THE DETERMINATION OF IMPURITIES IN HELIUM USED FOR REACTOR COOLING VIA GC/PDHID

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The growing world energy demand has led to the need to find sustainable energy sources with a low environmental impact. Nuclear energy can be considered a carbon free with long term sustainability energy generation system. In order to be able to offer efficient, economic, safe, with low radioactive waste and environmental impact energy production focus has been given to the development of advanced nuclear systems called Generation IV. Among the Generation IV nuclear systems VHTR which uses helium as coolant has received a great deal of attention. One of the key issues in this technology is the level of impurities in helium coolant. In this paper the purity of helium coolant for a HTHL as part of the infrastructure of gas cooled reactors in the Czech Republic was determined. The used analytical method was gas chromatography with pulsed discharge helium ionization detector (GC/PDHID). The PDHID is a universal, non-destructive and very sensitive detector. The analysed compounds in this paper are H_2, CO, CO_2, CH_4, N_2 and O_2.

Key words: high temperature reactor; helium loop; impurities in helium; GC/ PDHID

Received 10. 5. 2016, accepted 14. 6. 2016

1. Introduction

The growing world population is followed by an ever increasing demand of electrical energy. Currently in order to satisfy consumers demand the energy sector is heavily dependent on fossil fuels. It should be taken into account that fossil fuels are a limited resource and additionally their combustion is one of the main sources of atmospheric pollution. In fact for instance the EU continues to limit the burning of fossil fuels through various legislative instruments [1]. Therefore it is crucial to develop energy sources stable, economical and with low environmental impact. Nuclear energy due to its long term sustainability has attracted a lot of attention as a way of electricity generation [2].

The evolution of nuclear energy systems is generally divided into the four following generations [3]:

- Generation I (1950-1970): early prototypes of different designs;
- Generation II (1970-1995): reliable and competitive commercial power plants that are still operating today;
- Generation III/III+ (1995-2030): evolution of II generation in terms of significant advances in safety and economics. A number of such energy systems have been built, primarily in East Asia;
- Generation IV (2030+): designs called revolutionary given their separation from generation III systems.

The Generation IV systems are intended to provide significant advances compared with the current Generation III/III+ regarding efficiency, economic, safety, radioactive waste reduction, environmental performance, and proliferation resistance. However, the commercial application of Generation IV reactors is not expected sooner than 2030 [4].

1.1. Generation IV systems

In the year 2000 member countries of the Generation IV International Forum (GIF) began to discuss the necessity to support next-generation reactors [3]. The main characteristics of Generation IV systems are fast neutron reactors with closed fuel cycle and high temperature reactors [5]. The proposed Generation IV nuclear reactors can be divided in six types. Among these six types the two types that have received more attention and are being extensively researched are: Gas Cooled Fast Reactors (GFR) and Very High Temperature Reactors (VHTR). These two reactor types use helium as coolant in the primary circuit and both aim for high core outlet temperatures which should maximise the efficiency of electrical energy production. Moreover these reactors have the potential to be more sustainable by dramatically improving the utilisation of fissile material and as a result reducing the quantity and radiotoxicity of radioactive waste [6, 7].

Generation IV nuclear reactor present indeed a breakthrough compared to Generation III/III + reactors. In the case of GFR and VHTR core outlet temperature can be 850 and 1 000 °C, respectively. Given the stringent requirements materials employed in the current commercial reactors are not suitable for Generation IV reactors [8]. The material requirements for such nuclear systems should be able to withstand high temperature, high neutron flux, corrosive environment and lifetime expectancy. Materials of particular interest include graphite, high-temperature metallic materials and ceramics and composites [5, 9].

Regarding the coolant helium provides a safe non-reactive medium. However it should be noted that the coolant should have very high purity. Impurities even at very low concentrations can damage the construction materials by changing their structural and mechanical properties [6]. The most common but not limited to impurities are H_2, CO, CO_2, CH_4, N_2, O_2, H_2O [10].

