Methodological aspects of pH and EC measurements in geothermal water

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Abstract. A proper methodology for collecting samples of geothermal water makes it possible not on-ly to determine the hydrochemical characteristics of the water, but also to assess its temporal and spatial variability. The knowledge about the concentration of selected elements as well as the values of field measurements can help to indicate their impact on other environ-ments and the process-es that occur in a geothermal system. An important issue is the quality of the results obtained from in-situ measurements of unstable parameters, i.a. pH and electrical conductivity (EC). The results of measurements presented in the paper were completed with the use of three different devices in hot and cooled raw geothermal water (field test). The research was performed during two seasons of increased (winter) and lower (summer) exploitation of geothermal water. The percentage difference between EC at temperatures of 22ºC and 75ºC was 3.27%; however, for the pH the observed per-centage difference was only 0.26%. An additional experiment was carried out on a laboratory scale to indicate the influence of temperature changes on pH and EC measurements.

Introduction

A proper methodology for geothermal water sampling makes it possible not only to determine the hydrochemical characteristics of the water, but also to assess their temporal and spatial variability, as well as tracing flow lines, delineating recharge areas or carrying out geothermometry. The sampling procedures performed by one qualified sampler using proper containers and adequate methodology, according to ISO 5667-11: 2009 and the guidelines proposed by Ármannsson and Ólafsson (2010), determine the quality of the results obtained (Witczak et al. 2013). In the case of geothermal water, changes in the chemical composition are often noticeable earlier than changes in temperature, and therefore properly planned and conducted monitoring plays a major role in the early detection of trends (Kania 2003; Borsodi et al. 2016). Moreover, the results of chemical analyses help identify potential problems that may arise from water exploitation such as scal-

ing or corrosion (Tomaszewska 2008; Zeppenfeld 2010; Tomaszewska and Pająk 2012; Mehl and Johannsen 2018; Tomaszewska et al. 2018). They can provide information about the water mixing processes (Kania 2003; Kania and Olafsson 2005; Süer et al. 2008) and also provide geothermometric indicators (Diamond and Alt-Epping 2014; Apollaro et al. 2016; Hermandez-Morales and Wulf 2016) or aid research on the source of geothermal water (Guo et al. 2017; Yildirim and Özgür 2017a; Yilmaz and Özgür 2017b).

To control and monitor the physicochemical parameters of water with sufficient certainty and reliability the implementation of a quality assurance/ quality control (QA/QC) programme in field and laboratory practice is needed (Kmiecik 2018). *In-situ* measurements of pH and EC are considered simple and very often the measurements are not checked and controlled.

The main goal of the research was to evaluate the methodology and the quality assurance of *in-situ* measurements of unstable parameters (pH and EC).

Materials and Methods

The research material

Analysed solutions

Field study covered two geothermal water wells GT-1 and GT-2, which are used i.a. for heating purposes.

The study area is located in the south of Poland, using water from Poland's most effective geothermal water reservoir (Fig. 1). It is related to the Eocene carbonate series (Middle Eocene) with underlying Mesozoic formations, mainly Middle Triassic limestones and dolomites, Jurassic sandstones and carbonate rocks (Kępińska and Ciągło 2008; Bujakowski et al. 2016). The total depth of the GT-1 well is 3,242 m. The GT-2 well is a vertical well and its measured depth (MD) is 3,519.3 m (TVD is 3,400 m). The depth of the perforation zone is between 2,722.0 and 3,032.0 m in GT-1, and 2,706.2–3,500.0 m MD (2,587.1–3,380.7 m TVD) in GT-2. The ground ordinate of both wells is 672 m a.s.l. The water table is stable at +295.0 m (GT-1) and 211.6 m (GT-2) relative to the land surface (Korzec 2016). The hydrochemical type of water extracted from wells GT-1 and GT-2 is sulphate-chloride-sodium-calcium (according to the Szczukariew-Priklonski classification). The values of total dissolved solids are in the range from 2.3 to 3.0 g/L. The water temperature measured at the wellhead varies between 83ºC and 86ºC (Korzec 2016).

During the laboratory experiment, pH and EC values were measured in a sample of natural water heated from 17°C to 90°C.

The calibration solutions used were: pH buffers (DuraCal, Hamilton) and EC standards (Hamilton and VWR). Quality control of measurements was performed by the analysis of certified reference material ION-96.4 (Environment Canada).

Fig. 1. Location of study area

Analytical methods

Electrical conductivity and pH were measured using standardised methods. The parameters of methods used are summarised in Table 1.

