

DEVELOPMENT OF AN AUTOMATIC SAMPLING UNIT FOR MEASURING RADIOCARBON CONTENT OF GROUNDWATER

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ABSTRACT. An automatic water sampling unit was developed to monitor the radioactive emission (radiocarbon and other corrosion and fission products) from nuclear facilities into the groundwater. Automatic sampling is based on the principal of ion exchange using built-in resin columns in the submerging samplers. In this way, even the short-term emissions can be detected. According to our experiments, the ¹⁴C activity concentrations and the δ¹³C values of the samples made by the ion exchange method are systematically underestimated compared to the real values. The carbonate adsorption feature of the sampling unit was studied under laboratory and field conditions. For this purpose, a test method was developed. The observed sampling efficiencies and additionally some carbon contamination for the sampling method itself have to be taken into consideration when we estimate the amount of ¹⁴C contamination introduced into the groundwater from a nuclear facility. Therefore, a correction factor should be made for the ¹⁴C anion exchange sampling. With the help of this correction, the results converge to the expected value.

INTRODUCTION

In the monitoring of environmental loads from nuclear facilities, the role of groundwater is especially important due to its natural presence, biological role, rapid movement in the geosphere, and its reactive and solvent nature. Thus, sampling and monitoring of the radionuclide content of groundwater is one of the most prominent tasks in environmental control (Vrba 1988).

One of the most widespread approaches to control the areas of radioactive contamination is extensive isotope-analytical measurement of the groundwater in the affected area (Eggers 1976; Stow and Haase 1986; Hart and Spruill 1988; Mulsow et al. 1999). The simplest procedures can be used only for occasional sampling, and these illustrate the conditions at that given moment. In the course of these methods, 3–5 samples are taken from the monitoring well. A certain indicator parameter is monitored continuously until it becomes constant, at which point a sample is taken (Hazardous Waste Bureau 2001). In many cases, short-interval emissions cannot be monitored with these techniques.

Taking integrated samples seems to be more efficient, confident, and cheaper than measurement of the conditions at a given time. Numerous methods for this purpose are reported in the literature (e.g. King 1993). Simpler samplers with plastic membranes based on diffusion have been used to take gas, dissolved inorganic or organic compounds, and even groundwater bacteria samples (Ronen et al. 1987; Karp 1993; de Jonge and Rothenberg 2005; Divine et al. 2005; Petruzzi and Silliman 2006; Spalding and Watson 2007).

There were considerable efforts to enable automatic and more cost-effective sampling methods (Granato and Smith 1999; Jones et al. 1999). The Institute of Nuclear Research of the Hungarian Academy of Sciences (MTA ATOMKI) is developing a groundwater sampling system able to take integrated samples. The sampler consists of 3 main parts (Figure 1). The groundwater is collected in the sampling unit through a cotton filter. The second part of the device contains a control unit, a

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pump, a flow-meter, and batteries. The third part includes ion exchange resin columns. Two cation exchange columns and 1 anion-exchange column are in serial connection (50 cm length and 44 mm ID each column). The effluent from resins is carried by a spiral pipe out of the well.

