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Implementation of QA/QC program in research related to the membrane processes used in geothermal water treatment

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ABSTRACT

Testing physicochemical parameters of water with sufficient certainty and reliability requires always the implementation of quality assurance/quality control (QA/QC) systems in the laboratory practice. The paper presents the results of QA/QC program realized during nanofiltration (NF) process. The analyses of geothermal water (raw water), permeate and retentate in normal and control (duplicate) samples were conducted by the accredited hydrogeochemical laboratory. All samples were collected by a single sampler using the same sampling protocol and delivered to the laboratory within a short time (several hours). The samples were analysed by qualified analysts, using analytical methods that were validated for these purposes. A detailed analysis of test results is shown for one selected indicator – boron. The concentration of boron in samples of the permeate and the concentrate has not been particularly changed upon NF process. Therefore it was really important and necessary to estimate uncertainty of measurements for the results of such tests. On the basis of the data collected, the precision and uncertainty of determinations of this indicator were estimated in the context of the assessment of the quality of raw water, permeate and retentate. Relative measurement uncertainty of boron does not exceed 5%.

Keywords: Geothermal water; Boron; QA/QC; Duplicate (replicate) control samples

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1. Introduction

Nanofiltration (NF) is considered to be the most promising technique use for the production of high quality water from surface and brackish water. There are many examples of its use in practice [1–4]. Due to these properties, NF is considered a suitable pre-treatment process for desalination of waters with a high degree of hardness and a high concentration of sulphates and carbonates [5–10]. However, it was reported influence of biofouling of NF membrane on the performance of the membrane during boron removing from synthetic wastewater effluent [11].

Borates are widely found in nature, and they are present in oceans, sedimentary rocks, soil, coal and shale. Naturally occurring boron is found in groundwater, primarily as a result of leaching from rocks and soils that contain borates and borosilicates. Boron is found in surface water and groundwater in various locations around the world, including sea and river water, where it occurs mainly in the form

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of boric acid [11–13]. Geothermal waters are often characterised by high levels of boron (ranging from a few to around a dozen mg/L) [14–17].

During our research, NF process with NF-270 membrane has been tested as a pre-treatment process in geothermal water treatment conducted on a laboratory scale. The NF process has been analysed in order to decrease the number of divalent ions, especially for the softening feed water directed into the proper treatment in RO process. More details of the results of geothermal water pre-treatment during nanofiltration with NF-270 membrane tests can be found in [18].

For the analysis results obtained to be adequately reliable, it is necessary to implement an appropriate QA/QC program enabling the ongoing control of the tested indicators. In literature, numerous publications and guides can be found that deal with estimating measurement uncertainty, with particular emphasis on the sampling process as one of its main sources [19–66].

It is estimated that around 30% of errors are introduced in the process of sampling and transporting samples to the laboratory, another 60% are connected with the sample treatment process and the preparation of samples for analysis, and 10% of errors are associated with the analytical measurement itself [21].

The simplest method of estimating uncertainty, that also probably requires the least financial expenditure, is the duplicate sample method. This can be implemented using a balanced design or its simplified version [19,49]. Replicate samples are collected in parallel with normal samples, using the same sampling procedure and a single sampler. They are subsequently analysed in the same laboratory, using the same analytical methods and by the same analyst. This makes it possible to minimize sampling and analysis bias (systematic errors), which are not covered by this method for estimating uncertainty [30,49].

2. Materials and methods

In 2015, during the nanofiltration processes conducted using the NF-270 commercial membrane produced by Dow Filmtec with a cut-off of 200 Da, replicate (duplicate) samples were collected [18]. Filtration was performed under a transmembrane pressure in the range of 10 bar with cross-flow filtration. Tests were conducted for two different types of geothermal water with elevated mineralisation levels (TDS of 2.2–2.3 g/L), more than 600 mg $CaCO_3$/L and high silica concentrations.

Replicate samples of raw water, permeate and retentate were collected and analysed according to an extended balanced design – each normal (N) and replicate (D) samples were analysed twice (N1, N2, D1, D2) – Fig. 1a.

All samples were cooled and sent to the accredited Hydrogeochemical Laboratory of the Hydrogeology and Engineering Geology Department of the AGH University of Science and Technology in Kraków (PCA certificate No. AB 1050) within less than 24 h. Boron concentrations in the samples were analysed using the ICP-OES (inductively coupled plasma optical emission spectrometry) method [12].

