Determination of iodine in geothermal water samples – preliminary ICP-MS method validation results
A. Mika, K. Wątor, E. Kmiecik and K. Sekuła

ABSTRACT
Iodine is a microelement which occurs in natural water in different concentrations dependent on water type, origin and total dissolved solids concentration. The objects of research were natural geothermal water. In this paper, the fitness of the inductively coupled plasma mass spectrometry (ICP-MS) method for iodine determination in water with higher temperatures was tested and selected methodological problems were discussed. Basic method parameters (precision, accuracy, linearity, uncertainty) were determined. Calculated statistical parameters of the validated method fulfil the assumed criteria. The received results (correlation coefficient equal to 0.999) show that the linearity of the ICP-MS method is good. The accuracy was expressed as recovery (R) and according to the literature is at an acceptable level. The results of precision assessments (RSD) also correspond to the literature data.

Key words | geothermal water, ICP-MS, iodine, validation

IODINE – BASIC CHARACTERISTICS
Iodine is a nonmetallic element. It belongs to the halogen group. It is a necessary microelement for humans due to its important role in thyroid hormone synthesis and contribution to the growth of the brain (WHO 2007; PUBCHEM 2017). Iodine deficiency is responsible for thyroid diseases (goitre, hypothyroidism) and cretinism. Iodine deficiency is one of the most common sources of cognitive impairment (WHO 2008; PUBCHEM 2017). The brain is very sensitive to the effects of low iodine intake. The degree of damage depends on the timing and severity of the deficit (Zoeller & Rovet 2004). The recommended daily iodine intake is around 150 μg and is dependent on human age (Zimmermann & Anderson 2012). Iodine is used as an antiseptic for skin wounds and also as an emergency disinfectant of drinking water in the field. In hospitals, it is used as a disinfection agent (WHO 2003).

Iodine in water
Iodine is a microelement which occurs in natural water in different concentrations dependent on water type, origin and total dissolved solids concentration (Witczak et al. 2013). In groundwater iodine usually exists in the form of iodide ions. The highest concentrations are commonly associated with deep saline waters and brines (Wątor et al. 2016). Their occurrence is very often joined with hydrocarbon deposits (Bojarski 1966). In Poland, waters containing iodide in concentrations above 1 mg/L are referred to as curative specific iodide waters (RMH 2006; GML 2011). Iodide determination, especially in geothermal water, can be biased by different factors (inter alia high volatility – Wątor & Kmiecik 2017).

Methods of iodine determination
In the literature, plenty of methods are proposed for iodine determination. The choice of the method depends primarily on the type of tested material and the forms of iodine being measured (species). For water samples there are recommended inter alia: ion chromatography (IC), capillary electrophoresis (CE), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), total reflection X-ray fluorescence, electrochemical detection (ED), instrumental

ICP-MS has superior sensitivity for iodine determination in comparison with other detection techniques (Takaku et al. 1995). However, this method gives only information about total iodine content and no information about its species concentration. In the case of natural groundwater extracted from deep boreholes, where reductive conditions occur, the whole iodine can be considered as iodides (Wątor & Kmiecik 2017).

The aim of the presented research was the validation of the ICP-MS method for iodine determination in geothermal water samples.

MATERIALS AND METHODS

The object of the research was natural geothermal water. The hydrochemical type of water is sulphate–chloride–sodium–calcium (according to Szczukariew’s classification) (Dowgiallo 2002). The total dissolved solids values are about 2.5 g/L. The water temperature measured on the wellhead ranges between 80 and 86 °C. The concentration of iodine varies from 0.15 to 0.25 mg/L, according to archive data (Sekula 2017) and our own long-term research.

Reagents and samples

Samples were collected directly on the wellhead according to the procedure described in ISO 5667-11:2009. Before sample collection, the stability of selected water parameters, such as pH, electrical conductivity and temperature, were monitored in the online system. After stability of the measurements was obtained, samples were put into dark glass bottles without contact with air. Samples were neither filtered nor preserved (Witzczak et al. 2013). For the purpose of method validation, field control samples were also collected: field blank samples (deionised water collected in the field and treated like the normal sample), duplicate samples (duplicate of the normal sample) and spiked samples (normal sample with the known addition of a standard solution). In the laboratory, there were also prepared spiked deionised water samples (deionised water with the addition of an adequate amount of the standard). All these conditions accord with ISO 5667-14:2016.