Among the Generation IV VHTR is considered the one with the highest efficiency. In VHTR reactors it is very evident the significant advance in nuclear technology. This reactor type has the potential to not only produce carbon dioxide free electrical energy but can supply heat for a variety of high-temperature industrial applications such as petrochemical services, chemical industries, biofuels production, cement and ceramics [9]. Additionally out of the six Generation IV technologies VHTR is the only suitable system for high efficiency hydrogen production. The produced heat can be used for hydrogen production through thermo-chemical processes for splitting water which have high efficiency (40-57 %) but require high process heat ranging from 500 to 900 °C [11, 12].

1.2. Impurities in helium coolant for VHTR systems

Gaseous helium is an inert gas. Therefore is expected to have little impact on the corrosion and mechanical properties of the VHTR materials. However helium coolant is expected to contain trace amounts of contaminants such as H_2, CO, CO_2, CH_4, N_2, O_2, H_2O. The contamination of helium coolant can occur among others due to degassing, water or oil leaks and desorption from structural materials, such as graphite. The presence of these impurities even at slightly higher concentrations than the recommended ones can lead to corrosion or damage of the construction materials [6, 10, 13-15]. In **Fig. 1** the main sources of helium coolant impurities in the primary circuit are depicted.

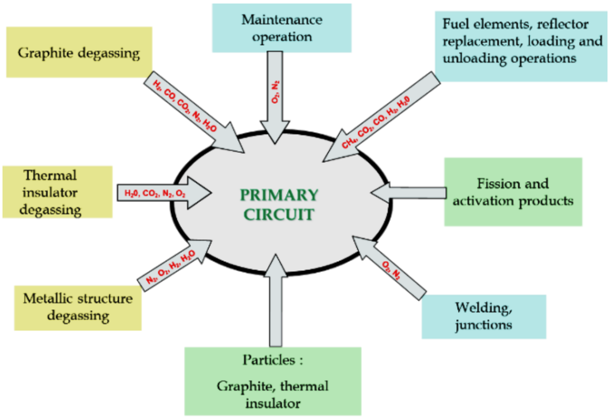

Fig. 1 Source of impurities in primary helium coolant [16]

Research concerning gas cooled reactors takes place within national and international research programs [17, 18]. The UCT Prague is also involved in these programs focusing mainly advanced materials and helium chemistry research. This paper focuses on the purity of helium for the high-temperature helium loop (HTHL) as part of the experimental infrastructure of advanced gas cooled reactors in the Czech Republic. The HTHL was built in the Nuclear Research Institute Rez. Detailed description of the construction and operation of the HTHL have been described in the previous works of Berka et. al [6, 19]. The determination of impurities in helium was performed within the infrastructure of UCT Prague. In **Tab. 1** are the expected concentration range of impurities in helium coolant for HTHL is depicted.

Tab. 1 Expected concentration range of impurities in helium coolant for HTHL [6].

Component	Expected concentration range $[ml \cdot m^{-3}]$
H_2	20 - 500
H_2O	< 1
CO	1 – 300
CH_4	2 - 40
CO_2	0,1 - 10
N_2	< 1,5
O_2	< 0,1

Impurities in helium coolant under very high temperatures can undergo several reactions which may cause equipment corrosion, graphite oxidation and mechanical damage. Therefore their concentration can constantly change. This paper focuses on the determination of H_2, CH_4, CO_2, CO, O_2 and N_2. The most important reactions and effects on the system of these compounds are as follows [20 - 27]:

Hydrogen

The main source of hydrogen in cycles which incorporate a steam turbine is diffusion from the steam cycle. Hydrogen reacts according to the Schikorr reaction as depicted in equation 1.

$$4H_2O + 3Fe \rightarrow Fe_3O_4 + 4H_2 \qquad (1)$$

Another hydrogen source can be desorption from structural materials or hydrocarbon leakage to the system. The formed hydrogen participates in the reverse steam-graphite reaction, equation 2; reverse water gas shift reaction, equation 3; methane reaction, equation 4; and equation 6.

