Environmental groundwater tracers: some new measurement methods and an example of application

Paweł Mochalski
Laboratory of Environmental Physics
Department of Environmental and Radiation Transport Physics
Laboratory of Environmental Physics

Development and application of gas chromatographic methods

Environmental Physics
- Greenhouse gases

Hydrology
- Trace gases: Freons, SF$_6$
- Noble gases: Ne, Ar
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Man-made trace gases in groundwater investigations:

- Freons: Freon-11, Freon-12, Freon-113
- $\text{SF}_6$

Application:

- young groundwater dating (up to 40 years)
- investigation of groundwater dynamics
Groundwater dating with freons and SF$_6$ requires:

- History of tropospheric tracer concentration
- Knowledge of tracer solubility in water
- Method for tracer determination in groundwater
Trace gases in hydrology
Analytical techniques

- Gas chromatography with electron capture detector
  - separate analytical systems for freons and SF$_6$
  - separate water samples for freons and SF$_6$

- Simultaneous measurement of freons and SF$_6$ restricts the estimation of groundwater age
New chromatographic system for analysis of freons and SF$_6$ in groundwater developed in IFJ PAN
New chromatographic system for analysis of freons and \(\text{SF}_6\) in groundwater developed in IFJ PAN

First in Europe and second in the world system for **simultaneous** measurements of \(\text{SF}_6\), freon-11, freon-12 and freon-113 in groundwater
## Comparison of detection limits

<table>
<thead>
<tr>
<th></th>
<th>SF$<em>6$ [fmol/L$</em>{H_2O}$]</th>
<th>Freon-11 [pg/L$_{H_2O}$]</th>
<th>Freon-12 [pg/L$_{H_2O}$]</th>
<th>Freon-113 [pg/L$_{H_2O}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our Lab</td>
<td>0.02</td>
<td>0.35</td>
<td>0.22</td>
<td>0.55</td>
</tr>
<tr>
<td>USGS Reston (USA)</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>USGS Reston (USA)</td>
<td>-</td>
<td>1.0</td>
<td>3.0</td>
<td>1.4</td>
</tr>
<tr>
<td>EAWAG Dubendorf (Switzerland)</td>
<td>-</td>
<td>1.0</td>
<td>2.1</td>
<td>-</td>
</tr>
</tbody>
</table>

**Required for groundwater dating detection limits**

|                     | 0.03                      | 4.0                       | 3.9                       | 0.07                      |
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Noble gases in hydrology

Reconstruction of paleoclimate:
- pale temperature

Groundwater investigations:
- recharge temperature
- recharge elevation
- climatic water age

Young groundwater dating:
- correction of SF$_6$ water age

Noble gases concentrations in groundwater
Analytical technique for noble gases analysis

Mass spectrometry

- high measurement precision
- isotopic ratio measurement

- high cost of apparatus
- complicated extraction and purification lines
- relatively long time of analysis
- high cost of analysis (up to 1000 $ per sample)

Routine noble gases measurements in groundwater are performed only in the USA and Switzerland
Alternative analytical technique for noble gases analysis in groundwater is sought

Gas chromatography
New chromatographic system for analysis of Ar and Ne in groundwater developed in IFJ PAN

- new mode of PD-HID detector
- neon doping
- new sample introducing system
- new method for O$_2$ removal

<table>
<thead>
<tr>
<th></th>
<th>Measurement precision [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ne</td>
</tr>
<tr>
<td><strong>Our Lab</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>Mass spectrometry</strong></td>
<td><strong>0.5 - 2</strong></td>
</tr>
</tbody>
</table>
New chromatographic system for analysis of Ar and Ne in groundwater developed in IFJ PAN

Advantages of a new method:
- simplicity of analytical system
- simple extraction method
- no additional purification lines
- short analysis time
- significantly lowered cost of analysis
An example of field study

<table>
<thead>
<tr>
<th>Groundwater Type</th>
<th>Recharge Temperature $[^\circ C]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice age groundwater</td>
<td>2.7±1</td>
</tr>
<tr>
<td>Holocene groundwater</td>
<td>9.4±1</td>
</tr>
<tr>
<td></td>
<td>(Southern Poland $9 ^\circ C$)</td>
</tr>
</tbody>
</table>
Future plans

- Development of GC methods for He, Kr and Xe analysis in groundwater

- Development of GC methods for measuring new groundwater tracers:
  - Perfluorocarbons: \( \text{C}_6\text{F}_{12}, \text{C}_8\text{F}_{16} \)
  - Telomars: \( \text{SF}_5\text{CF}_3, \text{SF}_5(\text{CF}_2)_3\text{Cl} \)