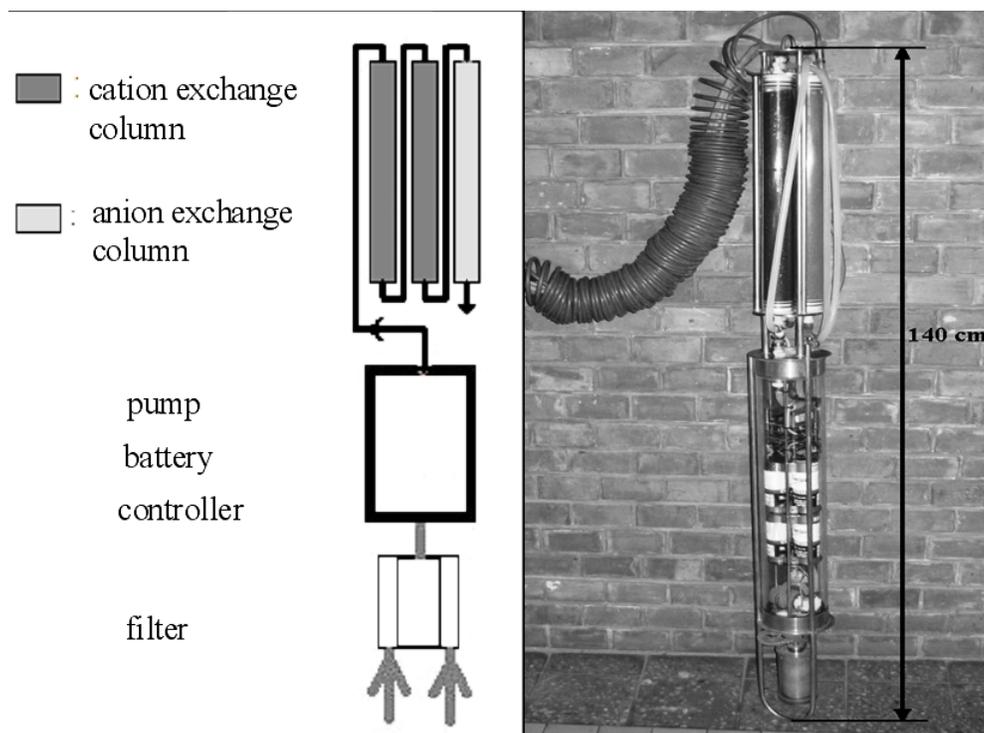


Figure 1 Automatic groundwater sampling unit

To control the release of radioactive isotopes, ^{14}C automatic samplers were installed in several observation wells near some Hungarian nuclear facilities (Püspökszilágy Radioactive Waste Disposal Facility and Paks nuclear power plant). The automatic sampling unit is able to take groundwater samples continuously, while the conventional ^{14}C sampling method (based on barium-chloride precipitation) can only be used for ad hoc sampling. In this way, even short emissions could be detected.

The automatic samplers contain columns filled with cation and anion exchange resin. The sampler works 2 m below the groundwater level with the help of water pumps. After a 2-month working period, the trapped ions are eluted from the resins. The activity of the gamma-emitters, ^{14}C , ^{90}Sr , and transuranium elements are measured from the eluate. The anion exchange resin exchanges the dissolved HCO_3^- ions for OH^- ions. The ^{14}C content of the dissolved HCO_3^- eluted from the resin is determined by conventional beta counting (gas proportional counting or liquid scintillation counting).

EXPERIMENTAL

In the course of normal laboratory experiments, the adsorption conditions of ion exchange resins are standard, and the sample solutions flow by an optimally set constant rate through the ion exchange columns. Those processes are relatively short; therefore, the ion migration due to diffusion has only a negligible influence on the ion exchange capacity. However, the whole sampling interval by our automatic sampling unit could be 2 months, and there is still water above the resin for a significant

part of this time. During this period, the ions already adsorbed onto the resin may migrate through the whole volume of the resin by ion diffusion. This phenomenon could decrease the efficiency of the ion exchange resins.

Materials Used

In the sampling units, we used Varian[®] AT-N, a strongly alkaline anion-exchange resin with quaternary ammonium active groups (changeable ion form: OH^- , particle size: 315–1250 μm), and Varian KS-N, a strongly acidic cation-exchange resin with sulfo-active groups (changeable ion form: H^+ , particle size: 315–1250 μm ; Nitrokémia Co.). The matrix of resins is styrene-divinylbenzene copolymer. All reagents used were of analytical grade (Scharlau[®], Spektrum-3D[®], Merck[®]).

Groundwater from a real sampling area was used in the experiments as model water. It is of key importance to know the water chemistry parameters of the groundwater to determine the efficiency of the ion exchange resin. The conductivity and the pH of the groundwater were $980 \pm 43 \mu\text{S}$ and 7.01, respectively. The elemental composition of the groundwater was measured by ICP-AES (Spectroflame[®]). The material of the aquifer is loessic river drift; therefore, the groundwater contains mostly calcium-hydrocarbonate. Table 1 shows the concentrations of the 8 major ions (Maucha 1932) being characteristic of the halobity of waters.