On the basis of the results obtained, the precision of the determination of boron by the ICP-OES method in test samples was evaluated and the uncertainty associated with the sampling and analytical processes was estimated.

In water quality monitoring (including geothermal water), the total variability of the parameters monitored (σ^2_{total}) is derived from three main sources (Fig. 1) [23–25]:

- the spatial and/or temporal natural variability of the indicator (geochemical variance, between target variance) – $\sigma^2_{geochemical}$;
- the errors that occur during sampling, sample transport and storage (sampling variance) – $\sigma^2_{sampling}$;
- analytical errors (analytical variance) – $\sigma^2_{analytical}$.

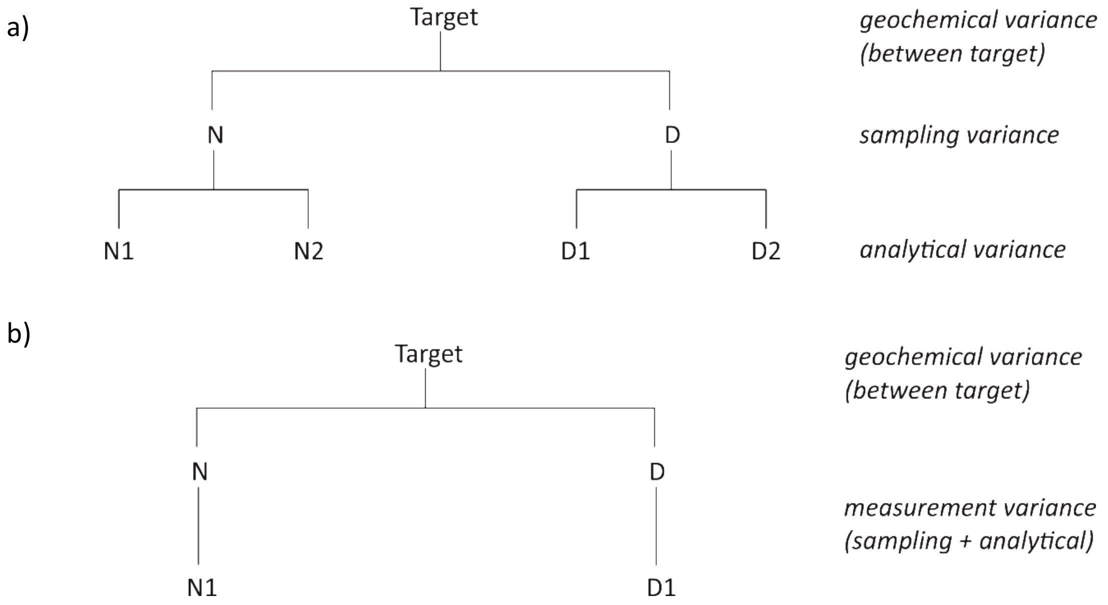

Fig. 1. Scheme a) extended; b) simplified for sampling replicate control samples and estimating individual types of variance.

$$\sigma^2_{total} = \sigma^2_{geochemical} + \sigma^2_{sampling} + \sigma^2_{analytical} = \sigma^2_{geochemical} + \sigma^2_{measurement} \quad (1)$$

Measurement (technical) variance is the sum of sampling and analytical variances.

This variability can be estimated based on the results of determinations for duplicate samples using variance estimators:

$$s^2_{total} = s^2_{geochemical} + s^2_{sampling} + s^2_{analytical} = s^2_{geochemical} + s^2_{measurement} \quad (2)$$

We can use these statistics to estimate standard uncertainties u:

$$u_{geochemical} = s_{geochemical} \quad (3)$$

$$u_{sampling} = s_{sampling} \quad (4)$$

$$u_{analytical} = s_{analytical} \quad (5)$$

$$u_{measurement} = s_{measurement} \quad (6)$$

To calculate expanded uncertainty (U) at a confidence level of e.g. 95%, we multiply the standard uncertainty value by the k coverage factor of 2, $U = 2u$:

$$U_{geochemical} = 2 \cdot s_{geochemical} \quad (7)$$

$$U_{sampling} = 2 \cdot s_{sampling} \quad (8)$$

$$U_{analytica\ l} = 2 \cdot s_{analytical} \quad (9)$$

$$U_{measurement} = 2 \cdot s_{measurement} \quad (10)$$

Relative uncertainties (U') with respect to the average value of the indicator analysed in normal and duplicate samples ($\bar{X}$) are calculated using the following formulas:

$$U'_{geochemical} = \frac{2s_{geochemical}}{\bar{x}} 100\ [\%] \quad (11)$$

$$U'_{sampling} = \frac{2s_{sampling}}{\bar{x}} 100\ [\%] \quad (12)$$

$$U'_{analytical} = \frac{2s_{analytical}}{\bar{x}} 100\ [\%] \quad (13)$$

$$U'_{measurement} = \frac{2s_{measurement}}{\bar{x}} 100\ [\%] \quad (14)$$

Estimates of uncertainty, according to the above formulas, can be obtained automatically in the ROBAN program[1] using the results of analyses of duplicate (replicate) samples. ROBAN accompanies AMC Technical Briefs No 40 "The Duplicate Method for the estimation of measurement uncertainty arising from sampling" [44].

The program presents in graphical form independent estimates of three components of total variance and their percentage shares. The estimate is based on the classical variance analysis (classical ANOVA) method and the robust ANOVA method, which uses a flexible statistical approach that allows for the presence of up to 10% of outliers in the data set analysed. For estimates using the robust method, the program also calculates standard uncertainty (standard deviation) u and extended relative uncertainty U' associated with these components.

The analysis of variance makes it possible to gain insights of total uncertainty structure. Fig. 2 shows the boundary values of relative shares of total uncertainty components resulting from measurements (sampling and analysis) and from the analysis itself (after [23]). If relative shares of total variance obtained through the duplicate sample method are higher than the boundary values shown in Fig. 2, appropriate action should be taken to reduce them.

The introduction of a QA/QC program in relation to duplicate samples in accordance to the extended analysis program is a costly undertaking. However, the use of a simplified program (Fig. 1b) where the normal and duplicate samples are analysed only once, provides no information about sampling and analytical uncertainty because only data on measurement uncertainty, which is the sum of these two components, are obtained [23]. The solution is to apply the unbalanced design and use e.g. the U-RANOVA program for estimating uncertainty [45,65,66].

U-RANOVA is an easy-to-use Excel application to assist in estimation of uncertainty by the duplicate method, which is fully described in the Eurachem guides [49–51].

U-RANOVA differs from previous methods in that it permits an unbalanced experimental design to be used. It enables estimates of the three variances described above to be made with fewer duplicated analyses, thus saving money on the chemical analysis. In this approach, the results of two measurements conducted for a normal sample and of one for the replicate sample are used. In this way, it is possible to reduce the number of tests performed.

In order for the uncertainty values obtained to be reliable, analysis results for at least 8 pairs of samples need to be used in calculations [49,51].

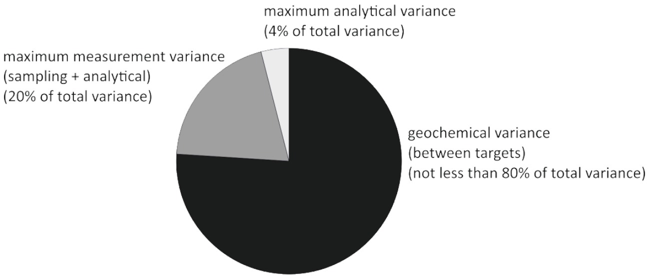

Fig. 2. Maximum permissible relative shares of sampling variance and analytical variance in total variance [23].

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[1] www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/ROBAN.asp

3. Results

The evaluation of precision and the estimation of the uncertainty (total, geochemical, measurement = sampling + analytical) for boron determination was conducted for three groups of samples: raw water, permeate and retentate obtained during the nanofiltration process. The measurement results obtained are summarised in Table 1.

Differences between boron concentrations in duplicate samples were marked on individual measurements control charts according to the ISO 5667-14 standard [53] (Fig. 3).

Each point plotted on the chart represents an individual measurement, difference of results or a summary statistic. The green/solid line is the centre line (CL) or the average of the data (bar-x). The two red dashed lines are the upper and lower control limits (UCL and LCL, ±3 standard deviations (3s) of the mean).

