

Methodological aspects concerning sampling and determination of total selenium and selenium species in geothermal waters



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Abstract. The work presents the results of geothermal water sample analysis with respect to the determination of total selenium concentration. For this purpose, geothermal water (GT) samples were collected from three different intakes (GT-1, GT-2, GT-3) with similar temperatures of about 85°C. Tests were carried out to see if the methodology of sample preparation influenced total selenium concentration during analysis by inductively coupled plasma mass spectrometry (ICP-MS). Samples (raw and filtered) were preserved with nitric acid (HNO₃) and mineralised in the laboratory. From the data obtained it was found that there is no significant difference between total selenium concentration in raw and filtered samples. Following mineralisation, the concentrations in the samples were below the limit of detection or limit of quantification. While different analytical steps or procedures are applied, the results of total selenium concentration can vary. Furthermore, high-performance liquid chromatography coupled with ICP-MS was used for the identification of selenium species. The results revealed that hexavalent selenium – Se(VI) – in the geothermal water was found only in samples collected from the GT-2 and GT-3 intakes.

Key words:
selenium species,
geothermal waters,
HPLC-ICP-MS,
chromatography,
mass spectrometry

Introduction

Selenium is a trace element that exists in the environment in several oxidation states. Like elements such as oxygen, sulphur, tellurium and polonium, it belongs to the 6th group of chalcogens in the periodic table and is characterised by transitional properties between metals and non-metals. In the environment, depending on the pH, redox potential (Eh) and microorganism activity, it can occur as selenide (Se(II): Se²⁻, HSe⁻, H₂Se_{aq}⁰), selenite (Se(IV):

SeO₃²⁻, HSeO₃⁻, H₂SeO_{3aq}⁰) or selenate (Se(VI): SeO₄²⁻, HSeO₄⁻, H₂SeO_{4aq}⁰) ions, elemental selenium (Se⁰) or organic selenium (selenomethionine, selenocysteine) compounds (Jacobs 1989; Neal 1995; Pyrzyńska 1996, 1998; Siepak 2005; Lenz and Lens 2009). They are presented in Figure 1.

In groundwater, selenium occurs due to weathering and leaching of rocks (i.e. Cretaceous shales), and dissolution or oxidation of soluble salts in soils. Thermodynamic calculations showed that Se(II) species should be found in reducing environments, Se(IV) species in moderately oxidising

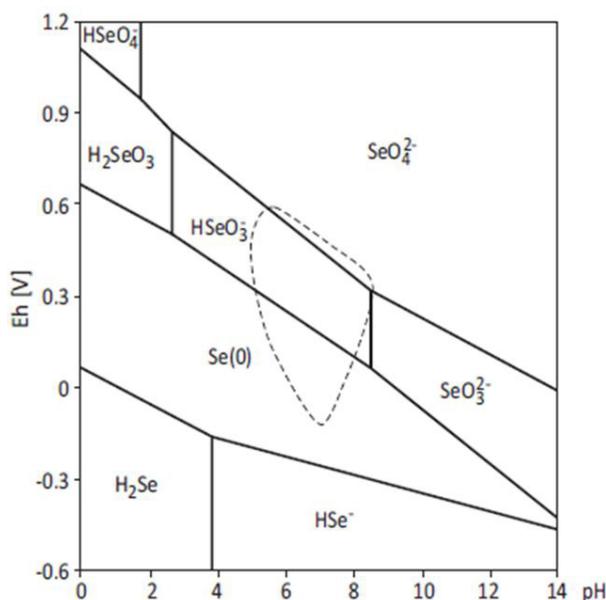


Fig. 1. Selenium species in relation to Eh and pH (Witczak et al. 2013 according to Séby et al. 2001) Calculation conditions: concentration of dissolved selenium in water at a level of 10^{-6} mol/L (ca. 0.08 $\mu\text{g/L}$), temperature = 25°C, pressure = 1 atmosphere

environments, and Se(VI) species in oxidising environments (Dauchy et al. 1994; Alfthan et al. 1995; Kumar and Riyazuddin 2011).

