Proceedings World Geothermal Congress 2015
Melbourne, Australia, 19-25 April 2015

Uncertainty Associated with the Sampling of Geothermal Water

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Keywords: geothermal water, sampling, control samples, measurement uncertainty

ABSTRACT

According to European Union directives (WFD, 2000; GDD, 2006) the identification and determination of uncertainty - also this associated with sampling, preservation and transport of samples - is an important part of the overall groundwater monitoring effort. Moreover, directive (DT 2009) indicate necessity of implementation the quality assurance and quality control program (QA/QC) of research in water monitoring. They also give the limit of quantification threshold value, as a 30% or less of environment quality norms.

Authors describe example of implementation of limit of quantification (LOQ) and practical limit of quantification (PLOQ) for the estimation of uncertainty involved in sampling and analytical processes during geothermal water monitoring from the Banska Nizna PG-P1 and PG-P3 wells. Physical parameters and chemical composition of geothermal waters can be changed during the long-term exploitation, so it is especially important to control quality of analyses (measurements), on the base of which we can confirm stability of the physico-chemical parameters.

1. INTRODUCTION

According to the European Union directive 2009/90/EC (DT, 2009): „Member States shall ensure that the minimum performance criteria for all methods of analysis applied are based on an uncertainty of measurement of 50% or below (k= 2) estimated at the level of relevant environmental quality standards and a limit of quantification equal or below a value of 30% of the relevant environmental quality standards".

Limit of detection means "the output signal or concentration value above which it can be affirmed, with a stated level of confidence that a sample is different from a blank sample containing no determinand of interest", but limit of quantification means "a stated multiple of the limit of detection at a concentration of the determinand that can reasonably be determined with an acceptable level of accuracy and precision. The limit of quantification can be calculated using an appropriate standard or sample, and may be obtained from the lowest calibration point on the calibration curve, excluding the blank" (DT, 2009).

Different methods of calculation of limits of quantification (LOQ) are suggested in the literature. For example Fleming et al. (1997) propose:

$$\mathrm{LOQ} = x_{\mathrm{blank}} + 6s_{\mathrm{blank}} \tag{1}$$

where:

$\bar{x}_{\mathrm{blank}}$ —mean concentration in laboratory blank samples,

s_{blank} — standard deviation.

No matter which definition of limit of quantification (LOQ) we choose, the LOQ value characterises only a performance of laboratory procedures. Unfortunately it does not provide any information about quality of sampling procedures such as sampling protocol, transport and storage conditions, preservatives added. Sampling protocols are never perfect. They are not able to describe the action required for every possible eventuality that may arise in the real world in which sampling occurs (Eurachem, 2006).

Reasonable way to assess uncertainties involved in monitoring process, including field and laboratory parts, seems to be implementation of practical limit of quantification (PLOQ) - the lowest concentration of analyte that can be quantified with a satisfying level of accuracy and precision in a field blank samples:

$$\mathrm{PLOQ} = x_{\mathrm{field\ blank}} + 6s_{\mathrm{field\ blank}} \tag{2}$$

where:

$\bar{x}_{\mathrm{field\ blank}}$ — mean concentration in field blank samples,

$s_{\mathrm{field\ blank}}$ — standard deviation.

Practical limit of quantification (PLOQ) could characterise performance of both laboratory methods and sampling procedures used during groundwater monitoring. PLOQ can be assessed using field blank samples that are treated and laboratory tested the same way as regular samples. PLOQ should be calculated from the same formula as limit of detection.

Under ideal conditions the values of LOD and PLOD would be approximately equal. The difference between these two values indicates uncertainties involved in sampling process.

2. MATERIAL AND METHODS

This paper presents preliminary results of QA/QC program of geothermal water monitoring started at march 2014. Control samples – blank and field blank – were collected for QA/QC purposes during standard monitoring campaign of geothermal water in Banska Nizna (Podhale region located in south Poland within the Inner Carpathians).

