



KWR | November 2018

## **KWR Proficiency Testing Services Program for 2019**

**KWR**



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**KWR | November 2018**

**Order number**

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**Project manager**

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**Client(s)**

Participating laboratories

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**Sent to**

Interested laboratories



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**More information**

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# Summary

We hereby offer you our new annual program for the KWR Proficiency Testing Services 2019. You will find, in addition to the annual program itself, a detailed explanation of the general course of events in participation, design and statistical processing.

In this program you will find all information about the composition of the PT's, the planning and the registration.

# Inhoud

<b>1</b>	<b>Introduction</b>	<b>6</b>
1.1	General	6
1.2	KWR proficiency testing	6
<b>2</b>	<b>General Information</b>	<b>8</b>
2.1	Subscription	8
2.2	Per proficiency test	8
2.3	Distribution of the samples and returning of packaging materials	9
2.4	Reporting your results	9
2.5	Reporting by KWR	9
2.6	Information	9
<b>3</b>	<b>Program 2019</b>	<b>10</b>
3.1	How to make a choice	10
3.2	Changes in the program 2019	10
3.3	Order confirmation and invoice	11
3.4	Discounts	11
3.5	Cancelling an order	11
3.6	KWR PT program 2019 and subscription form	11
<b>4</b>	<b>General overview KWR Proficiency Tests 2019</b>	<b>12</b>
<b>5</b>	<b>Parameter specifications for PT</b>	<b>13</b>
5.1	General- and inorganic parameters and (heavy) metals	13
5.2	Organic parameters	15
5.3	Microbiological parameters	19
<b>6</b>	<b>Lay-out of the final report</b>	<b>22</b>
6.1	Samples and standardsolutions	22
6.2	Graphical presentation of the results	23
6.3	Rapportcijfer	26
6.4	Z-score	27

# 1 Introduction

## 1.1 General

KWR Watercycle Research Institute, hereinafter abbreviated as KWR, is the competence centre for water and related nature and environmental aspects. It covers the entire area from catchment, treatment and distribution to the quality assessment of drinking, industrial, waste and domestic water. KWR supports water companies and third parties at home and abroad with research in the area of (drinking) water, water quality and water management.

Furthermore, KWR organizes proficiency tests for the matrix water. These proficiency tests are an important instrument in the harmonization of (environmental) analyses within The Netherlands as well as within Europe. The importance of proficiency testing for individual laboratories lies in the opportunity to compare own results with those from other (peer) laboratories. In practice, different analytical methods are being used and suitable reference materials are not always available. Therefore, it is sometimes impossible for laboratories to determine if (systematic) errors are present in their analytical procedures. Proficiency testing results can be helpful in visualizing these types of errors. Good results of a laboratory in a proficiency test can give additional value and trust towards customers and can play an important role in the assessment of the laboratory by accreditation bodies. Therefore, proficiency testing is more and more considered as a standard and integral part of the quality control system of a laboratory, by laboratories as well as accreditation bodies. For participants it is of utmost importance that the quality of the offered proficiency testing service is outstanding. Accrediting the organization of proficiency testing schemes is a tool to guarantee high quality schemes.

Depending on the objective, different types of proficiency tests can be organized. They can be divided into three types:

- method-evaluating test comparisons in which the performance of a (newly) developed method is tested;
- material-certifying test comparisons that primarily involve the production of a certified reference material for quality control purposes;
- laboratory-evaluating test comparisons (also called proficiency tests) that give participating laboratories the opportunity to evaluate their analytical methods and to compare their results with those from other (peer) laboratories.

## 1.2 KWR proficiency testing

Especially for the laboratory-evaluating comparisons KWR has set up a yearly program, which enables laboratories to test and evaluate their laboratory procedures on a regular basis. The primary objective of a proficiency test is to create an opportunity for laboratories to test their own performances under analytical conditions which are as normal as possible. To enable laboratories to get insight into their own performance in daily practice, they will receive samples which are made of practice water matrices. The analytical method to be applied by the laboratory is up to the laboratory, no mandatory methods are demanded by KWR. Assessment of the KWR Proficiency Testing Services by an independent institute, The Dutch Council for Accreditation, took place in 1996. Since thereon the complete package of KWR inter-laboratory test comparisons has been accredited and is registered under number R005. This accreditation according ISO/IEC 17043:2010 ensures participants that aspects such as high quality samples (homogeneous, stable, compatible with matrices offered in practice), suitable statistics, clear reports and impartiality of the organizer is guaranteed.

KWR proficiency tests:

- consist yearly of approximately 40 laboratory test comparisons for different types of water and more than 250 parameters;
- are based on Youden statistics for chemical parameters, which makes it possible to obtain a good indication if deviating results are caused by systematic and/or by relatively large random errors;
- present the results in table format and graphically;
- give information about the analytical methods applied by the participants. In this way assessment of the participants performance is simplified;
- assess the performance for chemical parameters of a group of (peer) laboratories by presenting a report mark;
- assess the individual performance of a laboratory by presenting the z-score.

In this brochure the procedure to be followed, when participating in KWR Watercycle Research Institute proficiency tests, is described. In chapter 2, the practical side of participating (subscription, sample distribution and receipt, reporting, etc.) is explained. The proficiency-testing program for 2019 together with the subscription form can be found in chapters 3, 4 and 5. In chapter 6 an extended explanation of the layout and statistics of the KWR Watercycle Research Institute proficiency tests is given.

## 2 General Information

### 2.1 Subscription

This brochure contains the program for the KWR proficiency tests for 2019. You can make your own selection from several proficiency tests offered by ticking the appropriate box(es) on the subscription form. In this way you can put together a tailor-made program.

All participants receive after registering a written confirmation of participation.

For the chemical and microbiological proficiency tests you may have different contact persons. If so, you can let us know by filling out the subscription form or by phoning us. You will also receive a set of keys to open the (cooling) containers. These keys remain in your possession for as long as you participate in the KWR scheme.

Finally, you will receive an instruction for entering and reporting your analysis results of a proficiency test.

### 2.2 Per proficiency test

KWR offers you for every parameter an opportunity to test your own performances under analytical conditions that are as normal as possible. To enable you to get insight into your own performance in daily practice, you will receive samples which are made from real drinking water, surface water, ground water, waste water or swimming water. Furthermore, for a number of chemical proficiency tests you will also receive standard solutions to check your instruments directly. It is, of course, important that you treat the proficiency testing samples the same as any other sample that is offered to your laboratory for analysis. In this way your results in the inter-laboratory test comparison represent daily practice and you will get the most out of your participation. For each proficiency test wherein you subscribe you will receive an e-mail with two accompanying files: a form to fill in your results and an instruction with the details.

This instruction refers to:

- the parameters to be analysed;
- an indication of the concentration levels;
- the matrices offered;
- the preservation of the samples (where applicable samples will be cooled during transportation);
- an advice relating to the storage life of the samples;
- the code numbers on the sample bottles;
- when to report back your results (closing date of the Proficiency Test) and how to return the packaging materials;
- the date when you can expect to receive the final report from KWR;
- any other information that could be of importance.

Results as well as applied analytical methods will be reported under a random code number in the final report.

The amount of sample material you will receive is based on the amount that is needed when using an accepted analytical method. If you require more sample material than provided, you may contact Mrs M. ten Broeke. She is also the person to contact when the sample material has been damaged during transport. If possible, you will then immediately receive new sample material.



### 2.3 Distribution of the samples and returning of packaging materials

The chemical samples will be delivered before 16:00 hours on the date mentioned in the program. The microbiological samples and proficiency tests which contain parameters with a limited storage life, they will be delivered before 12:00 hours after receipt of the samples and you can return the packaging materials by postal mail (preferably within two weeks after receiving the samples). Samples delivered outside the Netherlands and Belgium will arrive later.

### 2.4 Reporting your results

The files with your results and applied analytical methods (for verification purposes we also ask you to send a print out on paper) have to be at KWR within 4 weeks (for chemical Proficiency Tests) or within 3 weeks (for microbiological proficiency tests) after receiving the samples. The exact closing date stated in the instruction of the proficiency test. For delivering the results you need to use the RingDat Online program.

### 2.5 Reporting by KWR

The final report and the summary for all proficiency tests will be send to you by e-mail within 4 weeks after the closing date. In the KWR proficiency tests the results and analytical methods applied of all participants will be reported under a random code number to guarantee anonymity. A list of participants is given in the final report. If you do not want your company to be named in this list, it is possible to be named under code, which you can let us know by phone or by letter. The overview of analytical methods applied, given in the final report, can be of use in assessing deviating results. The results of the whole group of participants for the chemical proficiency tests is assessed in a so-called 'report mark'. In general one report mark is given per parameter and per matrix.