Table 1 Concentration of major anions and cations in groundwater sample.

Anions	(mg/dm^3)	Cations	(mg/dm^3)
HCO_3^-	$(4.28 \pm 0.21) \times 10^2$	Ca^{2+}	$(1.82 \pm 0.07) \times 10^2$
SO_4^{2-}	$(6.22 \pm 0.04) \times 10^1$	Mg^{2+}	$(3.29 \pm 0.03) \times 10^1$
Cl^-	$(2.51 \pm 0.02) \times 10^1$	Na^+	$(1.78 \pm 0.01) \times 10^1$
CO_3^{2-}	<2.1	K^+	1.80 ± 0.02

Model Test

Model tests with groundwater from the sampling area were executed under controlled laboratory conditions similar to the natural ones, to determine to what extent the field conditions influence the characteristics of the sample taken. In order to keep the temperature of the sample similar to the average groundwater temperature, the tests were carried out in a cold (15 °C) room of the laboratory. In order to avoid mixing of the resin, the groundwater flows into the columns in every case from above. During the tests, a pump system controlled by a PC pushes 1 L of water through the resin columns every 30 min for 30 hr. Altogether, 60 L of water sample were treated. Two parallel resin units (R1, R2) and a control line (C) without resin were used in the test. During these 6-hr periods, 1.5 L of untreated water sample was taken for ^{14}C measurement from the control line (conventional reference method: based on barium-chloride precipitation). The pH, conductivity, and temperature of these samples were also measured. The samples from the control line were treated by the conventional BaCl_2 precipitation method typically used for ^{14}C measurements.

Elution and CO_2 Recovery

After sampling, the anion-exchange resin columns are opened in a CO_2 -free manipulator box, and the resin is washed into the eluting column using high-purity distilled water. The adsorbed carbonate on the resins was eluted with 1300 mL of 10M NaNO_3 solution. The rate of elution was 10–12 mL/min. The BaCO_3 sample taken by conventional methods and the NaCO_3 taken by the automatic sampling unit were prepared for gas proportional counting.

Radiocarbon Measurement

We measured the ^{14}C activity of the samples using a gas proportional counting (Csongor and Hertelendi 1986; Hertelendi et al. 1989). To extract CO_2 from the samples, sulfuric acid was added to the NaCO_3 solution. Prior to its measurement, the liberated CO_2 gas was purified over charcoal, then frozen into a CO_2 trap with liquid nitrogen at $-196\text{ }^\circ\text{C}$, and the remaining non-condensable components were removed by a vacuum pump (Csongor et al. 1982). The standard deviation of a single $\Delta^{14}\text{C}$ measurement by this method was 4–5‰ after a 1-week-long measurement for each sample (Hertelendi 1990). The reported $\Delta^{14}\text{C}$ data were corrected for decay and $\delta^{13}\text{C}$ values measured by a ThermoFinnigan Delta^{Plus}XP stable isotope mass spectrometer.

RESULTS

The amount of the CO_2 collected and its ^{14}C activity concentration were measured after the recovery of carbonate samples taken by the automatic sampler and conventional barium-chloride precipitation. Differences were found between the results of the 2 methods in the amount of CO_2 , the $\delta^{13}\text{C}$ value, and the ^{14}C activity concentration (Table 2).

Table 2 Results of ^{14}C measurements.

Sample ^a	Water mass (kg)	Gained CO_2 (g/L water)	Excess CO_2 compared to the conventional method	$\delta^{13}\text{C}$ (‰) $\pm 0.2\text{‰}$	$^{14}\text{C}_c$ (pMC) ± 0.5 pMC
C	12.04	0.21	—	-11.04	104.1
R1	63.45	0.26	27%	-12.81	94.7
R2	63.74	0.30	44%	-12.85	94.4

^aSample C is a control sample taken by the conventional method. This sample was used as a reference.