The amount of selenium in water is related to the geochemistry of the environment. The highest concentrations of Se were found in waters infiltrating through selenium-rich geological formations. Igneous and sedimentary rocks contain less than 0.5 ppm of Se, while in sulphide minerals the Se concentration is above 100 ppm, and in sulphur deposits of volcanic origin its concentration is up to 200 ppm (Kabata-Pendias and Pendias 1999; WHO 2011; Alexander 2015). From the anthropogenic point of view the highest concentrations of Se are observed in waste disposal areas, industrial emissions coming from coal power plants, the use of phosphate fertilisers, and cement production. Selenium is also used in the glass industry, non-ferrous metal industries, veterinary medicine, paint production and even pesticides (Dojlido 1995; Kabata-Pendias and Pendias 1999; Kabata-Pendias and Szteke 2012; Liang et al. 2015; Nabavi Larimi et al. 2016).

Due to the continual development of science and technology, analytical methods for chemical com-

position analysis in different environmental matrices have significantly evolved. Methods of selenium determination in groundwater – not only total concentration but also detection of its particular species, both organic and inorganic – may be given as an example. The biotransformation of selenium in plants and the determination of Se species in animals have also been investigated (Kurek et al. 2009; Ruszczyńska et al. 2017).

During determination of selenium concentration, the presence of toxic species in the total concentration of selenium in natural waters, soils, food and biotas in general can be assessed, which is very important in the case of water intended for human consumption, agriculture and the food industry (Robberecht and Van Grieken 1982; Raessler et al. 2000; Hu et al. 2009; Torres et al. 2011; Jagtap and Maher 2016; Zhang et al. 2016). The non-carcinogenic risk or Hazard Quotient (HQ) can also be calculated, as has been presented by Al-Taani et al. (2012) or Dhillon and Dhillon (2016).

A comprehensive review of the analytical methods used for the determination of selenium species in natural waters is shown in Table 1. All of the methods described include a sample preparation step with the use of specific chemical reagents. Information can be found in the publications listed in the reference column. The limit of detection (LOD) of each method is also given. Information about analytical approaches for total selenium determination was not included since the most popular method in trace analysis is inductively coupled plasma mass spectrometry (ICP-MS), which was used in the research presented (APHA 2012; Witczak et al. 2013).

One of the problems with accurate determination of total selenium in geothermal samples is a complex matrix, *i.a.* high total dissolved solids (TDS) content. Plenty of analytical methods for selenium analysis are known (Table 1). However, it is necessary to know what impact sample collection and preparation (*i.e.* pre-concentration, microwave digestion, preparation for instrumental analysis) have on the representativeness of the results that will be used to interpret the object under investigation. Also, factors such as accuracy, purity of reagents, samples matrix or interferents have to be considered, and an appropriate analytical method has to be applied to ensure that it fits the purpose of the research (Casiot et al. 1999; Forrer et al.

Table 1. A review of analytical methods for the determination of selenium species

Technique	Analysed forms of Se ^{1,2}	LOD [$\mu\text{g/L}$]	Reference
ORS-ICP-MS Octopole reaction system – Inductively coupled plasma mass spectrometry	O/I	0.01	
HG-ETAAS Hydride generation – electrothermal atomic absorption spectrometry	O/I	0.005	
HG-AAS Hydride generation – atomic absorption spectrometry	Se(IV)	0.1	Pettine et al. 2015
HMDE-CSV Hanging mercury drop electrode – cathodic stripping voltammetry	Se(IV)	0.05–0.5	
NAA Neutron activation analysis	Se(IV) or Se(IV)+ Se(VI)	0.001	
Spectrophotometric methods	Se(IV)	10–100	
UV-HG HPLC-ICP-MS UV – hydride generation – high performance liquid chromatography – inductively coupled plasma mass spectrometry	Se(IV), Se(VI), SeMet, SeCyst	0.002–0.015	Darrouzès et al. 2008
UV detector	Se(IV), Se(VI)	100	Goyal et al. 1991; Dauchy et al. 1994
Conductimetry	Se(VI)	4.8	Sarzanini et al. 1990; Dauchy et al. 1994
Capillary electrophoresis	I	170 Se(VI) 290 (Se(VI))	Dzierzowska et al. 2003
CPE-ETV-ICP-MS Cloud point extraction – electrothermal vaporisation – inductively coupled plasma mass spectrometry-	Se(IV)	0.05	Li et al. 2008
On-line IL DLLME ETAAS Ionic liquid – dispersive liquid-liquid microextraction – electrothermal atomic absorption spectrometry	I	0.015	Martinis et al. 2011
HPLC-HG-AAS High-performance liquid chromatography – hydride generation – atomic absorption spectrometry	I	2.4 Se(IV) 18.6 Se(VI)	Niedzielski 2005
HG-QFAAS Hydride generation – quartz furnace atomic absorption spectrophotometry	Se(IV), Se(VI)	0.003	Apte and Howard 1986; Olivas et al. 1994
MFS Molecular fluorescence spectrometry	Se(IV), Se(VI)	0.005	Takayanagi and Wong 1983; Olivas et al. 1994
IC-HG-AAS Ion chromatography – hydride generation – atomic absorption spectrometry	Se(IV), Se(VI)	0.0010	Roden and Tallman 1982; Olivas et al. 1994
DPP Differential pulse polarography	Se(IV)	10	Campanella et al. 1987; Olivas et al. 1994;
DPCSV Differential pulse cathodic stripping voltammetry	Se(VI)	0.04	Campanella et al. 1987; Olivas et al. 1994
Indirect UV	Se(VI)	16.4	Gilon and Potin-Gautier 1996; Pyrzyńska 2001
Direct UV	Se(IV)	0.34	Liu and Lee 1998; Pyrzyńska 2001
SPE Solid phase extraction	Se(IV), Se(VI)	0.0056	Lin 2007
IC-ICP-MS Ion chromatography – Inductively coupled plasma mass spectrometry	Se(IV), Se(VI)	4	Londesborough et al. 1999; Vassileva et al. 2001

