

The analytical methods used in examining resistance of hydrogeological systems to anthropogenic pollution



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Introduction

In this work the method for evaluating resistance hydrogeological systems to anthropogenic pollution using environmental tracers is described. Resistance groundwater systems to anthropogenic pollution is correlated with the age of water, which can be determined by means of environmental tracers SF₆, F-11, F-12 [1] and He. To correct measured values of He and SF₆ the temperature of recharge and the excess air is needed and can be determined by measuring Ne and Ar concentrations in groundwater. This paper describes two measurement GC systems. First to determine the concentrations of greenhouse gases: sulfur hexafluoride (SF₆) and chlorofluorocarbons F-11, F-12 [2], the noble gases neon (Ne) argon (Ar) [3] and helium (He) [4] in groundwater. Second to determine the concentration of helium using system of enrichment.

Sampling and sample storage

Currently, the sampling system is adapted to pumped or artesian wells and consists only of copper or steel elements (tubes, valves). Water samples are taken into deactivated 2.9-L stainless steel vessels (Fig 1). Before sampling containers are carefully flushed with high-purity nitrogen to remove air. Wells are sampled under pressure to avoid sample degassing. Contamination by air is controlled by measurements of dissolved oxygen. Samples are stored in a laboratory refrigerator at 6 °C. However, an effort is made to analyse them within 2 days after sampling.



Figure 1. Sample vessel.

Analytical system for Ne, Ar, He, SF₆, F-11 and F-12 measurements

The scheme of analytical system is shown in Fig 2. Measured gases are extracted from water sample by a head-space extraction technique (HS) [2] The headspace volume is created in the sample vessel using high-purity nitrogen (99.9999%) and a syringe (S). Next the vessel is shaken mechanically for 20 minutes to obtain equilibrium between the gas and liquid phase. The equilibrated gas is transferred into the vacuum extraction and purification line (thickened lines in Fig. 2), where is dried (Nafion tube) and fills in two sample loops (P2 and P3) and a glass 125 ml-in-volume pipette.

Neon and Argon are analysed with a thermal conductivity detector (TCD1). A 2 ml of gas sample (loop P2) is separated in a 30m×0.56 capillary column (K3) filled with molecular sieve 5A. As a carrier gas He 6.0 is used. Separation of Ar and O₂ is achieved via a catalytic removal of oxygen from the sample at elevated temperature (grains of Cu at 200 °C) [3]. The catalyst is periodically activated by means of hydrogen.

Helium is measured with a gas chromatograph and thermal conductivity detector (GC-TCD2). Carrier gas (Ar 6.0) transports extracted HS gas from the P3 loop (1ml) into a 30m×0.56 capillary column filled with molecular sieve 5A.

SF₆ and CFCs are measured using two chromatographic columns operating in a back-flush mode, and the electron capture detector (ECD1) [5]. The extracted HS gas filling the glass pipette (125 ml) is cryofocused (77 K) under lowered pressure on a trap packed with glass pellets. After desorption gases are injected into a 2 m×1/8" column (K1) filled with n-octan on Porasil C. This column is connected for particular time intervals to a 3 m×1/4" column (K2) packed with 5A molecular sieve. Column K1 works in a back-flush mode. SF₆ and CFCs are detected in the ECD1 detector. The ECD1 detector works in a constant frequency mode to obtain optimal sensitivity for SF₆. The typical chromatograms of tracers and noble gases from groundwater sample are shown in Fig. 3.

