PRODUCT FOCUS: Master GC Turn-key Analysers for Total Petrochemical Solutions

The determination of volatile and semi-volatile components in petrochemicals is of utmost importance to fulfill research, quality control, and process monitoring purposes. With this in mind, DANI offers complete solutions, including instrumentation, applications, supplies, and services, providing specialised turn-key analysers to meet the most challenging analytical demands. The flexibility and upgradeability featured by the Master GC Fast Gas Chromatograph (Figure 1) easily support an array of custom configurations for special applications.

The Master GC can be equipped with up to three injectors and three detectors simultaneously and allows the use of auxiliary ovens, gas and liquid valves, methaniser, cryogenic cooling device, making the Master GC the most suitable unit for the development of complex analytical systems for the oil, gas refining, and petrochemical segments.

DANI offers a wide range of turn-key analysers covering, among others, natural gas, liquefied petroleum, oxygenates in gasoline, and biodiesel analyses, meeting the specifications given in international regulations. All systems are controlled by the Clarity™ Chromatography Station software, from data acquisition to processing.

Figure 1: Master GC Fast Gas Chromatograph equipped with MASTER AS Liquid Autosampler

Natural Gas Analysis (NGA)

As it is well-known, the commercial value of natural gas is based on its energy content; hence, composition analysis is strictly required to establish the heating value and BTU content. In view of the cost-driven natural gas marketplace, DANI offers the Master GC Turn-key Analyser which provides an innovative three-channel analysis to fulfill the demand of strict quality control routines.

The three-channel system (refer to Figure 2), based on micropacked columns - PLOT Q and Molsieve 5A, uses a μTCD: channel 1 with helium as carrier gas for the detection of permanent gases and channel 2 with nitrogen to enable the detection of helium and hydrogen. On the other hand, hydrocarbons from C_1 to

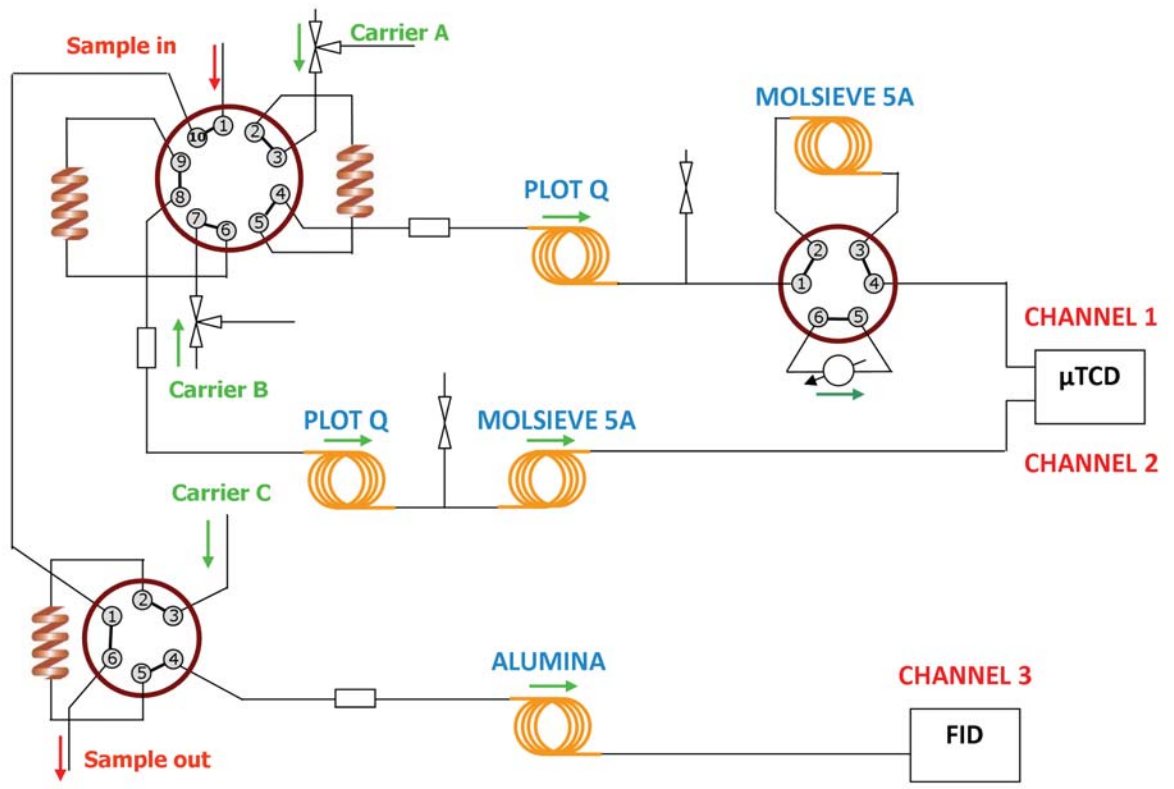

Figure 2: Scheme of the three-channel NGA system.