An individual assessment of the performance of each participant is given through reporting of the z-scores. Z-scores are calculated in relation to the group average and in relation to the theoretical value. In this way you can follow your own performance. The final report displays the results graphically and in table format. The report also contains a summary of your results. We refer to chapter 6 for an extended explanation of the lay-out, applied statistics and the report.

### 2.6 Information

For further information and requests, please contact:

- Asmail Asgadaouan (phone: +31 (0)30 60 69 595), e-mail: [Asmail.Asgadaouan@kwrwater.nl](mailto:Asmail.Asgadaouan@kwrwater.nl)
- Marieke ten Broeke (phone: +31 (0)30 60 69 612), e-mail: [Marieke.ten.Broeke@kwrwater.nl](mailto:Marieke.ten.Broeke@kwrwater.nl)
- Send an email to: [pt@kwrwater.nl](mailto:pt@kwrwater.nl)

## 3 Program 2019

### 3.1 How to make a choice

The KWR program consists of organic, inorganic and microbiological inter-laboratory test comparisons for more than 250 physical, chemical and microbiological parameters in the matrices drinking, surface, ground, waste and swimming water. By offering this program we hope that we can be of service to you in setting up your own personal proficiency testing program in 2019.

#### 3.1.1 Inorganic parameters

For the tests VIO 19-06 (urea, cyanuric acid, free chlorine, total chlorine and KMnO<sub>4</sub> in swimming water) we offer you also standard solutions.

#### 3.1.2 Organic parameters

In every organic proficiency test at least three matrices are offered and one standard solution. Per matrix two spiked samples are offered, excepted the proficiency test mineral oil in waste water (VIO 19-38).

#### 3.1.3 Microbiological parameters

For all the microbiological proficiency tests, excepted the parameters SSRC and *Clostridium perfringens*, we offer four samples.

For the proficiency tests *Legionella pneumophila* qPCR beside the water samples several concentrations genomic DNA samples are sent.

### 3.2 Changes in the program 2019

The program KWR proficiency tests for 2019 relative to previous years, some changes have been made.

- At the chemical proficiency tests:
  - The PT VIO 19-20 (sampling surface water on a location in The Netherlands) is now permanently included in the annual program.
  
- At the microbiological proficiency tests:
  - In this program the proficiency tests listed below are optional and will only proceed if there are sufficient participants. If you register for one of these proficiency tests, you will be automatically enrolled in one of the other similar proficiency tests:
    - VIO 19-42: Microbiological parameters in drinking water (plan date: October 15, 2019);
    - VIO 19-46: *Legionella* in drinking water (plan date: May 15, 2019);
    - VIO 19-54: Microbiological parameters in surface water (plan date: September 25, 2019);
    - VIO 19-56: *Legionella* in cooling water (plan date: September 4, 2019).
  - For the proficiency tests *Legionella pneumophila* qPCR VIO 19-59 (dw) and VIO 19-61(kw) the participants will only asked to report the results of the samples (possibly corrected for the yield) and the standards genomic DNA.

### 3.3 Order confirmation and invoice

Based on your subscription form we will calculate the costs and send you an overview of your participation. The total costs will be invoiced twice a year in two equal amounts, unless other agreements are made with you. If changes in your order occur during the year, an adapted cost accounting will be handled in the second period.

### 3.4 Discounts

At participating in several proficiency tests the following discounts are given:

Participation in 5-9 proficiency tests:	5% discount
Participation in 10-19 proficiency tests:	10% discount
Participation in more than 20 proficiency tests:	15% discount

The prices in the program are excluding carriage costs. Transport costs, based on actual transportation costs by post-calculation, will be charged.

The General Terms and Conditions for the Supply of Goods and Provision of Services and Purchase placed with KWR Watercycle Research Institute are applied on this tender. You can find this on KWR website [www.kwrwater.nl/voorwaarden/](http://www.kwrwater.nl/voorwaarden/).

### 3.5 Cancelling an order

If you wish to cancel a collaborative study, you need at least four weeks before the date of receipt of the collaborative study notify us in writing. After this period the cost of the ring test will be charged.

### 3.6 KWR PT program 2019 and subscription form

On pages 13 to 19 you will find our detailed program and on pages 20 and 21 the subscription form for 2019.

**You can subscribe for the KWR proficiency tests by using the subscription form. Please do this at least four weeks before the starting date of the proficiency tests.**

The subscription form can be sent to:

KWR Watercycle Research Institute

Attn.: Marieke ten Broeke

P.O. Box 1072

3430 BB NIEUWEGEIN

The Netherlands

FAX: (+31) 30 60 611 65

E-mail: [Marieke.ten.Broeke@kwrwater.nl](mailto:Marieke.ten.Broeke@kwrwater.nl) or [pt@kwrwater.nl](mailto:pt@kwrwater.nl)

**When less than eight participants subscribe, KWR reserves the right to cancel the proficiency test.**

## 4 General overview KWR Proficiency Tests 2019

Date	PT code	Matrix	Description
30 January	VIO 19-21	dw+sw+gw+ww	extractable organic halogens (EOX)
30 January	VIO 19-22	dw+sw+gw+ww	adsorbable organic halogens (AOX)
6 February	VIO 19-02	dw	◇ general- and macro parameters
12 February	VIO 19-41	dw	◇ microbiological parameters
6 March	VIO 19-30	dw+sw+gw	herbicides
13 March	VIO 19-06	zw	◇ urea, cyanuric acid, free chlorine, total chlorine, KMnO <sub>4</sub>
13 March	VIO 19-45	dw	◇ <i>Legionella</i>
13 March	VIO 19-55	kw	◇ <i>Legionella</i> (only according to NEN-EN-ISO 11731)
13 March	VIO 19-59	dw	◇ <i>Legionella pneumophila</i> qPCR
13 March	VIO 19-61	kw	◇ <i>Legionella pneumophila</i> qPCR
20 March	VIO 19-09b	sw	arsenic-3, arsenic-5, chromium-3 and chromium-6
20 March	VIO 19-25	dw+sw+gw+ww	polycyclic aromatic hydrocarbons (PAH)
26 March	VIO 19-48	dsw+dw	◇ ATP (Adenosine Tri Phosphate)/ Colonies on R <sub>2</sub> A medium
26 March	VIO 19-63	dw	◇ Total bacterial cell counting (incl. fraction dead and alive) using a flowcytometer
10 April	VIO 19-07	sw	◇ nutrients
10 April	VIO 19-18	dw+sw	bromide, bromate and chlorate
10 April	VIO 19-28	dw+sw+gw	pharmaceuticals
10 April	VIO 19-34	dw+sw+gw	glyphosate and AMPA
8 May	VIO 19-01	dw	(heavy) metals, as dissolved
8 May	VIO 19-09a	sw	(heavy) metals, as total
8 May	VIO 19-12	gw	(heavy) metals, as dissolved
15 May	VIO 19-46 <sup>#1</sup>	dw	◇ <i>Legionella</i>
22 May	VIO 19-23	dw+sw+gw+ww	pesticides (OCP)
22 May	VIO 19-24	dw+sw+gw	pesticides (PCB)
4 June	VIO 19-43	dw	◇ microbiological parameters
19 June	VIO 19-31	dw+sw+gw	chlorophenoxycarbonic acids (CPCA)/bentazone
19 June	VIO 19-39a	dw+sw+gw	chloridazon, dimethenamid-P and metabolites
25 June	VIO 19-53	sw	◇ microbiological parameters
26 June	VIO 19-17	zw	Sampling swimming water on location in The Netherlands
4 September	VIO 19-19	dw	odour and flavour (organoleptic)
4 September	VIO 19-26	dw+sw+gw+ww	volatile halogenated hydrocarbons (VHH)
4 September	VIO 19-47	dw	◇ <i>Legionella</i>
4 September	VIO 19-56 <sup>#1</sup>	kw	◇ <i>Legionella</i> (only according to NEN-EN-ISO 11731)
11 September	VIO 19-50	dw	◇ <i>Salmonella</i> , <i>Pseudomonas aeruginosa</i> , staphylococci
11 September	VIO 19-62	dw	◇ F-specific RNA-phages and Somatic coli-phages
25 September	VIO 19-39b	dw+sw+gw+ww	Non-target screening, semi-quantitative using a LC-MS
25 September	VIO 19-54 <sup>#1</sup>	sw	◇ microbiological parameters
9 October	VIO 19-27	dw+sw+gw+ww	volatile aromatic hydrocarbons (VAH)
15 October	VIO 19-42 <sup>#1</sup>	dw	◇ microbiological parameters
16 October	VIO 19-15	ww	◇ general- and macro parameters
16 October	VIO 19-16	ww	(heavy) metals, as total
6 November	VIO 19-13	gw	◇ general- and macro parameters
6 November	VIO 19-32	dw+sw+gw	phenylurea herbicides (PUH)
6 November	VIO 19-38	ww	mineral oil
19 November	VIO 19-20	sw	Sampling surface water on location in The Netherlands

<sup>#1</sup> This proficiency test is optional. Only if there are enough participants this test will go on.