The CO_2 amount obtained from the ion exchange resin was always higher by 30–40% than for samples taken by the conventional method. However, the ^{14}C content of the carbonate dissolved from the resin was always $\sim 10\%$ lower than the ^{14}C content of the barium carbonate precipitate. The $\delta^{13}\text{C}$ value of the elute was 1.7‰ lower than the sample taken by the conventional method (Figure 3).

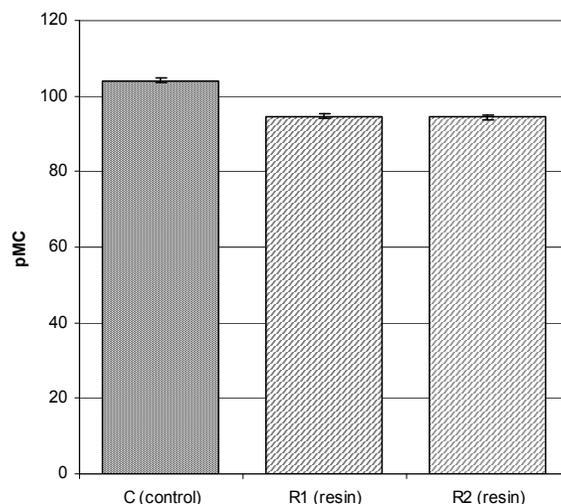


Figure 2 Comparison of ^{14}C activity concentration of the samples taken by the conventional and the automatic sampling method.

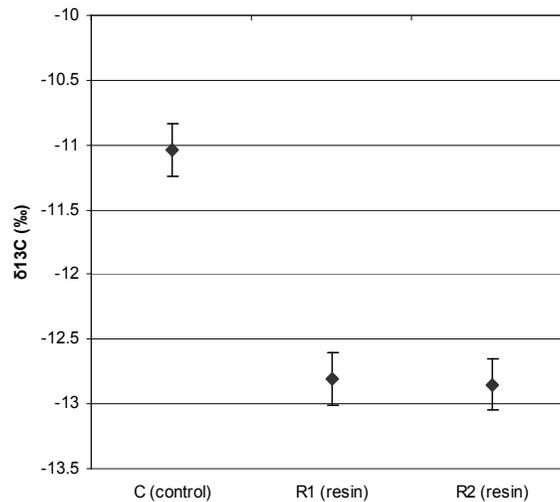


Figure 3 Comparison of $\delta^{13}\text{C}$ values of samples taken by the conventional and the automatic sampling method.

Phenomenon of Excess CO_2 being Proportional to the Amount of the Resin

It seems logical that the excess CO_2 derives from resin or other materials from the applied elution process. The real efficiency of elution is unknown, as we have some additional unknown amount of carbon after the elution. The following hypotheses were made in the course of calculation. The elution efficiency for the R2 test was assumed to be about 100% because it produced the higher specific yield. On the basis of this, calculating with the material balance, we have found that 684 cm^3 of resin gives 5.89 g of excess CO_2 (Table 3).

Table 3 Excess CO_2 proportional to the amount of the resin and the elution efficiency.

Sample	Volume of resin (cm^3)	Excess CO_2 (g)	Excess CO_2 (mg/cm^3 resin)	Efficiency ^a
R1	684	3.32	4.86	87%
R2	684	5.89	8.61	~100%

^aCalculated elution efficiency if the efficiency of R2 is ~100%.

Comparing the carbon isotope data obtained by the reference BaCO_3 precipitation method with the same data for the eluate, and considering the first values to be correct, we have determined the ^{14}C and $\delta^{13}\text{C}$ for the excess CO_2 . In this calculation, we assumed that the carbon isotope concentrations in the eluate are the weighted average of the groundwater- and resin-borne carbonate. The carbon isotope features of the excess CO_2 are 72.4 pMC for ^{14}C and -17‰ for $\delta^{13}\text{C}$ (VPDB).