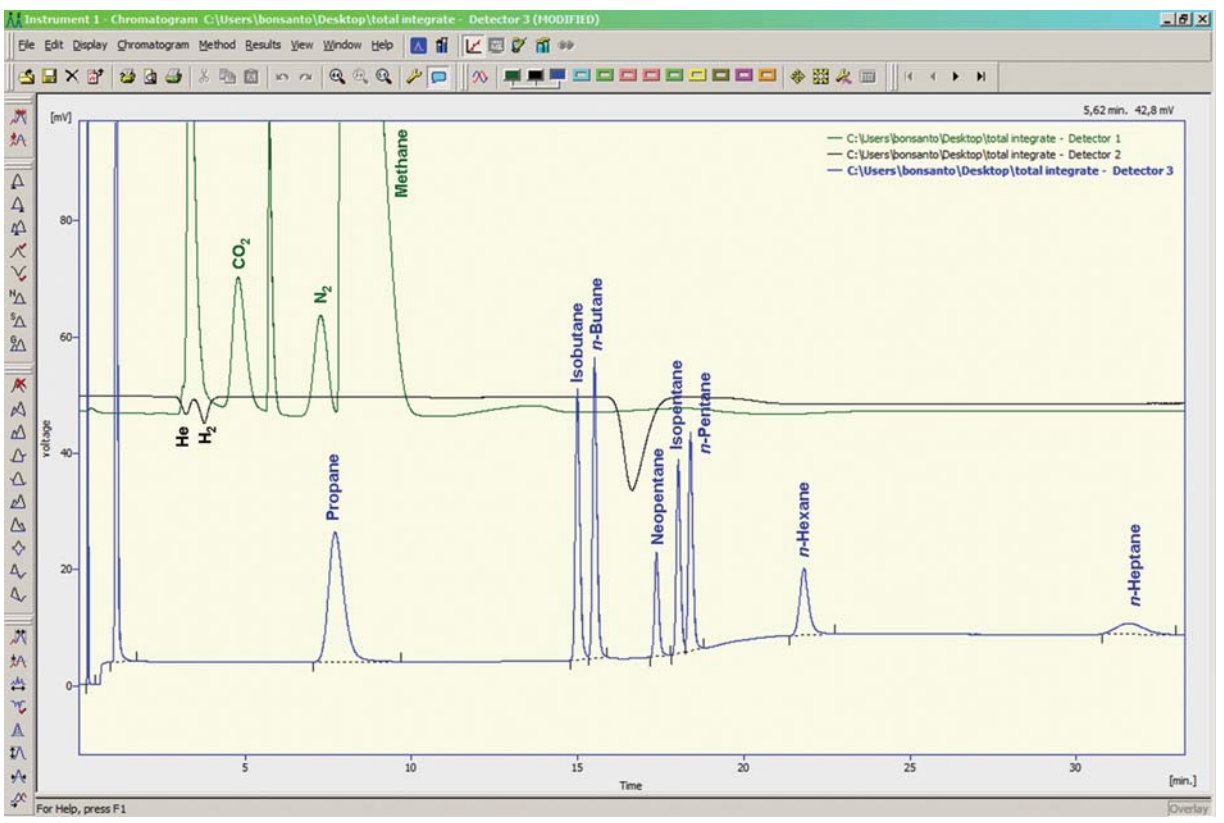

Figure 3: Chromatogram of a natural gas standard mixture (channel 1: green, channel 2: black, and channel 3: blue)

C_7 (or higher) are separated on a PLOT alumina column connected to an FID on channel 3. Sample injection is made through a 10-port sampling valve, while two 6-port switching valves are housed in the High Capacity Auxiliary Oven. Chromatograms simultaneously obtained on the three channels are presented in Figure 3.