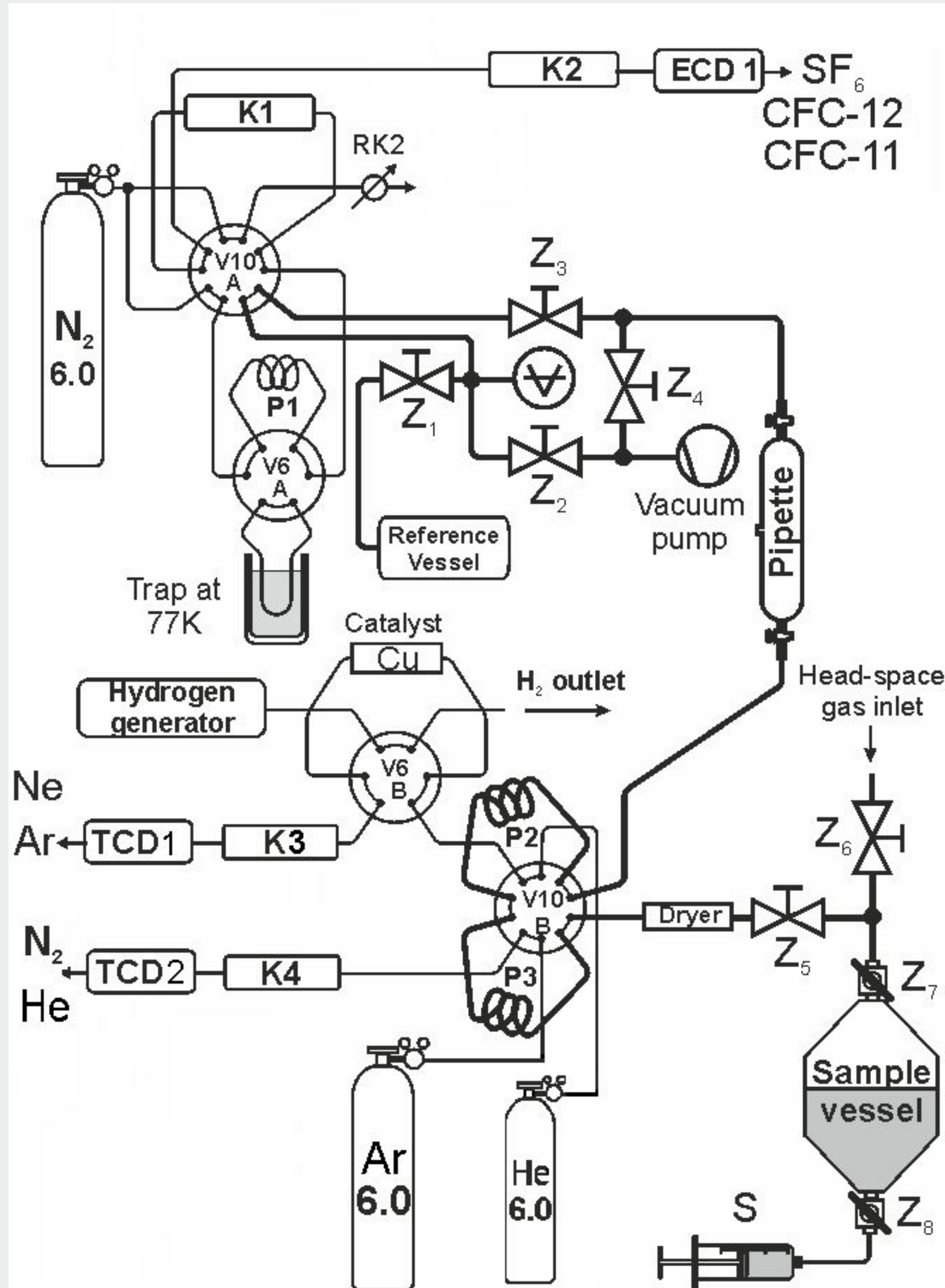


Figure 2. Scheme of measurement system.

The total analysis time is 50 minutes, including extraction and cryofocusing. The limits of detection (double noise amplitude) for measured tracers and noble gases are 0.055 fmol/L for SF₆, 0.5 pg/kg for CFC-11, 0.15 pg/kg for CFC-12, 0.3×10⁻⁷ cm³_{STP}/cm³ for Ne, 0.02×10⁻⁴ cm³_{STP}/cm³ for Ar and 14×10⁻⁸ cm³_{STP}/cm³ for He. The reproducibility estimated for modern water sample is 1.6% for Ne, 0.8% for Ar and 5% for SF₆ and CFCs.

Analytical system for He measurements using enrichment method

A scheme of the system for helium concentration measurements developed in the Institute of Nuclear Physics in Krakow is presented in Figure 5[4].