¹ O/I – both organic and inorganic species can be determined² I – only inorganic species

1999; Wang et al. 2001; Devi et al. 2017; Ferreira et al. 2019; Llaver and Wuilloud 2019). With the wider consideration of geothermal water as a drinking water supply, concentrations of contaminants should be precisely determined to apply a proper treatment strategy (Malhorta et al. 2020).

The current research aims to investigate the impact that the preparation of geothermal water samples has on total selenium determination by inductively coupled plasma mass spectrometry, and to recognise what selenium speciation is the predominant form in the analysed water. The investigations were conducted on geothermal water collected from three different intakes (GT-1, GT-2, GT-3). The hydrochemical type of water analysed is sulphate-calcium-sodium and sulphate-chloride-sodium-calcium. The total dissolved solids concentration changed from 2.5 to 3.0 g/L and the temperature measured at the wellhead varied from 82°C to 87°C. The geothermal water intakes are located within the Podhale trough (southern Poland, Lesser Poland Voivodeship). The GT-2 and GT-3 geothermal water intakes are located next to each other but drilled to different depths, and GT-1 is about 22 km south-west of them.

Material and methods

Sample collection

The sample collection was carried out as described in ISO 5667-11:2009 standard (ISO 2009). A geothermal well rinse (*ca.* 20 min.) was carried out in the field to avoid sample contamination with substances coming from the geothermal installation, to stabilise the chemical composition of the water and to ensure the representativeness of samples. Unstable parameters such as redox potential, temperature, pH, and electrical conductivity were also measured. If the measurements did not differ by 0.2°C for temperature, 0.1 unit for pH and 5% in the case of electrical conductivity (γ_{25}), the stability criterion is fulfilled (Witczak et al. 2013; Korzec et al. 2016; Kmiecik et al. 2019; Wątor et al. 2020). Two samples were collected from each intake – raw and filtered. All geothermal water samples were collect-

ed in bottles made from high-density polyethylene characterised by chemical and biological neutrality to avoid the contamination of water samples with compounds that can be leached from bottle material (ISO 2009; Witczak et al. 2013; Zdechlik et al. 2013). Two samples were taken from each intake – one directly from the wellhead without any sample preparation (GT-1, GT-2, GT-3) and a second filtered using a microporous filter with a pore diameter of 0.45 μm (GT-1_f, GT-2_f, GT-3_f) to check if the filtration process influences the selenium concentration results. Because both the total selenium concentration and its inorganic species were measured, samples were not preserved in the field. After collection, samples were chilled and immediately transported to the chemical laboratory of the Biological and Chemical Research Centre of the University of Warsaw. The laboratory analyses were performed using various analytical approaches (Fig. 2). The influence of sample filtration, acidification and mineralisation on selenium concentration in geothermal water samples was checked.

