An Innovative, Reliable, Easy Set-up for the Analysis of Permanent Gases via PDD and Gas Sampling Valve

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Abstract

The performance of an instant connect Pulsed Discharge Detector (PDD) and a gas sampling valve modules, installed in a gas chromatograph (GC) based on a new modular concept, is evaluated. These detector and injector modules are independent GC components which are fully self-sufficient sub-units of the GC, incorporating all electronic circuits and pneumatic controls together with the injector body or detector cell and storing calibration information, for results consistency. As gas analysis typically requires use of various packed or plot columns, sample loops, valves and a plumbing configuration, an auxiliary oven was mounted on one side of the GC. Some examples of the instant connect PDD module applicability to the analysis and characterization of gas samples are presented.

Introduction

The PDD uses metastable He atoms as an ionization source. These atoms are generated by electric sparks pulsed in a high purity grade He flow. Ionization of the compounds is due mainly to a broad band emission (Hopfield emission) arising from the transition of the diatomic helium He_2 into dissociative 2He ground state. The energy of the photons produced by this transition falls into 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 therefore to detect it in concentrations in the low ppb range. The PDD is a universal, non-destructive, high sensitivity detector particularly suited for the analysis of permanent gases.

In this poster, we introduce the innovative Thermo Scientific™ Instant Connect PDD (Figure 1), a versatile and self-sufficient module, including the electronic and pneumatic circuits necessary for its control and gas supply. This PDD can be installed on any TRACE 1300 Series GC regardless of its previous configuration.

Figure 1. Instant Connect PDD - Detector Module.

As gas analysis typically requires use of various packed or plot columns, sample loops, valves to switch columns and a plumbing configuration, an auxiliary oven was mounted on one side of the gas chromatograph. The examples in this poster illustrate the versatility of the Instant Connect PDD, coupled with the TRACE 1310 Auxiliary Oven, for a variety of applications with multiple column setups suitable for the analysis of pure gases.

Methods

Sample injection was performed by a valve-and-loop injector and the path of the analyte was controlled by switching valves in a time based way to send the different portions of the effluent carrier gas to the different columns, to the detector, or to the vent.

All of the examples in this poster use a TRACE 1310 GC equipped with an Instant Connect PDD Module and an TRACE 1310 Auxiliary Oven. Valve and column configurations differ from one example to the other.

Sample acquisition, system control and valve switching was handled by the Thermo Scientific Dionex™ Chromeleon™ 7.2 Chromatography Data System software.

Analysis of Impurities in Bulk Gases

For this application, the hardware configuration comprises three purged valves (VICI Valco Co. Inc.): one six-port sampling valve with a 0.5 mL external loop for the sample and two four-port switching valves. Two wide-bore Plot columns are used for the analyte separation: a 30 m Thermo Scientific TracePLOT™ TG-BOND Q GC column and a 30 m Thermo Scientific TracePLOT™ TG-BOND Msieve 5A GC column. The sample is split by a needle valve (VICI Valco Co.Inc.) mounted just before the first column connection. The analysis is performed by simply switching Valve 2 and Valve 3 in a time-based way, depending on the compound being analyzed. The system pneumatic scheme is illustrated in Figure 2. The gas mixtures analyzed are listed in Table 1.

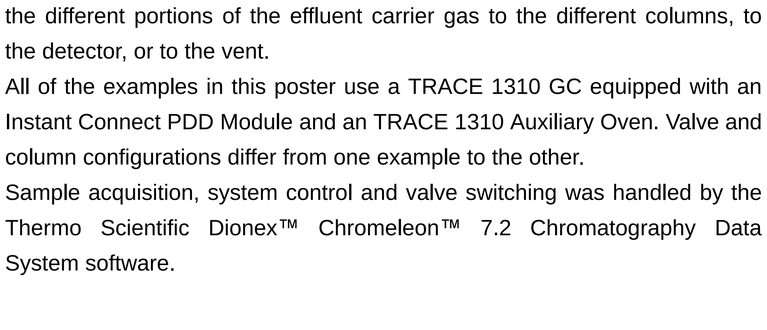

Figure 2. System schematics for gas impurities analysis.

Table 1. Analyzed gas mixes (all values in ppm unless stated otherwise).

He/N_2		He		Ar	
N_2	10%	N_2	2.0	H_2	50.0
O_2	2.0	O_2	0.5	N_2	6.0
CO_2	0.7	CO_2	0.5	O_2	2.6
CH_4	0.2	H_2	0.4	CH_4	0.2
		CO	0.2		
		CH_4	0.03		

Results

The area repeatability of all analyzed samples showed a %RSD <1.5. Figure 3 shows the chromatograms of the analysis for the impurities in helium and argon. The peak intensity for all analytes indicates the high sensitivity achieved in all of these analyses.

