Field measurement intercomparison

Field measurements of dissolved oxygen concentration

Mirja Leivuori, Teemu Näykki, Ivo Leito, Irja Helm, Lauri Jalukse, Lari Kaukonen, Panu Hänninen and Markku Ilmakunnas
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1 Introduction

In the framework of the European Metrology Research Programme (EMRP) project ENV05 OCEAN (Metrology for ocean salinity and acidity),\(^1\) the dissolved oxygen concentration field \((in situ)\) intercomparison (FieldOxy 2014) test was organized onboard R/V Aranda on April 23, 2014 in the Gulf of Finland (location called as “LL7”: 59°50.79’, 24°50.27’). The aim of the intercomparison was to enable the participants to assess their performance in measuring dissolved oxygen concentration in seawater under field conditions. The intercomparison measurement was organized jointly by the Finnish Environment Institute (Proftest SYKE, Envical SYKE) and University of Tartu (UT).

The proficiency test was carried out in accordance with the international guidelines ISO/IEC 17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi). This intercomparison test has not been carried out under the accreditation scope of the Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

The responsible for organizing the field intercomparison were Teemu Näykki and Lari Kaukonen (Envical SYKE), Mirja Leivuori (Proftest SYKE) and Ivo Leito (UT). Technical expertise was provided by Irja Helm, Lauri Jalukse (UT) and Keijo Tervonen (Proftest SYKE). Report layout was made by Markku Ilmakunnas (Proftest SYKE).

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\(^1\) For more information, please see the ENV05 website: http://www.ptb.de/emrp/env05.html
2.2 Participants

Total of 21 participants from 10 institutes in Finland, Estonia, France, Germany and Sweden participated in the intercomparison (Table 1, Figure 1). Totally, 13-18 oxygen sensors were tested depending of the test depth. 15 optical and 3 electrochemical oxygen sensors were used. Additionally, six Winkler titrimetric setups participated in the intercomparison. The sensors used by Proftest SYKE are shown as labcode 4, 18 and 21 in the result tables. The metrologically traceable Winkler titration result by UT (the assigned value) is shown as labcode 12.

Table 1. The participants in the test.

<table>
<thead>
<tr>
<th>Country</th>
<th>Participants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estonia</td>
<td>Estonian Marine Institute, University of Tartu</td>
</tr>
<tr>
<td></td>
<td>University of Tartu</td>
</tr>
<tr>
<td>Finland</td>
<td>EHP-Teknikka</td>
</tr>
<tr>
<td></td>
<td>HSY Käyttölaboratorio Pitkäkoski</td>
</tr>
<tr>
<td></td>
<td>Hyxo Oy</td>
</tr>
<tr>
<td></td>
<td>SYKE Laboratory of Hakuninmaa, Helsinki</td>
</tr>
<tr>
<td></td>
<td>SYKE Marine Research Centre, Helsinki</td>
</tr>
<tr>
<td></td>
<td>SYKE Freshwater Centre, Oulu</td>
</tr>
<tr>
<td>France</td>
<td>IFREMER France</td>
</tr>
<tr>
<td>Germany</td>
<td>Federal Maritime and Hydrographic Agency Germany</td>
</tr>
<tr>
<td>Sweden</td>
<td>Stockholm University, Department of Ecology, Environment and Plant Sciences</td>
</tr>
<tr>
<td></td>
<td>Umeå Marine Sciences Centre</td>
</tr>
</tbody>
</table>

Figure 1. Participants in the oxygen field intercomparison onboard Aranda 2014.
2.3 Testing site and times

The testing site situated two hours away in the offshore area in front of Helsinki (59°50.79', 24°50.27'). The station is called LL7 and it has been applied for a long time as monitoring site for water quality in the Baltic Sea. Based on the vertical water CTD profile measured onboard Aranda, the stable testing depths were chosen (Figure 2). The chosen testing depths were 5 m (D1), 23 m (D2) and 40 m (D3). Before the test the time of the participating sensors were synchronized with the provider’s time. The testing times were: for 5 m 11:54, for 23 m 13:45 and for 40 m 16:25. In the intercomparison, the water samples for Winkler titrations were collected using the water samplers mounted into Rosette onboard Aranda. Also the participant’s oxygen sensors were mounted on the Rosette (Figure 3) and they were transported to the testing depths using depth control and winch (Figure 4).

![Figure 2. The vertical CTD profile measured onboard Aranda at the testing site LL7. Please note, that in this figure the unit of DO (oxygen) concentration is ml/l deviating from the rest of report.](image-url)
Figure 3. The participant’s oxygen sensors mounted on the Rosette for transporting to the testing depths.

Figure 4. The tested oxygen sensors, CTDs and water samplers going-on down to the testing depths.
2.4 Homogeneity and stability studies

The homogeneity and temporal stability of the sea water at the intercomparison site was studied by measuring dissolved oxygen with three oxygen sensors YSI 600 XLM V2. These sensors were mounted in the three different positions on the Rosette for obtaining information on spatial heterogeneity at each testing depths (Figure 5). During the intercomparison homogeneity test measurements were carried out at each depth from 5 minutes before to 5 minutes after the testing time.

In addition, the contribution of inhomogeneity of DO concentration was numerically evaluated by Winkler titration performed with the UT setup from rosette sampling vessels 1, 4, 7 and 10 (Figure 5). The contribution of DO concentration inhomogeneity was taken into account in the uncertainty estimate of the assigned (reference) value.

Figure 5. A top view of the Rosette used water sample collection and mounting the sensors. Numbers 1-12 describe the 12 vessels applied for water sampling. Vessels marked with square were used for sampling the water for high-accuracy Winkler procedure (reference method). Positioning of the sensors (YSI 600 XLM V2) of PT provider for homogeneity testing are marked with letter “s”.
As the intercomparison was dealing with in situ measurements from naturally flowing water, the sources of uncertainties were not as easily controlled as in laboratory environment. By conducting the homogeneity testing simultaneously with the actual intercomparison experiments it was tried to ensure that the measured water was sufficiently homogeneous for all the participants.

For homogeneity test, 10 results were recorded within 10 minute’s timeframe by the sensor used by Proftest SYKE. Sensors recorded values measured from water body every fifth seconds. Two consecutive measurements were regarded as replicate measurements for one homogeneity test sample.

To assess whether the homogeneity is sufficient for the intercomparison, both spatial and between measurement time variability standard deviations during the test were obtained using ANOVA variance component analysis in accordance with the Eurachem/CITAC guide [4]. The total variation components were divided into three parts: time of the measurement (temporal heterogeneity), spatial heterogeneity of the test area and analytical precision (Appendix 1). The homogeneity of testing area was estimated based on the recommendation of the IUPAC Technical report [3], with the exception of using variation of temporal heterogeneity instead of variation due to heterogeneity of the test area. This was used as the sample column is not stable and time of measurement described better the flowing water. Because PT provider used three sensors for homogeneity testing (see Figure 5), the variation of heterogeneity of the test area included also analytical variability.