The results of normal and duplicate samples were used for estimating the uncertainty arising from the sampling procedure. The results of the analysis of geothermal water samples fortified with iodine as well as deionised water samples with iodide standard addition were used for accuracy and precision determination. To prepare spiked samples, the 10,000 mg/L iodide stock solution (WTW) was diluted with deionised water to yield 100 mg/L iodine solution. This solution was further added to deionised water and geothermal water. In the spiked deionised water samples the final concentrations were 0.1, 0.5, 1.0 and 2.0 mg/L whereas the addition of iodine to geothermal water samples (in the field) was appropriately 0.2, 0.5, and 1 mg/L. Field blank samples were collected for estimation of the practical limit of quantification (PLOQ). The results obtained for spiked deionised water samples were used for the calculation of the limit of quantification (LOQ).

Additionally laboratory blank samples with standard addition were prepared – deionised water was heated to 85 °C and iodine solution was added (with final concentrations 0.1, 0.25, 0.5 and 1 mg/L). These results were used to assess the linearity of the ICP-MS method for samples with higher temperatures.

Instrumentation

The analyses were conducted using the ICP-MS method with the use of the Elan 6100 spectrometer with argon plasma of the PerkinElmer company (USA). The analyses were performed in the Hydrogeochemical Laboratory of the Hydrogeology and Engineering Geology Department at the AGH University of Science and Technology in Krakow (Certificate of Polish Centre for Accreditation No. AB 1050). The $^{127}$I isotope was measured.

RESULTS AND DISCUSSION

Linearity

On the basis of results obtained for blank samples and spiked deionised water samples, method linearity was determined in
the range from 0.1 to 2 mg/L (Figure 1). The received results (correlation coefficient equal to 0.999) show that the linearity of the validated method is good (EURACHEM 2012).

Additionally, linearity was assessed on the basis of the heated spiked deionised water samples (Figure 2). The received results (correlation coefficient equal to 0.999) show that the linearity of the method tested is satisfactory also for samples with higher temperature.

Limit of quantification

LOQ means ‘a stated multiple of the limit of detection at a concentration of the determinant that can reasonably be determined with an acceptable level of accuracy and precision. The LOQ 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. The most commonly used is the formula proposed by Fleming et al. (1997):

\[ \text{LOQ} = \bar{x}_{\text{blank}} + 6s_{\text{blank}}, \]

where:

\( \bar{x}_{\text{blank}} \) – mean concentration in laboratory blank samples,

\( s_{\text{blank}} \) – standard deviation.

In the Hydrogeochemical Laboratory of the Hydrogeology and Engineering Geology Department at the AGH University of Science and Technology, the LOQ for iodine in natural water is estimated at the level of 0.01 mg/L. The LOQ calculated on the basis of laboratory blank samples analysed during the presented experiment is equal to 0.011 mg/L. A reasonable way to assess uncertainties involved in the monitoring process, including the field and laboratory parts, seems to be an implementation of the PLOQ – the lowest concentration of analyte that can be quantified with a satisfying level of accuracy and precision. It is calculated on the basis of field blank sample results from the following formula (Kmieciak & Postawa 2009; Postawa & Kmieciak 2010; Kmieciak & Korzec 2015):

\[ \text{PLOQ} = \bar{x}_{\text{field blank}} + 6s_{\text{field blank}} \]

where:

\( \bar{x}_{\text{field blank}} \) – mean concentration in field blank samples,

\( s_{\text{field blank}} \) – standard deviation.

The PLOQ calculated on the basis of the collected field blank samples is 0.014 mg/L. The PLOQ to LOQ ratio is equal to 1.3, which corresponds to the literature data (Szczepańska & Kmieciak 2005).

Precision

To assess the precision of the validated method, the relative standard deviation (RSD) was calculated on the basis of results obtained from analysis of natural geothermal water...
samples and geothermal water samples spiked with a known amount of the iodide standard solution. The received values are presented in Table 1.

According to literature data (AOAC 1998, 2011) RSD may vary from 1% at higher concentrations up to 30% when low concentrations are determined. The received results are very good and show that the precision of measurement is acceptable. Gilfedder et al. (2008) determined iodine concentration in rain, snow and aerosols using ICP-MS methods and gained RSD of 2.2%. Muramatsu et al. (2001) analysed iodine in saline waters and the precision was below 5% (calculated on the basis of two results). Saline waters were also studied by Tomaru et al. (2007). They received RSD below 5%. Similar results were obtained by Hurwitz et al. (2005). The results presented in Table 1 correspond to the literature data.