Apparatus

Mineralisation. The Ultra Wave (Milestone, Italy) microwave system was used for the digestion of geothermal water samples.

Elemental content. The quadrupole mass spectrometer with inductively coupled plasma ionisation that was used was an ICP-MS (Nexion 300D, Perkin Elmer Sciex, USA) equipped with a quartz cyclonic spray chamber, a Meinhard nebuliser and platinum sampler and skimmer cones. The working conditions of the spectrometer were optimised daily in order to obtain the maximal sensitivity and stability as well as the lowest level of oxides and double charged ions. Selenium isotopes ^{82}Se and ^{78}Se were monitored in the presence of ^{103}Rh at the concentration of 10 $\mu\text{g/L}$ as an internal standard.

Speciation. Agilent 1260 Infinity high performance liquid chromatography (Agilent Technologies, USA) was used with a Hamilton PRP-X100 (250'4.1 mm, particle size 10 μm) anion exchange column from Hamilton (USA) and coupled with polyetheretherketone (PEEK) tubing to an Elan 6100 DRC ICP-MS system (Perkin Elmer Sciex,

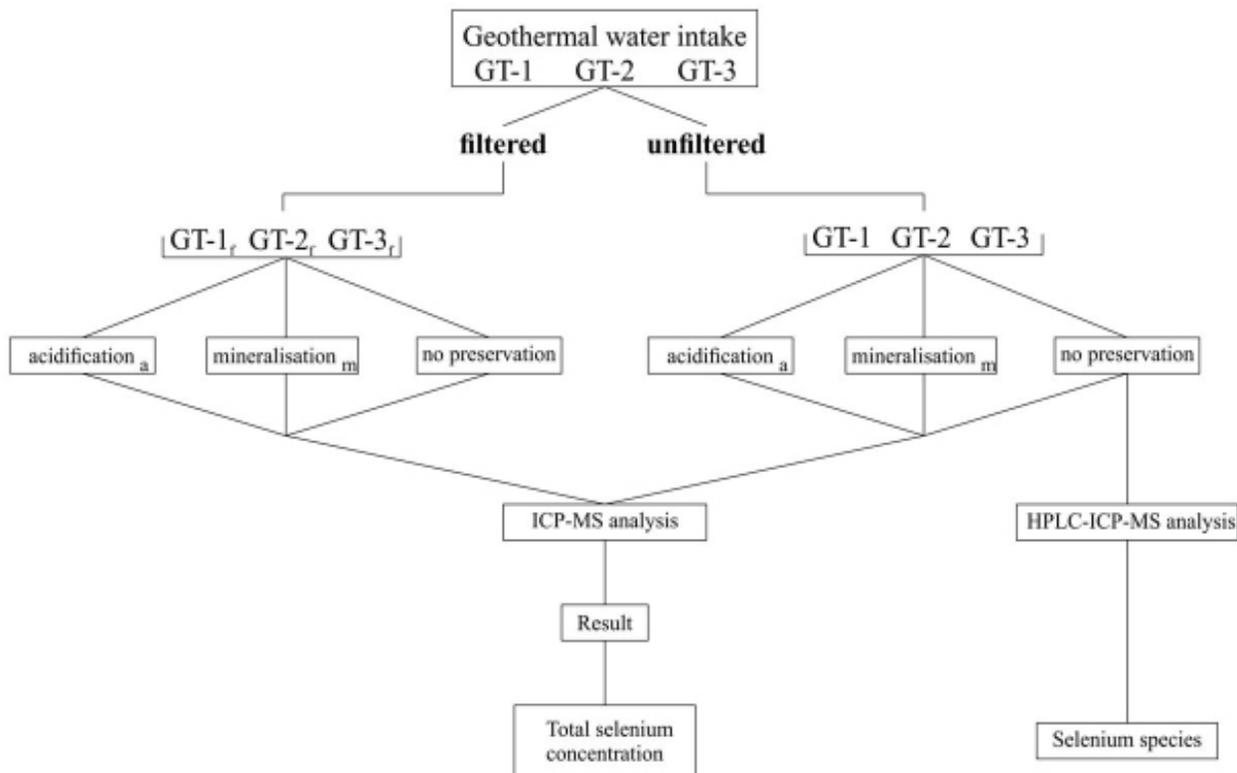


Fig. 2. Scheme of research on the path from sample collection to laboratory analyses
Key: f – filtered; a – acidified samples; m – mineralised samples

Canada) for HPLC-ICP-MS analysis in geothermal water samples.