◇ Proficiency tests marked with this symbol contain parameters that are only stable for 24 hours. Subscription to these tests may be possible after consulting Mrs M. ten Broeke. (See previous page for her contact data).

ww = waste water, dw = drinking water, gw = groundwater, kw = cooling water, sw = surface water, dsw = diluted surface water and zw = pool water

## 5 Parameter specifications for PT

### 5.1 General- and inorganic parameters and (heavy) metals

Date	PT code	Parameter	Matrix	Concentration range
8 May	VIO 19-01 <sup>#</sup>	<b>(Heavy) metals, as dissolved:</b> Hg, Ag <sup>+</sup> , Be <sup>+</sup> , Cd, Co <sup>+</sup> , V <sup>+</sup> , Al, As, Cr, Pb, Sb, Se, Sr <sup>+</sup> , Cu, Ni, Zn, B, Ba, Fe, Mn, Mo <sup>+</sup> , K, Mg, Ca, Na, total hardness.	dw	0,1-1 µg/l 0,1-10 µg/l 1-70 µg/l 1-200 µg/l 1-350 µg/l 0,5-50 mg/l 1-200 mg/l 0,5-6 mmol/l
6 February	VIO 19-02	NO <sub>2</sub> , F, NH <sub>4</sub> , turbidity, DOC, NO <sub>3</sub> , SO <sub>4</sub> , Cl, ortho-phosphate, total-phosphate, pH, SiO <sub>2</sub> , colour, CO <sub>3</sub> , EGV (at 25°C), HCO <sub>3</sub> , total cyanide.	dw ct	0,02-0,2 mg N/l 0,05-2 mg/l 0,05-2 mg N/l 0,1-2,5 FNE 0,1-15 mg C/l 0,5-50 mg N/l 1-200 mg/l 10-200 mg/l 0,05-2 mg P/l 4-11 pH 0,1-15 mg Si/l 2-20 mg Pt/l 0,5-50 mg/l 10-150 mS/m 1-300 mg/l 2,5-350 µg/l
13 March	VIO 19-06	urea, cyanuric acid, free chlorine, total chlorine, KMnO <sub>4</sub> <sup>+</sup> .	zw ct	0,5-5 mg/l 5-15 mg/l 0,1-20 mg/l 0,1-20 mg/l
10 April	VIO 19-07	NH <sub>4</sub> , NO <sub>2</sub> , NO <sub>3</sub> , ortho-phosphate, anion active detergents, F, Kjeldahl-N, total-phosphate, COD (CZV), SiO <sub>2</sub> , UV-absorption, colour, SO <sub>4</sub> , Cl, suspended solids, oxygen (dissolved).	sw ct	0,02-2 mg N/l 0,05-3 mg P/l 0,02-2,5 mg/l NalaurylSO <sub>4</sub> 0,02-2,5 mg/l 0,05-3 mg N/l 0,02-2 mg P/l 1-15 mg O <sub>2</sub> /l 1-15 mg Si/l 0,1-20 E/m 2-20 mg Pt/l 1-200 mg/l a.l. mg/l 1-15 mg O <sub>2</sub> /l
8 May	VIO 19-09a <sup>#</sup>	<b>(Heavy) metals, as total:</b> Ag <sup>+</sup> , Be, Cd, Hg, Sb <sup>+</sup> , Al, As, Co, Cr, Pb, Se, Sr <sup>+</sup> , V, B <sup>+</sup> , Ba, Cu, Mo <sup>+</sup> , Ni, Zn, Fe, Mn, K, Ca, Mg, Na.	sw	0,1-10 µg/l 1-70 µg/l 1-500 µg/l 0,01-1 mg/l 1-15 mg/l 1-200 mg/l
20 March	VIO 19-09b <sup>**</sup>	arsenic-3, arsenic-5 chromium-3, chromium-6	sw	0,1-10 µg/l 0,1-10 µg/l

Date	PT code	Parameter	Matrix	Concentration range
8 May	VIO 19-12 <sup>#</sup>	<b>(Heavy) metals, as dissolved:</b> Ag <sup>+</sup> , Be <sup>+</sup> , Cd, Hg, Sb <sup>+</sup> , As, Co, Cr, Pb, Se <sup>+</sup> , Sr <sup>+</sup> , V <sup>+</sup> , Al, B <sup>+</sup> , Cu, Mo, Ni, Zn, Ba, Fe, K <sup>+</sup> , Mn, Ca <sup>+</sup> , Mg <sup>+</sup> , Na <sup>+</sup> .	gw	0,1-10 µg/l 1-70 µg/l 1-300 µg/l 0,1-20 mg/l 1-200 mg/l
6 November	VIO 19-13	NH <sub>4</sub> , ortho-phosphate, pH, Mg, K, NO <sub>3</sub> , Na, Ca, SO <sub>4</sub> , HCO <sub>3</sub> .	gw ct	0,05-2 mg N/l 0,05-2 mg P/l 4-11 pH 0,5-50 mg/l 0,5-50 mg N/l 1-200 mg/l 1-300 mg/l
16 October	VIO 19-15	total-phosphate, ortho-phosphate, anion active detergents, F, DOC, SiO <sub>2</sub> , NO <sub>2</sub> , NH <sub>4</sub> , NO <sub>3</sub> , Kjeldahl-N, Cl, SO <sub>4</sub> , suspended solids, COD (CZV), total cyanide, free cyanide.	ww ct	0,1-5 mg P/l 0,1-10 mg/l NalaurylSO <sub>4</sub> 1-15 mg/l 1-15 mg C/l 1-15 mg Si/l 0,2-20 mg N/l 1-50 mg N/l 0,5-60 mg N/l 5-200 mg/l 7-300 mg O <sub>2</sub> /l 10-350 µg/l
16 October	VIO 19-16 <sup>#</sup>	<b>(Heavy) metals, as total:</b> Ag <sup>+</sup> , Be <sup>+</sup> , Co <sup>+</sup> , Hg, Sb <sup>+</sup> , As, B <sup>+</sup> , Ba <sup>+</sup> , Cd, Mo <sup>+</sup> , Se, Sr <sup>+</sup> , V <sup>+</sup> , Al, Cu, Fe, Mn, Ni, Zn, Cr, Pb, K <sup>+</sup> , Ca <sup>+</sup> , Mg <sup>+</sup> , Na <sup>+</sup> .	ww	0,5-50 µg/l 0,03-5 mg/l 0,03-5 mg/l 0,03-5 mg/l 1-15 mg/l 1-200 mg/l
26 June	VIO 19-17 <sup>**</sup>	Sampling on location in The Netherlands by participant; free chlorine, total chlorine, pH and temperature.	zw	a.l.
10 April	VIO 19-18 <sup>**</sup>	bromide, bromate, chlorate.	dw+sw ck	0,05-1 mg/l 1-10 µg/l 50-500 µg/l
4 September	VIO 19-19 <sup>**</sup>	odour and flavour (organoleptic)	dw ct	-
19 November	VIO 19-20 <sup>**</sup>	Sampling on location in The Netherlands: In addition to 'field parameters' such as O <sub>2</sub> , pH, EGV and temperature, sampling is performed for a number of chemical parameters.	sw	a.l.

dw = drinking water, sw = surface water, gw = ground water, zw = pool water and ww = waste water

ct = cooled transportation  
a.l. = actual level

\* This parameter is not accredited by the Dutch Accreditation Council RvA (R005);  
\*\* This proficiency test is not accredited by the Dutch Accreditation Council RvA (R005).