The efficient sampling technique allows protecting the Molsieve 5A columns, therefore ensuring a long analytical column life-time and highly reliable analytical results. In addition, the use of a μTCD, not only provides an advantageous increase in sensitivity when compared to a conventional TCD, but also eliminates considerable carrier gas costs. The novel three-channel method meets the specifications given in the ASTM 1945, ISO 6974, ISO 6975, and UOP 539 regulations. Additionally, gas properties calculations are automatically performed according to the selected norm by the NGA Extension of the Clarity™ software.

Liquefied Petroleum Gas (LPG) Analysis

The hydrocarbon composition of liquefied petroleum gas, derived either from petroleum refining or natural gas processing, and propene mixtures have to be accurately determined to ensure their uniform quality. As it is well-known, LPG is mainly composed of C_3 and C_4 with single and double bonds, such as propane, butane, propylene, and butylene. Moreover, the composition of LPG and concentration of each individual component should comply with the specifications given in the ASTM D2163 method.

LPG and propene mixture analyses can be easily performed on the MASTER GC equipped with a Split/Splitless injector (SL/IN) and an FID. Compound separation is carried out on a PLOT alumina column. Additionally, in order to introduce a sample that is representative of the LPG composition, the system is configured with an external two-position valve for liquid sampling, overcoming thereby the components' different vapor pressures.

Determination of Oxygenates in Gasoline

Oxygenated compounds are commonly added to gasoline as anti-knock agents to increase the octane number and decrease emissions by replacing organo-lead compounds. However, the U.S. EPA has specified a minimum of 2 % O_2 by weight (wo %) in gasoline as an attempt to reduce automobile emissions and improve air quality in polluted areas. MTBE is the most widely applied oxygenate and a gasoline concentration of about 12 w/w % MTBE already meets the 2 wo % requirement. Nevertheless, the wide-spread ground-water pollution and uncertain health effects of MTBE has led EPA to call for a substantial usage reduction and to reconsider the 2 wo % requirement.

As it is widely accepted, GC approaches predominate for the analysis of oxygenates in gasoline and the ASTM D4815 method, in particular, proposes the use of a multi-column chromatographic system. The Turn-key Analyser is composed of a MASTER GC equipped with two columns, a switching valve, and an FID. At first the injected sample passes onto a polar TCEP column, to retain oxygenates and heavy hydrocarbons, while lighter hydrocarbons elute to the vent. The retained components are then backflushed into a non-polar column enabling the separation of alcohols and ethers; see chromatogram in Figure 4. Type and concentration of target ethers (MTBE, DIPE, ETBE and TAME) and alcohols (C_1–C_4 alcohols and tert-pentanol) are specified to ensure acceptable commercial gasoline quality. It is worth to highlight that the system also fully meets specifications given in the ASTM D5580 method.