Reagents and solutions, reference materials

Analytical reagent grade chemicals purchased from Sigma Aldrich (Germany), Baker (Holland), Merck (Germany) and water (18.2 MΩcm) obtained using the Milli-Q system (Millipore, Bedford, MA) were used throughout. The multi-elemental standards for ICP-MS measurements were purchased from Merck. Working solutions were obtained by dilution with HNO₃ acidified deionised water as necessary. The reference materials for measurement of elements in water with certified values were used for validation of the analytical procedure: SPS-SW1 and SPS-SW2 (surface waters, Spectrapure Standards, Norway) and NIST 1640a (spring water, NIST, USA).

Analytical procedure of analysis

Total content of elements. Each water sample was introduced directly to the ICP-MS spectrometer (GT-1, GT-2, GT-3, GT-1_f, GT-2_f and GT-3_f – Fig. 2), the second just after acidification and appropriate dilution (GT-1_a, GT-2_a, GT-3_a, GT-1_{fa}, GT-2_{fa} and GT-3_{fa} – Fig. 2) while the third (2 mL) was reserved for mineralisation (GT-1_m, GT-2_m, GT-3_m, GT-1_{fm}, GT-2_{fm} and GT-3_{fm} – Fig. 2). The wet digestion procedure was carried out with the addition of 1 mL of 65% HNO₃ using a single reaction cell (SRC) microwave-assisted digestion unit. The microwave program was set to 250°C for 15 min after a 15-min heating up period at 120 bar and 1,500 W. After cooling down, the digests were diluted before introduction to the ICP-MS.

ICP-MS. Quantisation was achieved by a five-point external calibration (standards from 1 µg/L to 100 µg/L) and method evaluation by the analysis of certified reference materials. The purging time was

set at 60 s between sample measurements. The limit of detection was calculated from the results obtained for 10 repetitions of blanks (prepared from deionised water) undergoing the same procedures as samples (dilution and/or mineralisation) and calculated as the sum of mean and standard deviation multiplied by three (Fleming et al. 1997).

Speciation analysis

Selenium species. Raw samples GT-1, GT-2, GT-3 were directly intended for speciation analysis (with no filtration, preservation or mineralisation – Fig. 2).

HPLC-ICP-MS analysis. Mobile phases for anion exchange liquid chromatography were prepared by dissolving an appropriate amount of ammonium acetate in deionised water to obtain the required concentrations at pH=4.7: i) 5 mmol/L (solvent A) and ii) 100 mmol/L (solvent B). The mobile phase flow rate was 1 mL/min at 22°C. The solutions were filtered and degassed before use. The injection volume was 100 µL. Compounds were eluted with an increasing linear gradient from 0%–100% of solvent B within 25 min.

Results

Total selenium concentration

Three analytical approaches for sample preparation were implemented during the chemical analyses to check how the filtration process and preparation of samples for analysis (acidification and mineralisation) affect the final selenium concentrations. The results obtained differ from each other depending on the sample pre-treatment processes chosen, and the results are presented in Figure 3. The results of the individual analyses are discussed in detail in the later section of the paper.

When considering the Se_{tot} concentrations in the water samples with the addition of 1% of HNO_3 it can be seen that the selenium concentrations in the water collected from the GT-2 and GT-3 intakes (located next to each other but drilled to dif-