<sup>#</sup> Proficiency tests VIO 19-01 and VIO 19-12 concerning (heavy) metals to be analysed as 'dissolved'. (Heavy) metals in the proficiency tests VIO 19-09a and VIO 19-16 should be analysed as 'total'.

➤ **For the parameters that are only stable for 24 hours the samples are delivered within 24 hours after preparation in The Netherlands and Belgium.**

## 5.2 Organic parameters

Date	PT code	Parameter	Casnr.	Matrix <sup>1</sup>	Conc. range
30 January	VIO 19-21	<b>extractable organic halogens (EOX)</b>		dw+sw+gw ww <sup>***</sup>	0.02-5 µg/l 10-80 µg/l
30 January	VIO 19-22	<b>adsorbable organic halogens (AOX)</b>		dw+sw+gw ww <sup>***</sup>	2-50 µg/l 100-800 µg/l
22 May	VIO 19-23	<b>organic chlorinated pesticides (OCP)</b>		dw+sw+gw ww <sup>***</sup>	0.002-1 µg/l 0.1-10 µg/l
		aldrin	309-00-2		
		alpha-endosulfan	115-29-7		
		alpha-HCH	319-84-6		
		beta-HCH <sup>**</sup>	319-85-7		
		delta-HCH	319-86-8		
		dieldrin	60-57-1		
		endrin	72-20-8		
		gamma-HCH (lindane)	58-89-9		
		heptachlor	76-44-8		
		heptachlor endo epoxide isomer A	28044-83-9		
		heptachlor exo epoxide isomer B <sup>**</sup>	1024-57-3		
		hexachlorobenzene	118-74-1		
		isodrin <sup>**</sup>	465-73-6		
		o,p'-DDD	53-19-0		
		o,p'-DDE	3424-82-6		
		o,p'-DDT <sup>**</sup>	789-02-6		
		p,p'-DDT	50-29-3		
		p,p'-DDD	72-54-8		
		p,p'-DDE	72-55-9		
		pentachlorobenzene <sup>**</sup>	608-93-5		
		telodrin <sup>**</sup>	297-78-9		
		trans-chlordane <sup>**</sup>	5103-74-2		
22 May	VIO 19-24	<b>polychlorinated biphenyls (PCB)</b>		dw+sw+gw	0.002-1 µg/l
		PCB 28	7012-37-5		
		PCB 52	35693-99-3		
		PCB 101	37680-73-2		
		PCB 118	31508-00-6		
		PCB 138	35065-28-2		
		PCB 153	35065-27-1		
		PCB 180	35065-29-3		
20 March	VIO 19-25	<b>polycyclic aromatic hydrocarbons (PAH)</b>		dw+sw+gw ww	0.02-1 µg/l 0.1-20 µg/l
		acenaphthene	83-32-9		
		acenaphthylene	208-96-8		
		anthracene	120-12-7		
		benzo(a)anthracene	56-55-3		
		benzo(a)pyrene	50-32-8		
		benzo(b)fluoranthene	205-99-2		
		benzo(ghi)perylene	191-24-2		
		benzo(k)fluoranthene	207-08-9		
		chrysene	218-01-9		
		dibenzo(a,h)anthracene	53-70-3		
		fluoranthene	206-44-0		
		fluorene	86-73-7		
		indeno(1,2,3-cd)pyrene	193-39-5		
		naphthalene	91-20-3		
		phenanthrene	85-01-8		
		pyrene	129-00-0		

Date	PT code	Parameter	Casnr.	Matrix <sup>1</sup>	Conc. range		
4 September	VIO 19-26	<b>volatile halogenated hydrocarbons (VHH)</b>		dw+gw	0.1-2 µg/l		
				sw	0.5-2 µg/l		
				ww	2-200 µg/l		
				1,1,1,2-tetrachloro-ethane**	630-20-6		
				1,1,1-trichloro-ethane	71-55-6		
				1,1,2,2-tetrachloro-ethane	79-34-5		
				1,1,2-trichloro-ethane	79-00-5		
				1,1-dichloro-ethane	75-34-3		
				1,1-dichloro-ethene**	75-35-4		
				1,1-dichloropropane**	78-99-9		
				1,1-dichloropropene**	563-58-6		
				1,2,3-trichloropropane	96-18-4		
				1,2-dibromo-3-chloropropane**	96-12-8		
				1,2-dibromo-ethane**	106-93-4		
				1,2-dichloro-ethane	107-06-2		
				1,2-dichloropropane	78-87-5		
				1,3-dichloropropane**	142-28-9		
				2,2-dichloropropane**	594-20-7		
				bromochloromethane	74-97-5		
				bromodichloromethane	75-27-4		
				chloroform (trichloromethane)	67-66-3		
				cis-1,2-dichloro-ethene**	156-59-2		
				cis-1,3-dichloropropene	10061-01-5		
				dibromochloromethane	124-48-1		
				dibromomethane**	74-95-3		
				dichloromethane**	75-09-2		
				hexachloro-1,3-butadiene**	87-68-3		
				hexachloro-ethane**	67-72-1		
				tetrachloro-ethene	127-18-4		
				tetrachloromethane	56-23-5		
				trans-1,2-dichloro-ethene**	156-60-5		
				trans-1,3-dichloropropene	10061-02-6		
				tribromomethane	75-25-2		
				trichloro-ethene	79-01-6		
		trichlorofluoromethane**	75-69-4				
9 October	VIO 19-27	<b>volatile aromatic hydrocarbons (VAH)</b>		dw+gw	0.1-2 µg/l		
				sw	0.5-2 µg/l		
				ww	2-200 µg/l		
				1,2,3-trichlorobenzene**	87-61-6		
				1,2,3-trimethylbenzene	526-73-8		
				1,2,4-trichlorobenzene**	120-82-1		
				1,2,4-trimethylbenzene	95-63-6		
				1,2-dichlorobenzene**	95-50-1		
				1,3,5-trichlorobenzene**	108-70-3		
				1,3,5-trimethylbenzene**	108-67-8		
				1,3-dichlorobenzene**	541-73-1		
				1,4-dichlorobenzene**	106-46-7		
				2-chloromethylbenzene**	95-49-8		
				benzene	71-43-2		
				bromobenzene**	108-86-1		
				chlorobenzene	108-90-7		
				cyclohexane	110-82-7		
				dimethylbenzene, meta+para			
				dimethylbenzene, ortho	95-47-6		
				ethylbenzene	100-41-4		
				ethyl-tertiar-butylether (ETBE)**	637-92-3		
				iso-propylbenzene**	98-82-8		
				methylbenzene (toluene)	108-88-3		
				methyl-tertiar-butylether (MTBE)**	1634-04-4		
				naphthalene	91-20-3		
				n-butylbenzene**	104-51-8		
				n-propylbenzene	103-65-1		
				p-isopropyltoluene**	99-87-6		
		secundair-butylbenzene**	135-98-8				
		styrene (ethenylbenzene)**	100-42-5				
		tertiar-butylbenzene**	98-06-6				