In Podhale region geothermal waters are extracted from carbonate formations of the Middle Eocene and from Middle Triassic limestones and dolomites. They have relatively low mineralisation — from 2.358 g/L in the Bańska IG-1 well to 3.150 g/L in the Bańska PGP-1 well (Kępińska 2006). The temperature at the well outlet ranges from 69 to 86°C (Bujakowski et al., 2010).

Both regular and control samples (laboratory and field blank samples) were collected twice a month, by one sampler, in the same way, using the same sampling protocol, compatible with ISO standard 5667-11. Field blank samples give possibility to estimate practical detection limits for analyzed elements (Postawa, Kmiecik, 2010).

Blank samples were standard laboratory blank samples – deionized water collected and analyzed as regular samples (fixed).

Field blank samples (according to ISO standard 5667-14) were divided into three types samples prepared and treated in different way:

- *field blank (laboratory)* – deionized water collected and left in the laboratory (fixed),
- *field blank (filtered-fixed)* – blank sample filtrated with micropore filters (0,45 μm) and conserved by adding 0.5 mL of concentrated nitric acid per each 100 mL of sample, to achieve a pH less than 2,
- *field blank (unfiltered-unfixed)* – deionized water not filtrated and not fixed but transported with the rest of samples.

All samples were cooled and sent immediately after sampling (during some hours) to the laboratory.

The detailed analysis was performed for boron. *Boron* is a non-metallic element that belongs to group IIIA of the periodic table. It is never found in the elemental form in nature, exists as a mixture of the isotopes forms. Widely found in nature are borates. They present in oceans, sedimentary rocks, soil, coal and shale. Naturally occurring boron is present in groundwater, primary as a result of leaching from rocks and soils containing borates and borosilicates. Boron is detected in surface water and groundwater in various locations around the world, including sea and river waters, where it is occurs mainly in the form of boric acid. Value of boron concentration in drinking water is wide ranged, depending on the source of the drinking water, but for most of the world the range is judged to be between 0.1 and 0.3 mg/L (WHO, 2011). In seawater, the boron concentration ranges from 0.5 to 9.6 mg/L, averages at a value of 4.5 mg/L to 4.6 mg/L (Woods, 1994, Farhat et al. 2013, Kabay et al. 2010).

A high boron concentration is also a common feature of geothermal water sources, particularly when the TDS is greater than 1 g/L (Tomaszewska, 2011a, b; Tomaszewska, Bodzek, 2013). The presence of boron prevents from the direct use of geothermal waters as irrigation or potable water and causes chemical pollution and environmental problems in groundwaters and surface waters (Öner et al. 2011). Boron is also an essential micronutrient for plants, concentration level required for optimum growth differentiates among plant species. There is a narrow margin between boron deficiency and toxicity in some plants (Kot, 2009, Yavuz et al. 2013, Wolska, Bryjak 2013).

Boron in collected samples was measured in *one certified hydrogeochemical laboratory* of Hydrogeology and Engineering Geology Department at the AGH University of Science and Technology in Krakow (Certificate of Polish Centre for Accreditation No AB 1050) with inductively coupled plasma optical emission spectrometry (ICP-OES – PN-EN ISO 11885:2009), *by one operator*. This is reference method for boron determination in water (Standard methods, 2012; Witczak et al., 2013). Laboratory has implemented internal quality control/quality assurance (QA/QC) system. The laboratory compares its data and quality control system by participating in interlaboratory studies with other certified laboratories and by analysis of certified reference material — traceability.

2. RESULTS

Limits of quantification (LOQ) and practical limits of quantification (PLOQ) were calculated using (1) and (2) formulas (tab. 1).

Table 1. Limit of quantification (LOQ) and practical limits of quantification (PLOQ) for boron

Method of determination	Samples	No of samples/ analyses	LOQ [ug/L]	PLOQ [ug/L]	PLOQ/LOQ
ICP-OES	Blank (LOQ)	16	513	–	–
	Field blank (laboratory) – PLOQ1	10	–	453	0.9
	Field blank (filtered-fixed) – PLOQ2	10	–	521	1.02
	Field blank (unfiltered-unfixed)- PLOQ3	14	–	657	1.3

They are also presented using probability plot (fig. 1).

