

**University of Stuttgart**  
Germany



# Analytische Qualitätssicherung Baden-Württemberg

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Proficiency Test 6/19

- TW A4 – Other inorganic parameters -  
conductivity, oxidisability, selenium, antimony, arsenic

Final report

provided by

AQS Baden-Württemberg at

Institute for Sanitary Engineering, Water Quality and Solid Waste Management,  
University of Stuttgart

Bandtäle 2, 70569 Stuttgart-Büsnau, Germany



on behalf of the Ministry of Rural Affairs and  
Consumer Protection Baden-Württemberg

Stuttgart, in January 2020

**AQS Baden-Württemberg at  
Institute of Sanitary Engineering,  
Water Quality and Solid Waste Management  
at University of Stuttgart  
Bandtäle 2  
70569 Stuttgart-Büsnau  
Germany  
<http://www.aqsbw.de>  
Tel.: +49 (0)711 / 685-65446  
Fax: +49 (0)711 / 685-63769  
E-Mail: [info@aqsbw.de](mailto:info@aqsbw.de)**

**Responsibilities:**

<b>Scientific director:</b>	Dr.-Ing. Michael Koch	
<b>PT coordinator:</b>	Dr.-Ing. Frank Baumeister	
<b>Assistant PT coordinator</b>	Dipl.-Biol. Biljana Marić	
<b>Sample preparation</b>	Matthias Mischo	
<b>Release of the report:</b>	Dr.-Ing. Michael Koch	on
<b>Version of the report</b>	1	

## List of contents

1. General .....	1
2. PT design .....	1
3. Sample preparation .....	1
4. Sample distribution.....	2
5. Analytical methods .....	2
6. Submission of the results .....	2
7. Basic principle of evaluation and assessment .....	3
8. Evaluation.....	4
9. Explanation for the appendices .....	4
10. Measurement uncertainty.....	4
11. Traceable reference values .....	5
12. Internet.....	5

### Appendix A

CONDUCTIVITY .....	A-1
OXIDISABILITY.....	A-4
TOC .....	A-7
SELENIUM.....	A-17
ANTIMONY .....	A-27
ARSENIC.....	A-37

### Appendix B

### Appendix C

CONDUCTIVITY .....	C-1
OXIDISABILITY.....	C-37
TOC .....	C-64
SELENIUM.....	C-93
ANTIMONY .....	C-127
ARSENIC.....	C-162

## 1. General

This PT was provided in the context of the AQS Baden-Württemberg drinking water PT scheme. In this round conductivity, oxidisability, TOC, selenium, antimony and arsenic were to be determined.

The PT was executed according to the recommendations of the German Federal Environment Agency from December 2003. These recommendations “for the execution of PTs for the measurement of chemical parameter and indicator parameter for the external quality control of drinking water laboratories” (Bundesgesundheitsblatt 46 12, 1094-1095) require, that drinking water laboratories must demonstrate their competence for all parameters they are accredited for or they want to be accredited for by a successful participation in a PT round within a cycle of 2-3 years.

The PT was executed and evaluated according to the requirements of DIN 38402-A45 and ISO/TS 20612.

## 2. PT design

Each participant received the following samples:

- 3 samples for the determination of the oxidisability in 100-ml-plastic bottles. Stabilisation by adding sulphuric acid according to ISO 8467 (pH < 2).
- 3 samples for the determination of conductivity in 100-ml-plastic bottles.
- 3 samples for the determination of TOC in 100-ml-plastic bottles. Stabilisation by adding hydrochloric acid (pH ca. 2,1).
- 3 samples for the determination of antimony, arsenic and selenium in 500-ml-plastic bottles. Stabilisation by adding nitric acid (pH ca. 2,1).

9 different concentration levels/batches were produced. The concentration levels were randomly allocated to the participants. It was ensured that each participant received one concentration level from the lower concentration range (level 1–3).

## 3. Sample preparation

The samples were based on a real ground water matrix.

The ground water for the parameters oxidisability and TOC was filtered by using 5 µm and 1 µm filter cartridges to eliminate particles. To reduce germs, the ground water was irradiated with ultraviolet light and pasteurised at 80°C in a stainless steel vessel overnight. During pasteurisation, the ground water was aerated with a mixture composed of carbon dioxide and nitrogen to prevent calcium carbonate precipitation.