2.5 Feedback from the proficiency test

The feedback received from the PT participants was very positive. The arrangements were successful and facilities were fit for purpose. It was appreciated that they could participate for free of charge including meals and accommodation in the ship due to the financial support of the project. The participants wished that similar intercomparisons would be organized also in the future.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. More information about the statistical handling of the data is available from the Guide for participant [5].

2.6.2 Assigned values based on Winkler method

Winkler method (WM) was first published in 1888 by Hungarian analytical chemist Ludwig Wilhelm Winkler [6]. Although an old method, WM is still used for getting the reliable and traceable dissolved oxygen (DO) concentration values, because all sensors, in spite of being fast and convenient have a disadvantage: they all need to be calibrated with DO, the analyte.
The Winkler method is based on quantitative oxidation of Mn\(^{2+}\) to Mn\(^{3+}\) by oxygen in alkaline medium and on the subsequent quantitative oxidation of iodide to iodine by Mn\(^{3+}\) in acidic medium [7]. The formed iodine is titrated with thiosulfate.

First, two solutions (Winkler reagents) are added to the oxygen-containing sample: one containing I\(^-\) and OH\(^-\) and the other containing Mn\(^{2+}\). Oxygen reacts under alkaline conditions with Mn\(^{2+}\) ions forming manganese(III)hydroxide [7]:

\[
4\text{Mn}^{2+} + \text{O}_2 + 8\text{OH}^- + 2\text{H}_2\text{O} \rightarrow 4\text{Mn(OH)}_3\downarrow
\]  
(1)

The solution is then acidified. Under acidic conditions Mn\(^{3+}\) ions oxidize iodide to iodine, which eventually forms I\(^3^-\) ions with the excess of I\(^-\) [7]:

\[
2\text{Mn(OH)}_3\ (s) + 6\text{H}^+ \rightarrow 2\text{Mn}^{3+} + 3\text{H}_2\text{O}
\]  
(2)

\[
2\text{Mn}^{3+} + 2\text{I}^- \rightarrow 2\text{Mn}^{2+} + \text{I}_2
\]  
(3)

\[
\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-
\]  
(4)

The concentration of the formed I\(^3^-\) ions is usually determined by titration with sodium thiosulfate solution:

\[
\text{I}_3^- + 2\text{S}_2\text{O}_3^{2-} \rightarrow 3\text{I}^- + \text{S}_4\text{O}_6^{2-}
\]  
(5)

Thiosulfate solution is standardized using potassium iodate (KIO\(_3\)) standard solution. So, the DO concentration in the sample is traceable to the KIO\(_3\) mass. Under acidic conditions iodine is formed quantitatively according to the following reaction:

\[
\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}
\]  
(6)
The procedure used for assigned value determination in FieldOxy 2014 is mainly based on the high-accuracy Winkler procedure [8]. This procedure has a number of modifications compared to the classical Winkler method (available e.g. as standard EN 25813 [9]) in order to achieve higher accuracy:

1) Oxygen content in the Winkler reagents is determined and accounted for (instead of using approximate values from literature [10]);

2) Iodine loss by volatilization is determined and accounted for and is additionally minimized by pre-titration;

3) Possible sample contamination with air is determined and accounted for as an uncertainty source;

4) Titration end-point is detected amperometrically using two Pt-electrodes.

The procedure uses gravimetric measurement of titrant and the KIO₃ solution is prepared and its amount measured gravimetrically [8]. It is impossible to weigh accurately on a ship. Therefore volumetric titration instead of gravimetric was used. The titrant standardization was also performed volumetrically. Standard solution was prepared in the laboratory by weighing certain amount of KIO₃ and dissolving it in 1 dm³ (calibrated) flask. 5 ml of prepared standard solution was transferred into the titration vessel using calibrated glass pipette. Reagents were added and iodine was titrated. The Brand Liquid Handling Station LHS 600 was used for dosage of the titrant in case of titrant standardization as well as sample titrations.

The samples were not pure water (as in [8]), so the possible presence of oxidizing or reducing substances in the sea-water was determined after the testing cruise in the laboratory. It was done by using the same procedure as in the case of titrant standardization, but alternately (to eliminate all other influences) deionized water and sample water from the ship (5 ml each time in both cases) were added to the titrated solution. The relative differences between titrant concentrations in the case of these two titrations (at three depths, 5 replicates at every depth) and used as the estimates of uncertainty caused by possible interferences. They are converted to absolute (i.e. expressed in mg/dm³) uncertainty estimates by multiplying the relative value with oxygen concentration determined at the same depth, multiplying also with the average sample volume and dividing by 5 ml. The corresponding standard uncertainty estimates are obtained by dividing with square root of three. The summary data of uncertainty due to possible oxidizing or reducing substances in the sea-water are presented in Table 2.
Table 2. Determination of uncertainty due to possible oxidizing or reducing substances in the sea-water.

<table>
<thead>
<tr>
<th>Depth [m]</th>
<th>Relative differences between titrant concentrations [%]</th>
<th>( u_{\text{Interferences}} [\text{mg/dm}^3] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.118</td>
<td>0.023</td>
</tr>
<tr>
<td>23</td>
<td>0.148</td>
<td>0.027</td>
</tr>
<tr>
<td>40</td>
<td>0.062</td>
<td>0.011</td>
</tr>
</tbody>
</table>

In order to be sure that the uncertainty due to oxidizing or reducing substances is not underestimated, for all testing depths the estimate \( u_{\text{Interferences}} = 0.027 \text{ mg/dm}^3 \) was used.

In the intercomparison the DO concentration was determined separately by the above described high-accuracy Winkler procedure from the Rosette sampling vessels 1, 4, 7 and 10 at all testing depths (Figure 5). 17 sampling flasks (with calibrated volumes in the range of 11.1 to 11.5 ml) were used, so that 4 subsamples were taken from three sampling vessels and 5 from one. Some of the subsamples were discarded because of experimental failures (e.g. air bubbles in the flask, precipitate in the flask neck that was displaced by the reagent solution etc.). The numbers of used subsamples in the four sampling vessels at all depths are presented in Table 3. The subsamples were taken by thoroughly rinsing the sample bottles by ca 10-fold volume of the sampled water.

The results of determining the assigned values are presented in Table 3. At all depths the DO concentration assigned values (\( C_{O2,\text{Wink}} [\text{mg/l}] \)) are average values of the sampled Rosette vessels.

The measurement uncertainties were calculated mainly according to the same principles as in [8], except that volumetric solution measurement was used instead of weighing and the uncertainty source taking into account possible interferences (described above) was added. The uncertainty sources with their contributions in the case of one Rosette sampling vessel at one depth are presented in Figure 6 as an example (the descriptions of all input quantities not described here can be found in [8]).