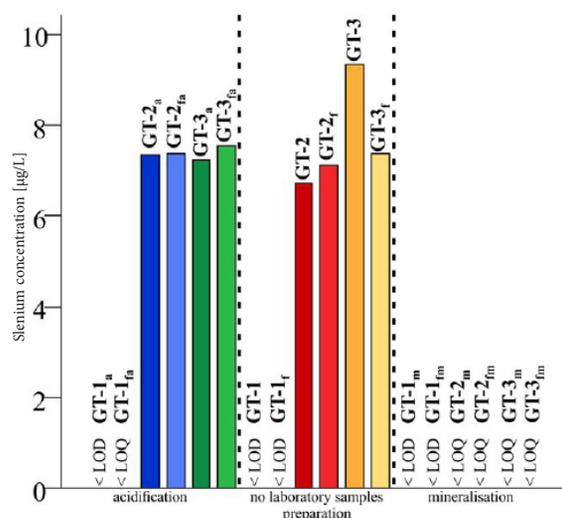


Fig. 3. Results obtained, by analytical approach

ferent depths) exploiting the same geothermal water are not very different. For intake GT-2 it is 7.35 µg Se/L and for GT-3 it is about 7.23 µg Se/L. In addition, the filtration process did not affect the selenium concentrations in the water samples analysed and the results obtained are similar to those of raw water (7.38 µg/L for GT-2 and 7.54 µg/L for GT-3). In water collected from intake GT-1 the total concentration of selenium in raw geothermal water was lower than the limit of detection (LOD) and after the filtration process it was below the limit of quan-

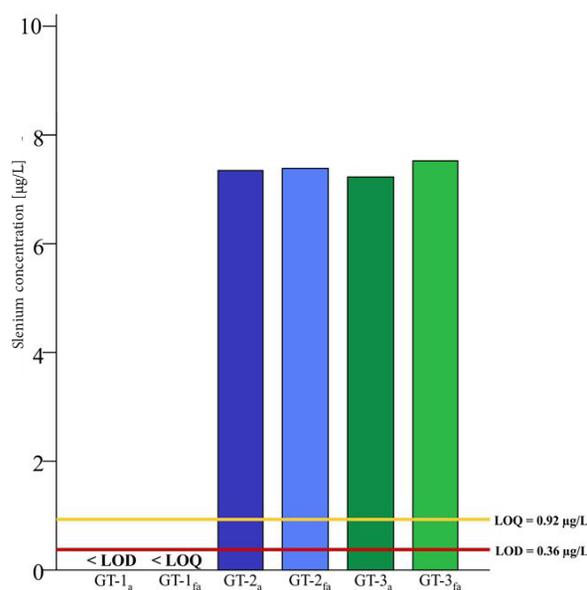


Fig. 4. Total selenium concentration changes in water subjected to preservation with HNO_3

tification (LOQ). The results are presented in Figure 4.

The increased Se concentration in the raw water collected from the GT-3 intake (Fig. 5) is higher than in a filtered water sample (GT-3_f) about 20% and could arise from the inhomogeneity of the sample (a suspension molecule could have gotten into the sample with water collected from the intake).

The differences in selenium concentrations in acidified and raw geothermal water samples coming from GT-2 and GT-3 intakes are not statistically significant, which was proven by the use of a pairwise comparison test calculated in PS IMAGO software (Table 2). PS IMAGO© is software provided by Predictive Solutions. IBM® SPSS Statistics® is an analytical engine of the PS IMAGO©. The significance level (2-tailed) is higher than 0.05, hence the differences between groups are negligible.

In the last variant of the total selenium concentration analysis, the water samples were subjected to a mineralisation process with the use of 65% nitric acid. The LOD is equal to 4.57 µg Se/L and LOQ = 11.26 µg Se/L. In all kinds of samples – raw and filtered – the selenium concentrations were below the detection limit (intake GT-1) or quantification limit (intakes GT-2 and GT-3). These limits are a few times higher than in the previous analysis, where they were calculated for non-mineralised geothermal water samples. As the results show, the LOQ in samples that have undergone the mineral-

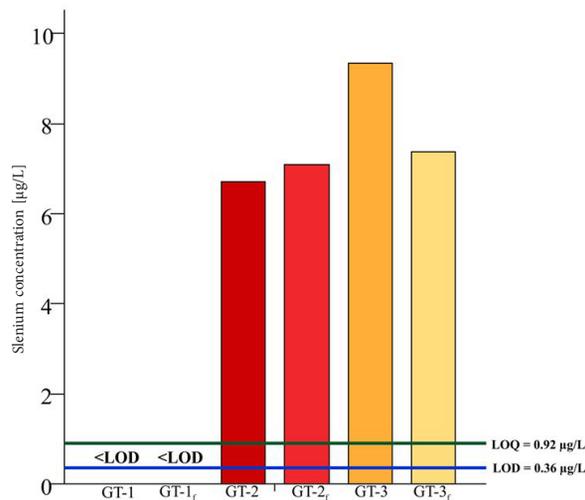


Fig. 5. Total selenium concentration changes in samples of raw geothermal water

isation process is higher than in the other analysis performed, which probably arises from the addition of reagents used for the mineralisation procedure and the more complex sample matrix or the loss of selenium in the form of volatile compounds that formed during mineralisation of the sample with oxidising acid.