When an analytical process is within control, approximately 68% of all values fall within ±1 standard deviation (1s) from the central line. Likewise, 95.5% of all values fall within ±2 standard deviations (2s) of the mean. About 4.5% of all data will be outside the ±2s limits when the analytical process is in control. Approximately 99.7% of all values are found to be within ±3 standard deviations (3s) of the mean. As only 0.3%, or 3 out of 1000 points, will fall outside the ±3s limits, any value outside of ±3s is considered to be associated with a significant error.

No point or sequential signals were identified on the charts (Fig. 3) and therefore differences between the results should be regarded as stable.

Table 1
Boron concentration measurement results in normal (N) and duplicate (D) samples

Date	Boron concentration [mg/L]				
	N1	N2	D1	D2	Difference N1-D1
Raw water					
2015-09-03	9.22	9.22	8.89	8.73	0.33
2015-09-07	8.70	8.06	8.69	8.57	0.01
2015-09-08	8.71	8.72	8.82	8.53	–0.11
2015-09-09	9.03	9.31	9.02	9.28	0.01
2015-09-11	7.89	7.89	7.87	7.87	0.02
2015-09-16	7.85	8.11	8.00	8.13	–0.15
2015-09-18	7.71	7.96	7.86	8.03	–0.15
2015-09-21	7.31	7.31	7.38	7.38	–0.07
Permeate					
2015-09-03	9.29	8.94	9.37	9.12	–0.08
2015-09-07	8.26	8.37	8.39	8.37	–0.13
2015-09-08	8.53	8.49	8.54	8.52	–0.01
2015-09-09	8.77	8.65	8.82	8.83	–0.05
2015-09-11	7.10	7.24	7.15	7.23	–0.05
2015-09-16	7.78	7.89	7.83	8.00	–0.05
2015-09-18	7.41	7.43	7.35	7.62	0.06
2015-09-21	7.01	7.20	7.05	7.26	–0.04
Retentate					
2015-09-03	9.76	9.50	9.87	9.36	–0.11
2015-09-07	8.96	8.28	8.96	8.84	0.00
2015-09-08	8.98	8.99	9.04	8.82	–0.06
2015-09-09	9.31	9.56	9.39	9.63	–0.08
2015-09-11	8.02	8.06	8.00	8.16	0.02
2015-09-16	8.12	8.01	8.17	8.08	–0.05
2015-09-18	7.73	7.88	7.75	7.99	–0.02
2015-09-21	7.21	7.51	7.30	7.46	–0.09

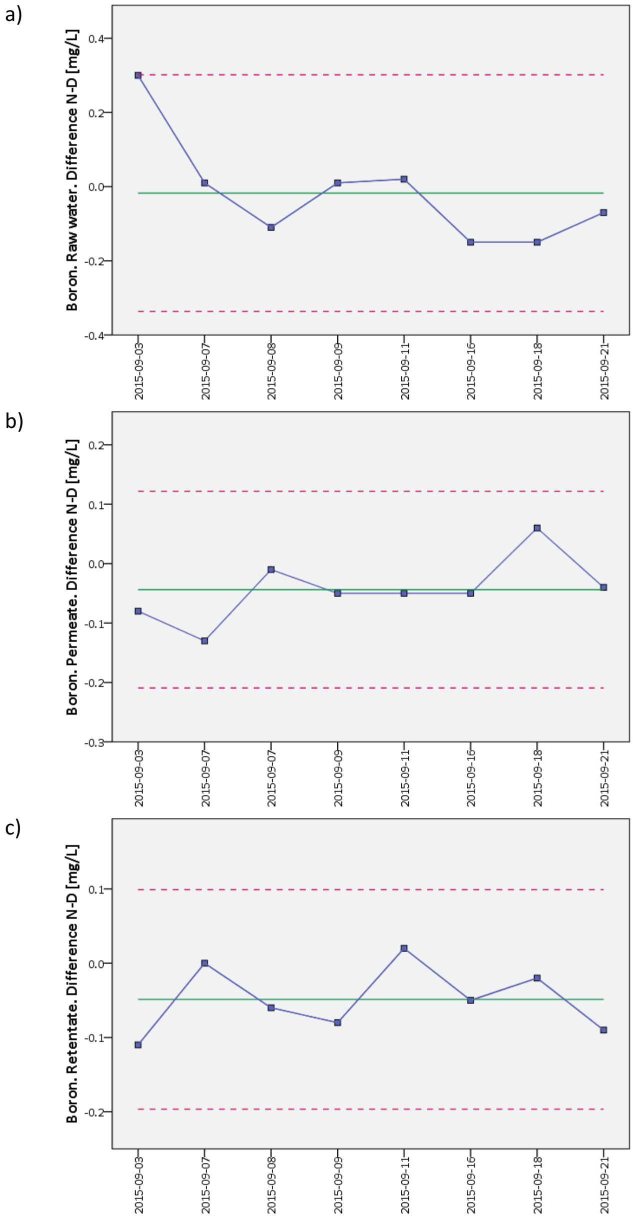

Fig. 3. Individual measurement control charts for concentration differences in normal and duplicate samples – a) raw water, b) permeate, c) retentate.

