

# APPLICATION NOTE

# LD16-05



## Refinery gas analyses with MultiDetek2 compact gas chromatograph and PlasmaDetek2 gas detector



The analysis of trace permanent gases has many different fields of application in the petrochemical industry. One of the most important is for controlling the manufacturing process and the product quality. For example, some contaminants as carbon monoxide and carbon dioxide tend to deteriorate the catalysts in the propylene and ethylene polymer grade production.

An instrument for monitoring trace impurities is then required. Many different GC techniques are available on the market. Most of the techniques use a combination of TCD, FID and methanizer for the trace analysis of H<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub>-CH<sub>4</sub>-CO-CO<sub>2</sub> in propylene and ethylene. More precisely, an FID and a methanizer are used to trace CH<sub>4</sub>-CO and CO<sub>2</sub>. A TCD with Hydrogen or Helium carrier gas is used to trace O<sub>2</sub>-N<sub>2</sub> detection. Finally, a second TCD with Argon or Nitrogen carrier gas must be added to trace H<sub>2</sub> detection. These solutions require complex GC solutions with multiple detectors and multiple gas sources for carrier, fuel and air. On top of that, an FPD must be added in some cases when the trace analysis of H<sub>2</sub>S is required.

### **LDETEK SOLUTION:**

The MultiDetek2 compact GC solution combined with the PlasmaDetek2 (PED) can perform the analysis of low concentration H<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub>-CH<sub>4</sub>-CO-CO<sub>2</sub> in different petrochemical gases as propylene, ethylene, propane, butylenes, butane and some others.

This solution offers the advantage of having a single detection technology based on plasma emission detector to achieve detection limits from ppb to ppm as required for this type of application. A single carrier gas source is necessary. It can be Helium or Argon depending on the availability of gases on site.

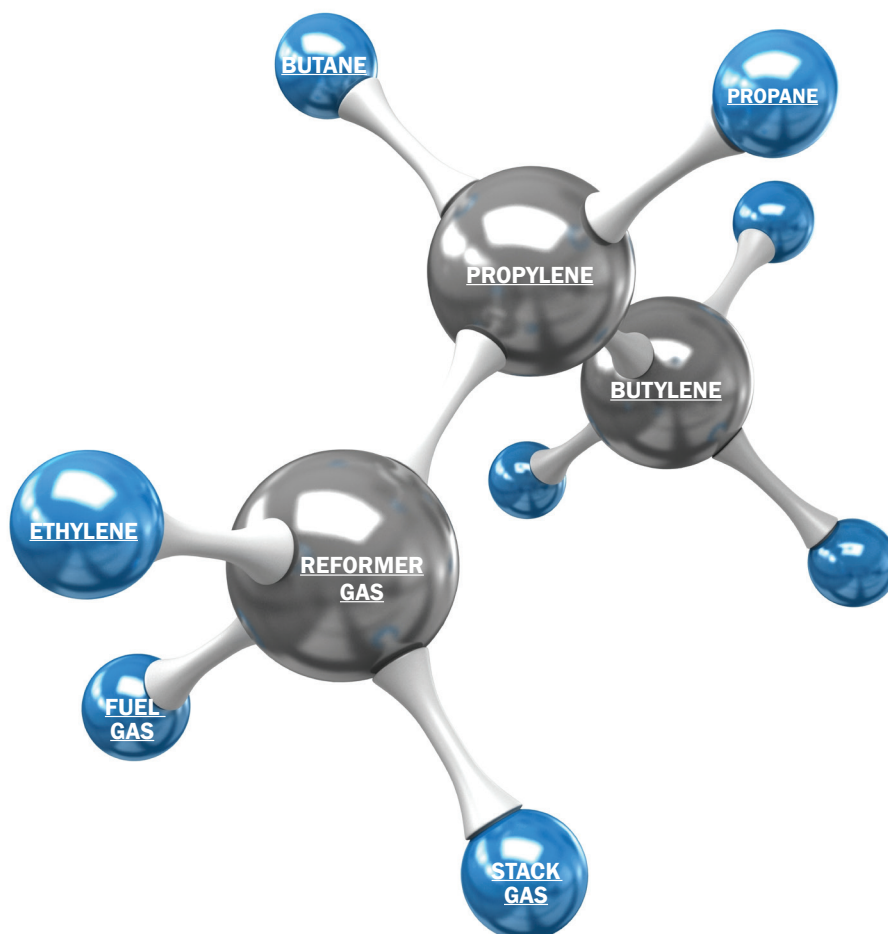
The method is configured with 2 channels merging in one PlasmaDetek2(PED). The first channel has a 10 port injection/backflush diaphragm valve with a Q Bond pre- column that allows the elution of H<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub>-CH<sub>4</sub>-CO as one peak and then vent out the heavier gases. The second column is a molecular sieve used for the separation of the previously mentioned impurities that will go one by one to the PED through a diaphragm selection valve. The second channel will use the same hardware configuration as the first channel except that no molecular sieve column will be added. Then, after the elution of CO<sub>2</sub> through the pre- column, the heavier impurities as propylene, ethylene and others will be vented out of the system. Again, the CO<sub>2</sub> will be redirected to the PlasmaDete2 through the selection valve.