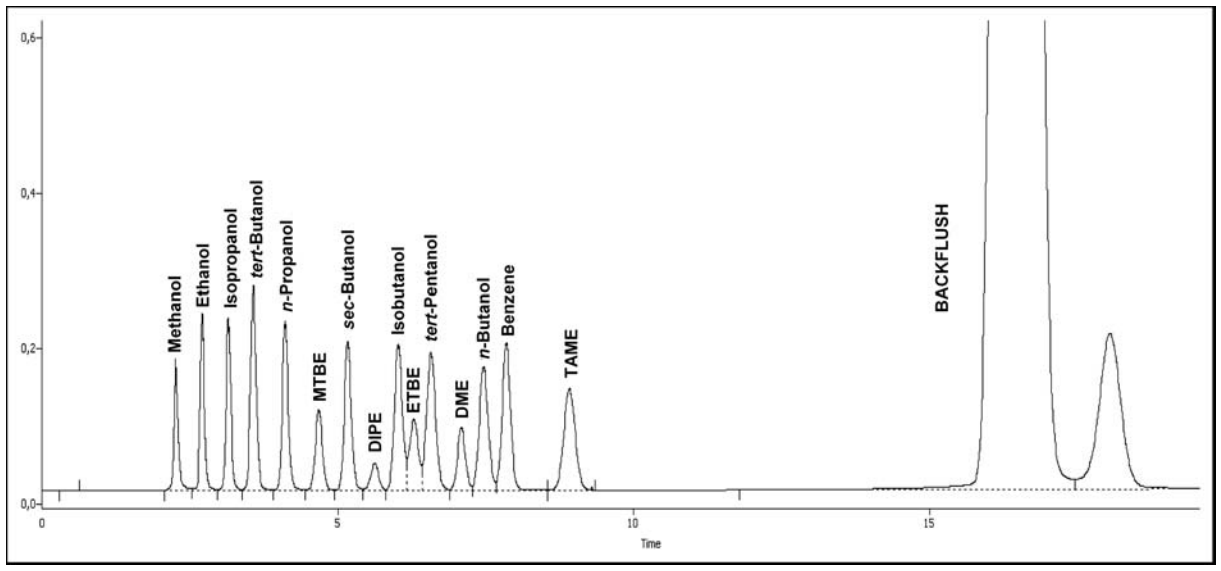

Figure 4: Chromatogram of oxygenate compounds in gasoline (ASTM D4815)

Biodiesel Monitoring

In the last years, the alternative to petroleum-diesel fuel, biodiesel, is receiving worldwide attention. This biofuel is mainly obtained from oil crops, such as rapeseed, palm, soybean, and sunflower, although waste oils from cooking and animal fats can also be used. The extracted oil is converted by transesterification to FAMEs and glycerol. Once isolated, fatty acid methyl esters, i.e. biodiesel, can be blended with petroleum diesel in various concentrations. These blends are widely used in compression-ignition diesel engines, usually as a 5% blend (B5) in cars and up to 20% blend (B20) in city buses.

Undoubtedly, to best characterise a fuel sample its origin and quality level has to be continuously monitored. Additionally, depending on the plant oils used for the production, biodiesel can consist of up to hundred different FAMEs. In this view, biodiesel samples have to meet the specifications given in the DIN EN 14214 in Europe and ASTM D6751 in U.S.A., which specify all legal limits for possible by-products. Within the European Biodiesel regulations EN 14214, EN 14105 sets the standards to determine free and total glycerol and glycerol esters in biodiesel oil, while EN 14110 describes the required method for methanol determination. Furthermore, as established in the EN 14103 to determine the ester content of FAMEs and amount of linolenic acid methyl ester, biodiesel must consist of 90 % (m/m) or more of FAMEs within the range of C14:0 up to C24:1.

It is certain that GC is the ideal technique for measuring important quality parameters in biodiesel. In this view, DANI has an analyser which combines all analytical capabilities in a single versatile unit. The Master GC, equipped with two SL/INs and a PTV, three FIDs and a Master AS Liquid Autosampler, is hyphenated to a HSS 86.50 Head Space Sampler (see Figure 5). Total glycerol and glycerol esters analysis is carried out in the PTV channel, whereas ester content of FAMEs and linolenic acid methyl ester determinations are performed in the SL/IN channel. On the other hand, the analysis of the methanol uses the well-known HSS 86.50 Head Space Sampler to enable the separation of low-boiling point methanol from high-boiling point FAMEs already during the sample preparation step. The HSS 86.50 applies the Valve & Loop technique, which is a renowned and proven headspace sampling mode able to merge robustness with reliability. Moreover, all analyses are performed on DN-BioDiesel columns.

Figure 5: Master GC unit combined with the Master AS Liquid Autosampler is easily hyphenated to the HSS 86.50 Head Space Sampler

Master GC Turn-key Analysers: extended Flexibility and Upgradeability

A wide selection of turn-key analysers is available, besides DANI is also actively engaged in the development of custom GC configurations for special applications. The flexibility and upgradeability featured by the Master GC easily support an array of custom configurations; from the retrofit of a single gas sampling valve and a packed column to four-valve three-channel systems with multiple columns.

An extended number of external devices are supported enabling the installation of different gas and liquid sampling and switching valves. Additionally, when low level CO and CO_2 detections are requested, the Master GC can be equipped with the methaniser to reach the sensitivity level of the FID.

Specific petrochemical applications require some compounds in a sample to be analysed at isothermal temperature, while others are to be analysed using temperature program. As a result, DANI produces two auxiliary ovens with different capacities to house valves and columns for specific multidimensional analyses.

DANI offers tailored and application-specific solutions, which provide everything that customers need for quick and easy setup and operation, efficiently meeting the most demanding analytical requests. Moreover, as regulations become more stringent, the DANI provides the analytical power required for the most demanding analyses.