

Determination of permanent gases and light hydrocarbon impurities in breathing Oxygen by Pulsed Discharge Detector (PDD)

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Key Words

- Purity Gases Certification
- Impurities in Breathing Oxygen
- Pulse Discharge Detector (PDD)

Introduction

Breathing Oxygen is a high purity grade gas. As it is an extremely important gas for our metabolism, it is used for a wide variety of applications whenever and wherever respiratory problems may occur. The most common applications are, with no doubt, in the medical field: hyperbaric therapies, respiratory aid, reanimation, burns and ulcerations treatment ect. However, besides this quite predictable area, there are several other not less important fields, in which its use may appear quite unexpected. An example of this may be the use the military aviation makes of it ("Avio Oxygen") in aiding pilots' respiration when flying at very high altitudes or during submarine activities, or its employment in high mountain climbing.

Needless to say that because of the effect that impurities possibly present may cause on the human body in such critical conditions, the purity of this gas has to be highly monitored. The official organism having responsibility over the control and certification of such gas is the Regional Health Ministry. This department, regardless the nationality, as far as the definition of the impurities and their tolerated limits, refers to the Pharmacopoeia* (two versions existing: for US and for EU) as official document.

Besides indication on the storage of this gas and the allowed content of solid contaminants, the document specifies the type of impurities to be detected and their limits.

The determination of the halogen containing compounds indicated is carried out by Electron Capture Detector and is not discussed in this application note. The maximum allowed concentrations of the compounds of interest are listed in the table below reported.

| COMPOUND | < PPM (V/V) |
|--------------------|-------------|
| Carbon dioxide | 5,0 |
| Nitrogen protoxide | 5,0 |
| Carbon monoxide | 5,0 |
| Methane | 60 |
| Acetylene | 0,1 |
| Ethylene | 1,0 |

In this method, the use of a Helium ionisation detector is mentioned as mandatory, although also the FID is indicated for the light hydrocarbons.

The Trace GC in the configuration equipped with the Pulsed Discharge Detector (PDD), is able to offer a modern and effective alternative solution, targeted for this specific application. In fact, in addition to being a Helium ionisation detector, the PDD does not feature any radioactive source thus allowing to eliminate the stringent and expensive steps of control and periodical re-certification such hazardous materials have to undergo.

The TRACE GC for the Determination of Impurities in Oxygen

Detection system

The Pulsed Discharge Detector (PDD) is a universal detector, which uses metastable He atoms as ionisation source.

These are generated by electric sparks pulsed in a high purity grade He flow. The photo-ionisation of the compounds is due mainly due to a broad band emission (Hopfield emission) arising from the transition of the diatomic helium He₂ into 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 ionise practically any compound present in the carrier gas, and therefore to detect it in concentrations ranging in the low ppb area.

It consists of a quartz cell in the upper part, in which high purity grade He, called “discharge gas”, flows. This gas reaches the discharge area consisting of a couple of electrodes connected to a high voltage pulse generator. The photons generated in the discharge zone pass in the lower part of the detector ionising the compounds eluted from the chromatographic column (see figure 1). The electrons so generated are accelerated and measured as electric signal by another couple of electrodes (polarising and collecting electrodes) connected to the electrometer.

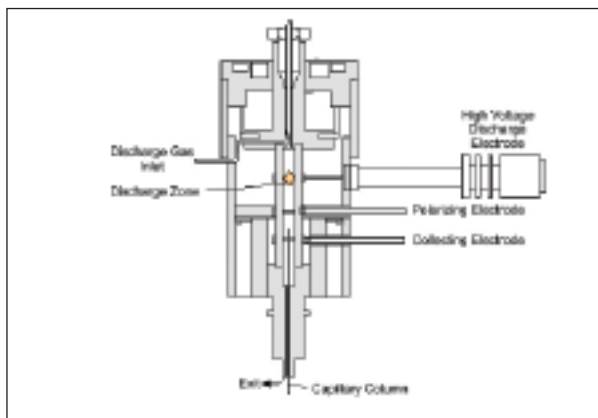


Figure 1: The PDD detector

The flow of the He discharge and the carrier gas are hence flowing in opposite directions (the former enters the detector from the high end the latter from the low end), so to avoid the column flow entering the discharge area where it might contaminate the electrodes. To allow this, a stable constant discharge gas flow of 30 ml/min is generated by setting a pressure of 60 Psi at the entrance of the pneumatic module.