Based on the above assumptions, not only the specific amount and the carbon isotopic data of the excess CO_2 should be known, but also the total amount of the eluate and the generated CO_2 , to correct the ^{14}C and $\delta^{13}\text{C}$ values measured in the eluate. The general correction formula is the following:

$$^{14}\text{C}_w = \frac{^{14}\text{C}_e \times m_e - ^{14}\text{C}_r \times m_r}{m_e - m_r}$$

where $^{14}\text{C}_w$, $^{14}\text{C}_e$, and $^{14}\text{C}_r$ are the specific ^{14}C content of the groundwater, the CO_2 from the eluate, and the excess CO_2 deriving from the resin, respectively (pMC). The m_e and m_r are the total amount of CO_2 deriving from the resin and excess CO_2 deriving from the resin (g).

The value of $^{14}\text{C}_r$ is 72.4 pMC according to these calculations, which is the ^{14}C content of the excess CO_2 from the resin. If the efficiency is not near 100% or it is highly variable, m_e should be corrected with the elution efficiency ($0 < \eta_e < 1$):

$$^{14}\text{C}_w = \frac{^{14}\text{C}_e \times \frac{m_e}{\eta_e} - 420}{\frac{m_e}{\eta_e} - 5.8}$$

Using the quantity and isotopic properties of the excess CO_2 , we calculated the real ^{14}C activity concentration and $\delta^{13}\text{C}$ value of the groundwater for the R1 test, without any influence of carbon from the resin. The correspondence between the corrected and the expected values reinforces our assumptions (Table 4 and Figures 4, 5).

Table 4 Correction of ^{14}C activity and the $\delta^{13}\text{C}$ value in R1 test according to the calculated excess CO_2 parameters.

Sample R1	Expected	Measured	Corrected
^{14}C (pMC) ± 0.5 pMC	104.1	94.7	104.6
$\delta^{13}\text{C}$ (‰) ± 0.2 ‰ (VPDB)	-11.04	-12.81	-10.97

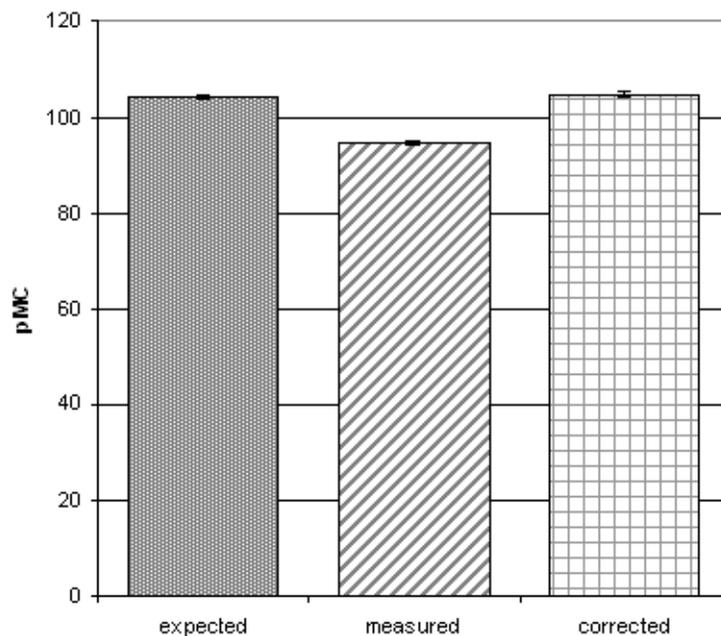
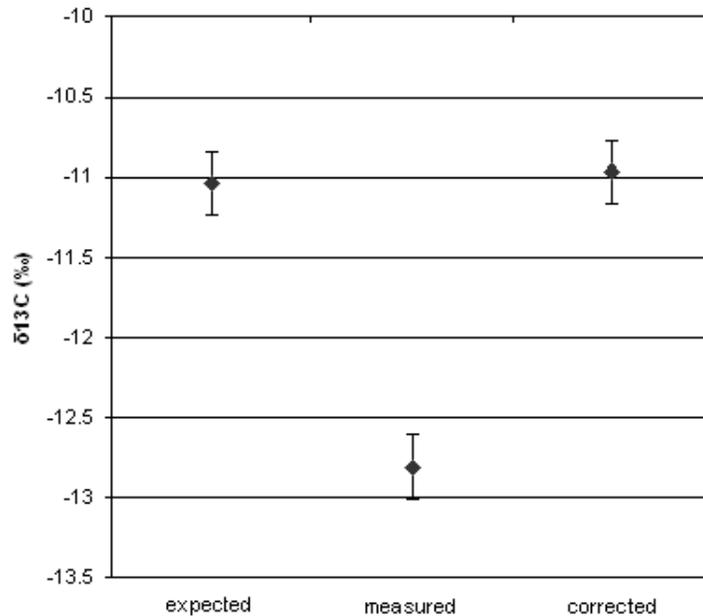