The estimation of uncertainty was conducted using the ROBAN and U-RANOVA programs using robust ANOVA method. The relative shares of geochemical (between targets), analytical and sampling variances are shown in Fig. 4.

The results obtained indicate that the primary source of variation in the concentrations analysed is the natural variability in the chemical composition of the water examined (due to heterogeneity of the objects – two kinds of geothermal waters). A sampling variance of zero points to a properly conducted sampling process and the small share of analytical variance in total variance (3–4%) is evidence of properly conducted analysis. In this case analytical variance is equal measurement variance.

The variance percentages determined in the ROBAN program using the extended scheme were compared with the results from the U-RANOVA program, where only a single analysis result was used for the duplicate sample. Also in this case the variances associated with sampling are equal to zero for all three types of solutions tested. In total variance, geochemical/natural (between target) variability dominates (96.5–98.5%), while analytical variance does not exceed 5%.

The standard, extended and relative uncertainty values were also determined (Table 2).

The uncertainty values determined using extended design sampling are similar for all three types of samples analysed – raw water, permeate and retentate. Relative

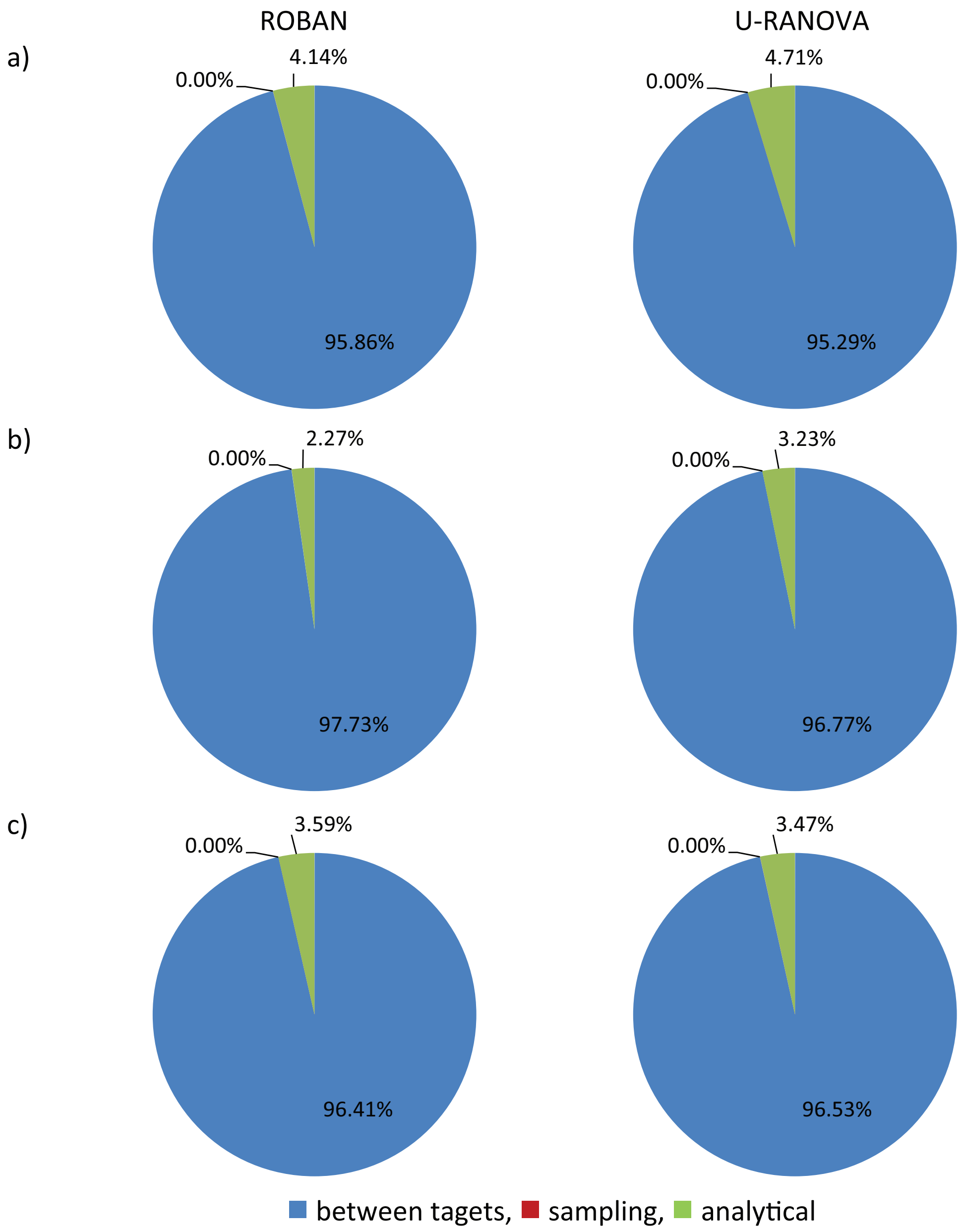

Fig. 4. Percentage variances for: a) raw water, b) permeate, c) retentate obtained using the ROBAN and U-RANOVA program.

Table 2
Boron determination standard (u), expanded (U) and relative (U') uncertainty values calculated on the basis of duplicate sample analysis results. Coverage factor $k = 2$ was assumed for a confidence interval of 95% – extended (ROBAN) or unbalanced design (U-RANOVA)

Parameter		Value	