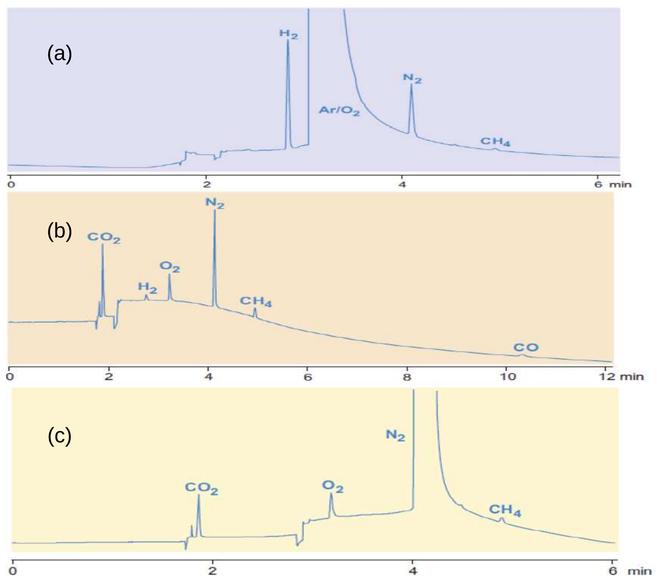

Figure 3. (a) argon, (b) helium, and (c) helium/nitrogen analyses.

Analysis of Impurities in Breathing Oxygen

Two valves are used: a six-port for gas sampling and a ten-port for column switching. The columns used are a TracePLOT TG-BOND Msieve (30 m, 0.53 mm ID) and a TG-BOND Q (30 m, 0.53 mm ID). The configuration is shown in Figure 4. The analyzed compounds are listed in Table 2.

Table 2. Impurities in oxygen (ppm).

CH_4	26.6
CO	5.8
CO_2	5.3
N_2O	4.1
C_2H_6	2.3
C_2H_4	1.0
C_2H_2	1.1

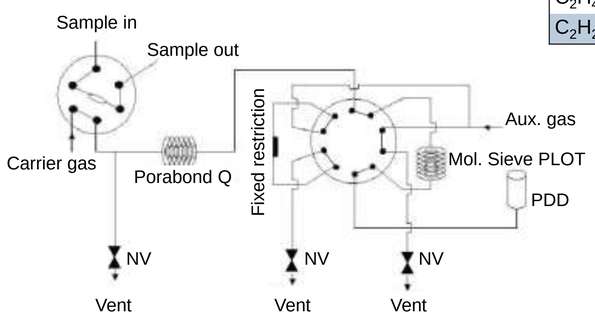

Figure 4. System schematics for analysis of breathing oxygen.

Results

Figure 5 shows the linearity plots for ethylene and acetylene tested on the oxygen mixture. Both show a R^2 greater than 0.999.

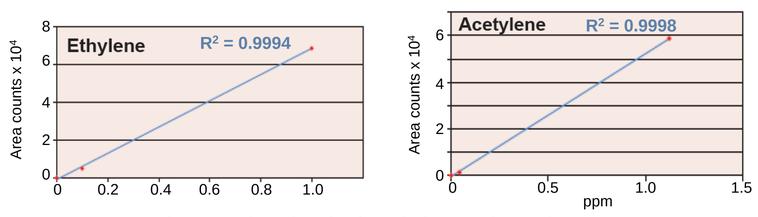

Figure 5. Linearity plot for ethylene and acetylene.

The repeatability of the areas of all samples analyzed showed an %RSD lower than 1.5, as reported in Table 3 along with the minimum detectable quantities. A chromatogram of the analysis is reported in Figure 6.

Table 3. Analysis results.

Compound	Area RSD%	Retention Time RSD%	MDQ (pg) S/N x 3
CH_4	0.494	0.0963	0.6
CO	0.975	0.0936	4.0
CO_2	0.900	0.0560	0.9
N_2O	0.579	0.0279	0.9
C_2H_6	0.612	0.0876	0.7
C_2H_4	1.184	0.0409	0.7
C_2H_2	0.463	0.0457	1.0

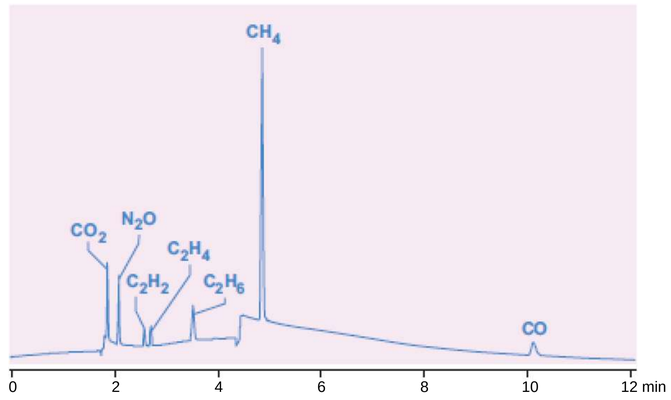

Figure 6. Oxygen analysis chromatogram.

