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Extended Abstracts

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title: **The gas chromatographic method in measurements of helium concentration in groundwater**

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INTRODUCTION

Helium concentration in groundwater is a fine indicator in water dating in a range from a hundred to tens of thousands of years and ^4He is also used for dating young waters (Andrews, 1989; Zuber et al., 2007).

Applications of helium method known so far, consisted of ^4He concentration measurements using special mass spectrometers (Beyerle et al., 2000). Such measurements unfortunately are expensive and not available in Poland. That is why this problem is tried to be solved using cheaper gas chromatographic method. The rate of $^3\text{He}/^4\text{He}$ in the atmosphere in temperature of 10°C , amounts to $140 \cdot 10^{-8}$ and is often signified by R_A . Helium originated only from the Earth's crust should have $R_c/R_A = 0.01$, and one that originates only from the Earth's mantle $R_m/R_A = 8$. This datasets show that $(^3\text{He}/^4\text{He})_c = 140 \cdot 10^{-10}$ and $(^3\text{He}/^4\text{He})_m = 1.1 \cdot 10^{-5}$, so the highest concentration of $^3\text{He} = 1.12 \cdot 10^{-5} \cdot ^4\text{He}$. Measurements of ^4He for groundwater dating can be substituted for the measurements of total helium concentration, because concentration of ^3He is in this case considerably low.

The aim of research was the elaboration of chromatographic measurement method of helium concentration in groundwater for hydrogeological purpose. In order to helium concentration in groundwater determination by gas chromatographic method, Thermal Conductivity Detector (TCD), head-space technique of gas extraction from water samples and cryogenic method of helium enrichment at abated pressure with the use of activated carbon was used.

EXPERIMENTAL

Measurement procedure

The determination of helium concentration in groundwater using developed GC method require: (1) sampling groundwater (from the well) without the contact with the air, (2) gas extraction from the water sample using head-space method, (3) cryogenic enrichment of gaseous sample, (4) analysis of the sample in chromatographic system equipped with the Thermal Conductivity Detector (TCD), (5) measurement results handling.

Sampling groundwater without the contact with the air

Groundwater samples are taken to the stainless steel vessels of volume equal to 2900 cm^3 designed in a way that application of head-space method is possible (Śliwka, Lasa, 2000). The vessel has two outlets ended with a spherical valves Z5, Z6. Used valves allow for easy connection of vessel with the system of pipes employed to sampling groundwater from the wells and allow to extract gases from sample in the laboratory. A scheme of the system of groundwater sampling is presented in Figure 1.

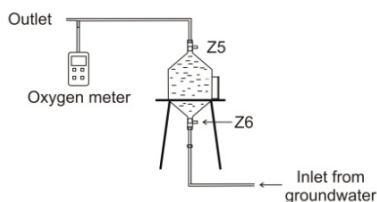


Figure 1. Scheme of the system of groundwater sampling.

During sampling the vessels are flushing with groundwater of volume equal to thirty liters. As noble gases are highly volatile it is very important to avoid gas exchange between the water sample and the atmosphere during sampling, transport or storage. To control the leaktightness of the sampling system during the sampling concentration of oxygen in the groundwater is measured. When the concentration of oxygen is higher than 2 mg/l sampling is being stopped.

Extraction of gases from groundwater samples using head-space method

The head-space method of gas extraction from the sample consist in analysis of gases (of volume of about V_{HS} , Figure 2(D)) from the space above (head space, HS) the measured groundwater sample closed in leak tightness vessel, after the previous bringing such system liquid-gas to the state of thermal equilibrium. In head-space method it is necessary to accomplish few activities. The first one is to introduce gas which doesn't consist helium to the measurement vessel filled with sample. Gas brought under pressure to the Z5 valve (Figure 2(D)) force out water from the vessel through the plastic drain pipe to the syringe. To accelerate establishment of thermal equilibrium state between gas and liquid phases vessel with created head-space phase is being shaken on the shaker for 30 minutes. Such gas phase is ready to analyze in chromatographic system.

Cryogenic enrichment and analysis of gas sample in the gas chromatographic system

A scheme of the measurement system developed in the Institute of Nuclear Physics in Cracow is presented in Figure 2. The system consists of a gas chromatograph equipped with a Valco TCD detector of $2\mu\text{l}$ volume; 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.

