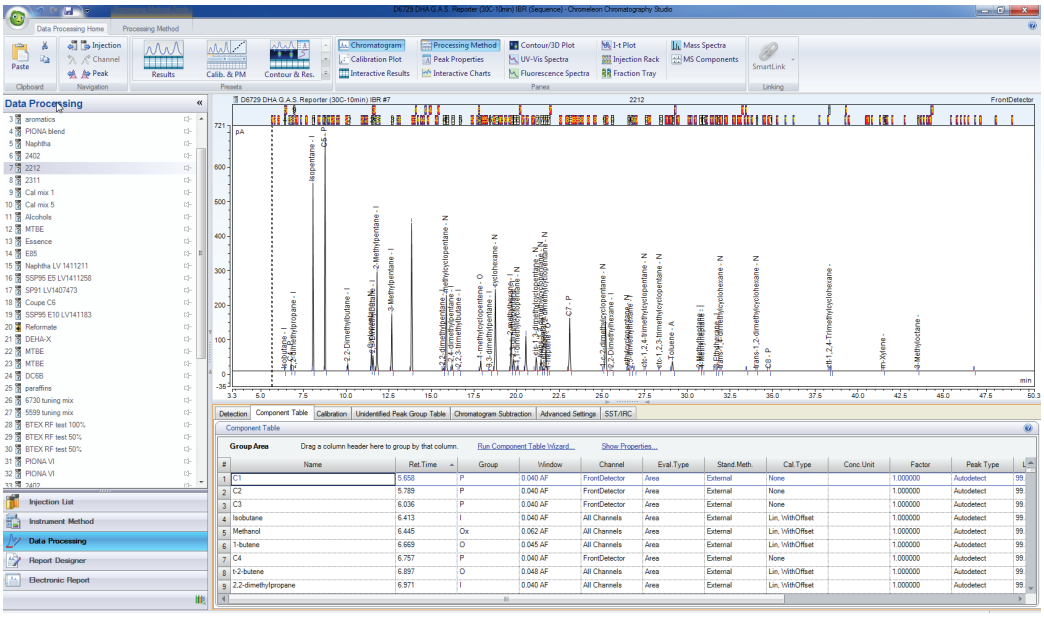

Figure 8. Chromeleom datasystem - DHA workflow



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