Figure 4 Correction of ^{14}C activity concentrations

Figure 5 Correction of $\delta^{13}\text{C}$ values

Verification by Field Test

The correction formula was applied for samples from the field. The value of m_e is equivalent with the amount of the total CO_2 recovered of the total amount of the eluate, if the elution efficiency is 100%. Therefore, m_e can be calculated on the basis of the amount of the CO_2 generated from the recovery process.

It is difficult to measure the efficiency of the elution; therefore, either it should be verified that the efficiency is close to 100%, or it should be reproducibly identical to correct with the m_e calculated on the basis of the recovery. The reproducibility seems to be fulfilled in the course of experiments.

The m_r is the excess CO_2 deriving from the resin, which can be calculated if the volume of the resin and the excess CO_2 per volume unit are known. The latter value is 8.5 mg of CO_2 per 1 cm^3 of resin; thus the m_r is ~ 5.8 g. The simplest formula for our sampling unit is thus:

$$^{14}\text{C}_w = \frac{^{14}\text{C}_e \times m_e - 420}{m_e - 5.8}$$

Results of the experiments were verified under field conditions. Samples were taken at the sampling area with the conventional method and by automatic sampler as well. The correction formula determined previously was applied for the results of the measurements. With the help of the correction formula, the ^{14}C activity concentrations of samples taken by the samplers correspond well with the values of the samples using the conventional BaCl_2 precipitation method (Figure 6).

CONCLUSION

An automatic water sampling unit was developed for the ^{14}C measurement of groundwater. The sampler was successfully tested under controlled laboratory conditions. A correction factor should

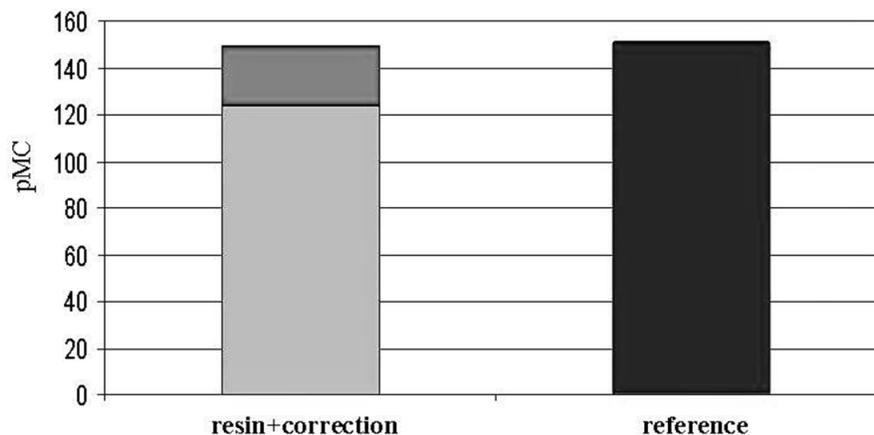


Figure 6 ^{14}C results of the field test

be introduced for the ^{14}C anion exchange sampling as the ^{14}C activity concentration of the groundwater measured by the ion exchange method is systematically underestimated using this system. The difference is well defined; therefore, it can be corrected. A correction formula was developed during reproducibility tests on the sampling unit, which takes the excess CO_2 deriving from the resin into consideration. The ^{14}C correction factor can give a more reliable picture and direction to the development of this system and possibly for new ion-exchange resin-based sampling systems.