$$H_2 + CO \leftrightarrow C + H_2O \qquad (2)$$

$$H_2 + CO_2 \leftrightarrow CO + H_2O \qquad (3)$$

$$2H_2 + C \leftrightarrow CH_4 \qquad (4)$$

$$H_2 + FeO \leftrightarrow Fe + H_2O \qquad (5)$$

Methane

One of the main sources of methane is oil or hydrocarbon leakage into the system. Methane formation can be comprehensively expressed via equation 4. Methane can seep in the helium coolant during fuel change and from reactor equipment. Methane concentration depends on temperature. At high temperatures methane decomposes therefore its concentration decreases, depicted by the reverse equation 4. Its concentration depends also on the reactions with other impurities as depicted in equation 6.

$$CH_4 + CO \leftrightarrow 2C + H_2O + H_2 \qquad (6)$$

Carbon dioxide

Carbon dioxide is formed at temperatures below 700 °C through the steam-graphite reaction. At higher temperatures the main product of this reaction is carbon monoxide. The concentration of CO_2 is directly proportional to the concentration of CO which is expressed by the Boudouard reaction as depicted in equation 7.

$$CO_2 + C \leftrightarrow 2CO \qquad (7)$$

With increasing temperature increases the ratio of CO and other reactions can take place such as those depicted in equation 2 and equation 3. It should be noted that the reaction depicted in equation 3 takes place only up until the moment of reaching CO equilibrium.

Carbon monoxide

Carbon dioxide concentration depends on a series of factors such as water presence, depicted in equation 2. Moreover its concentration is influenced by air leakage into the cooling system and desorption from fuel particles and structural material in the primary cycle. Carbon monoxide concentration also depends on the carbon dioxide concentration as depicted in equation 7.

Oxygen

Oxygen seeps into the system mostly due to air leakage during maintenance or fuel change. However, once in the reactor O_2 reacts very fast with graphite, as shown in equation 8.

$$\frac{1}{2}O_2 + C \rightarrow CO \qquad (8)$$

Nitrogen

The main source of nitrogen into the system is air. In the case of more prominent leakage N_2 is adsorbed in the structural materials and at higher temperatures is desorbed into the coolant. Another source of N_2 can be liquid nitrogen, which is used as coolant during the process of helium purification. The presence of N_2 is not very harmful; however it can partially react to form NO_x.

1.3. The pulsed discharge helium ionization detector

The Helium ionization detector (HID) was first commercially used in 1969 to analyse impurities in Grade A helium [28]. HID is a modified version of the original Lovelock`s argon ionization detector which was developed in the fifties. It should be noted that due to its drawbacks the argon ionization detector was substituted by the flame ionization detector (FID). The HID is a universal and very sensitive detector used mostly for the analysis of permanent gases and some organic compounds that have bad response or no response at all to the FID and that are present in too low concentrations to be detected by a thermal conductivity detector (TCD) [29, 30].

Nowadays there are two available versions of this detector, the HID and the pulsed discharge helium ionization detector (PDHID). The essential difference between these two models is the ionization source. The classical HID ionization mode is based on a radioactive source. Traditionally, β-emitters are used to initiate helium ionization and as a result metastable helium species are formed. These metastable species then ionize the analytes [31]. The second more recent version uses and electric pulsed discharge to generate metastable helium species, hence the name PDHID [32].

The PDHID was developed in 1992 by Wentworth et al. in collaboration with Valco Instruments Co. Inc [33]. The general configuration of the PDHID consists of two different zones: the discharge zone and the ionization zone. In the discharge zone are situated two electrodes between which the high voltage pulsed discharge occurs causing helium flow excitation. In the ionization zone are situated at least two electrodes, the bias electrode and the collector electrode. The excited helium flow is introduced in the discharge zone at the top while eluents from the chromatographic column at the bottom. Thus the eluents flowing counter to the flow of the excited helium are ionized. The separation of the production metastable helium and its interaction with eluents from the chromatographic column makes it a more robust and stable detector overcoming many of the difficulties associated with the HID [34].

