Application Note 10440

Detection of Impurities in Breathing Oxygen by Pulsed Discharge Detector (PDD)

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Key Words
Gas Chromatography, PDD, Pure Gases Analysis

Goal
To demonstrate the effectiveness of a system composed of a Thermo Scientific™ TRACE™ 1310 Series GC, a Thermo Scientific Instant Connect Pulsed Discharge Detector (PDD) Module and an auxiliary oven in the analysis of impurities in "Avio Oxygen" mixtures.

Introduction
Breathing oxygen is a high purity grade gas. It is used for a wide variety of applications. The most common applications are in the medical field, but it is also used in several similarly important fields. For example, breathing oxygen ("Avio Oxygen") is used in military aviation to help pilots breathe when flying at very high altitudes. In such critical conditions, potential impurities in the oxygen pose a threat to human body functions and need to be carefully monitored. Those with responsibility for the control and certification of such gases use to the Pharmacopoeia (either the US or EU version) as their official reference document. Besides instruction on the storage of this gas and the allowable levels of solid contaminants, the document specifies the types of impurities that must be monitored and their acceptable limits.

The Thermo Scientific™ Instant Connect Pulsed Discharge Detector (PDD), is able to offer a modern and effective solution, targeted for this specific application. The PDD is a universal detector, which uses metastable helium molecules as ionization source. These metastable molecules are generated by electric sparks pulsed in a high purity grade helium flow. The photo-ionization of the compounds is mainly due to a broad band emission (Hopfield emission) arising from the transition of the diatomic helium He2 into the dissociative 2He ground state.

The energy of the photons produced by this transition falls in the interval between 13.5 and 17.7 eV. This energy is high enough to ionize practically any compound present in the carrier gas, and detect it in concentrations in the low ppb area.

Due to its extreme sensitivity, the purity grade of both discharge and carrier gases is a mandatory requirement to avoid compromising the functionality of the system. The presence of impurities in the helium flow would result in incorrect determination/ quantification of compounds or high signal output. As a result, a helium purifier is supplied with the PDD.

The PDD module adds a modular design to the high sensitivity of the PDD allowing quick and easy installation on any TRACE 1300 Series GC, regardless of its previous configuration.

This application note describes a method for identifying and quantifying possible contaminants in breathing oxygen.

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System Setup

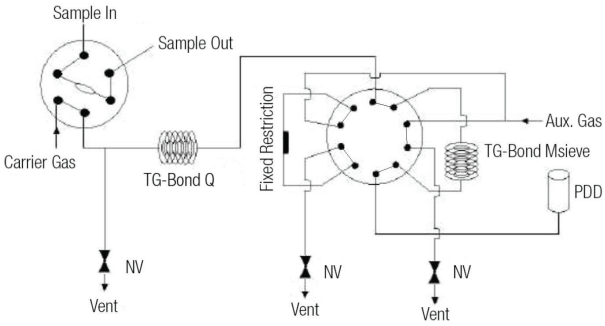

Figure 1. System schematics.

The system is composed of a TRACE 1310 Series GC equipped with an auxiliary carrier gas module and an auxiliary oven. Two valves must be used for gas sampling and column switching.

The sampling valve is a six-port valve equipped with a 250 µL loop, while a ten-port valve is used for column switching.

Both valves are helium-purged. Purging is mandatory because it prevents diffusion of atmospheric air into the gas lines during commutation of the valves. The purge gas is high purity grade helium coming from the helium purifier. Automated and accurate control of the timing of the valve is allowed by the data system. Heating the valves is not required because the sample is gaseous at ambient temperature.

The separation of permanent gases and light hydrocarbons may be successfully performed using a combination of TG Bond Q and Molecular Sieve columns. In this application, two wide bore (0.53 mm ID) columns are used.

The columns used for this application are:

- Thermo Scientific TracePLOT TG-Bond MSieve PLOT 30 m, 0.53 mm ID, p/n 26003-6100 for the separation of oxygen (matrix), nitrogen, methane, and carbon monoxide
- Thermo Scientific TracePLOT TG-Bond Q, 30 m, 0.53 mm ID, p/n 26004-6090 for the separation of carbon dioxide, nitrous oxide, ethylene, ethane, and acetylene.

