

KWR | November 2016

KWR Proficiency Testing Services

Program for 2017



KWR | November 2016

KWR Proficiency Testing Services Program for 2017

KWR | November 2016

Order number 401759

Project manager Ronald Italiaander

Client(s) Participating laboratories

Author Asmaïl Asgadaouan

Sent to Interested laboratories



Year of publication 2016

More information Asmail Asgadaouan +31 (0)30 60 69 595

pt@kwrwater.nl Е

PO Box 1072 3430 BB Nieuwegein The Netherlands

+31 (0)30 60 69 511 F +31 (0)30 60 61 165 info@kwrwater.nl Е www.kwrwater.nl





KWR | November 2016 © KWR

Al rights reserved. No part of this publication may be reproduce, stored in a database or retrieval system, or published, in any form or in any way, electronically, mechanically, by print, photo print, microfilm or any other means without prior written permission from the Publisher.

Content

| 1 | Introduction | 5 |
|-----|--|----|
| 1.1 | General | 5 |
| 1.2 | KWR proficiency testing | 5 |
| 2 | General Information | 7 |
| 2.1 | Subcription | 7 |
| 2.2 | Per proficiency test | 7 |
| 2.3 | Distribution of the samples and returning of packaging materials | 8 |
| 2.4 | Reporting your results | 8 |
| 2.5 | Reporting by KWR | 8 |
| 2.6 | Information | 8 |
| 3 | Program 2017 | 9 |
| 3.1 | How to make a choice | 9 |
| 3.2 | Changes in the program 2017 | 9 |
| 3.3 | Order confirmation and invoice | 10 |
| 3.4 | Discounts | 10 |
| 3.5 | Cancelling an order | 10 |
| 3.6 | KWR PT program 2017 and subscription form | 10 |
| 4 | General overview KWR Proficiency Tests 2017 | 11 |
| 5 | Parameter specifications for PT | 12 |
| 5.1 | Gerenal- and Inorganic parameters and (heavy) metals | 12 |
| 5.2 | Organic parameters | 14 |
| 5.3 | Microbiological parameters | 18 |
| 6 | Lay-out of the final report | 21 |
| 6.1 | Samples and standardsolutions | 21 |
| 6.2 | Graphical presentation of the results | 22 |
| 6.3 | Report mark | 25 |
| 6.4 | Z-score | 26 |

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 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 2017 together with the subscription form can be found in chapter 3. In chapter 4 an extended explanation of the layout and statistics of the KWR Watercycle Research Institute proficiency tests is given.

2 General Information

2.1 Subcription

This brochure contains the program for the KWR proficiency tests for 2017. 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 2 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 2 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 4 for an extended explanation of the lay-out, applied statistics and the report.

2.6 Information

For further information and requests, please contact:

- Asmaïl Asgadaouan (phone: +31 30 606 95 95) e-mail: <u>Asmail.Asgadaouan@kwrwater.nl</u> or
- Marieke ten Broeke (phone: +31 30 606 96 12) e-mail: <u>Marieke.ten.Broeke@kwrwater.nl</u> or
- Send an email to: pt@kwrwater.nl

3 Program 2017

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 2017.

3.1.1 Inorganic parameters

For the tests VIO 17-06 (urea, cyanuric acid, free chlorine, bound chlorine and $KMnO_4$ 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 17-38).

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 2017

The program KWR proficiency tests for 2017 relative to previous years, some changes have been made.

- At the chemical proficiency tests:
 - The proficiency test (VIO xx-20 "organic nanoparticles (fullerenes) in surface) has been removed from the program;
- At the microbiological proficiency tests:
 - Legionella pneumophila qPCR in drinking water and Legionella pneumophila qPCR in cooling water will only be organized in September 2017 and not, as in previous years in March and September;
 - In this program the profeiency 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 17-42: Microbiological parameters in drinking water (plan date: April 5, 2017);
 - VIO 17-46: Legionella in drinking water (plan date: May 31, 2017);
 - VIO 17-54: Microbiological parameters in surface water (plan date: September 6, 2017).

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% discountParticipation in 10-19 proficiency tests:10% discountParticipation 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 <u>www.kwrwater.nl/voorwaarden/</u>.

3.5 Cancelling an order

If you wish to cancel a collaborative study, you need at least <u>four</u> 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 2017 and subscription form

On pages 12 to 18 you will find our detailed program and on pages 19 and 20 the subscription form for 2017.