The combined standard uncertainties (\( u_c(C_{O2}) [\text{mg/l}] \), see Table 3) take into account the averaged uncertainty of the Winkler titration procedure (\( u_c(C_{O2,\text{Wink,averaged}}) [\text{mg/l}] \), calculated as the pooled standard uncertainties of all the subsamples, as well as the differences between the Rosette sampling vessels (\( u(\text{between vessels}) [\text{mg/l}] \)). The latter uncertainty (which is the dominating uncertainty contribution at 5 m and 40 m depths) is expected to account for the inhomogeneity of DO concentration around the Rosette. The expanded uncertainties \( U(C_{O2}) \) were found with 95% coverage probability, taking into account the effective number of degrees of freedom. Because the inhomogeneity is taken into account, the assigned values are expected to be valid assigned values for all DO measurement devices attached to the Rosette, as well as the Winkler titration results of samples taken from other sampling vessels.
Figure 6. Cause-effect diagram at depth 23 m (Rosette vessel no 4).

Table 3. Results of Winkler titration for determination of assigned values for the Fieldoxy 2014 intercomparison (Gulf of Finland, 23.04.2014).

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Rosette no</th>
<th>CO$_2$ Wink [mg/l]</th>
<th>$\bar{u}$ (CO$_2$ Wink) [mg/l]</th>
<th>Number of values obtained</th>
<th>$\bar{u}$ (CO$_2$ Wink averaged) [mg/l]</th>
<th>$\bar{u}$ (between vessels) [mg/l]</th>
<th>$\bar{u}$(CO$_2$) [mg/l]</th>
<th>Effective degrees of freedom</th>
<th>Assigned value, CO$_2$ [mg/l]</th>
<th>$k$ (95% coverage probability)</th>
<th>$\bar{u}$(CO$_2$) [mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>all averaged</td>
<td>14.932</td>
<td>0.047</td>
<td>17</td>
<td>0.051</td>
<td>0.101</td>
<td>0.11</td>
<td>4.7</td>
<td>14.93</td>
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<td>7</td>
<td>14.843</td>
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<td>15.067</td>
<td>0.039</td>
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<tr>
<td>23</td>
<td>all averaged</td>
<td>13.794</td>
<td>0.038</td>
<td>16</td>
<td>0.045</td>
<td>0.033</td>
<td>0.06</td>
<td>16.9</td>
<td>13.79</td>
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<td>0.12</td>
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<tr>
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<td>0.063</td>
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</table>
2.6.3 Standard deviation for proficiency assessment and z score

In this intercomparison, the assessment of the standard deviation for proficiency assessment ($s_p$) was based on perception and experience of the PT provider, taking into account the type of the sample, the concentration of the tested parameter, the results of homogeneity testing, the uncertainties of the assigned values and the long-term variation in previous proficiency tests for chemical laboratories. The target value for the standard deviation for proficiency assessment ($2s_p$) was set 8% for all testing depths. This is in accordance with the previous field intercomparison organized in 2013 [11, 12].

Additionally, the reliability was tested according to the criterion $u / s_p \leq 0.3$, where $u$ is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value ($U$) divided by the coverage factor, which is show in Table 3) and $s_p$ is the standard deviation for proficiency assessment [3]. The results show, that the criterion was fulfilled and the assigned values were considered reliable (Appendix 2).

The reliability of the target value of the standard deviation and the corresponding $z$ score was estimated by comparing the deviation for proficiency assessment ($s_p$) with the robust standard deviation of the reported results ($s_{rob}$) [3]. The criterion $s_{rob} / s_p < 1.2$ was fulfilled.

3 Results and conclusions

3.1 Results

The terms used in the result tables are explained in Appendix 3. The results and the performance of each laboratory are presented in Appendix 4 and the summary of the results in Table 4. Results of replicate DO concentration for the participants using Winkler titration is shown in Table 5. The reported results with their expanded uncertainties ($k = 2$) are presented in Appendix 5. The summary of the $z$ scores is shown in Appendix 6, participants’ $z$ scores in the ascending order in Appendix 7 and comparison of $z$ and zeta scores in Appendix 8. The robust standard deviations of the results varied from 2.4 to 4.2 % (Table 4). The variability of participants’ results was lower than expected for measurement in the field condition.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Sample</th>
<th>Unit</th>
<th>Assigned value</th>
<th>Mean</th>
<th>Rob. mean</th>
<th>Median</th>
<th>SD rob</th>
<th>SD rob %</th>
<th>$2s_p$ %</th>
<th>n</th>
<th>Acc $z$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>D1_05</td>
<td>mg/l</td>
<td>14.93</td>
<td>14.90</td>
<td>14.89</td>
<td>14.90</td>
<td>0.36</td>
<td>2.4</td>
<td>8</td>
<td>24</td>
<td>92</td>
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<td>mg/l</td>
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<td>13.79</td>
<td>13.66</td>
<td>13.70</td>
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<td>3.0</td>
<td>8</td>
<td>22</td>
<td>86</td>
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<td>D3_40</td>
<td>mg/l</td>
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<td>13.70</td>
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<td>13.63</td>
<td>0.57</td>
<td>4.2</td>
<td>8</td>
<td>19</td>
<td>84</td>
</tr>
</tbody>
</table>

Rob. mean: the robust mean, SD rob: the robust standard deviation, SD rob %: the robust standard deviation as percent, $2s_p$: the total standard deviation for proficiency assessment at the 95% confidence interval, Acc $z$: the results (%), where $|z| \leq 2$, n: the number of the participants.
Table 5. Results of the dissolved oxygen concentration (mg/l) for the participants using Winkler titration, who reported replicate results for their measurements. See results of laboratory 12 from Table 3.

<table>
<thead>
<tr>
<th>LabCode</th>
<th>D1_05</th>
<th>D2_23</th>
<th>D3_40</th>
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<tbody>
<tr>
<td>11</td>
<td>15.18</td>
<td>13.92</td>
<td>13.88</td>
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<tr>
<td></td>
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<td>13.89</td>
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<td></td>
<td>14.66</td>
<td>13.57</td>
<td>13.46</td>
</tr>
</tbody>
</table>

3.2 Used oxygen measurement instruments

The participants were allowed to use different analytical methods for the oxygen measurements in the intercomparison. The used analytical methods and results of the participants grouped by methods are shown in more detail in Appendix 9. The statistical comparison of the analytical methods was not carried out for the data due to the low number of the results was (n ≤ 5). Thus the comparison was carried out based on the graphical presentation.

**Optical and electrochemical sensors**

The participants used various oxygen sensors of which 15 were based on optical oxygen measurement and three were based on electrochemical oxygen measurement (Table 6). Based on the mean of the optical and electrochemical sensor and respectively recoveries, it is evident that the results of electrochemical oxygen sensors were lower than the results of optical oxygen sensors (Table 7).

Two possible reasons can be envisaged for the behavior of the electrochemical sensors. Firstly, the electrochemical sensors need water movement and if this is not sufficient then lowered readings are observed. Secondly, it is possible that the sensors’ parameters have drifted during the time period from last calibration to the intercomparison. Such drift almost always leads to lowering of the values (not increasing), which is also observed here.
Table 6. The used oxygen sensors and Winkler titrimetric instrumentation in the test.