The limit of quantification adopted was the minimum amount of the substance that gives a result for which the precision expressed as relative standard deviation (RSD) does not exceed 20%. The relative expanded uncertainty is the uncertainty declared by the laboratory and it takes into account shares associated with the analytical measurement and those resulting from the process of sampling.

The *in-situ* temperature measurement was carried out using the integrated temperature sensor of the meter's electrodes and calibrated glass thermometer.

The experiment on the measurement of pH and EC was performed using three different instruments:

A – OAKTON Waterproof PC300 (http://www.4oakton.com/Assets/Manual_pdfs/EOK_PC300_Oct02.pdf);

B – WTW Multi 3430 with electrodes specifically designed for thermal waters (www.globalw.com/downloads/WQ/multi3430.pdf);

C – WTW Multi 350i with electrodes designed for waters with a temperature lower than 40°C (www.geotechenv.com/Manuals/WTW_Manuals/Multi_350i.pdf).

Devices A and B were adapted for geothermal waters measurements (temperatures up to 120°C). The experiment was conducted for raw geothermal water (high temperature) and cooled water (<40°C). During the *in-situ* tests pH, EC as well as water temperature were measured. To check that water degasification had been avoided, alkalinity was also determined. For this purpose alkacymeric titration was used (Table 1).

Field test

In order to enable *in-situ* measurements and water sampling without contact with the air and to avoid water degasification, a glass flow cell was constructed. It is fully tight, enabling the continuous supply and discharge of the water tested. The method of geothermal water cooling without contact with the air was based on connecting a 100-metre-long coil of sampling hose and placing it in a container to which cold water was continuously provided. As a result the temperature of the water being tested decreased by 50°C, which allowed for the measurement of unstable parameters using standard electrodes while preventing water aeration, which was confirmed by additional alkalinity measurements. The measurements were conducted parallel in hot water flowing from the wells and in the cooled water.

The materials used during the experiments were compatible with the applicable guidelines (ISO 5667-11: 2009; Witczak et al. 2013; Korzec et al. 2016). The vessels and sampling hose were made of high density polyethylene (HDPE). Mineral precipitation from the solution was not observed.

Before the measurements, free flow of water through the sampling hose was allowed for about 15 minutes.

An important aspect of measuring pH and EC in geothermal water is the choice of the device used. An instrument suitable for measurement of the unstable parameters has electrodes that can be used in a broad temperature range. However, this results not only in the high cost of the meter itself, but

Table 1. Characteristics of analytical methods (according to the accreditation certificate of the Hydrogeochemical Laboratory)

Parameter	Analytical method	No. of standard	Limit of quantification	Relative expanded uncertainty U [%] (k=2, 95%)
pH	potentiometry	EN ISO 10523:2012	2	5.5
EC	conductometry	EN 27888:1993	2 µS/cm	9.0
Alkalinity (as HCO_3^-)	titration	ISO 9963-1:1994	24.4 mg/L	10.5

also in the high cost of its consumable parts (electrodes). If it is not possible to use a meter dedicated to high water temperature, a meter adapted to lower temperatures was proposed, which is much less expensive. This solution needs the construction of the above mentioned system in which the test water could be cooled without contact with atmospheric air.

An additional experiment was also conducted in order to verify that the proposed methodology would have no impact on the reliability of the results obtained. To determine if pCO_2 is changed during water cooling, an experiment of *in-situ* measurement of alkalinity was performed. The alkalinity was measured immediately in samples collected in three different ways. The first one was taken directly from the sampling pipe, the second one using a one-metre-long hose and the third one using a 100-metre-long hose.

Laboratory tests

Independent laboratory tests were carried out to indicate the difference in pH and EC of the water as a function of temperature. For this purpose, pH and EC values were measured (using the B meter) during water heating under laboratory conditions in the temperature range from 17°C to 90°C. The test was carried out using a standard laboratory thermostat with temperature rising in steps of about 5°C. The tested water was tap water.

Results and discussion

Field test

During the summer campaign three meters (A, B and C) were used to determine the pH and EC in hot and cooled water from the GT-1 and GT-2 wells. In winter the measurements were performed with the use of only two instruments dedicated to geothermal water (meters A and B). In this case the pH and EC values were measured in water from the GT-1 well. The EC value was measured with a temperature compensation of 25°C. When pH and

EC parameters are measured at the same time (both pH and EC electrodes are connected to the multimeter) the results are also recalculated to compensate for temperature. The following compensation methods can be selected: nonlinear, linear, manual or no temperature compensation. For natural water, the nonlinear function is recommended according to EN 27888:1993. All meters were calibrated at an appropriate temperature before field research using the same buffers (HAMILTON). The results of measurements are summarised in Table 2.