You can subscribe for the KWR proficiency tests by using the subscription form. Please do this at least <u>four</u> 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: <u>Marieke.ten.Broeke@kwrwater.nl</u> or <u>pt@kwrwater.nl</u>

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

4 General overview KWR Proficiency Tests 2017

| Date | Number | Matrix | Description |
|--------------|-------------------------|-------------|--|
| 1 February | VIO 17-21 | dw+sw+gw+ww | extractable and organic halogens (EOX) |
| 1 February | VIO 17-22 | dw+sw+gw+ww | adsorbable organic halogens (AOX) |
| 14 February | VIO 17-41 | dw | ♦ microbiological parameters |
| 22 February | VIO 17-30 | dw+sw+gw | herbicides |
| 8 March | VIO 17-02 | dw | ◊ general- and macro parameters |
| 15 March | VIO 17-48 | dsw | ATP (Adenosine Tri Phosphate)/ Colonies on R ₂ A medium |
| 15 March | VIO 17-62 | dw | ♦ F-specific RNA-phages and Somatic coli-phages |
| 15 March | VIO 17-63 | dw | \diamond Total bacterial cell counting (incl. fraction dead and alive) using a flowcytometer |
| 22 March | VIO 17-25 | dw+sw+gw+ww | polycyclic aromatic hydrocarbons (PAH) |
| 29 March | VIO 17-45 | dw | ◊ Legionella |
| 29 March | VIO 17-55 | kw | |
| 5 April | VIO 17-07 | SW | ◊ nutrients |
| 5 April | VIO 17-18 | dw+sw | bromide, bromate and chlorate |
| 5 April | VIO 17-28 | dw+sw+gw | pharmaceuticals |
| 5 April | VIO 17-34 | dw+sw+gw | glyphosate and AMPA |
| 5 April | VIO 17-42 ^{#1} | dw | microbiological parameters |
| 16 May | VIO 17-50 | dw | Salmonella, Pseudomonas aeruginosa, staphylococci |
| 17 May | VIO 17-09a | SW | (heavy) metals, as total |
| 17 May | VIO 17-09b | SW | arsenic-3, arsenic-5, chromium-3 and chromium-6 |
| 17 May | VIO 17-12 | gw | (heavy) metals, as dissolved |
| 17 May | VIO 17-23 | dw+sw+gw+ww | pesticides (OCP) |
| 17 May | VIO 17-24 | dw+sw+gw | pesticides (PCB) |
| 31 May | VIO 17-46 ^{#1} | dw | |
| 14 June | VIO 17-31 | dw+sw+gw | chlorophenoxycarbonic acids (CPCA)/bentazone |
| 14 June | VIO 17-39a | dw+sw+gw | chloridazon, dimethenamid-P and metabolites |
| 14 June | VIO 17-53 | SW | |
| 21 June | VIO 17-06 | ZW | \diamond urea, cyanuric acid, free chlorine, bound chlorine, KMnO $_{_4}$ |
| 21 June | VIO 17-17 | ZW | Sampling swimming water on location in The Netherlands |
| 6 September | VIO 17-01 | dw | (heavy) metals, as dissolved |
| 6 September | VIO 17-19 | dw | odor and flavour (organoleptic) |
| 6 September | VIO 17-26 | dw+sw+gw+ww | volatile halogenated hydrocarbons (VHH) |
| 6 September | VIO 17-54 ^{#1} | SW | ♦ microbiological parameters |
| 13 September | VIO 17-47 | dw | ◊ Legionella |
| 13 September | VIO 17-56 | kw | ◊ Legionella |
| 13 September | VIO 17-59 | dw | ◊ Legionella pneumophila qPCR |
| 13 September | VIO 17-61 | kw | ◊ Legionella pneumophila qPCR |
| 27 September | VIO 17-39b | dw+sw+gw+ww | Non-target screening, semi-quantitative using a LC-MS |
| 11 October | VIO 17-27 | dw+sw+gw+ww | volatile aromatic hydrocarbons (VAH) |
| 17 October | VIO 17-43 | dw | microbiological parameters |
| 18 October | VIO 17-15 | ww | general- and macro parameters |
| 18 October | VIO 17-16 | ww | (heavy) metals, as total |
| 8 November | VIO 17-13 | gw | general- and macro parameters |
| 8 November | VIO 17-32 | dw+sw+gw | phenylureaherbicides (PUH) |
| 8 November | VIO 17-38 | ww | mineral oil |

^{#1} 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).