Date	PT code	Parameter	Casnr.	Matrix <sup>1</sup>	Conc. range		
10 April	VIO 19-28**	<b>Pharmaceuticals</b>		dw+sw+gw	0.2-2 µg/l		
		diatrizoic acid	117-96-4				
		bezafibrate	41859-67-0				
		caffeine	58-08-2				
		carbamazepine	298-46-4				
		diclofenac	15307-86-5				
		phenazone	60-80-0				
		ibuprofen	15687-27-1				
		ketoprofen	22071-15-4				
		lincomycin	154-21-2				
		metoprolol	51384-51-1				
		propranolol	525-66-6				
		sotalol	3930-20-9				
sulfamethoxazole	723-46-6						
trimethoprim	738-70-5						
6 March	VIO 19-30	<b>N/P-pesticides</b>		dw+sw+gw	0.05-1 µg/l		
		atrazine	1912-24-9				
		azinfos-methyl**	86-50-0				
		BAM**					
		chlorofenvinfos (cis + trans)					
		cyanazine	21725-46-2				
		DEET**	134-62-3				
		desethylatrazine	6190-65-4				
		desisopropylatrazine	1007-28-9				
		desmetryn	1014-69-3				
		diazinon**	333-41-5				
		dichlorvos	62-73-7				
		dimethoate	60-51-5				
		ethoprophos	13194-48-4				
		malathion**	121-75-5				
		metribuzin	21087-64-9				
		parathion-ethyl	56-38-2				
		parathion-methyl**	298-00-0				
		pirimicarb	23103-98-2				
		prometryne	7287-19-6				
		propazine	139-40-2				
		pyrazofos**	13457-18-6				
		simazine	122-34-9				
		sulfotep**	3689-24-5				
		terbutryn	886-50-0				
		terbutylazine	5915-41-3				
		tetrachlorovinphos**	961-11-5				
		tolclofos-methyl**	57018-04-9				
		<b>chloroacetamides</b>				dw+sw+gw	0.05-1 µg/l
		alachlor	15972-60-8				
metazachlor	67129-08-2						
metolachlor	51218-45-2						
propachlor**	1918-16-7	dw+sw+gw	0.02-1 µg/l				
<b>bromacil</b>	314-40-9						
19 June	VIO 19-31	<b>chlorophenoxyacetic acids (CPCA)</b>		dw+sw+gw	0.05-1 µg/l		
		4,5-trichlorophenoxyacetic acid (2,4,5-T)**	93-76-5				
		2,4,5-trichlorophenoxypropionic acid (2,4,5-TP)**	93-72-1				
		2,4-dichlorophenoxyacetic acid (2,4-D)	94-75-7				
		2,4-dichlorophenoxybutanoic acid (2,4-DB)	94-82-6				
		4-chlorophenoxyacetic acid (4-CPA)**	122-88-3				
		3,6-dichloro-2-methoxybenzoic acid (dicamba)	1918-00-9				
		2-(2,4-dichlorophenoxy)-propanoic acid (dichlorprop)	120-36-5				
		(4-chloro-2-methylphenoxy)acetic acid (MCPA)	94-74-6				
		4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB)	94-81-5				
		2-(2-methyl-4-chlorophenoxy)propionic acid (MCP)	93-65-2				
		<b>bentazone</b>	25057-89-0			dw+sw+gw	0.02-1 µg/l

Date	PT code	Parameter	Casnr.	Matrix <sup>1</sup>	Conc. range
6 November	VIO 19-32	<b>Phenylurea herbicides (PUH)</b> chlorbromuron chlortoluron diuron isoproturon linuron methabenzthiazuron metobromuron metoxuron monolinuron monuron	13360-45-7 15545-48-9 330-54-1 34123-59-6 330-55-2 18691-97-9 3060-89-7 19937-59-8 1746-81-2 150-68-5	dw+sw+gw	0.02-1 µg/l
10 April	VIO 19-34**	<b>Glyphosate and AMPA</b> Glyphosate AMPA	1071-83-6 1066-51-9	dw+sw+gw	0.05-0.5 µg/l
6 November	VIO 19-38	<b>Mineral oil, only with the GC method</b>		ww	0.05-200 mg/l
19 June	VIO 19-39a**	<b>chloridazon, dimethenamid-P and metabolites</b> chloridazon desphenylchloridazon dimethenamid-P methyl-desphenylchloridazon	1698-60-8 6339-19-1 163515-14-8 17254-80-7	dw+sw+gw	0.05-2 µg/l
25 September	VIO 19-39b**	<b>non target screening, semi- quantitative</b> (semi)-quantification of various organic compounds using a LC-MS		dw+gw sw ww	0.1-1 µg/l 0.1-2 µg/l 1-10 µg/l
<sup>1</sup> dw = drinking water, sw = surface water, gw = ground water and ww = waste water					
* This compound is not accredited by the Dutch Accreditation Council RvA (R005);					
** This proficiency test is not accredited by the Dutch Accreditation Council RvA (R005);					
*** The matrix waste water is not accredited by the Dutch Accreditation Council RvA (R005).					
<b>All organic samples are cooled transported</b>					

## 5.3 Microbiological parameters

Date	PT code	Parameter	Matrix	Concentration range
12 February	VIO 19-41	bacteria of the coli group <i>E. coli</i> enterococci sulphite reducing clostridia (SRCs) <i>Clostridium perfringens</i> plate count 22°C plate count 36°C	dw	0-80 cfu /100 ml     0-300 cfu /ml
15 October	VIO 19-42	bacteria of the coli group <i>E. coli</i> enterococci <i>Aeromonas</i> 30°C <i>Aeromonas</i> 37°C sulphite reducing clostridia (SRCs) <i>Clostridium perfringens</i>	dw	0-80 cfu /100 ml
4 June	VIO 19-43	bacteria of the coli group <i>E. coli</i> <i>Aeromonas</i> 30°C <i>Aeromonas</i> 37°C plate count 22°C plate count 36°C	dw	0-80 cfu /100 ml     0-300 cfu /ml
13 March	VIO 19-45	<i>Legionella</i>	dw	0-30.000 cfu /l
15 May	VIO 19-46	<i>Legionella</i>	dw	0-30.000 cfu /l
4 September	VIO 19-47	<i>Legionella</i>	dw	0-30.000 cfu /l
26 March	VIO 19-48	ATP (Adenosine triphosphate) Colonies on R <sub>2</sub> A-medium (plate count)	diluted sw+dw*	0-100 ng/l 0-20.000 cfu /ml
11 September	VIO 19-50	<i>Salmonella</i> staphylococci <i>Pseudomonas aeruginosa</i>	dw	0-80 cfu /100 ml
25 June	VIO 19-53**	bacteria of the coli group thermotolerant bacteria of the coli group <i>E. coli</i> Faecal streptococci (intestinal) enterococci	sw	0-8.000 cfu /100 ml
25 September	VIO 19-54**	bacteria of the coli group thermotolerant bacteria of the coli group <i>E. coli</i> Faecal streptococci (intestinal) enterococci	sw	0-8.000 cfu /100 ml
13 March	VIO 19-55**	<i>Legionella</i>	kw	0-30.000 cfu /l
4 September	VIO 19-56**	<i>Legionella</i>	kw	0-30.000 cfu /l
13 March	VIO 19-59**	<i>Legionella pneumophila</i> qPCR	dw	0-1 · 10 <sup>6</sup> DNA-copies/l
13 March	VIO 19-61**	<i>Legionella pneumophila</i> qPCR	kw	0-1 · 10 <sup>6</sup> DNA-copies/l
11 September	VIO 19-62**	F-specific RNA-phages and somatic coli- phages	dw	0-150 pve/ml
26 March	VIO 19-63**	Total bacterial cell counting (incl. fraction dead and alive), flowcytometric	dw	1 · 10 <sup>3</sup> -1 · 10 <sup>6</sup> cells/ml

cfu = colony forming unit, dw = drinking water, sw = surface water, kw = cooling-water

\* In this PT, ATP is offered in drinking water and this matrix is not accredited by Dutch Accreditation Council (R005).

\*\* This proficiency test is not accredited by the Dutch Accreditation Council RvA (R005).

**Cooled transportation is provided for all microbiological samples. All samples are delivered within 24 hours after preparation in The Netherlands and Belgium.**

## Subscription form KWR Proficiency Tests 2019

You can indicate which proficiency tests you want subscription. You will receive a confirmation of participation.

PT	Description	Matrix	Price
<input type="checkbox"/> VIO 19-01	(Heavy) metals, as dissolved	dw	€ 1.185
<input type="checkbox"/> VIO 19-02	General- and macro parameters	dw	€ 1.670
<input type="checkbox"/> VIO 19-06	Urea, cyanuric acid, KMnO <sub>4</sub> , free chlorine and total chlorine	zw	€ 890
<input type="checkbox"/> VIO 19-07	Nutrients	sw	€ 1.600
<input type="checkbox"/> VIO 19-09a	(Heavy) metals, as total	sw	€ 1.185
<input type="checkbox"/> VIO 19-09b	Arsenic-3, arsenic-5, chromium-3 en chromium-6	sw	€ 495
<input type="checkbox"/> VIO 19-12	(Heavy) metals, as dissolved	gw	€ 1.125
<input type="checkbox"/> VIO 19-13	General- and macro parameters	gw	€ 1.240
<input type="checkbox"/> VIO 19-15	General- and macro parameters	ww	€ 1.240
<input type="checkbox"/> VIO 19-16	(Heavy) metals, as total	ww	€ 945
<input type="checkbox"/> VIO 19-17	Sampling on location in The Netherlands	zw	€ 475
<input type="checkbox"/> VIO 19-18	Bromide, bromate and chlorate	dw+sw	€ 495
<input type="checkbox"/> VIO 19-19	Odour and flavour, organoleptic	dw	€ 480
<input type="checkbox"/> VIO 19-20	Sampling on location in The Netherlands	sw	€ 630
<b>Total contribution inorganic proficiency tests</b>			<b>€</b>

dw = drinking water, sw = surface water, gw = ground water, ww = waste water and zw = pool water