The sample loaded on the loop is transferred to the analytical columns and split through the first needle valve (NV). In order to avoid overloading the columns, the NV is set to produce a 1/10 split ratio. Once oxygen, along with CO and CH_4 are eluted onto the MSieve column, the 10-port valve is switched. In this new phase, C_2 hydrocarbon isomers, CO_2 and N_2O reach the detector from the TG Bond Q column. During this period the second column is kept in a "store column"-like mode: a slight flow (5–7 mL/min), regulated by an auxiliary pressure regulator, is allowed through this column. The purpose of this minimum flow is to advance the retained compounds very slowly, avoiding any peak broadening and eventually air diffusion from the valve. In the following phase, the valve is switched back to the original position, and the compounds from the MSieve column are eluted to the detector.

A low isothermal oven temperature of 30 °C is used in both cases to enable optimal separation of the compounds.

The parameters set are:
Carrier pressure 150 kPa
Auxiliary gas pressure 50 kPa
Helium discharge flow 30 mL/min, split ratio 1/10
PDD temperature 120 °C

Results and Discussion

A four-point calibration curve was built, employing different gas standard mixtures whose component concentrations are reported in Table 1.

Table 1. Calibration point concentrations (ppm v/v).

	1	2	3	4
CO_2	4.35	5.16	10.5	15
N_2O	0.495	1.04	2.06	3.07
C_2H_2	0.0417	0.058	0.102	0.157
C_2H_4	0.1	0.217	0.317	0.621
C_2H_6	1.05	2.18	3.01	5.09
CH_4	14.3	24.8	46.8	58.9
CO	3.1	5.3	10.8	15.3