Xenon and Krypton Analysis

The system for this application (Figure 7) includes two analytical channels: the first includes three packed columns: Porapak QS (7 m), Porapak Q (2 m, 1/8”) installed in the valve oven, and MolSieve (2 m) installed in the GC oven. The sample is introduced through a valve (V4) with 1 mL sample loop. This channel should be used to analyze impurities that elute in the tail of Kr and Xe.

The second channel includes a 3 m MolSieve 5Å column installed in the GC oven. The sample is introduced through a valve (V1), with 1 mL sample loop. This channel should be used to analyze impurities such as C_2F_6, H_2, O_2, N_2, Kr, CH_4, and CO in pure Xe or C_2F_6, H_2, O_2, N_2, and Xe in pure Kr. Valves V1 and V4 are used for sample injection and for backflushing the packed column. Valves V2 and V3 direct the sample eluted out of the long Porapak QS column to the 2 m Porapak Q (2) or to the 2 m MolSieve (3) column.

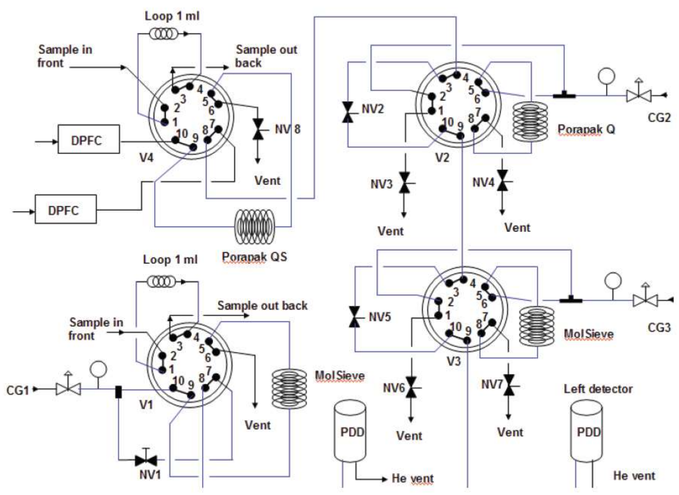

Figure 7. System schematics for Xenon an Krypton analysis.

The configuration in Figure 7 has been tested with different gas mixes in krypton and argon. Figure 8 shows that the CF_4 and C_2F_6 peaks are separate from the large krypton peak. Figure 9 shows the analysis of impurities in xenon.

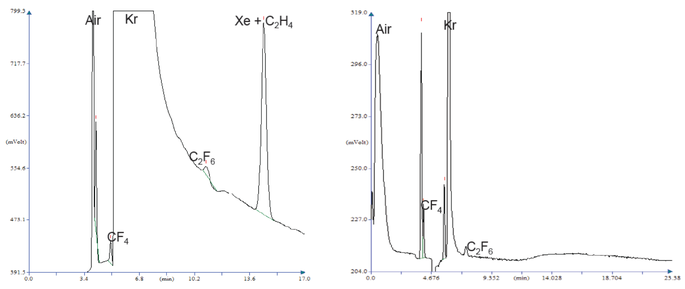

Figure 8. Krypton impurities analysis.

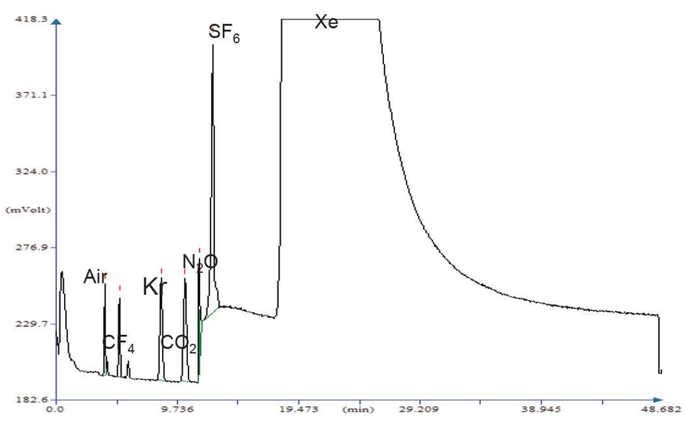

Figure 9. Xenon impurities analysis.

Conclusion

A PDD is an excellent detector for the characterization of gas samples due to its high sensitivity, allowing for the detection of trace impurities. Combined with different column and valve configurations, this detector is applicable to a vast range of analyses. The Thermo Scientific Instant Connect PDD module provides outstanding sensitivity and unmatched flexibility. PDD installation requires no modifications to the GC frame or plumbing.

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