REFERENCES

- Csongor É, Hertelendi E. 1986. Low-level counting facility for ^{14}C dating. *Nuclear Instruments and Methods in Physics Research B* 17(5–6):493–5.
- Csongor É, Szabó I, Hertelendi E. 1982. Preparation of counting gas of proportional counters for radiocarbon dating. *Radiochemical and Radioanalytical Letters* 55:303–7.
- de Jonge H, Rothenberg G. 2005. New device and method for flux-proportional sampling of mobile solutes in soil and groundwater. *Environmental Science & Technology* 9(1):274–82.
- Divine CE, Madsen LL, Andrews SD, Santangelo-Dreiling T. 2005. Passive diffusion ground water samplers at a site with heterogeneous hydrostratigraphy: pilot study results. *Ground Water Monitoring and Remediation* 25(1):90–9.
- Eggers DE. 1976. The application of borehole geophysics to the selection and monitoring of nuclear waste disposal sites. In: *Proceedings of 17th US Symposium on Rock Mechanics*. Snowbird, Utah, 25–27 August 1976. US National Committee for Rock Mechanics of the National Academy of Sciences, National Research Council. p 4B-1–4B-3-7.
- Granato GE, Smith KP. 1979. Robowell: an automated process for monitoring ground water quality using established sampling protocols. *Ground Water Monitoring and Remediation* 19(4):81–9.
- Hart RJ, Spruill TB. 1988. Description and hydrogeologic evaluation of nine hazardous-waste sites in Kansas, 1984–86. USGS Water Resources Investigations Report 88-4015.
- Hertelendi E. 1990. Developments of methods and equipment for isotope analytical purposes and their applications [CSc thesis]. Hungarian Academy of Sciences. In Hungarian.
- Hertelendi E, Csongor É, Záborszky L, Molnár J, Gál J, Györfi M, Nagy S. 1989. A counter system for high-precision ^{14}C dating. *Radiocarbon* 31(3):399–406.
- Hazardous Waste Bureau. 2001. Use of low-flow and other non-traditional sampling techniques for RCRA compliant groundwater monitoring. Position paper of Hazardous Waste Bureau of New Mexico Environment Department, Santa Fe, New Mexico, USA.
- Jones I, Lerner DN, Baines OP. 1999. Multiport sock samplers: a low-cost technology for effective multi-level ground water sampling. *Ground Water Monitoring and Remediation* 19(1):134–42.
- Karp KE. 1993. A diffusive sampler for passive monitoring of volatile organic compounds in ground water. *Ground Water* 31(5):735–9.
- King JA. 1993. Wastewater sampling. *The National Environmental Journal* 3(1):34–7.
- Maucha R. 1932. *Hydrochemische Methoden in der Limnologie*. Binnengewasser 12. Stuttgart: Schweizerbart. 173 p.
- Mulsow S, Coquery M, Dovlete C, Gastaud J, Ikeuchi Y, Pham MK, Povinec PP. 1999. Radionuclide concentrations in underground waters of Mururoa and Fanga-

- taufa atolls. *Science of the Total Environment* 237–238(1–3):287–300.
- Petruzzi NM, Silliman SE. 2006. A sampling device for collection of ground water bacteria under natural gradient flow conditions. *Ground Water Monitoring and Remediation* 26(1):85–91.
- Ronen D, Graber ER, Laor Y. 1987. Volatile organic compounds in the saturated-unsaturated interface region of a contaminated phreatic aquifer. *Vadose Zone Journal* 4(2):337–44.
- Spalding BP, Watson DB. 2007. Measurement of dissolved H_2 , O_2 , and CO_2 in groundwater using passive samplers for gas chromatographic analyses. *Environmental Science & Technology* 41(1):7861–7.
- Stow SH, Haase CS. 1986. Subsurface disposal of liquid low-level radioactive wastes at Oak Ridge, Tennessee. In: *Proceedings of the International Symposium on Subsurface Injection of Liquid Wastes*. Dublin, Ohio, USA: National Water Well Association. p 656–75.
- Vrba J. 1988. Groundwater quality monitoring as a tool of groundwater resources protection. In: *Karst Hydrogeology and Karst Environment Protection*. IAHS Publication 176, Volume 1. Wallingford: IAHS Press. p 88–97.