<table>
<thead>
<tr>
<th>LabCode</th>
<th>Method</th>
<th>Oxygen sensor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Optical</td>
<td>SBE37-SMP-ODOMicroCat</td>
</tr>
<tr>
<td>2</td>
<td>Optical</td>
<td>Ponsel OPTOD</td>
</tr>
<tr>
<td>3</td>
<td>Electrochemical</td>
<td>OxyGuard Ocean Probe, attached to SAIV SD204 CTD</td>
</tr>
<tr>
<td>4</td>
<td>Optical</td>
<td>YSI ROX oxygen sensor YSI 600 XLM V2</td>
</tr>
<tr>
<td>5</td>
<td>Winkler titration</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Optical</td>
<td>YSI 6150 rox attached YSI 6600 V2</td>
</tr>
<tr>
<td>7</td>
<td>Optical</td>
<td>Hach HQ30d with sensor LDO10130</td>
</tr>
<tr>
<td>8</td>
<td>Optical</td>
<td>Hach Lange LDO101-30</td>
</tr>
<tr>
<td>9</td>
<td>Electrochemical</td>
<td>RBR duo T.DO</td>
</tr>
<tr>
<td>10</td>
<td>Optical</td>
<td>Ysi ProODO</td>
</tr>
<tr>
<td>11</td>
<td>Winkler titration</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Winkler titration (assigned value)</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Optical</td>
<td>Ysi ProODO</td>
</tr>
<tr>
<td>14</td>
<td>Winkler titration</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Optical</td>
<td>SS DO Sensor, Sea and Sun</td>
</tr>
<tr>
<td>16</td>
<td>Optical</td>
<td>Sea&amp;Sun Fast Optical Oxygen Sensor (Optical DOSST)</td>
</tr>
<tr>
<td>17</td>
<td>Optical</td>
<td>Aanderaa Oxygen Optode 3835 + NKE Dortalogger</td>
</tr>
<tr>
<td>18</td>
<td>Optical</td>
<td>YSI ROX oxygen sensor YSI 600 XLM V2</td>
</tr>
<tr>
<td>19</td>
<td>Electrochemical</td>
<td>Dissolved Oxygen sensor SBE 13 attached Seabird SBE</td>
</tr>
<tr>
<td>20</td>
<td>Winkler titration</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Optical</td>
<td>YSI ROX oxygen sensor YSI 600 XLM V2</td>
</tr>
<tr>
<td>22</td>
<td>Optical</td>
<td>JFE Advantech, Rinko I arc-usb</td>
</tr>
<tr>
<td>23</td>
<td>Optical</td>
<td>Alec Rinko III</td>
</tr>
<tr>
<td>24</td>
<td>Winkler titration</td>
<td></td>
</tr>
</tbody>
</table>

Table 7. The mean and recovery of the results of the optical and electrochemical oxygen sensors.

<table>
<thead>
<tr>
<th>O₂ / sample</th>
<th>Optical</th>
<th>Electrochemical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean (mg/l)</td>
<td>Recovery (%)¹</td>
</tr>
<tr>
<td>D1_05</td>
<td>14.99</td>
<td>100.4</td>
</tr>
<tr>
<td>D1_23</td>
<td>13.83</td>
<td>100.3</td>
</tr>
<tr>
<td>D1_40</td>
<td>13.80</td>
<td>101.2</td>
</tr>
</tbody>
</table>

¹Recovery (%) = 100*mean/assigned value

**Winkler titrations**

Four participants used iodometric method based on standard EN 25813 [9] in Winkler titrimetric titrations, one participant used the withdrawn SFS 3040 titrimetric method and UT used a high-accuracy titrimetric method [8]. The latter one was applied for establishing the metrologically traceable assigned values of DO concentration in the intercomparison. As seen in the Figures in Appendix 9 all the results based on Winkler titrimetric method were in the same range and all of them were acceptable for the intercomparison.
3.3 Measurement uncertainties of the results

Very few participants reported measurement uncertainties. The reported ones were mainly for Winkler titrimetric procedures and for some optical oxygen sensors operated by SYKE and UT. The comparison of z and zeta scores is shown in Appendix 8 for those participants who reported their measurement uncertainties.

Participants were encouraged to improve their analytical results by providing information about uncertainty of the measurement result. According to ISO 11352 [13] and Nordtest Handbook for measurement uncertainty estimation [14], uncertainty is broken down into two main components: (1) within-laboratory reproducibility and (2) method and laboratory bias. The first one covers the random effects of analytical results i.e. standard deviation of the measurement results. Sensor operator may for example record at least 10 replicate measurement results of same sample water in repeatability conditions and repeat this during five different days with the instrument calibrated just before the measurements. After that the (pooled) standard deviation \((u_{Rw})\) of the measurement results can be estimated.

The bias be calculated using the results of this PT. More detailed information for calculation of bias using PT results is described in Nordtest TR 537 [14]. Nordtest TR handbook suggests having at least six different PT results. However in this PT there were only three individual results available. When more PT data are available, the participants should revise their bias estimates. As the use of PT results for bias estimate is inferior to use of certified reference material for same purpose, the participants should also consider setting up facility for production of “in-house” reference material, water saturated with air, for dissolved oxygen determination. This is described in detail in reference [8].

4 Evaluation of the results

The evaluation of the participants was based on z scores, which were calculated using the assigned values and the estimated target values for the total standard deviation (Appendix 3). The z scores were interpreted as follows:

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>(</td>
<td>z</td>
</tr>
<tr>
<td>(2 &lt;</td>
<td>z</td>
</tr>
<tr>
<td>(</td>
<td>z</td>
</tr>
</tbody>
</table>

In total, 88 % of the results were satisfactory when total deviation of 8 % from the assigned values were accepted. More detailed summary of the type of oxygen sensor used or Winkler titrimetric results are shown in Table 8. Only three results were questionable and five results were unsatisfactory (Table 8, Appendix 7). The unsatisfactory results were found only for electrochemical oxygen sensors, which are based on the Clark cell type [16] measurement principle. Clark cell sensors measure DO indirectly through an electrochemical reaction. They are known to need careful and skilled maintenance, more frequent calibration and skilled
operation in order to perform well. This finding was similar than noticed in the previous intercomparisons [11, 15].

All electrochemical DO sensors have some flow dependency because they consume oxygen at the membrane surface. Therefore, water should be moving to obtain good measurement results, and in slow-moving water, mechanical stirring is necessary for most models. Under the sea conditions the Rosette is constantly moving due to movement of the ship in the sea. Also the water currents are moving around the Rosette and the sensors. In connection to this PT, additional tests were carried out by collaborator of EMPR project ENV05 (IOW Liebniz-Institute for Baltic Sea research Warnemünde, Rostock, Germany) for flow dependency of DO measurement results on water flow rate in the surface of the sensor (SBE43; Seabird). It was noticed that flow velocities ca. 6-14 cm/s yielded DO results within 1.5% at 8.9 mg/l concentration level. If the flow rate of water was 0 cm/s, then the DO results were decreased dramatically resulting DO concentration ca 65% lower than compared to flow speed of 14 cm/s. However, the movement of the water during the PT may have been insufficient for the electrochemical sensors, and based on this dissolved oxygen concentration field measurement intercomparison, it cannot be reliably concluded that the electrochemical measurement principle is inferior to the optical one. For some oxygen sensors, the results were affected by the measurement depth and the measurement results were noticed to be systematically higher or lower. In these cases, the calibration and depth compensation of the oxygen sensor should be checked.
Table 8. Summary of the used oxygen sensor’s type and performance (z score) in the field intercomparison.