		Extended design	Unbalanced design
Raw water			
Mean value [mg/L]		8.31	8.31
Total uncertainty	u_{total} [mg/L]	0.727	0.746
	U_{total} [mg/L]	1.45	1.49
	U'_{total} [%]	17.50	17.95
Geochemical uncertainty	$u_{\text{geochemical}}$ [mg/L]	0.711	0.729
	$U_{\text{geochemical}}$ [mg/L]	1.42	1.46
	$U'_{\text{geochemical}}$ [%]	17.11	17.55
Analytical uncertainty	$u_{\text{analytical}}$ [mg/L]	0.148	0.162
	$U_{\text{analytical}}$ [mg/L]	0.30	0.32
	$U'_{\text{analytical}}$ [%]	3.55	3.89
Sampling uncertainty	u_{sampling} [mg/L]	0	0
	U_{sampling} [mg/L]	0	0
	U'_{sampling} [%]	0	0
Permeate			
Mean value [mg/L]		8.343	8.037
Total uncertainty	u_{total} [mg/L]	0.935	0.902
	U_{total} [mg/L]	1.87	1.804
	U'_{total} [%]	22.41	22.45
Geochemical uncertainty	$u_{\text{geochemical}}$ [mg/L]	0.925	0.895
	$U_{\text{geochemical}}$ [mg/L]	1.85	1.79
	$U'_{\text{geochemical}}$ [%]	22.17	22.27
Analytical uncertainty	$u_{\text{analytical}}$ [mg/L]	0.141	0.11
	$U_{\text{analytical}}$ [mg/L]	0.282	0.21
	$U'_{\text{analytical}}$ [%]	3.38	2.47
Sampling uncertainty	u_{sampling} [mg/L]	0	0
	U_{sampling} [mg/L]	0	0
	U'_{sampling} [%]	0	0
Retentate			
Mean value [mg/L]		8.522	8.515
Total uncertainty	u_{total} [mg/L]	0.93	0.963
	U_{total} [mg/L]	1.86	1.926
	U'_{total} [%]	21.83	22.62
Geochemical uncertainty	$u_{\text{geochemical}}$ [mg/L]	0.913	0.947
	$U_{\text{geochemical}}$ [mg/L]	1.826	1.894
	$U'_{\text{geochemical}}$ [%]	21.43	22.24
Analytical uncertainty	$u_{\text{analytical}}$ [mg/L]	0.176	0.18
	$U_{\text{analytical}}$ [mg/L]	0.352	0.36
	$U'_{\text{analytical}}$ [%]	4.13	4.23
Sampling uncertainty	u_{sampling} [mg/L]	0	0
	U_{sampling} [mg/L]	0	0
	U'_{sampling} [%]	0	0

total uncertainty is the lowest for raw water (17.5%) and the highest for the permeate (22.4%). Analytical uncertainty (which in this case is measurement uncertainty because sampling uncertainty equals zero) ranges from 3.4 to 4.1%.