5 Parameter specifications for PT

5.1 Gerenal- and Inorganic parameters and (heavy) metals

| Date | Number | Parameter | Matrix | Concentratio | on range |
|-------------|--------------|---|----------|--|---|
| 6 September | VIO 17-01# | (Heavy)metals, as dissolved: Hg, Cd, Ag [*] , Be [*] , Co [*] , V [*] Al, As, Cr, Pb, Sb, Se, Sr [*] Cu, Ni, Zn, B, Ba, Fe, Mn, K, Mg, Na, Ca, total hardness. | dw | 0,1-1 0,1-10 1-70 1-200 1-350 0,5-50 1-200 0,5-6 | μg/l μg/l μg/l μg/l μg/l mg/l mg/l mmol/l |
| 8 March | VIO 17-02 | NO ² , F, NH₄, turbidity, DOC, NO ³ , SO₄, Cl, ortho-phosphate, total-phosphate, pH, SiO ₂ , color, CO ₃ , EGV (25°C), HCO ₃ , total cyanide. | dw ct | 0,02-0,2 0,05-2 0,1-2,5 0,1-15 0,5-50 1-200 10-200 0,05-2 4-11 0,1-15 2-20 0,5-50 10-150 1-300 2,5-350 | mg N/l mg/l mg N/l FNE mg C/l mg N/l mg/l mg/l mg P/l pH mg Si/l mg Pt/l mg/l mS/m mg/l μg/l |
| 21 June | VIO 17-06 | urea, cyanuric acid, free chlorine, bound chlorine, KMnO4°. | zw ct | 0,5-5 5-15 0,1-20 0,1-20 | mg/l mg/l mg/l mg/l |
| 21 June | VIO 17-17** | Sampling on location by participant; free chlorine, bound chlorine, pH and temperature. | ZW | a.l. | |
| 5 April | VIO 17-07 | NH4, NO2, NO3, ortho-phosphate, anion active detergents, F, Kjeldahl-N, total-phosphate, COD (CZV), SiO2, UV-absorption, color, SO4, Cl, suspended matter, oxygen (dissolved). | sw ct | 0,02-2 0,05-3 0,02-2,5 0,02-2,5 0,05-3 0,02-2 1-15 1-15 0,1-20 2-20 1-200 a.l. 1-15 | mg N/l mg P/l mg/l NalaurylSO4 mg/l mg N/l mg P/l mg O ₂ /l mg Si/l E/m mg Pt/l mg/l mg/l mg O ₂ /l |
| 17 May | VIO 17-09a* | (Heavy)metals, as total: Be, Cd, Hg, Ag [°] , Sb [°] , Cr, As, Se, V, Co, Al, Pb, Cu, Zn, Ni, Ba, Fe, Mn, K, Ca, Mg, Na. | sw | 0,1-10 1-70 1-500 0,01-1 1-15 1-200 | μg/l μg/l μg/l mg/l mg/l mg/l |
| 17 May | VIO 17-09b** | arsenic-3, arsenic-5 chromium-3, chromium-6 | SW | 0,1-10 0,1-10 | μg/l μg/l |

| Date | Number | Parameter | Matrix | Concentration range |
|-------------|------------------------|--|-------------|--|
| 17 May | VIO 17-12* | (Heavy)metals, as dissolved: Cd, Hg, As, Cr, Co, Pb, Sr°, Cu, Ni, Zn, Mo, Al, Ba, Fe, Mn. | gw | 0,1-10 µg/l 1-70 µg/l 1-300 µg/l 0,1-20 mg/l |
| 8 November | VIO 17-13 | NH4, ortho-phosphate, pH, Mg, K, NO3, Na, Ca, SO4, HCO3. | 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 |
| 18 October | VIO 17-15 | total-phosphate, ortho-phosphate, anion active detergents, F, DOC, SiO ₂ , NO ₂ , NH ₄ , NO ₃ , Kjeldahl-N, Cl, SO ₄ , suspended matter, COD (CZV), total cyanide, fee cyanide. | ww ct | 0,1-5 mg P/l 0,1-10 mg/l NalauryISO₄ 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 O₂/l 10-350 μg/l |
| 18 October | VIO 17-16 [#] | (Heavy)metals, as total: Hg, Ag [°] , As, Cd, Se, Al, Cu, Fe, Mn, Ni, Zn, Cr, Pb. | ww | 0,5-50 μg/l 0,03-5 mg/l 0,03-5 mg/l 0,03-5 mg/l |
| 5 April | VIO 17-18** | bromide, bromate, chlorate. | dw+sw ct | 0,05-1 mg/l 1-10 μg/l 50-500 μg/l |
| 6 September | VIO 17-19** | odor and flavour (organoleptic) | dw ct | - |

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

ct = cooled transportation

a.l = actual level

* These parameters are not accredited by the Dutch Accreditation Council RvA (R005).

**These proficiency tests are not accredited by the Dutch Accreditation Council RvA (R005).

* Proficiency tests VIO 17-01 and VIO 17-12 concerning (heavy) metals to be analysed as 'dissolved'. (Heavy) metals in the proficiency tests VIO 17-09a and VIO 17-16 should be analysed as 'total'.