Overall PDD operations on Trace GC are quite simple since all relevant parameters (discharge pulse width and period, bias voltage and He discharge flow rate) are preset and optimised to achieve the highest performance. The only “parameter” to be set is the on/off function, used to activate the pulse generator and activated from the Trace GC keyboard.

Due to its extreme sensitivity, the presence of impurities would result in incorrect determination/quantification of compounds or high signal output.

It is therefore a fundamental requirement for the system to be leak free. Additionally the purity grade of both discharge and carrier gas is a mandatory requirement to avoid compromising the functionality. Because of this, a He purifier is supplied together with the PDD.

A 0.7 mm ID deactivated capillary column piece (15 cm) allows the sample to enter directly in the ionisation chamber thus avoiding any undesired dead volume effect (peak broadening).

Injection and switching system

Two valves **MUST** be used for sampling of the gas and switching of the columns. The sampling valve is a six-port valve while a ten-port valve is used for column switching. Both are He purged. Purging is mandatory because it prevents from any diffusion of atmospheric air into the gas lines during commutation of the valves. The purge gas is still high purity grade He coming from the He purifier.

Automated and accurate control of the timing of the valve is allowed by the Trace GC keyboard.

No heating of the valves is required since the sample is gaseous at ambient temperature.

Analytical columns

The separation of permanent gases and light hydrocarbons is generally successfully carried out using a combination of Porapak and Molecular Sieve columns. In this application two Wide Bore (0.53mm ID) columns are used. Due to their higher efficiency, peaks are narrower with respect to traditional packed columns, and therefore sensitivity can be lowered even if splitting is required.

The columns used for this application are the following:

- Mol Sieve PLOT 30m, 0.53mm ID, for the separation of Oxygen (matrix), Nitrogen, Methane and Carbon monoxide
- Porabond Q, 25m, 0.53mm ID, for the separation of Carbon dioxide, Nitrous oxide, Ethylene, Ethane, Acetylene.

The Analysis

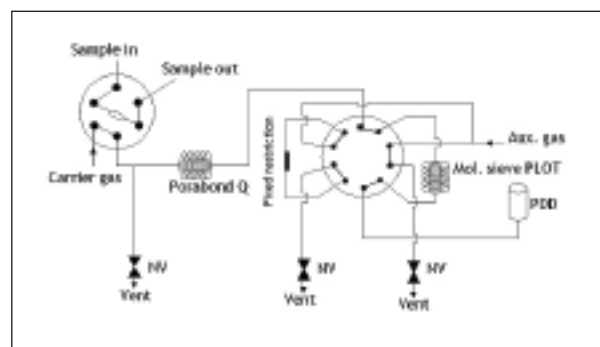


Figure 2: Column configuration

Figure 2 shows the configuration of the instrument for the analysis of impurities in Breathing Oxygen.

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 of the columns the NV is set to produce a 1/10 split ratio. Once oxygen along with CO and CH₄ are eluted onto the MS PLOT, the 10 port valve is switched. In this new phase C₂ hydrocarbon isomers, CO₂ and N₂O reach the detector from the Porabond Q. During this period the second column is kept in “store column” like mode. A slight flow (5-7ml/min) regulated by an auxiliary pressure regulator, is allowed through this column. The purpose of this minimum flow is to very slowly push ahead the compounds retained thus avoiding any peak broadening and eventually air diffusion from the valve. In the following phase the valve is switched back in the original position, and the compounds from the MS PLOT 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, He discharge flow 30 ml/min, split ratio 1/10, auxiliary gas pressure 50kPa.