**Accuracy**

The accuracy of the validated method was determined on the basis of the results of spiked geothermal water samples and standard solutions diluted with deionised water (Table 2). The accuracy is expressed as recovery (R). The true value is the calculated expected concentration in the spiked geothermal water samples.

According to literature data, the recovery can change from 50% to 120% when low concentrations are measured (AOAC 1998, 2011). The results obtained during validation of the ICP-MS method for the purpose of iodine determination in geothermal water varied from 86% to 116% when natural water fortified with the standard solution was measured and from 100% to 108% in the case of standards. The worse results for recovery were obtained for geothermal water samples, which could be caused by the effect of the matrix or natural high temperature of the water tested.

### Table 1 | The precision of the validated method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of replicates</th>
<th>Mean iodine concentration [mg/L]</th>
<th>RSD [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal sample</td>
<td>8</td>
<td>0.24</td>
<td>5.4</td>
</tr>
<tr>
<td>Spiked sample 1</td>
<td>8</td>
<td>0.52</td>
<td>10.1</td>
</tr>
<tr>
<td>Spiked sample 2</td>
<td>8</td>
<td>0.64</td>
<td>2.2</td>
</tr>
<tr>
<td>Spiked sample 3</td>
<td>8</td>
<td>1.18</td>
<td>5.2</td>
</tr>
</tbody>
</table>

### Table 2 | The accuracy of the validated method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of replicates</th>
<th>True value [mg/L]</th>
<th>Mean iodine concentration [mg/L]</th>
<th>R [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spiked sample 1</td>
<td>8</td>
<td>0.44</td>
<td>0.52</td>
<td>116.1</td>
</tr>
<tr>
<td>Spiked sample 2</td>
<td>8</td>
<td>0.74</td>
<td>0.64</td>
<td>86.1</td>
</tr>
<tr>
<td>Spiked sample 3</td>
<td>8</td>
<td>1.24</td>
<td>1.18</td>
<td>94.6</td>
</tr>
<tr>
<td>Spiked deionised water sample 1</td>
<td>1</td>
<td>0.50</td>
<td>0.54</td>
<td>108.0</td>
</tr>
<tr>
<td>Spiked deionised water sample 2</td>
<td>1</td>
<td>1.00</td>
<td>1.06</td>
<td>106.0</td>
</tr>
<tr>
<td>Spiked deionised water sample 3</td>
<td>1</td>
<td>2.00</td>
<td>2.00</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Uncertainty

To assess the measurement uncertainty the results of eight pairs of normal and duplicate samples were taken into account. The analysis of variance was carried out using methodology described by Kmiecik (2011), Mika et al. (2017), Kmiecik & Tomaszewska (2017), and Kmiecik (2018).

The following information was derived on the basis of calculation made with the use of ROBAN software (www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/ROBAN.asp):

- The total variance separated into geochemical, sampling and analytical variance:

\[ s^2_{\text{total}} = s^2_{\text{geochemical}} + s^2_{\text{sampling}} + s^2_{\text{analytical}} \]

\[ s^2_{\text{total}} = s^2_{\text{geochemical}} + s^2_{\text{meas}} \]

- Calculation of standard and relative uncertainties \((u)\) associated with these components:

\[ u_{\text{geochemical}} = s_{\text{geochemical}}, \quad u_{\text{sampling}} = s_{\text{sampling}}, \quad u_{\text{analytical}} = s_{\text{analytical}}, \quad u_{\text{meas}} = s_{\text{meas}} \]

- Calculation of expanded uncertainty \((U)\) for 95% confidence level:

\[ U_{\text{geochemical}} = 2s_{\text{geochemical}}, \quad U_{\text{sampling}} = 2s_{\text{sampling}}, \quad U_{\text{analytical}} = 2s_{\text{analytical}}, \quad U_{\text{meas}} = 2s_{\text{meas}} \]