The ground water for the parameters conductivity, antimony, arsenic and selenium was filtered by using 5 µm and 1 µm filter cartridges to eliminate particles, but not pasteurised.

The matrix for antimony, arsenic and selenium was pre-stabilised with nitric acid and was stored in a plastic tank prior use.

For the parameter conductivity the matrix was prepared directly prior use and was stored in a plastic vessel.

For preparation of the samples, with exception of the parameter conductivity, the matrix was spiked with stock solutions and the concentrations covered drinking and ground water relevant ranges.

The samples for the conductivity were prepared by diluting the ground water with UV irradiated pure water.

The samples were cooled directly after preparation and freezer packs were added for the shipment.

#### 4. Sample distribution

The samples were dispatched on 30 September 2019 by express service (TNT).

#### 5. Analytical methods

The participants were free to choose a suitable method, but following limits of quantification were required.

<b>parameter</b>	<b>limit of quantification</b>
oxidisability	0,5 mg/l O <sub>2</sub>
conductivity	100 µS/cm
TOC	0,8 mg/l
antimony	1 µg/l
arsenic	1 µg/l
selenium	1 µg/l

The participants were informed that the samples had to be analysed in the own laboratory, with own personal and own equipment. Subcontracting of the analysis was not allowed.

The samples had to be analysed in duplicate over the complete method (sample preparation and measurement). The participants were asked to report the results for the oxidisability in mg/l O<sub>2</sub>, for the conductivity in µS/cm at 25 °C, for the parameter TOC in mg/l and for antimony, arsenic, selenium in µg/l with three significant digits.

#### 6. Submission of the results

The deadline for the submission of results was on 21 October 2019.

## 7. Basic principle of evaluation and assessment

The basic principle of the evaluation and assessment of the PTs from AQS Baden-Württemberg are described in the document „Evaluation of the PTs and information for the report“, which can be downloaded from [www.aqsbw.de/pdf/ausw\\_berichte\\_v1\\_en.pdf](http://www.aqsbw.de/pdf/ausw_berichte_v1_en.pdf).

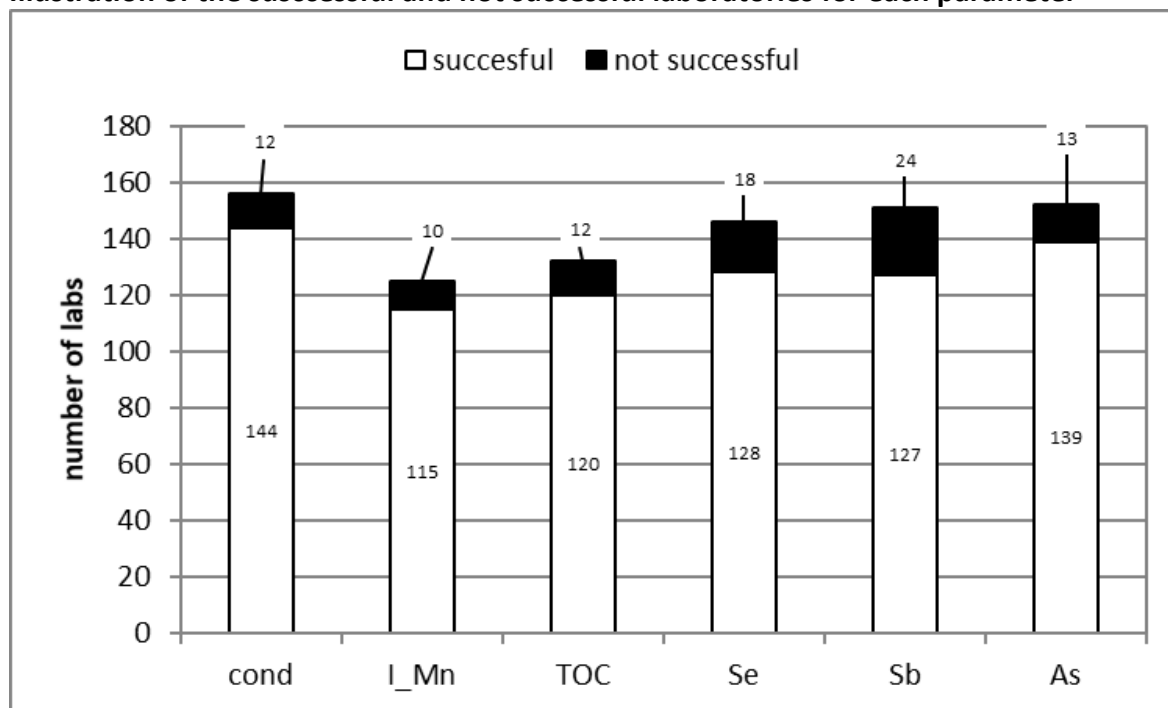
This PT was evaluated as follows:

<b>Assigned value <math>x_{pt}</math>:</b>	Reference value: <ul style="list-style-type: none"> <li>- TOC</li> <li>- selenium</li> <li>- antimony</li> <li>- arsenic</li> </ul> Consensus value (Hampel estimator): <ul style="list-style-type: none"> <li>- conductivity</li> <li>- oxidisability</li> </ul>						
<b>Standard deviation for proficiency assessment <math>\sigma_{pt}</math>:</b>	Q method Variance function						
<b>Upper limit of <math>\sigma_{pt}</math>:</b>	25 %						
<b>Lower limit of <math>\sigma_{pt}</math>:</b>	5 %						
<b>Assessment:</b>	$z_U$ -Score						
<b>Classification of the single results:</b>	<table style="border: none; width: 100%;"> <tr> <td style="padding-right: 20px;"><math> z_u  \leq 2,0</math></td> <td>successful</td> </tr> <tr> <td><math>2,0 &lt;  z_u  &lt; 3,0</math></td> <td>questionable</td> </tr> <tr> <td><math> z_u  \geq 3,0</math></td> <td>unsatisfactory</td> </tr> </table>	$ z_u  \leq 2,0$	successful	$2,0 <  z_u  < 3,0$	questionable	$ z_u  \geq 3,0$	unsatisfactory
$ z_u  \leq 2,0$	successful						
$2,0 <  z_u  < 3,0$	questionable						
$ z_u  \geq 3,0$	unsatisfactory						
<b>Parameter assessment:</b>	A parameter was assessed as successful, if more than half of the values were correctly determined (2 out of 3 values are within the tolerance limits).						

## 8. Evaluation

<b>Number of participants:</b>	166
<b>Number of reported values</b>	2585
<b>Number of accepted values:</b>	2305 (89,17%)

### Illustration of the successful and not successful laboratories for each parameter



## 9. Explanation for the appendices

The explanations for the appendices can be found in the document „Evaluation of the PTs and information for the report“, which can be downloaded from [www.agsbw.de/pdf/ausw\\_berichte\\_v1\\_en.pdf](http://www.agsbw.de/pdf/ausw_berichte_v1_en.pdf).

## 10. Measurement uncertainty

### General:

Number of labs with valid values	164
Number of labs with valid values and reported measurement uncertainties	95 (57,93%)
Number of valid values	2585
Number of valid values with measurement uncertainties	1508 (58,34%)

**Measurement uncertainties against the accreditation status**

Accreditation status of the values	Number of values	Number of values with measurement uncertainty
accredited	2358	1434 (60,81%)
not accredited	110	53 (48,18%)
not specified	117	21 (17,95 %)

**Interpretation of the reported measurement uncertainties:**

If measurement uncertainties are underestimated values assessed as “satisfactory” in the PT ( $|z_U| \leq 2$ ), will have a large  $\zeta$ -score.  $|\zeta| > 2$  means that the “own” requirements (defined in terms of estimated uncertainty) are not fulfilled.

<b>Number of values with reported measurement uncertainty having a <math> z_U  \leq 2,0</math></b>	1353
<b>Number of values with a magnitude of <math>\zeta</math>-scores <math>&gt; 2</math></b> The own requirements of the laboratory are not fulfilled and the estimation of the measurement uncertainty is too low	131 (10,3%)

**11. Traceable reference values**

The explanations about traceable reference values can be found in the document „Evaluation of the PTs and information for the report“, which can be downloaded from [www.aqsbw.de/pdf/ausw\\_berichte\\_v1\\_en.pdf](http://www.aqsbw.de/pdf/ausw_berichte_v1_en.pdf)

**12. Internet**

The report is available on the following webpage: [http://www.aqsbw/pdf/report\\_201.pdf](http://www.aqsbw/pdf/report_201.pdf)