For some other RGA applications, it is also required to measure some light hydrocarbons and sulfurs. For these cases, the MultiDetek2 is so flexible that the configuration can be modified to achieve such measurement capability in the same compact chassis.

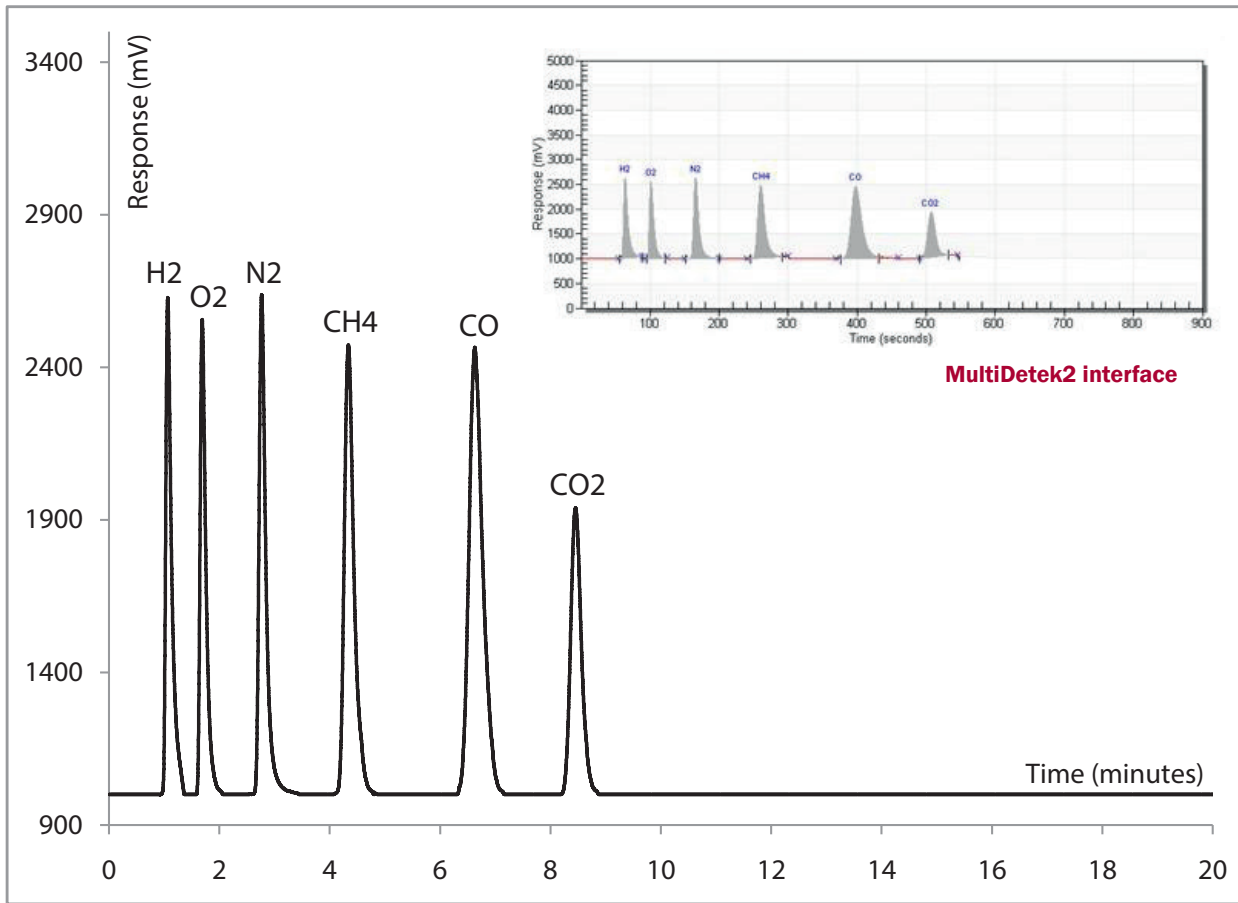
For example, the trace H<sub>2</sub>S analysis can be added in the same channel as the one already used to trace CO<sub>2</sub> with the Q Bond column. No need to add extra detector as FPD or PFPD as generally used since the same PlasmaDetek2 can detect low concentration sulfurs. In the case that H<sub>2</sub>S is added, then coated gas lines must be used to reduce surface adsorption. The detector doesn't have to be modified since it is made of Quartz, which is perfectly inert to trace sulfur.