The temperature of the Pulsed Discharge detector is of 120°C while the sampling occurs through a 0,250 mL loop mounted on the purged valve.

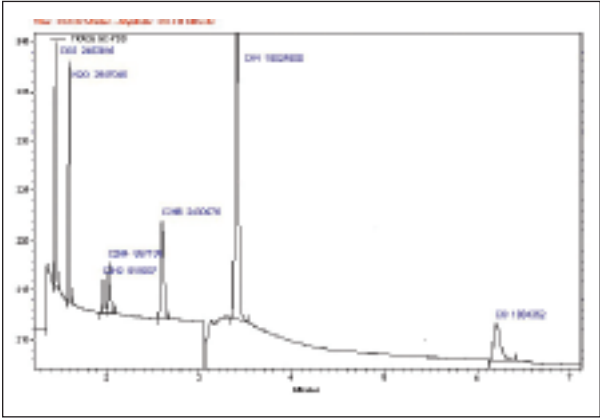


Figure 3: Chromatogram showing the elution order of the compounds analysed

Figure 3 reports the chromatogram obtained. The baseline distortion between the C₂H₆ and the CH₄ peaks is due to the 10 port valve’s switching after the store column phase. The analysis is carried out in less than 7 minutes!

| MINIMUM DETECTABLE QUANTITIES REVEALED BY THE SYSTEM | | |
|---|---|---|
| IMPURITIES | STANDARD MIXTURE CONCENTRATION (ppm v/v) | MINIMUM DETECTABLE QUANTITIES (pg) S/N=3 |
| Carbon Dioxide | 5.0 | 0.9 |
| Carbon Monoxide | 5.0 | 4.0 |
| Nitrous Oxide | 4.0 | 0.9 |
| Methane | 26.0 | 0.6 |
| Acetylene | 1.0 | 1.0 |
| Ethylene | 1.0 | 0.7 |
| Ethane | 2.0 | 0.7 |

Figure 4: The table indicates the compound’s concentration in the standard mixture and the calculated MDQs.

Table 4 indicates and the compound concentration of the standard used, together with the calculated MDL with a 3/1 signal to noise ratio. The exceptional results in terms of peak area repeatability based on 10 consecutive runs of all compounds are summarized in figure 5; as can easily be seen all RSD% of the peak areas are below 1.2%!!

| | | CO ₂ | N ₂ O | C ₂ H ₂ | C ₂ H ₄ | C ₂ H ₆ | CH ₄ | CO |
|--------------------------------------|-----------|-----------------|------------------|-------------------------------|-------------------------------|-------------------------------|-----------------|----------|
| Peak | Mean | 3630019 | 3215883 | 622280 | 998488 | 3027146 | 21403232 | 2132629 |
| Area (Counts) | Std. Dev. | 32657 | 18605 | 2882 | 11818 | 18535 | 105739 | 20786 |
| | RSD% | 0.900 | 0.579 | 0.463 | 1.184 | 0.612 | 0.494 | 0.975 |
| Retention Times (min) | Mean | 1.390 | 1.544 | 1.910 | 1.979 | 2.546 | 3.303 | 6.029 |
| | Std. Dev. | 0.000789 | 0.000430 | 0.000873 | 0.000809 | 0.002231 | 0.003181 | 0.005641 |
| | RSD% | 0.0568 | 0.0279 | 0.0457 | 0.0409 | 0.0876 | 0.0963 | 0.0936 |

Figure 5: Area reproducibility of permanent gases and light hydrocarbons detected in breathing Oxygen

Conclusions

The simplicity, rapidity and quantitative reliability besides the superior results delivered by the Trace GC equipped with the PDD detector are in line with, and sometimes even exceed, the stringent requirements of the highly regulated market segment of the purity gases certification, not only for breathing Oxygen.

The non-radioactive ionisation source of the PDD detector is a further key benefit of this system, which does not have to undergo periodical, expensive wipe test certifications.

Considering that control and/or certification of these gases is required at all levels (from the producer to the end user) this is an extremely versatile solution for a large number of applications.

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