Measurements of helium concentration in groundwater using gas chromatographic method

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Gas chromatography (GC) measurements of helium [1] can be used as an alternative to mass spectrometry (MS) determinations of $^4$He for groundwater dating.

A scheme of the measurement system developed in the Institute of Nuclear Physics in Cracow is presented in Figure 1. The system consists of a gas chromatograph equipped with a Valco TCD detector of 2μl volume; 10 port valve V10; three chromatographic columns K1 (1.5 m), K2 (7 m) and K3 (2 m); sample loop Vp; 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 cm$^3$. Helium is extracted from water samples by the head-space (HS) method [2,3]. The HS gas of volume $V = 200$ cm$^3$ 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 Vp, 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) [4]. 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%) to the TCD detector. The signal from the detector is registered in a computer equipped with appropriate software.

Examples of the chromatograms of the helium concentration analysis in air, surface water and groundwater obtained through the chromatographic method described above are shown in Figs 2, 3, 4 and 5, respectively. Figure 6 shows the results of calibration of the system with the standard 101±5 ppm helium in argon (produced by Linde Gas).

Fig. 2. The chromatogram of helium concentration analysis in 10 cm$^3$ of air without the system of enrichment (LOD of TCD: 2.8 ng He).

Fig. 1. Scheme of the chromatographic system measuring helium concentration in groundwater.

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Fig. 3. The chromatogram of helium concentration analysis in 200 cm$^3$ of air with the system of enrichment.

Fig. 4. The chromatogram of helium concentration analysis in surface water with the system of enrichment.

Fig. 5. The chromatogram of helium concentration analysis in groundwater of glacial age in Cracow with the system of enrichment.

Fig. 6. The results of the calibration of the TCD detector, (1 ng = 560·10$^{-8}$ cm$^3$ STP).

Examples of comparisons of He analyses performed with the aid of GC system with those performed earlier by MS technique in water of glacial age in the Cracow area are shown in Table 1.

Table 1. Helium in 10$^{-8}$ cm$^3$STP/g measured by MS in 1992 [5] with uncertainty lower than 4%, and by GC in 2006.

<table>
<thead>
<tr>
<th>Well</th>
<th>$^4$He (MS)</th>
<th>He (GC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>185</td>
<td>225±6</td>
</tr>
<tr>
<td>15</td>
<td>212</td>
<td>184±5</td>
</tr>
<tr>
<td>16</td>
<td>225</td>
<td>240±7</td>
</tr>
</tbody>
</table>

In the Busko area, southern Poland, mineral waters of interglacial age occur with $^4$He$_{exc}$ of (12000 to 15400)·10$^{-8}$ cm$^3$STP/g [6]. Similar water was found in a recently drilled well about 10 km SE of Busko with He content of (9500)·10$^{-8}$ cm$^3$STP/g as determined with the aid of GC technique.

In conclusion, the developed system can be regarded as suitable for helium determinations in groundwater for dating purposes.

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References