



Dissolved Oxygen Concentration Interlaboratory Comparison Measurement ESTDO-2012

Final Report

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1. Introduction

Dissolved oxygen (below DO) content in natural waters is an indispensable quantity whenever background data is collected for investigations of nature from hydrobiological, ecological or environmental protection viewpoint. Sufficient concentration of DO is critical for the survival of most aquatic plants and animals as well as in waste water treatment. DO concentration is a key parameter characterizing natural and wastewaters and for assessing the state of environment in general. Yet DO concentration is a highly unstable parameter of water. Thus preparation of reference solutions that are stable for extended period of time is almost impossible. This complicates the standardization of the measurements and preparation of certified reference materials. Intercomparison measurements, however, are a viable means of underpinning measurement quality even with this unstable analyte.

It is difficult to organize DO intercomparisons with sending samples to the participating laboratories as is usually done in the case of interlaboratory comparisons in other chemical measurements. Given that most DO measurement instruments¹ can be transported *in situ* interlaboratory comparisons are a good alternative. In situ interlaboratory comparisons are intercomparison measurements, where all the participants (with their technical equipment and using their own competence) measure the same sample continuously at the same time, at the same site. This arrangement provides the best possibility for assessing participant² performance in determining DO content in water.

ESTDO-2012 *in situ* interlaboratory comparison measurement of **dissolved oxygen concentration** took place on March 23, 2012 at Testing Centre of University of Tartu (below UT), Estonia. This report presents the results and conclusions of the intercomparison.

The purpose of the intercomparison was twofold:

1. To assess the agreement between the results of DO measurements performed by the personnel of the participant laboratories with their instruments according to their usual working procedures.
2. To improve the measurement competence of the participants.

¹ The instrument (also called analyzer) generally consists of an amperometric or optical sensor connected to a data processing and displaying unit.

² Participant – laboratory participating in the intercomparison and sending a worker and an instrument to the intercomparison.

The intercomparison measurements' participants, conditions and results are discussed in Section 2 and conclusions are presented in Section 3.

2. DO Intercomparison

2.1 Participants

There were thirteen participants to the DO intercomparison (below denoted³ as: **A, B, C, D, E, F, G, H, J, K, L and M**). The participants are listed in this report but the results are presented in random order, so that the results cannot be traced back to the participants. Every participant received a private letter revealing his/her result number and permitting assessment of performance.

Table 1. List of participants.

Participant	Country
AS Tartu Veevärk	Estonia
AS Pärnu Vesi	Estonia
Baltic Sea Research Institute	Germany
Eesti Keskkonnauuringute Keskus OÜ	Estonia
EKUK Pärnumaa Filiaal	Estonia
EKUK Virumaa Filiaal Jõhvi labor	Estonia
EMÜ Limnoloogiakeskus	Estonia
IFREMER Centre de Brest	France
Saaremaa Veterinaar-ja Toidulabor	Estonia
Tartu Ülikooli Katsekoda	Estonia
EKUK Virumaa Filiaal Kohtla-Järve keskkonnalabor	Estonia
Finnish Environment Institute SYKE	Finland
EKUK Tartu Filiaal	Estonia

2.2 Apparatus for creating the reference medium

The best comparison of measurement results is possible when the measured value is determined by the participants for the same object in the same location at the same time. The measurements were carried out in water produced by a MilliQ Advantage A10 setup (below MilliQ water) at four saturation concentrations (according to ISO 5814:1990⁴), in tap water and in oxygen-free environment at concentration of practically 0 mg/l. The DO measurements were carried out in the apparatus shown in Annex 1. At saturation condition measurements were carried out follows. Air-saturated MilliQ water was used as the

³ The participants are listed in this report but the results are presented in random order, so that the results cannot be traced back to the participants!

⁴ ISO 5814:1990 *Water quality – Determination of dissolved oxygen – Electrochemical probe method*. ISO, 1990.

reference medium (equilibrium saturation medium). The pressure, humidity and temperature of the air used for saturation were controlled and taken into account. The saturation medium was created in a modified (a second bath and a mechanical stirrer were added) thermostat CC2-K12 (Peter Huber Kältemaschinenbau GmbH, Germany) in MilliQ water with overall volume 3.9 dm³. The obtained temperature stability was lower than 0.01 °C (standard deviation). See the Annex 1. The air used for saturation was taken from the air inlet situated on the roof of the building. The air flow velocity during calibration was around 1 dm³ min⁻¹. The ordinary aquarium spray was used for bubbling (at depth of 13 cm). The estimated diameter of the bubbles was between 0.8 to 1.8 mm. The measured environment was stirred with constant speed. Thus the DO probes of the participants were arranged concentrically in the bath and were immersed approximately to the same depth for achieving the same velocity of water movement in the location of each sensor. This setup permitted to achieve the best possible uniformity of the measurement conditions between the participants.