For the light hydrocarbon analysis using the same MultiDetek2, a diaphragm valve network channel combined with Alumina type column and a second PlasmaDetek2 configured for hydrocarbons can be added. It is also possible to add an FID detector in the same unit if required.

**The MultiDetek2 can be used in many different application fields related to the refinery gas analyses.**



**RESULTS:**



**Figure 1:** Chromatogram of trace impurities in balance Propylene

Historic Values

|      | H2    | O2    | N2     | CH4   | CO    | CO2   |
|------|-------|-------|--------|-------|-------|-------|
| 0:31 | 8.103 | 9.177 | 10.531 | 9.687 | 9.675 | 5.186 |
| 7:05 | 8.090 | 9.163 | 10.532 | 9.680 | 9.578 | 5.193 |
| 3:39 | 8.140 | 9.185 | 10.545 | 9.674 | 9.544 | 5.198 |
| 0:14 | 8.113 | 9.184 | 10.537 | 9.657 | 9.578 | 5.171 |
| 4:03 | 8.044 | 8.981 | 10.532 | 9.657 | 9.475 | 5.188 |
| 0:37 | 8.155 | 9.197 | 10.564 | 9.695 | 9.578 | 5.198 |
| 7:11 | 8.155 | 9.209 | 10.586 | 9.694 | 9.695 | 5.113 |
| 3:46 | 8.253 | 9.129 | 10.596 | 9.668 | 9.578 | 5.138 |
| 0:19 | 8.232 | 9.163 | 10.655 | 9.638 | 9.535 | 5.198 |
| 5:53 | 8.233 | 9.226 | 10.612 | 9.602 | 9.544 | 5.226 |
| 3:28 | 8.017 | 9.163 | 10.564 | 9.628 | 9.475 | 5.193 |
| 0:02 | 8.265 | 9.271 | 10.545 | 9.602 | 9.475 | 5.233 |
| 5:35 | 8.218 | 9.267 | 10.579 | 9.644 | 9.578 | 5.198 |
| 3:10 | 8.155 | 9.129 | 10.564 | 9.657 | 9.696 | 5.236 |

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**Figure 2:** Results showing stability from a mixture cylinder containing trace impurities in balance gas Propylene

| <b>COMPONENT</b> | <b>CONCENTRATION</b> | <b>PEAK HEIGHT</b> | <b>NOISE</b> | <b>LDL (3X NOISE)</b> |
|------------------|----------------------|--------------------|--------------|-----------------------|
| H <sub>2</sub>   | 8.155 ppm            | 2701 mV            | 2.2 mV       | 0.020 ppm             |
| O <sub>2</sub>   | 9.129 ppm            | 2655 mV            | 1.5 mV       | 0.015 ppm             |
| N <sub>2</sub>   | 10.564 ppm           | 2740 mV            | 1.1 mV       | 0.012 ppm             |
| CH <sub>4</sub>  | 9.657 ppm            | 2501 mV            | 2 mV         | 0.023 ppm             |
| CO               | 9.696 ppm            | 2482 mV            | 2.5 mV       | 0.029 ppm             |
| CO <sub>2</sub>  | 5.236 ppm            | 2010 mV            | 2.1 mV       | 0.016 ppm             |

Note: other LDL could be obtained with different injection volume and chromatographic conditions

**Figure 3: LDL based on 3 times noise ratio**

## CONCLUSION:

With this simple method, the MultiDetek2 compact and robust GC brings an innovative solution for this type of application. The platform also offers the standard industrial communication protocols, the remote connectivity and a built-in or external PC with software interface. The refinery gas analysis market can now have a compact, robust and flexible GC analyzer using a single detector type (PlasmaDetek2) and a single carrier type to cover the whole range of applications.



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