PT	Description	Matrix	Price
<input type="checkbox"/> VIO 19-21	Extractable organic halogens (EOX)	dw sw gw ww	€ 1.005
<input type="checkbox"/> VIO 19-22	Adsorbable organic halogens(AOX)	dw sw gw ww	€ 1.005
<input type="checkbox"/> VIO 19-23	Organic chlorinated pesticides (OCP)	dw sw gw ww	€ 1.170
<input type="checkbox"/> VIO 19-24	Polychlorinated biphenyls (PCB)	dw sw gw	€ 915
<input type="checkbox"/> VIO 19-25	Polycyclic aromatic hydrocarbons (PAH)	dw sw gw ww	€ 1.040
<input type="checkbox"/> VIO 19-26	Volatile halogenated hydrocarbons (VHH)	dw sw gw ww	€ 1.185
<input type="checkbox"/> VIO 19-27	Volatile aromatic hydrocarbons (VAH)	dw sw gw ww	€ 1.185
<input type="checkbox"/> VIO 19-28	Pharmaceuticals	dw sw gw	€ 1.185
<input type="checkbox"/> VIO 19-30	N/P-pesticides	dw sw gw	€ 1.170
<input type="checkbox"/> VIO 19-31	Chlorophenoxyacetic acids (CPCA)/bentazone	dw sw gw	€ 1.185
<input type="checkbox"/> VIO 19-32	Phenylurea herbicides (PUH)	dw sw gw	€ 910
<input type="checkbox"/> VIO 19-34	Glyphosate and AMPA	dw sw gw	€ 1.005
<input type="checkbox"/> VIO 19-38	Mineral oil, only with GC method	ww	€ 255
<input type="checkbox"/> VIO 19-39a	Chloridazon, dimethenamid-P and metabolites	dw sw gw	€ 910
<input type="checkbox"/> VIO 19-39b	Non-target screening, semi-quantitative LC-MS	dw sw gw ww	€ 1.005
<b>Total contribution organic proficiency tests</b>			<b>€</b>

dw = drinking water, sw = surface water, gw = ground water and ww = waste water

PT	Description	Matrix	Price
<input type="checkbox"/> VIO 19-41	Bacteriological parameters	dw	€ 875
<input type="checkbox"/> VIO 19-42 <sup>#1</sup>	Bacteriological parameters	dw	€ 875
<input type="checkbox"/> VIO 19-43	Bacteriological parameters	dw	€ 875
<input type="checkbox"/> VIO 19-45	<i>Legionella</i>	dw	€ 580
<input type="checkbox"/> VIO 19-46 <sup>#1</sup>	<i>Legionella</i>	dw	€ 580
<input type="checkbox"/> VIO 19-47	<i>Legionella</i>	dw	€ 580
<input type="checkbox"/> VIO 19-48	ATP/Colonies on R <sub>2</sub> A-medium	diluted sw + dw	€ 910
<input type="checkbox"/> VIO 19-50	<i>Salmonella</i> , staphylococci and <i>Pseudomonas aeruginosa</i>	dw	€ 875
<input type="checkbox"/> VIO 19-53	Bacteriological parameters	sw	€ 875
<input type="checkbox"/> VIO 19-54 <sup>#1</sup>	Bacteriological parameters	sw	€ 875
<input type="checkbox"/> VIO 19-55	<i>Legionella</i>	kw	€ 580
<input type="checkbox"/> VIO 19-56 <sup>#1</sup>	<i>Legionella</i>	kw	€ 580
<input type="checkbox"/> VIO 19-59	<i>Legionella pneumophila</i> qPCR	dw	€ 525
<input type="checkbox"/> VIO 19-61	<i>Legionella pneumophila</i> qPCR	kw	€ 525
<input type="checkbox"/> VIO 19-62	F-specific RNA-phages and somatic coli-phages	dw	€ 655
<input type="checkbox"/> VIO 19-63	Total bacterial cell counting (incl. fraction dead and alive), flowcytometric	dw	€ 655
<sup>#1</sup> This proficiency test is optional. Only if there are enough participants this test will go on.			€
<b>Total contribution microbiological proficiency tests</b>			€

dw = drinking water, sw = surface water and kw = cooling water

Total contribution proficiency tests			€
<b>Discount</b>	participation in 5-9 proficiency tests	- 5%	- €
	participation in 10-19 proficiency tests	- 10%	- €
	participation in > 20 proficiency tests	- 15%	- €
<b>Total contribution in euros</b>			€
✓ When less than eight participants subscribe, KWR reserves the right to cancel the proficiency test. You will then be informed by email in time.			
✓ The total costs will be invoiced in two equal amounts, unless other agreements are made with you. If changes in your order occur during the year, an adapted cost accounting will be handled in the second period.			
✓ The prices in the program are excluding carriage costs. Transport costs, based on actual transportation costs by post-calculation, will be charged.			
✓ If you wish to cancel a proficiency test, you need at least four weeks before the date of receipt of the proficiency test notify us in writing. After this period the costs of the test will be charged.			
✓ The General Terms and Conditions for the Supply of Goods and Provision of Services and Purchase placed with KWR are applied on this tender. You can find these terms and conditions on KWR website <a href="http://www.kwrwater.nl/voorwaarden/">www.kwrwater.nl/voorwaarden/</a> .			
		<b>Your data</b>	
<b>Company</b>		<b>Date of entry</b>	
<b>Correspondention attn.</b>			
<b>Telephone</b>			
<b>PO-box</b>		<b>Client</b>	
<b>Zip code/Place/Country</b>			
<b>Samples attn.</b>			
<b>Telephone</b>		<b>Autograph</b>	
<b>Address</b>			
<b>Zip code/Place/Country</b>			
<b>Email</b>			
<b>Company</b>			

## 6 Lay-out of the final report

### 6.1 Samples and standardsolutions

The chemical proficiency tests of KWR use the so-called Youden. This implies that per parameter at least two samples are distributed for analysis. These two samples are practically identical for the parameter to be analysed. There is only a slight difference in concentration between the two samples, by adding known amounts of the parameter (by 'spiking'). This lay-out enables participants to obtain a good indication if deviating results are caused by systematic errors and/or by relatively large random errors. The within laboratory reproducibility and/or repeatability of the individual participants are not tested. Because of the difference in concentration between the samples of a Youden pair is known (theoretical value), the accuracy can also be assessed. Unfortunately, for a number of parameters this is not possible since they are part of an equilibrium (e.g. carbonate and hydrogen carbonate), or because some parameters are not stable over a longer period of time (e.g. nitrite; because of bacterial activity the concentration of nitrite will decrease in time). In these situations an indication of the theoretical value will be given if possible.

In a number of chemical proficiency tests also one or two standard solutions (the parameter to be analysed is added to a solvent matrix or ultra-pure water) are offered. It is known that for many analytical methods matrix problems and/or problems with preparation and pre-concentration of the sample play a role. To examine this and to simplify the interpretation of the analytical results, one or two standard solutions are offered for analysis. The results for the standard solutions are not involved in the final assessment (report mark and Z-scores).

In the microbiological proficiency tests, the Youden lay-out is not applied. In these tests four samples are usually being distributed. Every sample is assessed separately and furthermore one combined assessment is given for all four samples (Good, Moderate, Bad).

#### 6.1.1 *Criteria minimum number of laboratory results*

The minimum number of laboratory results (observations for a parameter/sample set combination) that must be present in order to perform statistical analysis on has been set at eleven results. If the number of laboratory results is less than eleven, then the usual statistical key figures (mean, standard deviation, etc.) including the Z-scores were calculated. Only the judgment (Good, Moderate, Bad) based on the Z-scores than omitted. And if there are less than four laboratory results, the Youden plots (only for chemical tests) are not made.

#### 6.1.2 *Consensus Value as assigned value*

The arithmetic mean of the results of the participants after removal of outliers – the consensus value – is used as assigned value for the calculation of the Z-score compared to the group average, so based on this Z-score the participant can be assessed compared to the group average.

#### 6.1.3 *Difference from additions as assigned value*

For some chemical proficiency testing the difference addition from Youden sample-pairs – referred to as the theoretical value – is also used as assigned value. Since its information can be obtained on the addition-recovery and a systematic error of the measurement (both important for the report mark). Furthermore, for each participant the Z-score compared to the theoretical value ( $Z_t$ ) is calculated.