5.2 Organic parameters¹

| Date | Number | Parameter | Casnr. | Matrix | Conc. Range |
|------------|-----------|------------------------|--------|----------|-------------|
| 1 February | VIO 17-21 | extractable | | dw+sw+gw | 0,02-5 µg/l |
| | | organic halogens (EOX) | | ww* | 10-80 µg/l |

| | | | | | • |
|-----|------------|-----------|------------------------|-----------------|--------------|
| ſ | 1 February | VIO 17-22 | adsorbable | dw+sw+gw | 2-50 µg/l |
| | | | organic halogens (AOX) | ww [*] | 100-800 µg/l |
| ••• | | | | | |

| 17 May | VIO 17-23 | organic chlorinated pesticides (OCP) aldrin alpha-endosulfan alpha-HCH beta-HCH delta-HCH dieldrin endrin gamma-HCH (lindane) heptachlor endo epoxide isomer A heptachlor endo epoxide isomer A heptachlor exo epoxide isomer B" hexachlorobenzene isodrin" o,p'-DDD o,p'-DDD o,p'-DDT p,p'-DDT p,p'-DDD p,p'-DDE pentachlorobenzene" telodrin" trans-chlordane" | 309-00-2 115-29-7 319-84-6 319-85-7 319-86-8 60-57-1 72-20-8 58-89-9 76-44-8 28044-83-9 1024-57-3 118-74-1 465-73-6 53-19-0 3424-82-6 789-02-6 50-29-3 72-54-8 72-54-8 72-55-9 608-93-5 297-78-9 5103-74-2 | dw+sw+gw ww* | 0,002-1 0,1-10 | |
|----------|-----------|--|--|-----------------|-------------------|------|
| 17 May | VIO 17-24 | polychlorinated biphenyls (PCB) PCB 28 PCB 52 PCB 101 PCB 118 PCB 138 PCB 153 PCB 180 | 7012-37-5 35693-99-3 37680-73-2 31508-00-6 35065-28-2 35065-27-1 35065-29-3 | dw+sw+gw | 0,002-1 | µg/l |
| 22 March | VIO 17-25 | polycyclic aromatic hydrocarbons (PAH) acenaphtene acenaphtylene anthracene | 83-32-9 208-96-8 120-12-7 | dw+sw+gw ww | 0,02-1 0,1-20 | |

| acenaphtylene | 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(123-cd)pyrene | 193-39-5 |
| naphthalene | 91-20-3 |
| phenanthrene | 85-01-8 |
| , pyrene | 129-00-0 |

¹ DISCLAIMER

For the preparation of the organic proficiency tests, KWR deviates from the guide ISO/IEC 17043. For the testing of the homogeneity the method described in §4.4.3 is not followed. KWR follows a self-designed procedure.

| Date | Number | Parameter | Casnr. | Matrix | Conc. Range |
|-------------|-----------|--|---------------------|--------|-------------|
| 6 September | VIO 17-26 | volatile halogenated | | dw+gw | 0,1-2 µg/l |
| | | hydrocarbons (VHH) | | SW | 0,5-2 µg/l |
| | | 1,1,1,2-tetrachloro-ethane** | 630-20-6 | WW | 2-200 µg/l |
| | | 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 1,1-dichloro-ethene** | 75-34-3 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 ^{**} dichloromethane ^{**} | 74-95-3 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 | | |
| | | | | | |
| 11 October | VIO 17-27 | volatile aromatic | | dw+gw | 0,1-2 µg/l |
| | | hydrocarbons (VAH) | | SW | 0,5-2 µg/l |
| | | 1,2,3-trichlorobenzene** | 87-61-6 | WW | 2-200 µg/l |
| | | 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 ^{**} 2-chloromethylbenzene ^{**} | 106-46-7 95-49-8 | | |
| | | benzene | 71-43-2 | | |
| | | bromobenzene | 108-86-1 | | |
| | | chlorobenzene | 108-90-7 | | |
| | | cyclohexane | 110-82-7 | | |
| | | dimethylbenzene, meta+para | 110 02 7 | | |
| | | dimethylbenzene, ortho | 95-47-6 | | |
| | | ethylbenzene | 100-41-4 | | |
| | | ethyl-tertiair-butylether (ETBE)** | 637-92-3 | | |
| | | iso-propylbenzene** | 98-82-8 | | |
| | | methylbenzene (toluene) | 108-88-3 | | |
| | | methyl-tertiair-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 98-06-6 | | |
| | | tertiair-butylbenzene** | 90-00-0 | | |