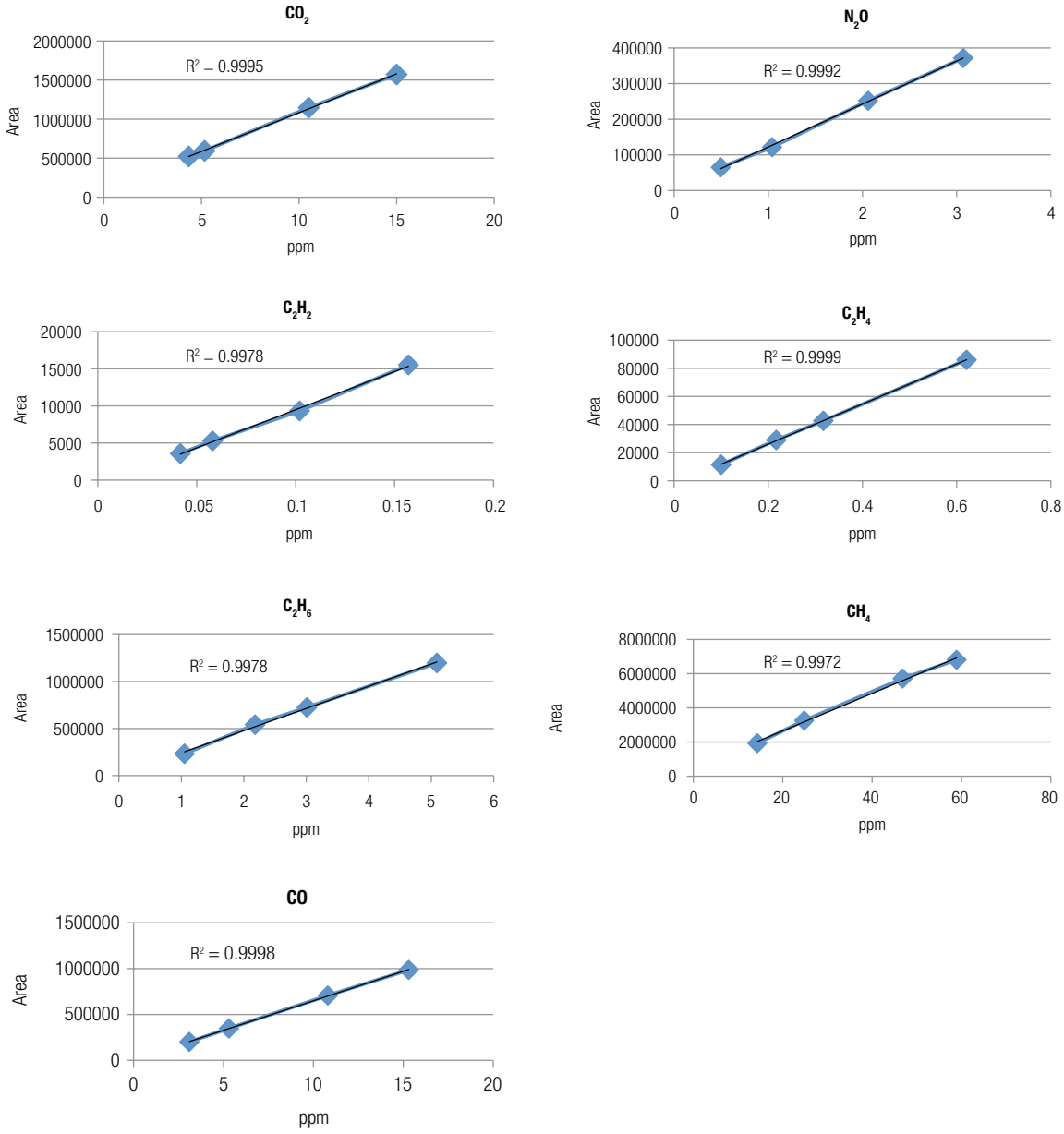

Figure 2. Calibration results.

The calibration shows excellent results in terms of linearity for all of the analyzed compounds, as shown in Figure 2.

Repeatability and method detection limit (MDL) have been calculated employing a different mixture concentration. Table 2 indicates the compound concentration of the standard used, together with the calculated MDL with a 3/1 signal to noise ratio.

Table 2. Standard concentration and MDL.

	Conc (ppm v/v)	MDL (pg)
CO_2	5	0.9
N_2O	5	4.0
C_2H_2	4	0.9
C_2H_4	26	0.6
C_2H_6	1	1.0
CH_4	1	0.7
CO	2	0.7

Table 3. Peak area repeatability.

		CO_2	N_2O	C_2H_2	C_2H_4	C_2H_6	CH_4	CO
Area	avg	3630019	3215883	622280	998488	3027146	21403232	2132629
	Std.Dev	32657	18605	2882	11818	18535	105739	20786
	RSD%	0.9	0.58	0.46	1.18	0.61	0.49	0.98

Table 4. Retention time repeatability.

		CO_2	N_2O	C_2H_2	C_2H_4	C_2H_6	CH_4	CO
R.T.	avg	1.39	1.544	1.91	1.979	2.546	3.303	6.029
	Std.Dev	0.0008	0.0004	0.0009	0.0008	0.0022	0.0032	0.0056
	RSD%	0.057	0.003	0.046	0.041	0.088	0.096	0.094

The results in terms of peak area repeatability, based on 10 consecutive runs of all compounds are summarized in Table 3. All RSD% of the peak areas are below 1.2%

Conclusion

The results delivered by the TRACE 1300 Series GC equipped with the PDD and auxiliary oven are in line with, and sometimes superior to, the stringent requirements of the highly regulated oxygen certification market. The easy-to-install and operate PDD module is a key benefit of this system. All of the maintenance interventions and configuration changes are easy to perform without stopping the gas chromatograph from completing other analyses and assuring continuous productivity.

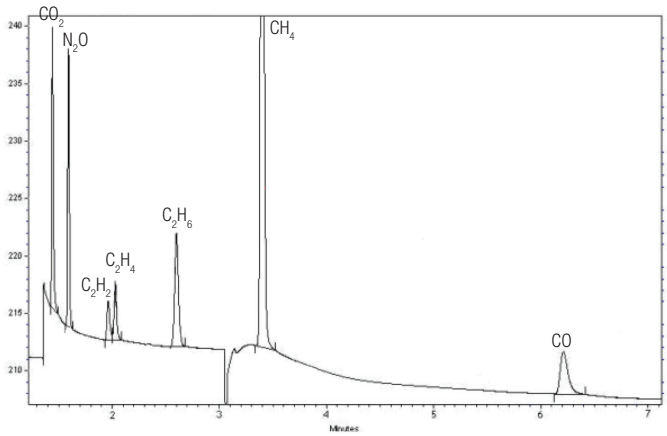

Figure 3. Gas standard chromatogram. The baseline distortion between the C_2H_6 and the CH_4 peaks is due to the 10-port valve switching after the store column phase.

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