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Dating of groundwater using anthropogenic gaseous tracers (SF6, SF5CF3, CFC-12, HC-1311): methodological aspects

J. Bartyzel (1), J. Rosiek (1), I. Śliwka (2), and K. Rozanski (1)

(1) AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, 30 Mickiewicza Ave., 30-059 Krakow, Poland, (2) Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, 152 Radzikowskiego St., 31-342 Cracow, Poland

Groundwater is an important source of potable water in many countries. Nowadays, this strategic resource is at risk due to anthropogenic pollutants of various nature entering shallow aquifers. Proper management of groundwater resources requires precise understanding of groundwater dynamics on time scales characteristic for the history of pollutant input to groundwater. Several anthropogenic trace substances present in the atmosphere, such as freons (CFC-11, CFC-12) and sulfur hexafluoride (SF_6) play an increasingly important role as environmental tracers allowing a better insight into the dynamic of groundwater systems. The concentration of SF_6 in the atmosphere is increasing steadily, with the growth rate in the order of 5% per year. Recently, a new trace gas (trifluoromethyl sulphur pentafluoride - SF_5CF_3) has been discovered in the atmosphere. The atmospheric concentrations of SF_5CF_3 reconstructed from archive air samples have been increasing during the late 1980s and 1990s with the growth of ca. 6 % per year, with the sings of leveling-off during the last decade.

We present here a dedicated analytical system capable to determine environmental levels of several gaseous tracers (SF_6, SF_5CF_3, CFC-12, HC-1311) in air and water, with the precision and accuracy sufficiently low do use them for groundwater dating. In addition, the system is capable to measure in the same water sample the concentrations of Ne and Ar. This allows corrections for excess air to be made and the calculations of recharge temperatures.

The field sampling system is based on a dynamic head-space method. The analysed water is pumped continuously through the extraction system where the dynamic head-space is created. Approximately 100 liters of water has to be pumped through the system before the dynamic equilibrium is reached in the head-space volume. Then, gaseous sample is collected from the head-space volume (ca. 200 ml) and transferred to the laboratory.

The mixing ratio measurements are performed using a dedicated gas chromatograph (Agilent 6890) equipped with μ-ECD detector. Due to extremely low atmospheric mixing ratios and poor solubility in water of the analyzed gases, cryogenic enrichment of the gaseous sample prior to detection is employed. A specially designed, automatic cryogenic trap is used for this purpose. Before the cryogenic enrichment, a small fraction of the gaseous sample (5-10 ml) is diverted for measurements of Ne and Ar content in the analysed water sample.

Analytical performance of the detection system is presented, supplemented by several examples of field analyses of the discussed gaseous tracers in groundwater systems in Poland.

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