<table>
<thead>
<tr>
<th>LabCode</th>
<th>Sample depth (m)</th>
<th>z score</th>
<th>Oxygen sensor</th>
<th>Measurement principle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D1_05</td>
<td>-0.37</td>
<td>SBE37-SMP-ODOMicroCat</td>
<td>Optical</td>
</tr>
<tr>
<td>1</td>
<td>D2_23</td>
<td>-0.62</td>
<td>SBE37-SMP-ODOMicroCat</td>
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</tr>
<tr>
<td>1</td>
<td>D3_40</td>
<td>-0.51</td>
<td>SBE37-SMP-ODOMicroCat</td>
<td>Optical</td>
</tr>
<tr>
<td>2</td>
<td>D1_05</td>
<td>-0.22</td>
<td>Ponsel OPTOD</td>
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</tr>
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</tr>
<tr>
<td>3</td>
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</tr>
<tr>
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<tr>
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<td>4</td>
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<td>-0.77</td>
<td>YSI ROX oxygen sensor attached YSI 600 XLM V2</td>
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<tr>
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<td>Winkler</td>
<td>Winkler</td>
</tr>
<tr>
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<td>D2_23</td>
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<td>Winkler</td>
<td>Winkler</td>
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<tr>
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<td>D3_40</td>
<td>0.25</td>
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</tr>
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<td>6</td>
<td>D2_23</td>
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<tr>
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<td>D2_23</td>
<td>-3.50</td>
<td>RBR duo T.DO</td>
<td>Electrochemical</td>
</tr>
<tr>
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<tr>
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<td>Winkler</td>
</tr>
<tr>
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<td>D2_23</td>
<td>0.21</td>
<td>Winkler</td>
<td>Winkler</td>
</tr>
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<td>D3_40</td>
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<td>Winkler</td>
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<td>Winkler (assigned value)</td>
<td>Winkler</td>
</tr>
<tr>
<td>12</td>
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<td>NA</td>
<td>Winkler (assigned value)</td>
<td>Winkler</td>
</tr>
<tr>
<td>12</td>
<td>D3_40</td>
<td>NA</td>
<td>Winkler (assigned value)</td>
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</tr>
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<td>0.28</td>
<td>Ysi ProODO</td>
<td>Optical</td>
</tr>
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<td>D1_05</td>
<td>0.10</td>
<td>Winkler</td>
<td>Winkler</td>
</tr>
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<td>D2_23</td>
<td>0.35</td>
<td>Winkler</td>
<td>Winkler</td>
</tr>
<tr>
<td>14</td>
<td>D3_40</td>
<td>0.29</td>
<td>Winkler</td>
<td>Winkler</td>
</tr>
<tr>
<td>LabCode</td>
<td>Sample depth (m)</td>
<td>z score</td>
<td>Oxygen sensor</td>
<td>Measurement principle</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------</td>
<td>---------</td>
<td>---------------</td>
<td>-----------------------</td>
</tr>
<tr>
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<td>D1_05</td>
<td>1.16</td>
<td>SS DO Sensor, Sea and Sun</td>
<td>Optical</td>
</tr>
<tr>
<td>15</td>
<td>D2_23</td>
<td>1.65</td>
<td>SS DO Sensor, Sea and Sun</td>
<td>Optical</td>
</tr>
<tr>
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<td>D3_40</td>
<td>1.82</td>
<td>SS DO Sensor, Sea and Sun</td>
<td>Optical</td>
</tr>
<tr>
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<td>0.52</td>
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<td>1.00</td>
<td>Sea&amp;Sun Fast Optical Oxygen Sensor (Optical DOSST)</td>
<td>Optical</td>
</tr>
<tr>
<td>16</td>
<td>D3_40</td>
<td>1.32</td>
<td>Sea&amp;Sun Fast Optical Oxygen Sensor (Optical DOSST)</td>
<td>Optical</td>
</tr>
<tr>
<td>17</td>
<td>D1_05</td>
<td>-0.37</td>
<td>Aanderaa Oxygen Optode 3835 + NKE Dortalogger</td>
<td>Optical</td>
</tr>
<tr>
<td>17</td>
<td>D2_23</td>
<td>-0.53</td>
<td>Aanderaa Oxygen Optode 3835 + NKE Dortalogger</td>
<td>Optical</td>
</tr>
<tr>
<td>17</td>
<td>D3_40</td>
<td>-0.02</td>
<td>Aanderaa Oxygen Optode 3835 + NKE Dortalogger</td>
<td>Optical</td>
</tr>
<tr>
<td>18</td>
<td>D1_05</td>
<td>-0.07</td>
<td>YSI ROX oxygen sensor attached YSI 600 XLM V2</td>
<td>Optical</td>
</tr>
<tr>
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<td>D2_23</td>
<td>-0.42</td>
<td>YSI ROX oxygen sensor attached YSI 600 XLM V2</td>
<td>Optical</td>
</tr>
<tr>
<td>18</td>
<td>D3_40</td>
<td>-0.72</td>
<td>YSI ROX oxygen sensor attached YSI 600 XLM V2</td>
<td>Optical</td>
</tr>
<tr>
<td>19</td>
<td>D1_05</td>
<td>-1.01</td>
<td>Dissolved Oxygen sensor SBE 13 attached Seabird SBE 43</td>
<td>Electrochemical</td>
</tr>
<tr>
<td>19</td>
<td>D2_23</td>
<td>-1.01</td>
<td>Dissolved Oxygen sensor SBE 13 attached Seabird SBE 43</td>
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<td>Dissolved Oxygen sensor SBE 13 attached Seabird SBE 43</td>
<td>Electrochemical</td>
</tr>
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<td>20</td>
<td>D1_05</td>
<td>-0.28</td>
<td>Winkler</td>
<td>Winkler</td>
</tr>
<tr>
<td>20</td>
<td>D2_23</td>
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<td>20</td>
<td>D3_40</td>
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<td>21</td>
<td>D1_05</td>
<td>-0.03</td>
<td>YSI ROX oxygen sensor attached YSI 600 XLM V2</td>
<td>Optical</td>
</tr>
<tr>
<td>21</td>
<td>D2_23</td>
<td>-0.45</td>
<td>YSI ROX oxygen sensor attached YSI 600 XLM V2</td>
<td>Optical</td>
</tr>
<tr>
<td>21</td>
<td>D3_40</td>
<td>-0.75</td>
<td>YSI ROX oxygen sensor attached YSI 600 XLM V2</td>
<td>Optical</td>
</tr>
<tr>
<td>22</td>
<td>D1_05</td>
<td>2.33</td>
<td>JFE Advantech, Rinko I aro-usb</td>
<td>Optical</td>
</tr>
<tr>
<td>22</td>
<td>D2_23</td>
<td>2.28</td>
<td>JFE Advantech, Rinko I aro-usb</td>
<td>Optical</td>
</tr>
<tr>
<td>22</td>
<td>D3_40</td>
<td>2.15</td>
<td>JFE Advantech, Rinko I aro-usb</td>
<td>Optical</td>
</tr>
<tr>
<td>23</td>
<td>D1_05</td>
<td>0.45</td>
<td>Alec Rinko III</td>
<td>Optical</td>
</tr>
<tr>
<td>23</td>
<td>D2_23</td>
<td>0.27</td>
<td>Alec Rinko III</td>
<td>Optical</td>
</tr>
<tr>
<td>23</td>
<td>D3_40</td>
<td>0.35</td>
<td>Alec Rinko III</td>
<td>Optical</td>
</tr>
<tr>
<td>24</td>
<td>D1_05</td>
<td>-0.47</td>
<td>Winkler</td>
<td>Winkler</td>
</tr>
<tr>
<td>24</td>
<td>D2_23</td>
<td>-0.41</td>
<td>Winkler</td>
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<td>D3_40</td>
<td>-0.27</td>
<td>Winkler</td>
<td>Winkler</td>
</tr>
</tbody>
</table>
5 Summary