- Calculation of relative uncertainties \((U')\) related to the mean values of the analysed element for normal and duplicate samples:

\[ U'_{\text{geochemical}} = (2s_{\text{geochemical}}/\bar{x}_{\text{mean}}) \times 100[\%], \]
\[ U'_{\text{sampling}} = (2s_{\text{sampling}}/\bar{x}_{\text{mean}}) \times 100[\%], \]
\[ U'_{\text{analytical}} = (2s_{\text{analytical}}/\bar{x}_{\text{mean}}) \times 100[\%], \]
\[ U'_{\text{meas}} = (2s_{\text{meas}}/\bar{x}_{\text{mean}}) \times 100[\%]. \]

The calculated measurement variance does not exceed the limit value of 20% (Ramsey et al. 1992) and therefore can be accepted. Further calculations (estimation of uncertainty) are made for robust results \((k = 2)\). The expanded relative analytical uncertainty \((U'_{\text{analytical}})\) is 15.47%, whereas the total relative uncertainty is 43.09% and mostly depends on the natural geochemical variability of iodine concentration in water. The measurement uncertainty \((U'_{\text{meas}})\) is 17.68% (Table 3) and the uncertainty arising from sampling is below 9%. This estimation based on the experimental data takes into account only random effects and any systematic errors are not included.

For the purpose of the estimation of combined uncertainty, the results of precision, accuracy and sampling uncertainty determination were used. Uncertainty associated with the precision of the method tested was assumed to be equal to the highest value of RSD calculated — 10.1% (Table 1). The uncertainty contribution arising from the accuracy of the method was assumed to be 16.1% for the concentrations below 1 mg/L and 8% in the case of solutions with iodine concentration above 1 mg/L (Table 2). The total combined uncertainty calculated on the basis of these results is equal to 21% for lower iodine amounts and 15.6% when concentrations are higher than 1 mg/L. The expanded uncertainty \((k = 2, 95\%)\) is 42% and 31.2% respectively. The expanded uncertainty declared by the laboratory varies from 12% to 26% depending on the iodine concentration. Dwornik et al. (2015) calculated the uncertainty of iodine measurements in surface and mine waters.

**Table 3 | Uncertainty of the validated method**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(u_{\text{geochemical}}) [mg/L]</td>
<td>0.035</td>
</tr>
<tr>
<td>(u_{\text{geochemical}}) [mg/L]</td>
<td>0.070</td>
</tr>
<tr>
<td>(U'_{\text{geochemical}}) [%]</td>
<td>38.67</td>
</tr>
<tr>
<td>(u_{\text{sampling}}) [mg/L]</td>
<td>0.008</td>
</tr>
<tr>
<td>(U'_{\text{sampling}}) [mg/L]</td>
<td>0.016</td>
</tr>
<tr>
<td>(U'_{\text{sampling}}) [%]</td>
<td>8.84</td>
</tr>
<tr>
<td>(u_{\text{analytical}}) [mg/L]</td>
<td>0.014</td>
</tr>
<tr>
<td>(U'_{\text{analytical}}) [mg/L]</td>
<td>0.028</td>
</tr>
<tr>
<td>(U'_{\text{analytical}}) [%]</td>
<td>15.47</td>
</tr>
<tr>
<td>(u_{\text{meas}}) [mg/L]</td>
<td>0.016</td>
</tr>
<tr>
<td>(U'_{\text{meas}}) [mg/L]</td>
<td>0.032</td>
</tr>
<tr>
<td>(U'_{\text{meas}}) [%]</td>
<td>17.68</td>
</tr>
<tr>
<td>(U_{\text{total}}) [mg/L]</td>
<td>0.078</td>
</tr>
<tr>
<td>(U_{\text{total}}) [mg/L]</td>
<td>43.09</td>
</tr>
</tbody>
</table>
using ICP-MS methods and obtained worse results – the expanded relative measurement uncertainty was above 57% and resulted from a high sampling uncertainty of 56%. This could be caused by the more complicated sampling of those types of samples. The analytical uncertainty was above 9%. Higher analytical uncertainty determined for the geothermal water samples analysis can result from the high temperature of the water.

CONCLUSIONS

The ICP-MS method is useful for iodine determination in geothermal water samples. The method parameters determined during the validation experiment are at a satisfactory level. The high temperature and increased mineralisation of the water tested have not influenced the results obtained. To prove the correctness of the reached results an additional experiment was performed. The deionised water was heated and iodine stock solution added. This experiment proved that the temperature does not have a significant impact on the results.

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