When interpreting the results obtained, one should take into account that three different meters were used, i.e. three different calibration curves were used, which results in differences between the results of the measurements. However, the expanded uncertainty takes into account all these factors.

The expanded uncertainty of field parameter measurements assumed by the laboratory conducting physical and chemical analyses of geothermal waters is 5.5% (calculated for the measured mV prior to pH unit conversion) for pH and 9% for EC (with an expansion coefficient of k=2 – Table 1). The percentage differences between the results obtained for cooled and hot geothermal water calculated on the basis of the results of experiment did not exceed these values, which confirms the correctness of the methodology adopted. These differences vary from 0.6 to 4% for EC and from 1 to 4% in the case of pH measurement and they are not dependent on the hot or cooled water temperature (Table 2). The results show that the use of a flow cell during measurement of unstable water parameters could give comparable values for both cold and hot water when the appropriate temperature compensation is chosen and the observed differences are not statistically significant (t-test significance p>0.05). The differences between the results obtained using the three different meters were also calculated (Table 3).

The results indicated that there is no statistically significant difference between the results of the electrical conductivity of cold water measured with the OAKTON Waterproof PC300 (A) and WTW Multi 350i (C) even though the percentage difference for the results obtained varies by about 10% (Table 3). The pH and EC values measured with the use of three different instruments are similar and the

Table 2. Results of unstable parameter measurements using different meters

Well	Meter/ Water	Measured value of specific electrical conductivity EC [mS/cm]	Percentage difference between measured value of specific electrolytic conductivity EC [mS/cm] in cold and hot water [%]	Measured value of pH [–]	Percentage difference between measured value of pH [–] in cold and hot water [%]	Water temperature during measurement [°C]	Outdoor temperature [°C]
GT-1 (summer)	A/Hot	3.22	-0.94	6.71	1.19	76.3	22.0
	A/Cold	3.19		6.79		21.5	
	B/Hot	3.3	-1.80	6.74	-1.19	78.4	
	B/Cold	3.36		6.66		22.6	
	C/Cold	3.54	—	6.4	—	30.4	
GT-2 (summer)	A/Hot	3.33	-2.43	6.72	-3.95	71.6	
	A/Cold	3.25		6.46		29.9	
	B/Hot	3.38	4.06	6.73	-3.94	71.4	
	B/Cold	3.52		6.47		21.2	
	C/Cold	3.6	—	6.52	—	21.2	
GT-1 (winter)	A/Hot	3.38	-3.00	6.74	-2.71	56.2	-2.0
	A/Cold	3.28		6.56		1.6	
	B/Hot	3.32	0.60	6.78	1.03	55.8	
	B/Cold	3.34		6.85		1.6	

differences observed are not statistically significant (t-test significance p>0.05).

It is very important to measure correctly pH and EC values, especially when vertical stratification of these parameters is in the interest of the researcher (Nielsen [ed.] 2005; Jover et. al 2007; Witczak et al. 2013). Furthermore, when the spatial distribution of pH and EC values is considered, the measurements should be provided over a short time period and the same buffers should be used during calibration.

The results of alkalinity measurements show that, during water cooling with the use of the hose, the alkalinity did not change greatly; however the HCO_3^- concentration (Table 4) as well as pH value (Table 3) are higher, which means that CO_2 concentration decreases when a long hose is used (Boyd 2000).

The differences between the results obtained for the alkalinity measurements were not greater than 7% and they are lower than the measurement uncertainty (Table 1).

Laboratory tests

The additional independent laboratory tests were carried out. The results of pH and EC values measured during the heating of tap water under laboratory conditions are presented in Figure 2.

During water heating from 17 to 40°C the EC value changed in a very small range (from 0.371 to 0.374 mS/cm). Furthermore, an increase in temperature caused a decrease in the EC value from 0.374 to 0.358 mS/cm regardless of the fact that nonlinear temperature compensation was used as recommended. The percentage difference between the EC in temperatures of 22°C and 75°C is 3.27%. This is comparable with the results obtained during field measurements for hot and cold water (Table 3) and is much lower than the relative expanded uncertainty of these types of measurements (Table 1).