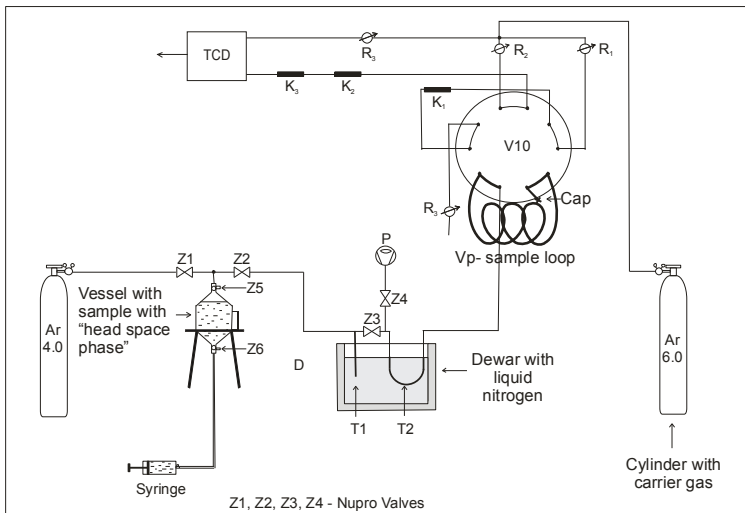


Figure 2. Scheme of the chromatographic system measuring the helium concentration in groundwater.

Water samples are taken to the stainless steel containers of volume 2900 cm^3 with a special procedure without contamination with air. The construction of stainless steel vessels allow to

apply the head space (HS) method for helium extraction from water (Śliwka, Lasa, 2000). The gas sample of volume $V_{HS} = 200 \text{ cm}^3$ 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) (Sugisaki et al., 1981; Sugisaki et al., 1987). 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 50%/50% (Zieliński, 1961)) to the TCD detector. The signal from the detector is registered in a computer equipped with appropriate software.

RESULTS

The difficulties with measurements of helium concentration in groundwater derive from: (a) lack of proper detector for He detection and (b) difficulty with separation helium from neon in room temperature. Peaks of helium and neon appear together, when columns are in room temperature. To separate them long columns (K1-1.5m., K2-7m., K3-2m) in room temperature were applied. Additionally, application of a third column K3 packed with a mixture of molecular sieve 5A and activated charcoal, gave advisable effects. The detection limit for the TCD detector obtained in this system is 2,8 ng He. The results from the analyses of helium concentration in groundwater and in the atmosphere, obtained through the chromatographic method described above are shown in Figures 3a, 3b and 3c.

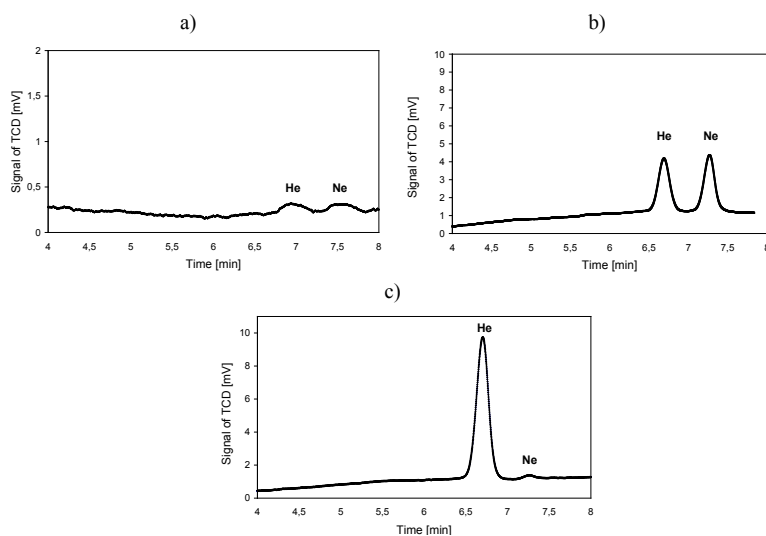


Figure 3. The chromatograms of helium concentration analysis in: a) 10 cm^3 of air without using the system of enrichment (LOD of TCD: 2.8 ng He), b) 200 cm^3 of air with using the system of enrichment, c) groundwater of glacial age in Cracow with using the system of enrichment.