| Date | Number | Parameter | Casnr. | Matrix | Conc. Range | |
|-------------|--------------|--|--|--|--|---|
| 5 April | VIO 17-28*** | Pharmaceuticals diatrizoic acid bezafibrate caffeine carbamazepine diclofenac phenazone ibuprofen ketoprofen lincomycin metoprolol propranolol sotalol sulfamethoxazole trimethoprim | 117-96-4 41859-67-0 58-08-2 298-46-4 15307-86-5 60-80-0 15687-27-1 22071-15-4 154-21-2 51384-51-1 525-66-6 3930-20-9 723-46-6 738-70-5 | dw+sw+gw | 0,2-2 μg/ | |
| 22 February | VIO 17-30 | N/P-pesticides atrazine azinfos-methyl ^{**} BAM ^{**} chlorofenvinfos (cis + trans) cyanazine DEET ^{**} desethylatrazine desisopropylatrazine desmetryn diazinon ^{**} dichlorvos dimethoate ethoprophos malathion ^{**} metribuzin parathion-ethyl parathion-methyl ^{**} pirimicarb prometryne propazine pyrazofos ^{**} simazine sulfotep ^{**} terbutryn terbutylazine tetrachlorovinphos ^{**} tolclofos-methyl ^{**} chloroacetamides alachlor metazachlor metolachlor propachlor ^{**} bromacil pyrazole ^{**} | 1912-24-9 86-50-0 21725-46-2 134-62-3 6190-65-4 1007-28-9 1014-69-3 333-41-5 62-73-7 60-51-5 13194-48-4 121-75-5 21087-64-9 56-38-2 298-00-0 23103-98-2 7287-19-6 139-40-2 13457-18-6 122-34-9 3689-24-5 886-50-0 5915-41-3 961-11-5 57018-04-9 15972-60-8 67129-08-2 51218-45-2 1918-16-7 314-40-9 288-13-1 | dw+sw+gw dw+sw+gw dw+sw+gw dw+sw+gw | 0,05-1 μg/ 0,05-1 μg/ 0,02-1 μg/ 0,05-1 μg/ | 1 |
| 14 June | VIO 17-31 | chlorophenoxycarbonic acids (CPCA) 4,5-trichlorophenoxyacetic acid (2,4,5-T)" 2,4,5-trichlorophenoxypropionic acid (2,4,5-TP)" 2,4-dichlorophenoxyacetic acid (2,4-D) 2,4-dichlorophenoxybutanoic acid (2,4-D) 4-chlorophenoxyacetic acid (4-CPA)" 2-(2,4-dichlorophenoxy)-propanoic acid (dichlorprop) 3,6-dichloro-2-methoxybenzoic acid (dicamba) (4-chloro-2-methylphenoxy)acetic acid (MCPA) 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB) 2-(2-methyl-4-chlorophenoxy)propionic acid (MCPP) bentazone | 93-76-5 93-72-1 94-75-7 94-82-6 122-88-3 120-36-5 1918-00-9 94-74-6 94-81-5 93-65-2 25057-89-0 | dw+sw+gw dw+sw+gw | 0,05-1 µg/ 0,02-1 µg/ | |

| 8 November VI | 10 17-32 | Phenylureaherbicides (PUH) | | | | |
|---------------|----------|------------------------------|------------|----------|--------|------|
| | | riteriyiureanerbiciues (PUH) | | dw+sw+gw | 0,02-1 | µg/l |
| | | chlorbromuron | 13360-45-7 | | ŕ | , |
| | | chlortoluron | 15545-48-9 | | | |
| | | diuron | 330-54-1 | | | |
| | | isoproturon | 34123-59-6 | | | |
| | | linuron | 330-55-2 | | | |
| | | methabenzthiazuron | 18691-97-9 | | | |
| | | metobromuron | 3060-89-7 | | | |
| | | metoxuron | 19937-59-8 | | | |
| | | monolinuron | 1746-81-2 | | | |
| | | monuron | 150-68-5 | | | |

| 5 April | VIO 17-34*** | Glyphosate and AMPA | | dw+sw+gw | 0,05-0,5 µg/l |
|---------|--------------|---------------------|-----------|----------|---------------|
| | | Glyphosate | 1071-83-6 | | |
| | | AMPA | 1066-51-9 | | |

| | 8 November | VIO 17-38 | Mineral oil, only with the GC method | WW | 0,05-200 | mg/l |
|---|------------|---------------|--------------------------------------|-------------|----------|------|
| I | | | | | | |
| | 14 June | VIO 17-39a*** | chloridazon, dimethenamid-P and | dw+sw+gw | 0,05-2 | µg/l |
| | | | metabolites chloridazon | 1698-60-8 | | |
| | | | dimethenamid-P | 163515-14-8 | | |
| | | | | 6339-19-1 | | |
| | | | methyl-desphenylchloridazon | 17254-80-7 | | |

| | 27 Septer | nber | VIO 17-39b*** | Non-target screening, semi-quantitative (semi)-quantification of various organic compounds using a LC-MS | dw+sw+gw ww | 0,1-1 μg/l 0,5-1 μg/l |
|--|-----------|------|---------------|--|----------------|--------------------------|
|--|-----------|------|---------------|--|----------------|--------------------------|

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

The matrix waste water is not accredited by the Dutch Accreditation Council RvA (R005).