The system consists of a gas chromatograph equipped with a Valco TCD detector; 10 port valve V10; three chromatographic columns K1 (1.5 m), K2 (7 m) and K3 (2 m); sample loop V_p; system of helium enrichment and the vacuum pump, P. As a carrier gas argon 6.0 is used. Water samples are taken to the stainless steel containers of volume 2900 cm³ with a special procedure without contact with the air. The construction of stainless steel vessels allow to apply the head space (HS) method for helium extraction from water. The gas sample of volume V_{HS} = 200 cm³ obtained using the head-space method passes through a system of two (vacuumed earlier) traps, T1 and T2 immersed in liquid nitrogen, D. In the first trap T1, the water vapour is stopped. In the second trap T2 filled with activated charcoal, oxygen and nitrogen are adsorbed whereas helium and neon are not adsorbed and fill the volume of the sample loop V_p, the trap T2 and a pipe connections (also earlier vacuumed). After changing the position of V10, helium and neon from sample loop are dosed to the first column K1 (filled with molecular sieve 5A). When helium and neon gets to the second column K2 (also filled with molecular sieve 5A), the position of V10 is changed back and the compounds which remained in the column K1 are removed from the system. The columns K1 and K2 are working in the "back flush" mode. For a better separation, both gases (i.e. helium and neon) pass through the third column K3 (filled with a mixture of molecular sieve 5A and activated charcoal 1/1) to the TCD detector (with LOD 2,8 ng He). The typical chromatogram of He from groundwater sample analysis is shown in Fig. 4.

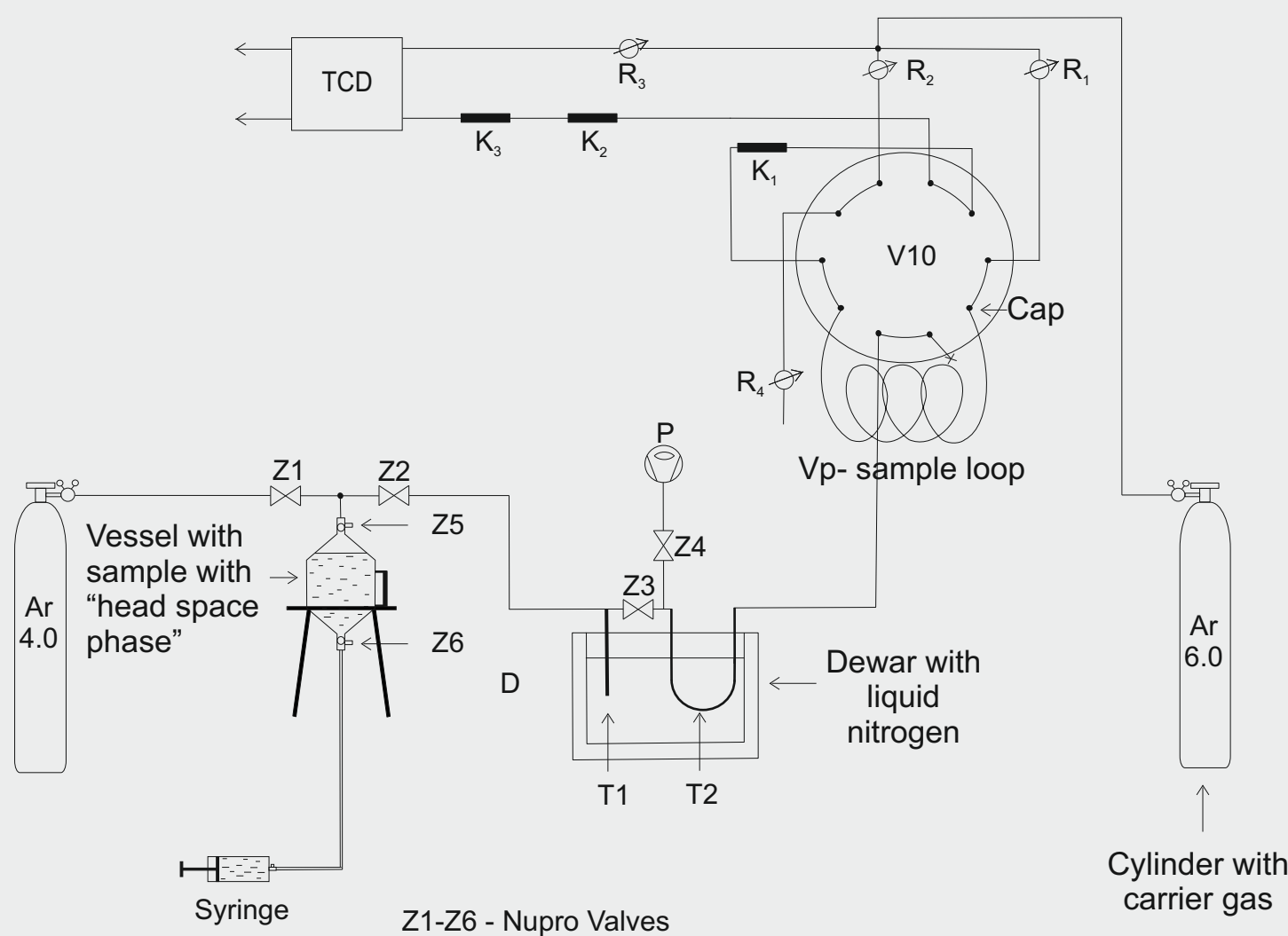


Figure 5. Scheme and the picture of the system for helium concentration measurements.