Result from measurement of helium concentration in the atmosphere without using the system of enrichment is shown in Figure 3a. In Figure 3b result from measurements of helium concentration in the atmosphere with the use of system of enrichment in a trap T2 is presented. Example of the chromatogram of the helium concentration analysis in groundwater from Kraków obtained through the chromatographic method described above is shown in Figure 3c. Figure 4 shows the results of calibration of the system with the standard 101 ± 5 ppm helium in argon (produced by Linde Gas).

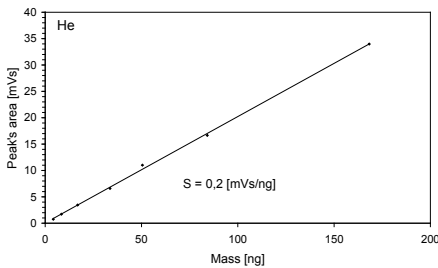


Figure 4. The results of the calibration of the TCD detector, (S - sensitivity of detection for helium $0,20$ mVs/ng He; $1 \text{ ng} = 560 \cdot 10^{-8} \text{ cm}^3 \text{ STP}$).

In aim of verification of elaborated method groundwaters of Cracow's area were analysed and the results were compared with the results obtained using mass spectrometer (MS) technique in 1992 (Zuber et al., 2004). Examples of comparisons of He analyses performed with the aid of GC system with those performed earlier by MS technique in groundwater of glacial age in the Cracow's area are shown in Table 1.

Table 1. Helium concentration in $10^{-8} \text{ cm}^3 \text{ STP/g}$ measured by MS in 1992 (Zuber et al., 2004) with uncertainty lower than 4%, and by GC in 2006.

| Well | ^4He (MS) | He (GC) |
|------|--------------------|--------------|
| 11 | 185 | 184 ± 13 |
| 15 | 212 | 225 ± 16 |
| 16 | 225 | 240 ± 19 |

On the basis of the results shown in Table 1 one can see that results obtained by chromatographic method overlap the results from MS technique in the margin of error. In conclusion, the developed system can be regarded as suitable for helium determinations in groundwater for dating purposes.

CONCLUSIONS

The developed chromatographic system described here, can be used for measurements of helium concentration in groundwater. The obtained level of helium detection for groundwater samples of volume equal to 2900 cm^3 , where helium was extracted to 200 cm^3 head-space gas phase, amounts to $0,67 \cdot 10^{-8} \text{ cm}^3 \text{ STP/g}_{\text{H}_2\text{O}}$.

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REFERENCES

- Andrews J.N., 1989: *Isotopes of noble gases as tracers in environmental studies*. International Atomic Energy Agency, Vienna.
- Beyerle U., Aeschbach-Hwertig W., Imboden D.M., Baur H., Graf T., Kipfer R., 2000: *A mass spectrometric system for the analysis of noble gases and tritium from water samples*. Environ. Sci. Technol., 34, 2042 p.
- Sugisaki R., Hiroshi T., Kawabe I., Miyazaki H., 1981: *Simplified gas chromatographic analysis of H₂, He, Ne, Ar, N₂ and CH₄ in subsurface gases for seismo-geochemical studies*. Chemical Geology, 36, pp. 217–226.
- Sugisaki R., Taki K., 1987: *Simplified analyses of He, Ne, and Ar dissolved in natural waters*. Geochemical Journal, 21, pp. 21 to 23–27.
- Śliwka I., Lasa J., 2000: *Optimisation of the head-space method in measurements of SF₆ concentration in water*. Chemia analityczna (Chemical analysis), 45, 59 p.
- Zieliński E., 1961: *Praktyczne aspekty oznaczania helu i neonu metodą chromatograficzną*. Chemia analityczna, (Chemical analysis), 6, 787 p.
- Zuber A., Ciężkowski W., Róžański K., (red.), 2007: *Metody znacznikowe w hydrogeologii – poradnik metodyczny*. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław.
- Zuber A., Weise S.M., Motyka J., Osenbrück K., Róžański K., 2004: *Age and flow pattern of groundwater in a Jurassic limestone aquifer and related Tertiary sands derived from isotope, noble gas and chemical data*. J. Hydrol. 286, 1-4, pp. 87–112.



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