** These compounds are not accredited by the Dutch Accreditation Council RvA (R005).

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

> All organic samples are cooled transported

5.3 Microbiological parameters

| Date | Number | Parameter | Matrix | Concentra | tion Range |
|--------------------------|--------------------------|--|------------|---------------------|-------------------------|
| 14 February | VIO 17-41 | bacteria of the coli group <i>E. coli</i> enterococci sulphite reducing clostridia (SRCs) <i>Clostridium perfringens</i> plate count 22°C | dw | 0-80 | cfu/100 ml |
| | | plate count 36°C | | 0-300 | cfu/ml |
| 5 April | VIO 17-42 | bacteria of the coli group | dw | 0-80 | cfu/100 ml |
| | | E. coli enterococci Aeromonas 30°C Aeromonas 37°C sulphite reducing clostridia (SRCs) Clostridium perfringens | | | |
| 17 October | VIO 17-43 | bacteria of the coli group <i>E. coli</i> <i>Aeromonas 30°C</i> <i>Aeromonas 37°C</i> plate count 22°C | dw | 0-80 | cfu/100 ml cfu/ml |
| L | | plate count 36°C | | | |
| 29 March | VIO 17-45 | Legionella | dw | 0-30.000 | cfu/l |
| 31 May | VIO 17-46 | Legionella | dw | 0-30.000 | cfu/l |
| 13 September | VIO 17-47 | Legionella | dw | 0-30.000 | cfu/l |
| | | | | | |
| 15 March | VIO 17-48 | ATP (Adenosine triphosphate) Colonies on R2A-medium (plate count) | diluted sw | 0-100 0-20.000 | ng/l cfu/ml |
| 16 May | VIO 17-50 | Salmonella staphylococci Pseudomonas aeruginosa | dw | 0-80 | cfu/100ml |
| 14 June | VIO 17-53* | bacteria of the coli group | SW | 0-8.000 | cfu/100ml |
| 14 June | | thermotolerant bacteria of the coli group <i>E. coli</i> Faecal streptococci (intestinal) enterococci | 5₩ | 0-8.000 | |
| | | | | | |
| 6 September | VIO 17-54* | bacteria of the coli group thermotolerant bacteria of the coli group <i>E. coli</i> Faecal streptococci (intestinal) enterococci | SW | 0-8.000 | cfu/100ml |
| | | Logicualla | lav | 0.20.000 | of /l |
| 29 March 13 September | VIO 17-55* VIO 17-56* | Legionella Legionella | kw kw | 0-30.000 | cfu/l cfu/l |
| | VIO 17-30 | суютени | kw | 0-30.000 | |
| 13 September | VIO 17-59* | Legionella pneumophila qPCR | dw | 0-1.10 ⁶ | DNA-copies/l |
| 13 September | VIO 17-61* | Legionella pneumophila qPCR | kw | 0-1.10 ⁶ | DNA-copies/l |
| 15 March | VIO 17-62* | F-specific RNA-phages and somatic coli- phages | dw | 0-150 | pve/ml |
| 15 March | VIO 17-63* | Total bacterial cell counting (incl. fraction dead and alive), flowcytometric | dw | 1 · 10³-1 · 1 | 0 ⁶ cells/ml |

- * These proficiency tests are 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 within The Netherlands and Belgium.

Page 19 of 27

Subscription form KWR Proficiency Tests 2017

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

| РТ | Description | Matrix | Price |
|--------------|--|--------|---------|
| UIO 17-01 | (heavy) metals, as dissolved | dw | € 1.110 |
| UIO 17-02 | general- and macro parameters | dw | € 1.570 |
| UIO 17-06 | Urea, cyanuric acid, KMnO4, free chlorine and bound chlorine | zw | € 835 |
| UIO 17-07 | nutrients | sw | € 1.500 |
| 🗌 VIO 17-09a | (heavy) metals, as total | sw | € 1.110 |
| UIO 17-09b | arsenic-3, arsenic-5, chromium-3 en chromium-6 | sw | € 465 |
| UIO 17-12 | (heavy) metals, as dissolved | gw | € 1.055 |
| UIO 17-13 | general- and macro parameters | gw | € 1.165 |
| UIO 17-15 | general- and macro parameters | ww | € 1.165 |
| UIO 17-16 | (heavy) metals, as total | ww | € 885 |
| UIO 17-17 | Sampling on location by participants | zw | € 445 |
| UIO 17-18 | bromide, bromate and chlorate | dw+sw | € 465 |
| UIO 17-19 | odor and flavour, organoleptic | dw | € 450 |
| | | | |