Speciation analysis

Each raw geothermal water sample was introduced to the HPLC-ICP-MS apparatus. The chromatogram was obtained with ⁸²Se isotope being monitored. The results considered in this section concern only the qualitative analysis of Se species to check which forms of selenium (in which oxidation states) are present in the examined geothermal waters. The research conducted constituted pilot studies and therefore the concentrations of the forms detected were not determined. Four samples were analysed: blank, GT-1, GT-2 and GT-3.

Only hexavalent selenium (inorganic species) was indicated during the HPLC-ICP-MS analysis. One can see that the Se(VI) peak on the elution curve was obtained at retention time $t_R = 12.47$ min with a detector reading several dozen of counts for the GT-2 and GT-3 water samples. Inorganic species of selenium was only observed in these two samples. It can be assumed that tetravalent selenium was not detected. The detector showed a comparable number of counts for Se(IV) in the geothermal water intakes investigated as in a blank sample (Fig. 6).

The research is continuing. Concentrations of the selenium species will be determined and the influence of sample temperature on the results obtained will be tested on different kind of geothermal water from the Podhale region.

Discussion

The work presented a pilot study of selenium determination in geothermal water samples that was conducted in the Podhale region in Poland. Samples were collected using the approach included in the ISO 5667 standard (ISO 2009) from three differ-

Table 2. Pairwise comparison (dependent T-test) Key: GT-2, GT-3* – geothermal intakes; a – acidified samples

Differences in dependent variables								
	Mean	Standard deviation	Std. error of mean	95% confidence interval for difference of mean		t	df	Sig. level (2-tailed)
				Lower	Upper			
GT-2 - GT-2 _a	-0.458	0.251	0.178	-2.713	1.798	-2.577	1	0.236
GT-3 - GT-3a	0.975	1.603	1.134	-13.428	15.377	0.860	1	0.548

*Samples within the internal groups include information about the filtration process

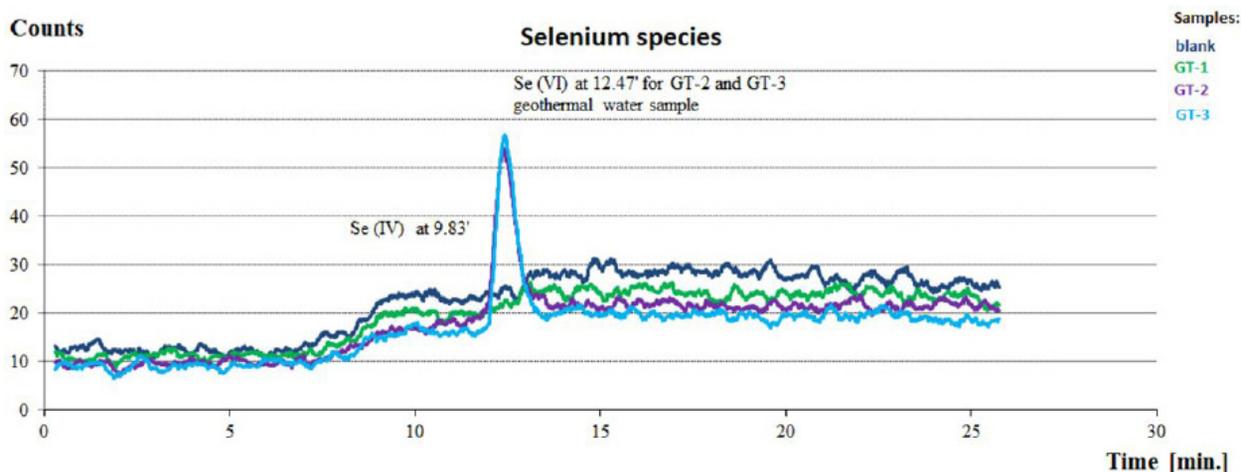


Fig. 6. Elution curve for determination of selenium species with the use of the HPLC-ICP-MS method

ent geothermal water intakes. The raw geothermal water was collected to bottles made of high-density polyethylene. Second water samples were also collected that were filtered with a microporous filter (pore diameter of 0.45 μm) to check if the filtration process influenced the total selenium concentrations in geothermal waters. During the analysis, the impact of acidification and sample mineralisation of total selenium content was checked.