Example of application

In table 1 the measured He, Ne, Ar, SF₆, CFC-11 and CFC-12 concentrations in three wells of the Saint Lambert aquifer (France) are presented. The Ar and Ne data were used to calculate the values of the recharge temperatures and excess air (graphical method).

Table 1. The results of measurements of the concentration of neon, argon and helium in groundwater from the area of Saint Lambert aquifer in 2012 along with the calculated excess air and NGT which allowed to correct SF₆ and helium He.

Well	Date of analysis	He × 10 ⁻⁸ [cm ³ _{STP} /cm ³]	SF ₆ [fmol/l]	F-11 [pg/kg]	F-12 [pg/kg]	Ne × 10 ⁻⁷ [cm ³ _{STP} /cm ³]	Ar × 10 ⁻⁴ [cm ³ _{STP} /cm ³]	NGT [°C]	Excess air [cm ³ /L]
P4	06.03.2012 13.03.2012	9,0±2,3	0,38±0,02	66,05±2,9	37,875±6,5	2,99±0,04	4,52±0,09	8,1±1,3	5,4±0,5
P5	13.03.2012 08.03.2012	8,4±1,9	0,16±0,01	24,65±1,9	11,45±0,5	3,09±0,10	4,57±0,02	8,1±1,2	5,9±0,8
Albian	15.03.2012	413±29	0,15±0,01	7,85±0,5	2,25±0,2	2,76±0,02	4,83±0,06	3,5±1,2	3,4±0,5
LOD		1,2	0,055	0,5	0,15	0,3	0,02		

Conclusions

Simultaneous chromatographic measurement of Ne, Ar, He, SF₆, CFC-11 and CFC-12 in groundwater has numerous advantages:

- ✓ Reduced number of groundwater samples needed to obtain all tracers data,
- ✓ Shortened sampling time,
- ✓ Decreased laboratory effort,
- ✓ Lowered analysis cost.

Gas chromatographic method for helium concentration measurements using enrichment system allows for analysis of helium in a wide range of concentrations (LOD 1,2×10⁻⁸ cm³_{STP}/cm³ for He).

Acknowledgements

Authors wish to acknowledge dr Paweł Mochalski from Medical University Innsbruck for his help. Work performed within the strategic research project "Technologies supporting the development of safe nuclear power" financed by the National Centre for Research and Development (NCBiR). Research Task "Development of methods to assure nuclear safety and radiation protection for current and future needs of nuclear power plants", contract No. SP/JJ/6/143339/11. This work was also supported by grant No. N N525 3488 38 from the Polish National Science Centre.

References

- [1] I. Śliwka, et al., Long-Term Measurements of CFCs and SF₆ Concentration in Air, Polish J. of Environ. Stud. Vol. 19, No. 4, 811-815, 2010.
- [2] I. Śliwka, et al., Headspace Extraction Method for Simultaneous Determination of SF₆, CCl₃F₂, CCl₂F₂ and CCl₂FCClF₂ in Water, Chem. Anal. (Warsaw) 49,535, 2004.
- [3] P. Mochalski, Chromatographic method for the determination of Ar, Ne and N₂ in water, Ph.D. thesis, Institute of Nuclear Physics Polish Academy of Sciences in Krakow, 2003 (in polish).
- [4] J. Najman, Development of chromatographic measurement method of helium concentration in groundwater for the purpose of dating in the hydrological issues, Ph.D. thesis, Institute of Nuclear Physics Polish Academy of Sciences in Krakow, 2008, http://www.ifj.edu.pl/SD/rozprawy_dr/rozpr_Najman.pdf?lang=pl (in polish).
- [5] I. Śliwka, J. Lasa. Chem. Anal. (Warsaw), 45 (2000), p. 59.

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