Total contribution inorganic proficiency tests €

| РТ | Description | Matrix | Price |
|--------------|---|-------------|---------|
| 🗌 VIO 17-21 | Extractable organic halogens (EOX) | dw sw gw ww | € 940 |
| 🗌 VIO 17-22 | Adsorbable organic halogens(AOX) | dw sw gw ww | € 940 |
| 🗌 VIO 17-23 | Organic chlorinated pesticides (OCP) | dw sw gw ww | € 1.095 |
| 🗌 VIO 17-24 | Polychlorinated biphenyls (PCB) | dw sw gw | € 860 |
| 🗌 VIO 17-25 | Polycyclic aromatic hydrocarbons (PAH) | dw sw gw ww | € 975 |
| 🗌 VIO 17-26 | Volatile halogenated hydrocarbons (VHH) | dw sw gw ww | € 1.110 |
| 🗌 VIO 17-27 | Volatile aromatic hydrocarbons (VAH) | dw sw gw ww | € 1.110 |
| 🗌 VIO 17-28 | Pharmaceuticals | dw sw gw | € 1.110 |
| 🗌 VIO 17-30 | N/P-pesticides | dw sw gw | € 1.095 |
| 🗌 VIO 17-31 | Chlorophenoxycarbonic acids (CPCA)/bentazone | dw sw gw | € 1.110 |
| 🗌 VIO 17-32 | Phenylureaherbicides (PUH) | dw sw gw | € 855 |
| 🗌 VIO 17-34 | Glyphosate and AMPA | dw sw gw | € 940 |
| 🗌 VIO 17-38 | Mineral oil, only with GC method | ww | € 235 |
| 🗌 VIO 17-39a | Chloridazon, dimethenamid-P and metabolites | dw sw gw | € 855 |
| 🗌 VIO 17-39b | Non-target screening, semi-quantitative LC-MS | dw sw gw ww | € 940 |
| | | | |

Total contribution organic proficiency tests €

| РТ | Description | Matrix | Price |
|-------------------------|---|-------------------|-------|
| 🗌 VIO 17-41 | Bacteriological parameters | dw | € 820 |
| VIO 17-42 ^{#1} | Bacteriological parameters | dw | € 820 |
| 🗌 VIO 17-43 | Bacteriological parameters | dw | € 820 |
| 🗌 VIO 17-45 | Legionella | dw | € 545 |
| VIO 17-46 ^{#1} | Legionella | dw | € 545 |
| 🗌 VIO 17-47 | Legionella | dw | € 545 |
| 🗌 VIO 17-48 | ATP/Colonies on R ₂ A-medium | diluted sw | € 855 |
| 🗌 VIO 17-50 | Salmonella, staphylococci and Pseudomonas aeruginosa | dw | € 820 |
| 🗌 VIO 17-53 | Bacteriological parameters | SW | € 820 |
| VIO 17-54 ^{#1} | Bacteriological parameters | SW | € 820 |
| 🗌 VIO 17-55 | Legionella | kw | € 545 |
| 🗌 VIO 17-56 | Legionella | kw | € 545 |
| 🗌 VIO 17-59 | Legionella pneumophila qPCR | dw | € 490 |
| 🗌 VIO 17-61 | Legionella pneumophila qPCR | kw | € 490 |
| 🗌 VIO 17-62 | F-specific RNA-phages and somatic coli-phages | dw | €615 |
| UIO 17-63 | Total bacterial cell counting (incl. fraction dead and alive), flowcytometric | dw | €615 |
| | Total contribution microbiological | proficiency tests | € |

dw = drinking water, sw = surface water, gw = ground water, ww = waste water, zw = swimming water and kw = cooling water

| | Total contribution proficiency tests | | |
|-------------------|---|----------------------------|----------------------------------|
| Discounts | participation in 5-9 proficiency tests | - 5% | -€ |
| | participation in 10-19 proficiency tests | - 10% | -€ |
| | participation in > 20 proficiency tests | - 15% | -€ |
| | Total c | € | |
| The total costs w | ill be invoiced in two equal amounts, unless other agreements are | e made with you. If change | s 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 <u>four</u> 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 <u>www.kwrwater.nl/voorwaarden/</u>.

| | Your data | |
|------------------------|-----------|---------------|
| Company | | Date of entry |
| Correspondention attn. | | |
| Telephone | | |
| PO-box | | Client |
| Zip code/Place/Country | | |
| Samples attn. | | |
| Telephone | | Autograph |
| Address | | |
| Zip code/Place/Country | | |
| Email | | |

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 assesses 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 eight results. If the number of laboratory results is less than eight, then the usual statistical key figures (mean, standard deviation, etc.) including the Z-scores were calculated. Only the judgement (Good, Moderate, Bad) based on the Z-scores than omitted. And if there are less than four laboratory results, the Youdenplots (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 (Zt) 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 Saw tooth plot

In the saw tooth plot the results of the participants are presented graphically under their successive random code numbers. Each plot shows the results of one or two samples or one standard solution. The average or median of the group is indicated by an uninterrupted line and the 2s-border or 5- and 95-percentile by an interrupted line. The interrupted lines for indicating the 2s-border or 5- and 95-percentile differ from each other when it concerns a plot with two different samples. A <-value is represented by a square marker in the saw tooth plot. For real measured values a round marker is used. The matrix and the concentration level are taken into account when presenting two parameters in one plot.