In the PDHID analyte ionization occurs through a number of different processes. However the two main contributors to the ionization of the eluents from the chromatographic column are metastable species causing direct analyte ionization and photoemission ($h\nu$) during the transition of diatomic helium to dissociative helium, the so called Hopfield emission, causing analyte photoionization, equation (1) [35]:

$$\mathrm{He}_2(\mathrm{A}^1\textstyle\sum_{\mathrm{u}}^{+}) \rightarrow 2\,\mathrm{He}(1^1\,\mathrm{S}) + \mathrm{h}\nu \qquad (8)$$

It should be noted that it is believed that photoionization is the principal mechanism of analyte ionization. The actual ionization efficiency is 0.01 – 0.1 %. This characteristic makes PDHID an essentially non-destructive detector which permits to use it in combination with other detectors. The energy of the excited helium continuum is from 13.5 eV to 17.7 eV making possible the ionization of any compound except Ne which has an ionization potential of 21.5 eV [32, 36].

Even though originally the PDHID was primarily used for the analysis of permanent gases and some volatile compounds with poor response to the FID, nowadays given its ability to ionize any compound with the exception of Ne can be considered a universal detector. It should be noted that for organic compounds FID is still the preferred choice since it is easier to operate [34]. However in a number of studies the PDHID has been used for the analysis of inorganic and organic compounds either separately or simultaneously [35, 37-40].

2. Experimental

2.1. Reagents and Materials

Standards containing various concentrations H_2, CO, CO_2, CH_4, O_2 and N_2 in He were purchased from Linde Gas (The Linde Group, Germany). The standard concentrations for each individual compound in ml · m^{-3} were as follows:

H_2: 41.2; 149.7; 396.0
CH_4: 33.7; 41.4; 50.0
CO_2: 5.05; 41.2; 99.7
CO: 10.0; 40.4; 100.0
O_2: 2.01; 30.2; 100.1
N_2: 10.2; 50.1; 99.9

2.2. Laboratory apparatus

All analytical experiments were carried out o an Agilent 7890B gas chromatograph (Agilent Technologies, USA) equipped with a PD-D3-I detector (VICI AG International, Switzerland). A six port valve with a 0.5 mL sample loop was used for sample injection. For sample separation a micropacked column 2 m x 1 mm, with OD 1/16” and packed with a 100/120 mesh ShinCarbon (ShinCarbon ST Micropacked Column, Restek Corporation, USA), was used.

The performance of PDHID is adversely affected by the presence of impurities in the gas stream. In order to maintain a stable, low noise discharge the detector requires very high purity helium [41]. Therefore as carries gas, discharge gas and purging gas was used helium of 99.9999 % vol. purity. Additionally to ensure gas purification to sub-ppm levels of gaseous impurities a miniature helium purifier HPM (VICI AG International, Switzerland) was installed. The discharge flow rate was set at 30 ml · min^{-1}, which is within the range recommended by the manufacturer. In Fig. 1 the scheme of the detector gas connections for the detector system is depicted.

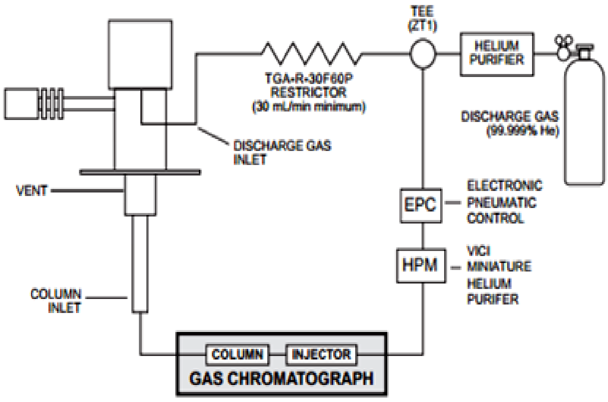

Fig. 2 Scheme of the detector gas connections for the detector system[42]

2.3. Sampling

Helium sampling from the HTHL in two canisters (SilicoCan, maximum pressure 40 psig, Restek, USA) was performed. Sampling canisters had an internal volume of 6 l and before sampling were regenerated and evacuated. Sampling was performed via the sampling line which was prior to sampling evacuated. The canisters were pressurized at absolute pressure 300 kPa. Sample injection into the GC/PDHID via the sampling line was carried out. Prior to injection the sampling line was evacuated and rinsed with the sample itself. Evacuation and rinsing was carried out in order to minimize surrounding air diffusion into the sample.