Also in the unbalanced design with a single duplicate sample analysis relative total uncertainty ranges from 20.2 to 22.6% and relative analytical uncertainty (measurement uncertainty) does not exceed 4.23%.

The boron measurement uncertainty estimated by the laboratory stands at about 20%. It is higher than these estimated on the basis of analyses for duplicate samples.

When uncertainty estimates are based on duplicate control samples, systematic factors are not accounted for (they were minimized – one sampler, one procedure, one laboratory, one method, one analyst etc.). Laboratory in uncertainty estimating process also took into account the systematic factors resulting e.g. from reproducibility conditions (changing the sampler, changing the analyst etc.).

In Fig. 5 the results of boron determination in normal samples with estimated on the basis of replicate samples expanded uncertainty intervals are presented.

They show measurement uncertainty as a range around the measured value that should encompass the 'true value' of the measure and with known probability (95%).

The differences between single results of boron concentration in three types of analysed samples are small. When we take into account the measurement uncertainty ranges, we can see that the 'true' levels of boron concentration in those samples could be different.

Measurement uncertainty needs to be estimated since it is an intrinsic part of the measurement result. Its value allows an objective and independent interpretation of the measurement result and can be used to check quality and prove the adequacy of the measurement for its intended use. It does not imply doubt about the validity of a measurement, on the contrary, knowledge of the uncertainty

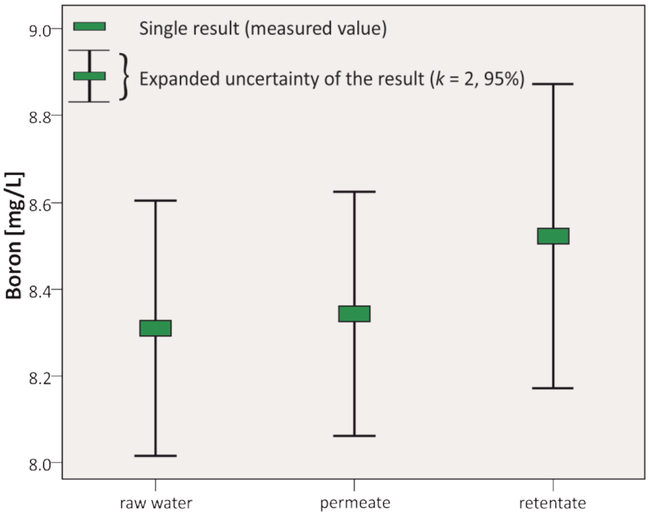

Fig. 5. Single results of boron determination in normal samples (2015-09-03) with expanded measurement uncertainty intervals.

implies increased confidence in the validity of a measurement result [67,68].

So the knowledge about measurement uncertainty is really important especially when we assess effectiveness of membrane processes [69].

4. Conclusions

Obtaining sufficiently certain and reliable measurements of physicochemical parameters of water entails the need for the laboratory to implement a quality assurance/quality control (QA/QC) system.

The results of the quality control/quality assurance process implemented indicate that the geothermal water treatment process is a stable one. For all three solutions analysed (raw water, permeate and retentate), individual measurement control charts do not exhibit any point or sequential signals for the differences between the results obtained for the normal and duplicate samples. Moreover, the sampling variances determined for the extended design using the ROBAN program and the unbalanced design using the U-RANOVA program are equal to zero in both cases. In total variance, the component resulting from the natural variability of the solutions tested dominates and analytical variance is no higher than 5%. Thus the number of control samples can be reduced, which will make it possible to reduce analysis cost, and the unbalanced design can be used, in which a normal sample is analysed twice and the duplicate sample only once.

The uncertainty values determined are similar for all three types of solutions. Relative total uncertainty determined on the basis of the extended design is the lowest for raw water (17.4%) and the highest for the permeate (22.4%). Analytical uncertainty (which is in this case measurement uncertainty) ranges from 3.4 to 4.1%. Similar results were obtained using the unbalanced design with a single analysis for duplicate samples. Relative total uncertainty ranges from 20.2 to 22.6% and relative analytical uncertainty does not exceed 4.23%.

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