Selenium was also found in geothermal water of southern Poland. In the Iwonicz-Zdrój spa selenium was determined in concentrations below 0.005 mg/L. The next place where selenium has been documented is Uniejów in the centre of Poland, where its concentration is equal to 0.011 mg/L (Sapińska-Śliwa et al. 2009). The results of our research revealed that the Se amount in the examined geothermal wells is two times higher than in Iwonicz-Zdrój and about 3 $\mu\text{g/L}$ lower than in the city of Uniejów. Geothermal waters in France are more rich in Se; for instance, at La Roche Posay, where the Se concentration is about 0.053 mg/L. Analyses

performed using the ICP-MS method were used for checking the proposition that filtration, preservation and mineralisation of geothermal waters have a significant influence on the Se concentrations in this water. As the results showed, the effect of filtration and addition of HNO_3 on the determination of Se concentrations is indiscernible. The concentrations are very close to one another and any differences between them can be caused by the preparation of the apparatus for analysis each time for each water series, or the preparation of a new blank sample for each series of analytical samples (different LOD and LOQ).

Submitting geothermal water to mineralisation proved that this process has an appreciable impact on the calculated parameters of research methods such as the limit of detection (LOD) and limit of quantification (LOQ). As mentioned earlier, the experimental approaches to the preparation of geothermal water samples for chemical analysis proved that the chosen methods (preservation, filtration, mineralisation) are very important stages in the an-

alytical procedure while considering the task and the results one wishes to obtain.

Depending on the research methodology adopted for preparing samples for analysis, there is variation in the limits of detection and quantification. For raw and acidified geothermal water samples, these were comparatively low (LOD = 0.36 µg/L, LOQ = 0.92 µg/L). After samples had undergone the mineralisation process, the LOD and LOQ parameters increased to the level of 4.57 µg/L and 11.26 µg/L, respectively. The changes in these parameters can affect the results obtained at low concentrations of the elements analysed. In the context of groundwater monitoring, mineralisation of water samples is not carried out in the standard procedures. In the field, a filtration and acidification method is commonly used for quantitative analysis of the total concentrations of particular elements.

Conclusions

Based on the results obtained from the experiment it can be stated that high-performance liquid chromatography coupled with a mass spectrometer can be successfully used for the determination of inorganic selenium species in geothermal waters. Hence, the purpose of the research being performed must be clarified and, thence, appropriate methods applied for sample collection, preservation and preparation for analysis. The major findings of our research are that the filtration of geothermal water samples did not impact the concentration of total selenium, but that mineralisation can affect the limits of determination (particularly, increasing them) such that the selenium cannot be detected or quantified in relatively low concentrations.

In accordance with the methodology, samples for species analysis cannot be preserved with the use of, for example, nitric acid, due to its high oxidation properties, which in consequence could lead to the determination of only one form of the chosen element at the highest oxidation state. Moreover, the samples were collected with a natural temperature of 86°C, but before they were delivered to the laboratory the unstable parameters altered, i.e. temperature, Eh and pH, which in consequence led to changes in ionic equilibrium. Due to this fact,

the selenium species in the geothermal waters also changed and, for example, Se(IV) could have been oxidised to Se(VI). In the geothermal water samples examined, only hexavalent selenium was determined in the GT-2 and GT-3 intakes. The elution curve also indicated the presence of Se(IV), but, due to higher readings by the HPLC detector for the blank sample than for the water samples analysed, it was assumed that Se(IV) concentrations were very low and they are not significant at this stage of the analytical procedure. Probably, there are other species of selenium in this water – maybe its organic forms. The results obtained from the experiment can be verified in a theoretical manner by solving a hydrogeochemical model based on the physicochemical parameters of the water analysed (concentration of particular elements, pH, Eh, temperature, dissolved gases, etc.) and entered into a specialist programme, e.g. PHREEQC.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Author contributions

Study design: PR, AR, KW, EB, EK; data collection PR, AR, KW, EB, EK; statistical analysis: PR, AR, KW, EB, EK; result interpretation PR, AR, KW, EB,

EK; manuscript preparation PR, AR, KW, EB, EK;
literature review: PR, AR, KW, EB, EK.

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