Sampling was carried out 200 h after the start-up of the HTHL during a 1 000 h corrosion experiment. Prior to experiment start an alloy 800 H testing sample was placed inside the loop. Afterwards the HTHL was filled with a gaseous mixture with the following composition: 50 ml · m^{-3} CO, 10 ml · m^{-3} H_2 and 10 ml · m^{-3} CH_4 in helium. Experiments in the active section of the HTHL at 760 °C and 4 MPa were carried out.

2.4. Calibration curves and sample analysis

Prior to sample analysis calibration curves with the gaseous standards were performed. For both standard and sample analysis the initial column temperature was set at 40 °C and maintained constant for 2 min. With a temperature gradient of 20 °C · min^{-1} the column was heated at 160 °C and kept constant for 3 additional minutes. Total time of analysis was 11 min.

3. Results and discussion

3.1. Calibration

After analysis via the GC/PDHID setup linear response was indicated with a correlation factor of at least 0.9986 for all compounds of interest. Calibration curves for the analysed compounds are depicted in Fig 3-8.

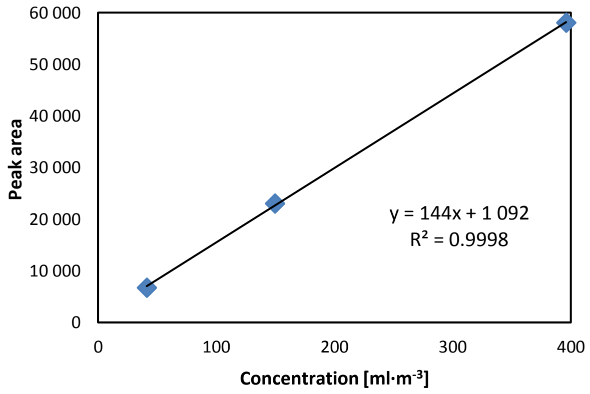

Fig. 3 Hydrogen calibration curve

The response of all analysed compounds was stable almost immediately with the exception of O_2 and N_2, as expected.