## 6.2 Graphical presentation of the results

In the final report a graphical presentation is given by means of a saw tooth plot and, if applicable, a Youden plot (see also figures 1 and 2). Furthermore, a graphical presentation of the Z-score is given (see figure 6).

### 6.2.1 Sawtooth plot

The saw tooth plot is a graphical representation of the results of all participants for a standard solution and for the samples. On the x-axis the random numbers are shown and on the y-axis the measured values. Using the saw tooth plot, the individual result of each of the laboratories can be compared with the results of the other participating laboratories. In the plots, the results of the participating laboratories are displayed without any outliers.

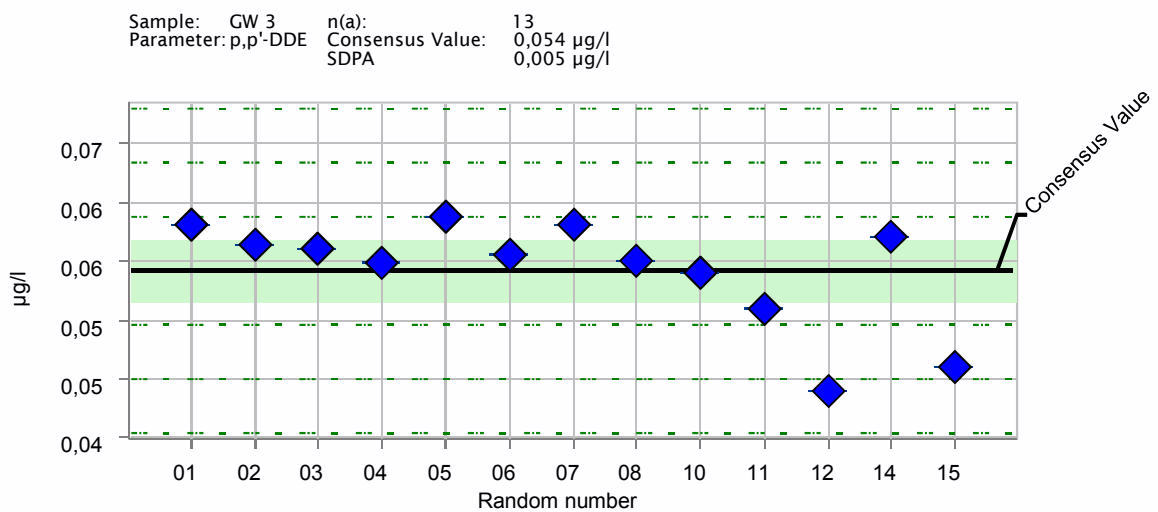


Figure 1: Example of a sawtooth plot

The dotted lines in the graph show  $1 \times$  SDPA,  $2 \times$  SDPA and  $3 \times$  SDPA respectively. The light green marked part concerns the 95% confidence interval.

### 6.2.2 Youden plot

The Youden plot is a graphical representation of the results for the two samples of a Youden pair. For each laboratory, the result of the first sample (on the x-axis) is plotted against the result of the second sample (on the y-axis). The lines perpendicular to the x-axis and the y-axis are the averages of the two samples. The radius of the circles are determined by the standard deviation caused by random errors. If there are no systematic errors, with a normal distribution about 95% of the results will lie within the smallest circle and about 99% of the results will lie within the largest circle. Furthermore, the results will also be equally distributed over the four quadrants. Also, a 45°-line through the 1st and 3rd quadrant is also displayed in the plot. From the Youden plot it can be established whether the mistake made is accidental or systematic.

To apply the special statistics, as developed by Youden, the following conditions must be met:

- the minimum number of participants is 4 (after also applying the test on outliers);
- the random error is of the same level for all laboratories;
- the systematic error for both samples is of the same order of magnitude within one laboratory;
- to enable a sound interpretation of the circles in the Youden plot, the results should come from a normal distribution.

The following interpretation can be made from the Youden plot:

The further away a laboratory is from the center of the plot along the diagonal line, the greater a systematic error of that laboratory. Laboratories that lie within the radius show neither systematic error nor poor repeatability at the indicated significance level (5%, 1% or 0.1%).

Systematic errors will cause observations to occur in the first and third quadrant of the Youden plot. When there are no random errors all points will lie on the 45°-line that passes through the 1st and 3rd quadrant (the 1st quadrant is situated top right, the other ones run up clockwise). With random errors, inevitable in practice, in combination with detectable systematic errors the points will lie in a drawn-out ellipse round the 45°-line. The length of the perpendicular from the plotted point of the laboratory to the 45°-line will be a measure for the random error of that laboratory. The distance along the 45°-line, from the centre of the circle to the point of intersection with the perpendicular is a measure for the systematic error of the laboratory. The Youden plot concerns only one combined observation in time, therefore no more than a global indication of the type of errors (random or systematic) can be obtained. When a laboratory has participated in more inter-laboratory test comparisons with the same parameters, the results can indeed confirm a pattern in the type of errors.

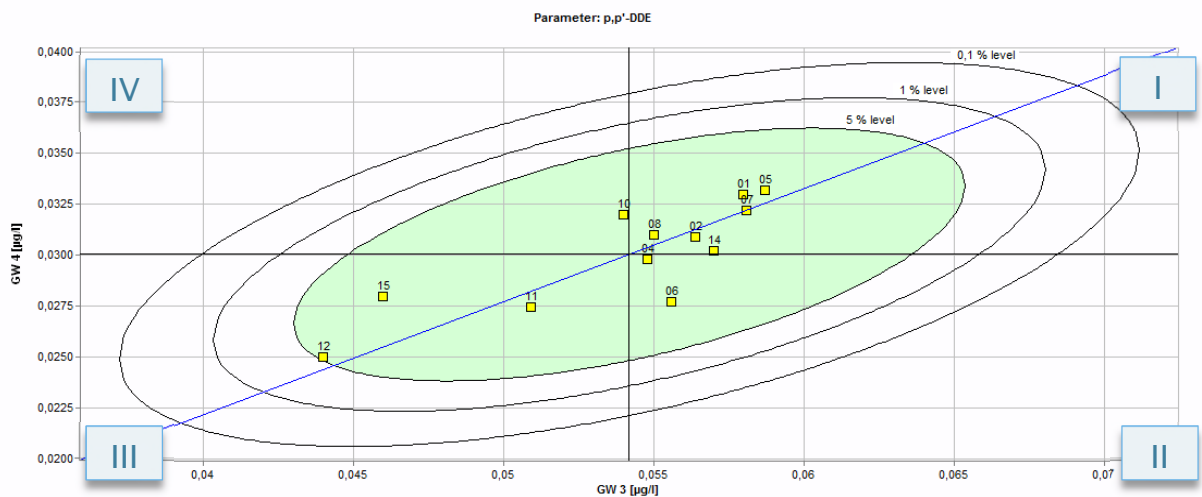


Figure 2: Example of a Youden plot



Some examples of how to interpret a Youden plot are given below.

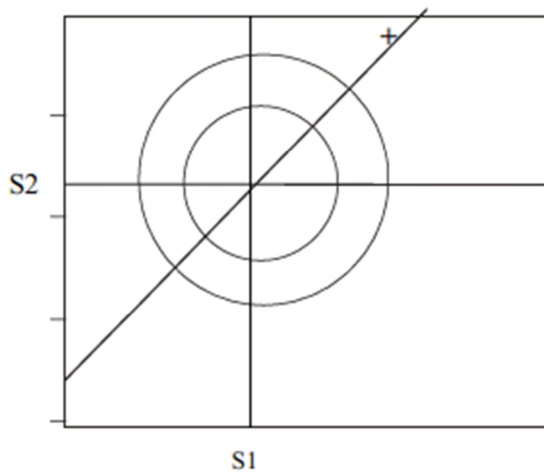


Figure 3: Example of a large systematic error, above the average of the group

In this example the results of a participant are shown with a '+'. The samples (S1 and S2) are samples from one Youden pair. There is only a slight difference in concentration between the two samples. On the x-axis the result of sample 1 is plotted and on the y-axis the result of sample 2. In this graph you can clearly see that the reported concentrations for both sample 1 and sample 2 are too high. This indicates the presence of a large systematic error. It is possible that this participant has a problem with its blank procedure.