In the framework of the European Metrology Research Programme (EMRP) project ENV05 OCEAN (Metrology for ocean salinity and acidity), the dissolved oxygen field (in situ) intercomparison (FieldOxy 2014) test was organized onboard R/V Aranda on April 23, 2014 in the Gulf of Finland (location called as “LL7”: 59°50.79’, 24°50.27’). The aim of the intercomparison was to enable the participants to assess their performance in measuring dissolved oxygen concentration in seawater under field conditions. The intercomparison measurement was organized jointly by the Finnish Environment Institute (Proftest SYKE, Envical SYKE) and University of Tartu (UT).

Total of 21 participants from 10 institutes in Finland, Estonia, France, Germany and Sweden participated in the intercomparison. Totally, 13-18 oxygen sensors were tested depending of the test depth. Additionally, six Winkler titrimetric setups participated in the intercomparison. The metrologically traceable Winkler titration result (the assigned value) was measured by the Winkler setup of University of Tartu onboard R/V Aranda.

In total, 88 % of the results were satisfactory when total deviation of 8 % from the assigned values were accepted. Only three results were questionable and five results were unsatisfactory. A possible reason for several unsatisfactory results might be problems with calibration of electrochemical oxygen sensors. The electrochemical sensors need water movement and if this is not sufficient then lowered readings are observed. The movement of the water during the PT may have been insufficient for the electrochemical sensors, and based on this intercomparison, it cannot be reliably concluded that the electrochemical measurement principle is inferior to the optical one. For the most part the share of satisfactory results was very good.

6 Summary in Finnish

Euroopan metrologian tutkimusohjelman (EMRP) projektissa ENV05 OCEAN (Metrology for ocean salinity and acidity) järjestettiin meriveden liuennen hapen kenttämittausverailu Arandalla 23.4.2014. Vertailun tarkoituksena oli arvioida kentällä suoritettavien happimääritysten luokitus ja keskinäistä vertailtavuutta. Vertailukokeen järjestivät Suomen Ympäristökeskus ja Tarton Yliopisto.


Kenttämittausverailussa kaiken kaikkiaan 88 % tuloksista oli hyväksyttyäviä, kun tulosten sallittiin vaihdella 8 % vertailuarvosta. Vain kolme tulosta oli kyseenalaisia ja viisi tulosta ei-hyväksyttyäviä. Jälkimäiseen tulokseen saattaa olla syynä elektrokemiallisten happisensorien...
REFERENCES


# APPENDIX 1: Homogeneity of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean</th>
<th>Unit</th>
<th>$s_h$ (%)</th>
<th>$s_p$ (%)</th>
<th>$s_{obs}$ (%)</th>
<th>$s_a$</th>
<th>$s_t$</th>
<th>$s_t/s_h&lt;0.5$?</th>
<th>$c$</th>
<th>$s^2&lt;c^2$?</th>
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<tbody>
<tr>
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<td>0.003</td>
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</table>

$s_h$ = Target standard deviation for homogeneity; $s_p$ = Standard deviation for proficiency assessment; $s_{obs}$ = Observed total standard deviation = $\sqrt{s_a^2 + s_t^2 + s_s^2}$; $s_a$ = Variation due to analytical precision; $s_t$ = Variation due to temporal heterogeneity; $s_s$ = Variation due to heterogeneity of the test area (sampling); $c = F_1 \times s_{all}^2 + F_2 \times s_s^2$; $s_{all}^2 = (0.3 \times s_p^2)$; $F_1 = 1.46$ and $F_2 = 0.93$.

**Conclusion:** The analytical deviation fulfilled the criteria $s_a/s_p<0.5$ for each sample. Also in each case the $s^2$ was smaller than the criteria $c$. The testing area could be regarded as homogenous.
APPENDIX 2: Evaluation of the assigned values and their uncertainties

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Sample</th>
<th>Unit</th>
<th>Assigned value</th>
<th>Standard uncertainty</th>
<th>Standard uncertainty, %</th>
<th>Evaluation method of assigned value</th>
<th>( u/s )</th>
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</thead>
<tbody>
<tr>
<td>O₂</td>
<td>D₁₀₅</td>
<td>mg/l</td>
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<td>0.11</td>
<td>0.76</td>
<td>Metrologically traceable</td>
<td>0.16</td>
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<td>0.08</td>
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<td>Metrologically traceable</td>
<td>0.15</td>
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</tbody>
</table>

Criterion for reliability of the assigned value \( u/s_p \leq 0.3 \), where:
- \( s_p \) = target value of the standard deviation for proficiency assessment
- \( u \) = standard uncertainty of the assigned value

Conclusion: The criterion was fulfilled and the assigned values were considered to be reliable.
APPENDIX 3: Terms in the results tables

<table>
<thead>
<tr>
<th>Results of each participant</th>
<th>Analyte</th>
<th>The determined chemical species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td></td>
<td>The code of the sample</td>
</tr>
<tr>
<td>z score</td>
<td></td>
<td>Calculated as follows:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[ z = (x_i - X)/s_p ] where</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( x_i ) = the result of the individual laboratory</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( X ) = the assigned value (reference value)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( s_p ) = the target value of the standard deviation for proficiency assessment</td>
</tr>
<tr>
<td>Assigned value</td>
<td></td>
<td>The reference value</td>
</tr>
<tr>
<td>2* s_p %</td>
<td></td>
<td>The target value of total standard deviation for proficiency assessment (s_p) at the 95 % confidence level</td>
</tr>
<tr>
<td>Lab’s result</td>
<td></td>
<td>The result reported by the participant (the mean value of the replicates)</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>Median</td>
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<tr>
<td>SD</td>
<td></td>
<td>Standard deviation</td>
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<tr>
<td>SD%</td>
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<td>Standard deviation, %</td>
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<tr>
<td>n (stat)</td>
<td></td>
<td>Number of results in statistical processing</td>
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</table>