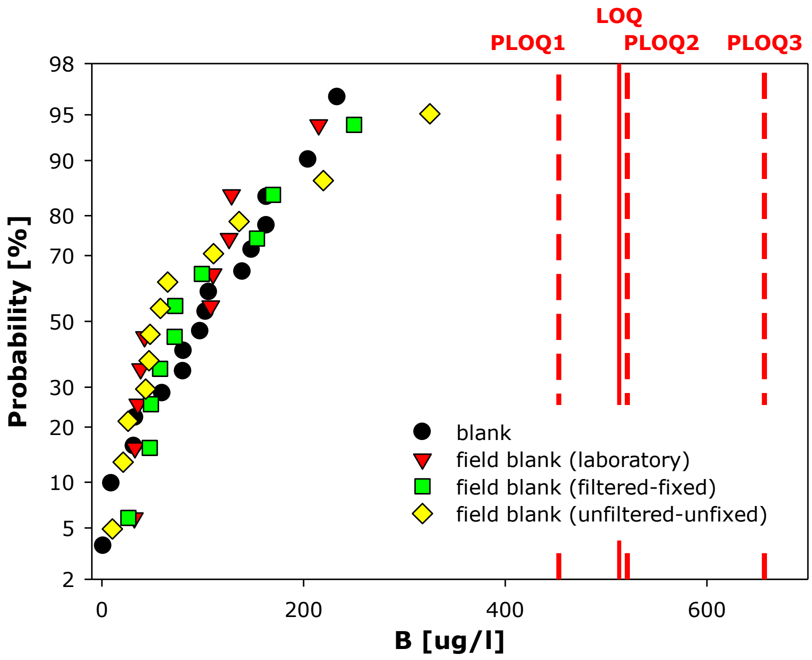

Figure 1. Limit of quantification (LOQ) and practical limits of quantification (PLOQ) for boron. Explanation – see tab. 1

Calculated practical limits of quantification (PLOQ) are comparable with limit of quantification (LOQ) determined in laboratory tests (see tab. 1). PLOQ2 and PLOQ3 are higher than laboratory limit of quantification, however the difference is not too high. PLOQ1 and PLOQ3 are lower than LOQ. The PLOQ/LOQ ratios vary from 0.9 to 1.3.

That may suggest that addition of nitric acid affects the boron concentrations in control samples. In practice higher PLOQ/LOQ ratios are observed when samples are collected by many samplers, not one – like in that case. Even if the samplers are experienced and all procedures are kept, it can be stated that uncertainties associated with sampling process always increase with increasing number of samplers taking part in sampling campaign. Changes of samplers during a sampling campaign may result with significant increase of both random and systematic errors (Kmiecik, Podgorni, 2009; Postawa, Kmiecik, 2010).

3. CONCLUSIONS

Practical limit of quantification (PLOQ) value, determined by analysing field blank samples, is usually higher than limit of quantification determined and declared by the laboratory (Szczepanska Kmiecik, 2005; Postawa, Kmiecik, 2010; Witczak et al., 2013).

PLOQ allows assessing the performance of monitoring process as the whole – starting from sampling, through samples treatment, transportation and laboratory procedures.

In order to achieve satisfyingly level uncertainty required due to formal regulations (e.g. EU directives or national regulations) extended quality assurance/quality control (QA/QC) program comprising control samples should be undertaken to improve monitoring data quality. In this example (monitoring of geothermal water in Banska Nizna), such a program is in progress. On the base of duplicate control samples there will be estimated measurement uncertainty. Additionaly some possible sources of measurement uncertainty will be examined – e.g. nitric acid used to sampling preservation or type of sample containers.

ACKNOWLEDGMENTS

The study was partially supported by AGH-UST 11.11.140.026.

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