The saw tooth plot enables participants to compare their individual results with the results of the other participants. When one or more outliers have been found in the group of results, an additional saw tooth plot without the outlier(s) is given.

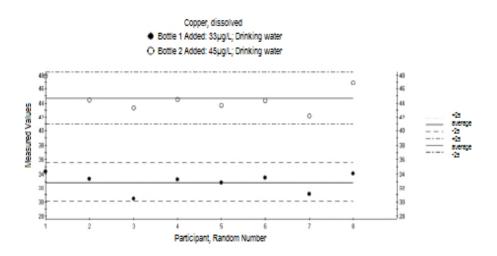


Figure 1. Example of a saw tooth plot

6.2.2 Youden plot

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 Youden plot gives an indication whether an error is random or systematic. Per 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 statistical analysis according to Youden calculates a variance (s²), which is split up into two parts. The first part relates to systematic errors and the second part relates to random errors. This is the reason why the two samples of a Youden pair have to be of the same matrix and of comparable concentration levels.

The radius of the circle in the Youden plot is a measure for the standard deviation that has been caused by random errors. The lines perpendicular to the x-axis and the y-axis are the averages of the two samples. When there are no systematic errors and the results come from a normal distribution, about 70% of the results will lie within the smallest circle and about 96% will lie within the largest circle. Furthermore, the results will also be equally distributed over the four quadrants. When the results do not follow a normal distribution a Youden plot will still be drawn, excluding the 1-s and 2-s circles, because these circles lose their meaning if the results do not follow a normal distribution.

The radius of the smallest circle is $1.55 \times$ the standard deviation calculated according to Youden and corresponds with 0.71 × the standard deviation of the difference between both results. The largest circle has a radius of 2.45 × the standard deviation calculated according to Youden.

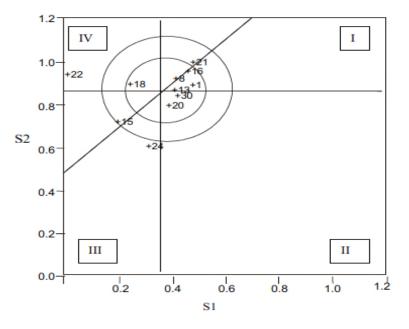


Figure 2. Example of a Youden plot

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. In case of (a) outlier(s) an additional Youden plot is presented without the(se) outlier(s).

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

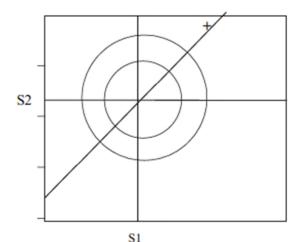


Figure 3. Example of a large systematic error, above the average of the group

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.

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.

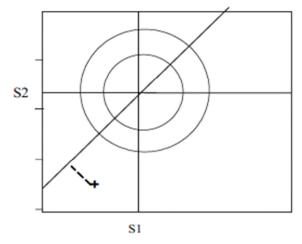
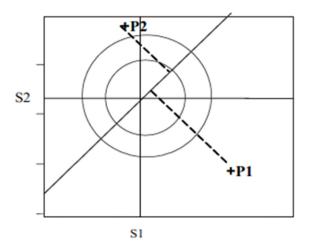
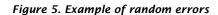


Figure 4. Example of a large systematic error, below the average of the group



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 Report mark

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 (s,); 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.

| VIO xx-xx parameter y | Youden pair | Score | |
|----------------------------------|------------------|---------------|---|
| Samples: S1, S2 | δ = -0,0700 ug/l | | |
| 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 | 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 | 5,5 | 7,3 | |
| | | alternative * | |

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

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 the 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 ones own laboratory, a distinction is made between the assessment of the following performances:

- of ones own laboratory with regard to the group average (or for a number of microbiological parameters with regard to the average of the 50% 'highest' results of the group);
- of ones own laboratory with regard to the theoretical value (the real difference in spikes of the two samples) and
- of ones 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_o) 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), which is calculated from the Youden pair.

If there are less than 8 results, after removal of outliers, KWR chooses to make the calculation of the average and the standard deviation to calculate <u>alternative</u> 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 / DIS 13528.

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

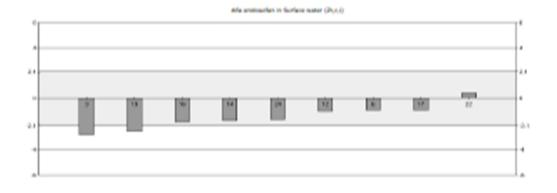


Figure 6. Example of the graphically presentation of the z-scores