Summary on the z scores
- S – satisfactory ( -2 \( \leq \) z \( \leq \) 2)
- Q – questionable ( 2 < z < 3), positive error. the result deviates more than 2 \( \cdot \) s_p from the assigned value
- q – questionable ( -3 < z < -2), negative error. the result deviates more than 2 \( \cdot \) s_p from the assigned value
- U – unsatisfactory (z \( \geq \) 3), positive error. the result deviates more than 3 \( \cdot \) s_p from the assigned value
- u – unsatisfactory (z \( \leq \) -3), negative error. the result deviates more than 3 \( \cdot \) s_p from the assigned value

Robust analysis
The items of data are sorted into increasing order, \( x_1, x_2, x_p \) .... \( x_p \).
Initial values for \( x^* \) and \( s^* \) are calculated as:
\[
\begin{align*}
  x^* &= \text{median of } x_i \ (i = 1, 2, ..., p) \\
  s^* &= 1.483 \cdot \text{median of } |x_i - x^*| \ (i = 1, 2, ..., p)
\end{align*}
\]
The mean \( x^* \) and \( s^* \) are updated as follows:
Calculate \( \varphi = 1.5 \cdot s^* \). A new value is then calculated for each result \( x_i \) (i = 1, 2 ...p):
\[
\begin{align*}
x_i^* &= \begin{cases} 
  x_i - \varphi, & \text{if } x_i < x^* - \varphi \\
  x_i + \varphi, & \text{if } x_i > x^* + \varphi \\
  x_i, & \text{otherwise}
\end{cases}
\end{align*}
\]
The new values of \( x^* \) and \( s^* \) are calculated from:
\[
\begin{align*}
x^* &= \frac{\sum x_i^*}{p} \\

s^* &= 1.134 \sqrt{\frac{\sum (x_i^* - x^*)^2}{(p-1)}}
\end{align*}
\]
The robust estimates \( x^* \) and \( s^* \) can be derived by an iterative calculation, i.e. by updating the values of \( x^* \) and \( s^* \) several times, until the process convergences [2].
APPENDIX 4: Results of each participant

Laboratory 1

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Unit</th>
<th>Sample</th>
<th>z score</th>
<th>Assigned value</th>
<th>2's p, %</th>
<th>Lab's result</th>
<th>Md</th>
<th>Mean</th>
<th>SD</th>
<th>SD%</th>
<th>n (stat)</th>
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<tbody>
<tr>
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<tr>
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Laboratory 2

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<th>Lab's result</th>
<th>Md</th>
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Laboratory 3

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Laboratory 4

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<th>2's p, %</th>
<th>Lab's result</th>
<th>Md</th>
<th>Mean</th>
<th>SD</th>
<th>SD%</th>
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Laboratory 5

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<th>Lab's result</th>
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Laboratory 6

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Laboratory 7

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<th>2's p, %</th>
<th>Lab's result</th>
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<th>Mean</th>
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Laboratory 8

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<th>$2\sigma$, %</th>
<th>Lab's result</th>
<th>Md</th>
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### Laboratory 10

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<th>Assigned value</th>
<th>$2\sigma$, %</th>
<th>Lab's result</th>
<th>Md</th>
<th>Mean</th>
<th>SD</th>
<th>SD%</th>
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<th>Md</th>
<th>Mean</th>
<th>SD</th>
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APPENDIX 5: Results of participants and their uncertainties

In figures:
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.
Analyte $O_2$ Sample D3_40

Laboratory

mg/l
## APPENDIX 6: Summary of the $z$ scores

| Analyte | Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | % |
|---------|--------|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| $O_2$   | D1.05  | S | S | S | S | S | S | S | S | u | S | S | S | S | S | S | S | S | S | S | Q | S | 91.7 |
|         | D2.23  | S | S | S | u | S | S | S | S | S | S | S | S | S | S | S | S | S | S | S | Q | S | 86.4 |
|         | D3.40  | S | u | S | S | S | S | S | S | . | u | S | S | S | S | S | S | S | S | S | S | Q | S | 84.2 |
| %       |        | 100 | 100 | 33 | 100 | 100 | 0 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 0 | 100 | 0 | 100 | 0 | 100 | 0 |
| accredited |     | 3 | 3 | 2 | 2 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |

| Analyte | Sample | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | % |
| $O_2$   | D1.05  | $\text{S}$ | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | 91.7 |
|         | D2.23  | $\text{S}$ | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | 86.4 |
|         | D3.40  | $\text{S}$ | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | . | 84.2 |
| %       |        | 100 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| accredited |     | 3 | | | | | | | | | | | | | | | | | | | | | | | | | | | |

- **S** - satisfactory ($-2 < z < 2$), **Q** - questionable ($2 < z < 3$), **q** - questionable ($-3 < z < -2$), **U** - unsatisfactory ($z \geq 3$), **u** - unsatisfactory ($z \leq -3$), **bold** - accredited, **italics** - non-accredited, **normal** - other

Percentage of satisfactory results: **Totally satisfactory, % in all: 88**  
% in accredited: 93  
% in non-accredited: 80
APPENDIX 7: z scores in ascending order

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<table>
<thead>
<tr>
<th>Analyte O₂</th>
<th>Sample D3_40</th>
<th>z score</th>
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<tbody>
<tr>
<td></td>
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<td>9</td>
</tr>
<tr>
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<td>3</td>
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<tr>
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<td>19</td>
</tr>
<tr>
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<td></td>
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</tr>
<tr>
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<td></td>
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<tr>
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<tr>
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<td></td>
<td></td>
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<td></td>
<td>11</td>
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<td></td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22</td>
</tr>
</tbody>
</table>

- Analyte O₂: z scores in ascending order
- Laboratory: 9, 19, 3, 6, 24, 1, 17, 4, 20, 2, 5, 18, 21, 12, 14, 7, 13, 11, 10, 8, 23, 16, 15, 22
- Analysis of z scores for different samples and laboratories.
APPENDIX 8: Summary of the z and zeta scores

Zeta scores are not used for the evaluation of the performance of the laboratories. This information is however very useful when you re-evaluate the measurement uncertainties for your own laboratory (see below).