The same as in figure 3, but now the participant is analysing systematically too low. A low recovery could be the problem. The length of the perpendicular (dotted line) to the 45°-line is representative for the size of the random error. The distance along the 45°-line, from the centre of the circle to the point of intersection with the perpendicular represents the size of the systematic error. Most errors will be a combination of random and systematic errors.

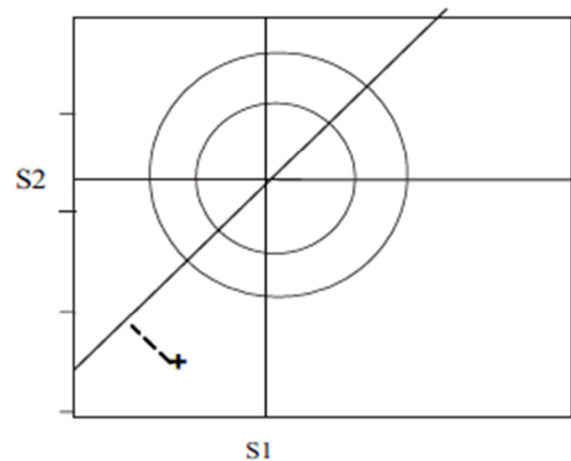


Figure 4: Example of a large systematic error, below the average of the group

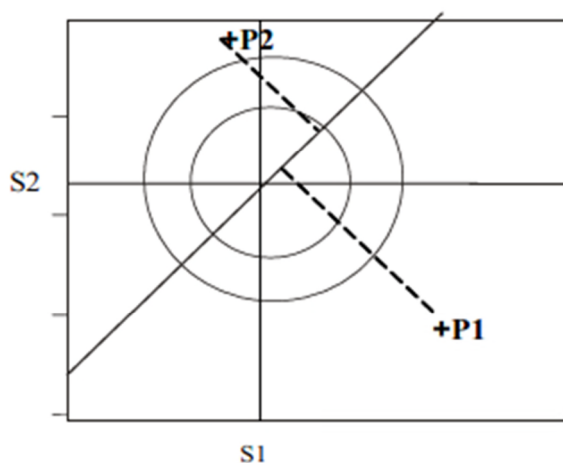


Figure 5. Example of random errors

In this plot two examples of random errors are given. Participant 1 (P1) finds for sample 1 a higher value and for sample 2 a lower value than the average value of the group. Both samples are not correctly analysed and/or reported. This may indicate a sample exchange. Participant 2 (P2) scores very close to the average group value for sample 1, but for sample 2 far above the average group value and for both samples (Youden) outside the 2s border. It is not possible to draw a conclusion on systematic basis and therefore these errors may be considered as random. You could think of a once-only error, e.g. adding no reagent samples during the analysis.

When a participant has a deviating score or is even an outlier, it is of utmost importance to find the cause(s). KWR Watercycle Research Institute herewith would like to point out that it is absolutely useful first to check for trivial causes, such as sample exchange, typing errors, dilution errors etc. Research performed by KWR Watercycle Research Institute in 1996 showed that 30% of all proficiency testing relating errors were trivial. This first check is very easy to perform with a fairly large chance of getting results. When no causes are found after this first and quick check, it is useful to check the analytical method applied.

### 6.3 Rapportcijfer

The report mark gives an idea of the performance of a group on a scale of 0 to 10, and is an instrument to assess group performances over a longer period of time. It can be used to identify for which parameters the analytical method has to be reconsidered or to see certain trends in results as a consequence of (inter)national harmonisation of analytical methods. The report mark is only calculated in the chemical proficiency tests.

The mark is calculated by weighing the scores for the following items:

- percentage of outliers (the outliers in the group of differences of the two results of a Youden pair);
- recovery of the spike, where applicable;
- occurrence of systematic errors (only with normal distribution of the results);
- coefficient of variation of the reproducibility.

The report marks are calculated per real sample matrix and per parameter. However, in some cases no 'theoretical value' is known. Consequently, it is not possible to calculate a recovery of the spike or a systematic error with regard to the theoretical value (known as "systematic error with marginal note"). In these cases an alternative report mark will be calculated that does not take into account these two items. This alternative report mark is always calculated. The table with the basic statistics for the calculation of the report mark also presents a standard deviation of the repeatability (sr); this can be seen as an average for the participating group. The special Youden lay-out enables the calculation of this statistical number, even though there are no repeated measurements. An underlying assumption however, is that in each laboratory both samples were analysed in the same series of measurements

*Example of a report mark calculation of a Youden pair with known theoretical value:*

VIO xx-xx, parameter y Samples: S1, S2	Youden pair $\delta = 0,0800 \text{ mg/l}$	Score
Participating laboratories	15	
Outliers	(0) 0 %	10
Remaining laboratories	15	
Normal distribution	Yes	Yes
Average difference	-0,0554 ug/l	
Median difference	-0,0560 ug/l	
Recovery of spike	79,1 %	6
Syst. Error of the measurement	1%>=P	0
Syst. Error between laboratories	1%>=P	0
Group average result	0,1177 ug/l	
Stand.dev. repeatability	0,0129 ug/l	
Stand.dev. reproducibility	0,0283 ug/l	
Coëff. of var. reproducibility	24,0%	6
Report Mark	<b>5,5</b>	<b>7,3</b> alternative *

## 6.4 Z-score

To enable a participant in a proficiency test to assess his or her results in an equivocal way, Z-scores are presented. Z-scores are an internationally accepted way to assess the performance of an individual laboratory. It also enables participants to follow their own performance in time. The Z-score presents the deviation from the group average or the theoretical value and is related to the standard deviation of the group.

For the assessment of the performance of one's own laboratory, a distinction is made between the assessment of the following performances:

- of one's own laboratory with regard to the group average;
- of one's own laboratory with regard to the theoretical value (the real difference in spikes of the two samples) and
- of one's own laboratory in time (not given in the final report)

For the calculation of the Z-scores with regard to the group average, the standard deviation of the reproducibility ( $s_R$ ) of the individual samples is used.

For the calculation of the Z-scores with regard to the theoretical value, KWR Watercycle Research Institute has chosen to use the standard deviation of the repeatability ( $s_r$ ), which is calculated from the Youden pair.

If there are less than 11 results, after removal of outliers, KWR chooses to make the calculation of the average and the standard deviation to calculate alternative Z-scores ( $Z_{alt}$  - score) wherein the uncertainty of the value assigned to (consensus value) is included. This is an approach which is also specified in ISO 13528.

The various Z-scores are also presented graphically. An example is shown in figure 6.

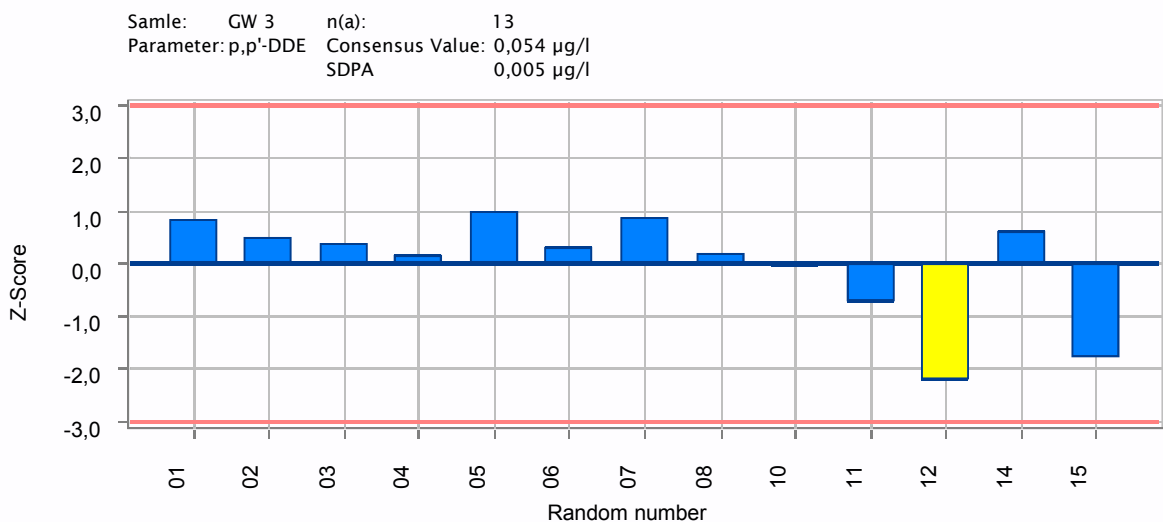


Figure 6: Example of the graphical presentation of the Z-scores