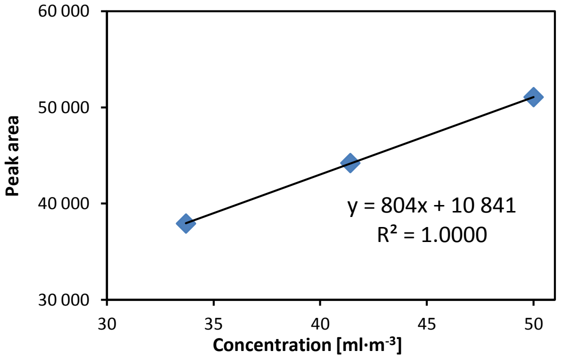

Fig. 4 Methane calibration curve

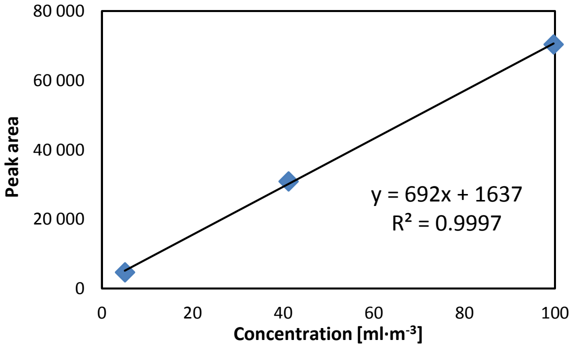

Fig. 5 Carbon dioxide calibration curve

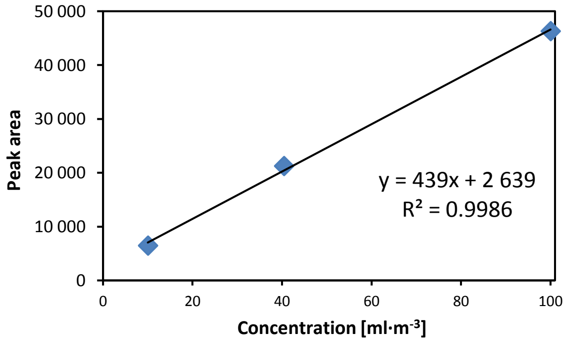

Fig. 6 Carbon monoxide calibration curve

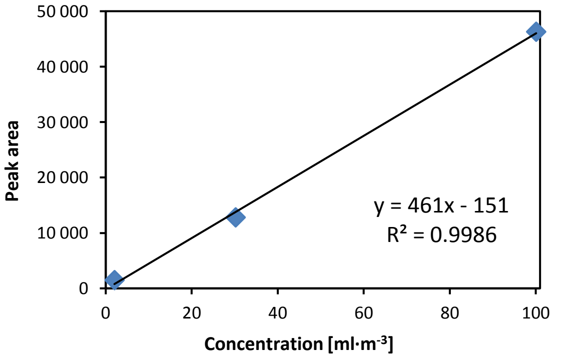

Fig. 7 Oxygen calibration curve

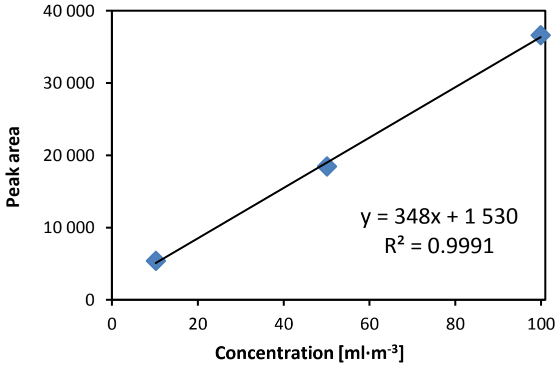

Fig. 8 Nitrogen calibration curve

Probably the most important step of the whole analytical process when determining extremely low concentrations of small-molecular substances is, in addition to a continuous rinse, to secure the tightness of the whole sampling and injection lines (connecting capillaries, vents, injectors). This is very important especially when the compounds of interest are oxygen and nitrogen. Due to the effect of air diffusion not only during sampling but also analysis it is crucial to have sufficient amount of sample to perform a minimum of 10 - 15 injections. During certified standards analysis containing O_2 and N_2 a peak area decrease from the first injection to the second of 61 % and 55 % respectively was observed. After the tenth injection the area response for both compounds was over 96 % lower compared to the first injection. The effect of air diffusion can be clearly seen in **Fig. 9** where a comparison between the chromatographic response after the first and tenth injection of the same standard containing both O_2 and N_2 is depicted.

3.2. Sample analysis

Taking into consideration the effect of air diffusion and the limited sample amount it was possible to determine only the content of H_2, CH_4, CO_2 and CO. In **Tab. 2** the concentration of the analysed impurities in helium is depicted. The results are depicted for each sampling canister separately.

Tab. 2 The concentration of the analysed impurities in helium coolant.

Component	Sampling canister 1 [ml · m^{-3}]	Sampling canister 2 [ml · m^{-3}]
H_2	0.3	0.4
CH_4	0.2	0.2
CO_2	0.2	0.3
CO	1.1	1.4

From the obtained results it is clear that the concentration of H_2, CH_4 and CO is 30 - 45 times lower than in the initial gas mixture.