**Explanations' for the z and zeta score sheet**

Assigned value = the reference value  
$k \times u = $ the expanded uncertainty of the assigned value (%), the coverage factor $k$ is shown in Table 3  
$2 \times s_p \% = $ the target value for the total standard deviation at 95 % confidence interval  

$$z = \frac{x - X}{s_p}, \text{ where}$$

$x =$ the result of the individual participant  
$X =$ the assigned value  
$s_p =$ the standard deviation for proficiency assessment  

$$\text{zeta} = \frac{x - X}{\sqrt{u_{lab}^2 + u_C^2}}, \text{ where}$$

$x =$ the result the assigned value of the individual participant  
$X =$ the assigned value  
$u_{lab} =$ the standard uncertainty of the participant's result  
$u_C =$ the standard uncertainty of the assigned value

**How to interpret these results?**

<table>
<thead>
<tr>
<th>z score</th>
<th>zeta score</th>
<th>Action to take</th>
</tr>
</thead>
<tbody>
<tr>
<td>Satisfactory</td>
<td>Satisfactory</td>
<td>No action; the result is good!</td>
</tr>
<tr>
<td>Satisfactory</td>
<td>Not satisfactory</td>
<td>The claimed uncertainty is too low, but it fills the requirement of the proficiency test.</td>
</tr>
<tr>
<td>Not satisfactory</td>
<td>Satisfactory</td>
<td>The result is within your claimed uncertainty, but not within the limits of proficiency test. The uncertainty might therefore be too high and should be checked against the uncertainty requirement of your client.</td>
</tr>
<tr>
<td>Not satisfactory</td>
<td>Not satisfactory</td>
<td>The result is too much biased and the reason should be clarified.</td>
</tr>
</tbody>
</table>
### Assigned value $k_u$ $zeta_u$ %

|        | 14.93 | 2.1  | 8.0 |

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Mean $U_{k_u}$</th>
<th>$zeta_u$</th>
<th>$z$ score</th>
<th>$zeta$ score</th>
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<tbody>
<tr>
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<td>0.33</td>
<td>0.11</td>
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<tr>
<td>7</td>
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<td>2.4</td>
<td>0.12</td>
<td>0.29</td>
</tr>
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<td>11</td>
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<td>1.9</td>
<td>0.37</td>
<td>1.27</td>
</tr>
<tr>
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<td>0.00</td>
<td>0.00</td>
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<td>0.10</td>
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<td>7.5</td>
<td>1.00</td>
<td>1.14</td>
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<td>14.77</td>
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<td>0.28</td>
<td>0.88</td>
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<tr>
<td>21</td>
<td>14.91</td>
<td>1.6</td>
<td>0.03</td>
<td>0.70</td>
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<tr>
<td>24</td>
<td>14.65</td>
<td>7.5</td>
<td>0.47</td>
<td>0.52</td>
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</table>
Assigned value (u, %): 13.79

<table>
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<tr>
<th>Laboratory</th>
<th>Mean</th>
<th>U, %</th>
<th>z</th>
<th>zeta</th>
</tr>
</thead>
<tbody>
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<td>13.40</td>
<td>6.0</td>
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<td>0.98</td>
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<td>7</td>
<td>13.49</td>
<td>6.4</td>
<td>0.52</td>
<td>1.70</td>
</tr>
<tr>
<td>11</td>
<td>13.91</td>
<td>1.9</td>
<td>0.23</td>
<td>1.35</td>
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<td>0.9</td>
<td>0.00</td>
<td>0.02</td>
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<td>13.56</td>
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<td>0.47</td>
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</table>
### Assigned value (x): $36_\%$

<table>
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<tr>
<th>Laboratory</th>
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<th>$z$</th>
<th>zeta score</th>
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</thead>
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<td>3.63</td>
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<td>14</td>
<td>3.79</td>
<td>0.2</td>
<td>2.20</td>
</tr>
<tr>
<td>18</td>
<td>3.34</td>
<td>0.3</td>
<td>0.72</td>
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<tr>
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<td>3.14</td>
<td>0.5</td>
<td>0.66</td>
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<td>3.67</td>
<td>0.9</td>
<td>0.97</td>
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<tr>
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**APPENDIX 9: Analytical methods**

**Results grouped according to the methods**

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<tr>
<th>Analyte O&lt;sub&gt;2&lt;/sub&gt; Sample D1_05</th>
<th>Analyte O&lt;sub&gt;2&lt;/sub&gt; Sample D2_23</th>
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</thead>
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<td>13,6</td>
</tr>
<tr>
<td>17,3</td>
<td>14,0</td>
</tr>
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</table>

*Methods and abbreviations used:*
- EN 25813 Iodometric method (Winkler)
- Withdrawn SFS 3040 Titrimetric method (Winkler)
- High accuracy Winkler method
- Optical oxygen sensor
- Electrochemical oxygen sensor
APPENDIX 9 (2/2)

EN 25813 Iodometric method (Winkler)
Withdrawn SFS 3040 Titrimetric method (Winkler)
High accuracy Winkler
Optical oxygen sensor
Electrochemical oxygen sensor
# Kenttämittausvertailu


Kenttämittausvertailussa kaiken kaikkiaan 88 % tuloksista oli hyväksyttäviä, kun tulosten sallittiin vaihdella 8 % vertailuarvosta. Vain kolme tulosta oli kyseenalaisia ja viisi tulosta ei-hyväksyttäviä. Jälkimmäiseen tulokseen saattaa olla syynä elektrokemiallisen happisensoreiden kalibrointiongelmat. Jälkimmäiseen tulokseen saattaa olla syynä elektrokemiallisen mittauksen kannalta riittävää, mikä on voinut aiheuttaa poikkeamaa mittaustuloksiin.
In the framework of the European Metrology Research Programme (EMRP) project ENV05 OCEAN (Metrology for ocean salinity and acidity), the dissolved oxygen field \textit{(in situ)} intercomparison (FieldOxy 2014) test was organized onboard R/V Aranda on April 23, 2014 in the Gulf of Finland. The aim of the intercomparison was to enable the participants to assess their performance in measuring dissolved oxygen concentration in seawater under field conditions. The intercomparison measurement was organized jointly by the Finnish Environment Institute (Proftest SYKE. Envical SYKE) and University of Tartu.

Total of 21 participants from 10 institutes in Finland, Estonia, France, Germany and Sweden participated in the intercomparison. Totally, 13-18 oxygen sensors were tested depending of the test depth. Additionally, six Winkler titrimetric setups participated in the intercomparison. The metrologically traceable Winkler titration result (the assigned value) was measured by the Winkler setup of University of Tartu onboard R/V Aranda.

In total, 88 % of the results were satisfactory when total deviation of 8 % from the assigned values were accepted. Only three results were questionable and five results were unsatisfactory. A possible reason for several of the unsatisfactory results might be problems with calibration of electrochemical oxygen sensors. The movement of the water during the PT may have been insufficient for the electrochemical sensors, which may have resulted biased measurement results. Overall the share of satisfactory results was very good.

Som referensvärde av upplöst syre användes Tartu universitets Winkler titrerings resultat, som är metrologiskt spårbart. Resultaten värderades med hjälp av z-värden. I jämförelsen var 88 % av alla resultaten tillfredsställande, när 8 % totalavvikelsen från referensvärdet accepterades. Bara tre resultat var tvivelaktiga och fem resultat oacceptabla. En möjlig förklaring till de oacceptabla resultaten var problem med kalibreringen av elektrokemiska syresensorer, som är svårt i stillastående vatten. Överlag var andelen acceptabla resultat mycket god.

Nyckelord: EMPR, Aranda, fältmätning, jämförelseprov, utlöst syre, vattenanalyser, Proftest, Envical, provningsjämförelse, vatten- och miljölaboratorier.
Field measurement intercomparison

Field measurements of dissolved oxygen concentration

Mirja Leivuori, Teemu Nääkkö, Ivo Leito, Irja Helm, Lauri Jalukse, Lari Kaukonen, Panu Hamrin and Markku Ilmakunnas