The measurement of EC is an important part of water study, because there is a correlation between the EC value and the amount of total dissolved solids in the sample (Witczak et al. 2013). The conversion coefficient can vary between 0.54 and 0.96

Table 3. Differences between the results of pH and EC measurements using meters dedicated to geothermal water and a standard meter for water with a temperature below 40°C

Meters	Parameter	GT-1 (Summer)		GT-2 (Summer)		GT-1 (Winter)	
		Water					
		Cold	Hot	Cold	Hot	Cold	Hot
		Difference between results obtained using different meters [%]					
A and C	pH	5.91	—	0.92	—	—	—
	EC	10.40	—	10.22	—	—	—
B and C	pH	3.98	—	0.77	—	—	—
	EC	5.22	—	2.25	—	—	—
A and B	pH	0.45	1.93	0.15	0.15	4.33	0.59
	EC	2.45	5.19	7.98	1.49	1.81	1.79

Table 4. Results of alkalinity determination during field experiment

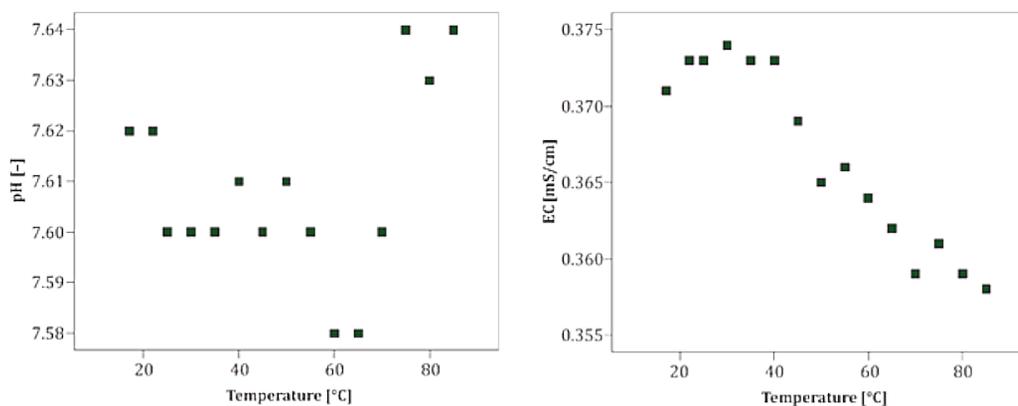| Well	Sampling method	HCO$_3^-$ [mg/L]
GT-1	directly from wellhead	309.5
	3-m hose	322.0
	100-m hose	326.8
GT-2	directly from wellhead	306.0
	3-m hose	326.8
	100-m hose	316.4

Fig. 2. pH (a) and EC (b) changes with increase in temperature in tap water. Laboratory test

(Hem 1989) and depends on the chemical composition of water. It can be calculated when both the TDS and EC are measured for a period of time and the measurements must be conducted properly. The results should not be dependent on the type of meter and chosen temperature compensation. It is also necessary to obtain the correct results of the pH parameter, in particular when geochemical modelling is considered and different forms of elements (speciation) are analysed (Tomaszewska 2008; Dobrzyński et al. 2018). The results of the research indicated that for the pH parameter the changes ob-

served are not visible as in the case of EC measurements. The pH varies from 7.58 to 7.64 in the whole of the temperature range analysed. The percentage difference between the values measured at the temperatures of 22°C and 75°C is 0.26%. This indicates that the reported pH is not dependent on temperature when temperature compensation is carried out during measurements.

Conclusions

The main purpose of the research presented in this paper was to determine the appropriate method of *in-situ* measurements of unstable parameters (pH and EC) in geothermal water. The field experiment was completed using three meters. The study demonstrated that the proposed system for cooling geothermal water without contact with air did not affect the measurement results. The percentage differences between the results for cooled and raw water are in the range of 0.60%–4.06% for electrical conductivity and from 1.03% to 3.95% for pH values. This falls within the boundaries of measurement uncertainty declared by the laboratory and is comparable with the results obtained during additional laboratory measurement.

For the pH parameter, the observed results vary from 7.58 to 7.64 over the temperature range examined. The percentage difference between the values measured in temperatures of 22°C and 75°C is 0.26%. These differences are not statistically significant, which means that the pH value is not dependent on temperature if compensation is used when taking measurements.

The presented experiment demonstrated that it is possible to use matching solutions enabling the guidelines for the sampling of geothermal water to comply with the use of readily available materials and instruments. However, it is necessary to implement an appropriate field QA/QC programme in order to obtain reliable measurement results. In addition, when different meters are used, an independent experiment should be performed to confirm the proper procedure for unstable parameter measurements.

Disclosure statement

No potential conflict of interest was reported by the authors.

Author Contributions

Study design: E.K., K.W., B.T., K.S., A.M.; data collection E.K., K.W., B.T., K.S., A.M.; statistical analysis: E.K., K.W., B.T., K.S., A.M.; result interpretation E.K., K.W., B.T., K.S., A.M.; manuscript preparation E.K., K.W., B.T., K.S., A.M.; literature review: E.K., K.W., B.T., K.S., A.M.

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