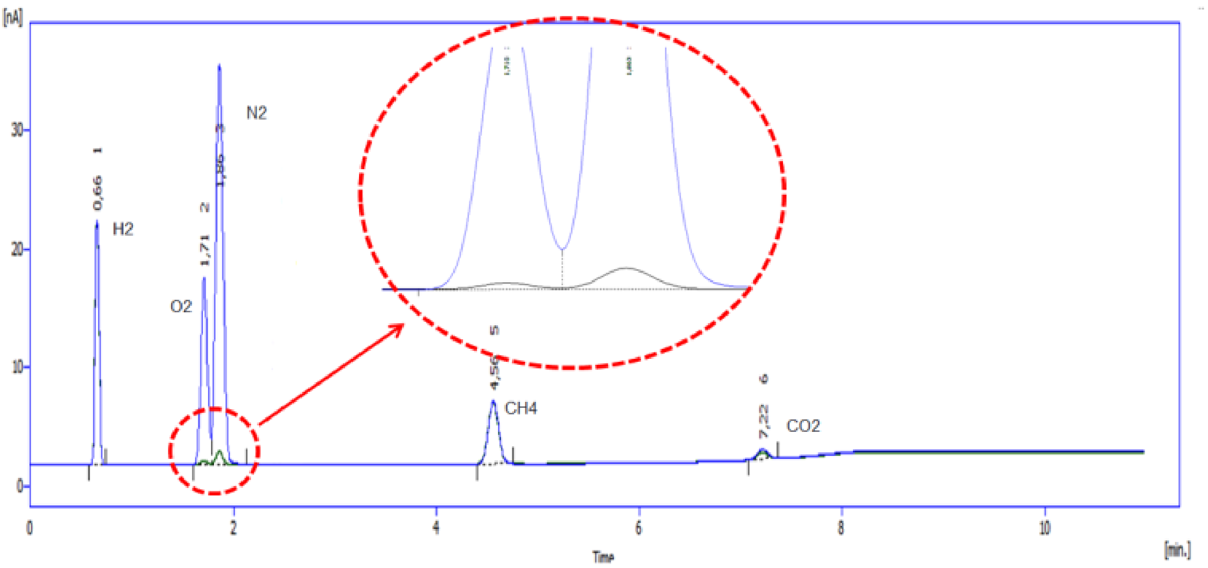

Fig. 9 A comparison between the chromatographic response for O_2 and N_2 after the first injection (blue) and tenth injection (green).

This decrease can be attributed to the reaction of these compounds with alloy 800 H, the structural material of the loop itself or/and adsorption in the inner surface of the hot and cold loop areas. The presence of CO_2 which was not present in the initial mixture it is most probably related to reactions 3 and 7 taking place.

Despite the taken percussions the effect of air diffusion in the sampling and injection lines was prominent. The determination of O_2 and N_2 was not possible since there were not enough samples to perform the minimum amount of desired injections in order to obtain a stable and reliable detector response for these two compounds. A possible solution to this problem could be thoroughly rinsing the injection line with the sample itself and using a higher sample flow rate. This approach can potentially minimize air diffusion but requires a larger sample amount.

4. Conclusions

The most common impurities found in helium coolant are H_2, CO, CO_2, CH_4, N_2, O_2. GC/PDHID is a very sensitive and suitable analytical setup for the determination of these compounds. The PDHID is able to detect and determine these compounds of interest at very low concentrations. However a great deal of attention should be given to the sampling and injection procedures since the PDHID is very susceptible of impurities that can diffuse in the system, most notably air, especially when the compounds of interest are O_2 and N_2.

Helium from a HTHL as part of the infrastructure of advanced gas cooled reactors built in the Nuclear Research Institute Rez was sampled and analysed via GC/PDHID. Sampling in two canisters was carried out. As expected, O_2 and N_2 could not be determined due to the diffusion of air in the injection lines and/or sampling lines. The other compounds of interest i.e. H_2, CO, CO_2, CH_4, where determined. Their average concentration was as follows: 0.35 $ml \cdot m^{-3}$ of H_2; 0.20 $ml \cdot m^{-3}$ of CH_4; 0.25 $ml \cdot m^{-3}$ of CO_2; 1.25 $ml \cdot m^{-3}$ of CO. The GC/PDHID is a universal and sensitive analytical whose sampling and injection line should be optimized when the compounds of interest are O_2 and N_2. In future works attention will be focused on the minimization of air leakage into the sampling and analytical lines.

Acknowledgments

The presented work was financially supported by IGA – 2015_FTOP_2015_030 and TACR – Alfa Project TA03010849 and TA03020850.

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