2.3 Calibration of Measurement Equipment

As stated above the purpose of the intercomparison was to assess the agreement between the participant results obtained using their *routine work procedures*. Therefore the participants were requested to carry out calibration of their measurement instruments in the same way as they would in the case of ordinary field work according to their own procedures and calibration intervals.

2.4 The Measurement Conditions

The reference values of DO saturation concentrations were calculated as described in the standard ISO 5814:1990⁴. The experimental setup for creating the water saturated with air under carefully controlled conditions and the calculation method for obtaining the reference values and their uncertainties have been verified using the gravimetric Winkler titration method⁵. The uncertainty of the reference value was estimated according to the ISO GUM. All the major uncertainty sources, such as temperature measurement, temperature instability, air pressure, air humidity, oxygen concentration in air, the mathematical model itself, possible over- or undersaturation, etc were taken into account. The two most important uncertainty sources are possible over- or undersaturation and the uncertainty of the mathematical model itself⁵. The uncertainties of the reference DO concentrations used

⁵A highly accurate method for determination of dissolved oxygen: Gravimetric Winkler method. I. Helm, L. Jalukse, I. Leito, *Analytica Chimica Acta* **2012**, 741, 21-31.

in this intercomparison were conservatively estimated as ± 0.15 mg/l ($k = 2$). The temperature of the MilliQ water was measured by calibrated digital thermometer Chub-E4 (model nr 1529, serial nr A44623, manufacturer Hart Scientific) with two Pt100 sensors (Ser. No. 0818 and 0855). The last calibration was made in May 2011 (by the Estonian NMI, AS Metrosert). The uncertainties of all temperature measurements (including bath instability uncertainty source) are ± 0.05 °C ($k = 2$). The atmospheric pressure was measured by digital barometer PTB330 (Ser No G37300007, manufactured by Vaisala Oyj, Finland, calibrated by manufacturer 19.09.2011) with uncertainty 10 Pa ($k = 2$). The level of air humidity after the second saturation vessel was measured using digital hygrometer Almemo 2290-8 with sensor ALMEMO FH A646 E1C (manufacturer AHLBORN Mess- und Regelungstechnik GmbH). The humidity of the air bubbled through the water in the second bath was around 100% RH. The uncertainties of all relative humidity measurements are ± 5 %RH ($k = 2$).

The timeline of the intercomparison is presented in Table 2. The measurements started at the highest temperature and every next temperature was lower than the preceding one. Lowering the temperature for arriving at the next temperature level started immediately after taking the readings of the participant and reference instruments at the preceding temperature. Sufficient time was allowed for stabilization of the temperature and dissolved oxygen content. Both parameters were monitored and measurements were started only after a stable plateau was seen. The criterion of stability was that DO reading of the monitoring instrument (with optical sensor) did not change by more than 0.01 mg/l during 10 minutes. Temperature always stabilized faster than the DO reading, therefore the stability of the DO reading automatically meant also the stability of the temperature reading.

Table 2. Time table, Reference Values and Uncertainties.

Time window start-end (h.min)	reference value of DO concentration U, k=2		reference value of temperature U, k=2		air pressure mean U, k=2		Medium
	mg/l	mg/l	°C	°C	Pa	Pa	Comment
10.39 10.47	8.24	0.15	24.84	0.05	100757	10	MilliQ water saturated with air (below: SAT25)
12.45 12.46	9.07	0.15	19.91	0.05	100757	10	MilliQ water saturated with air (below: SAT20)
14.38 14.42	10.05	0.15	15.04	0.05	100926	10	MilliQ water saturated with air (below: SAT15)
16.56 17.00	12.74	0.15	5.07	0.05	100932	10	MilliQ water saturated with air (below: SAT5)
17.25 17.28	-	-	-	-			Tapwater at room temperature (below: TAPW)
17.31 17.39	0.0	0.01					Oxygen-free tapwater (added: Na ₂ SO ₃ + CoCl ₂) (below: ZERO)

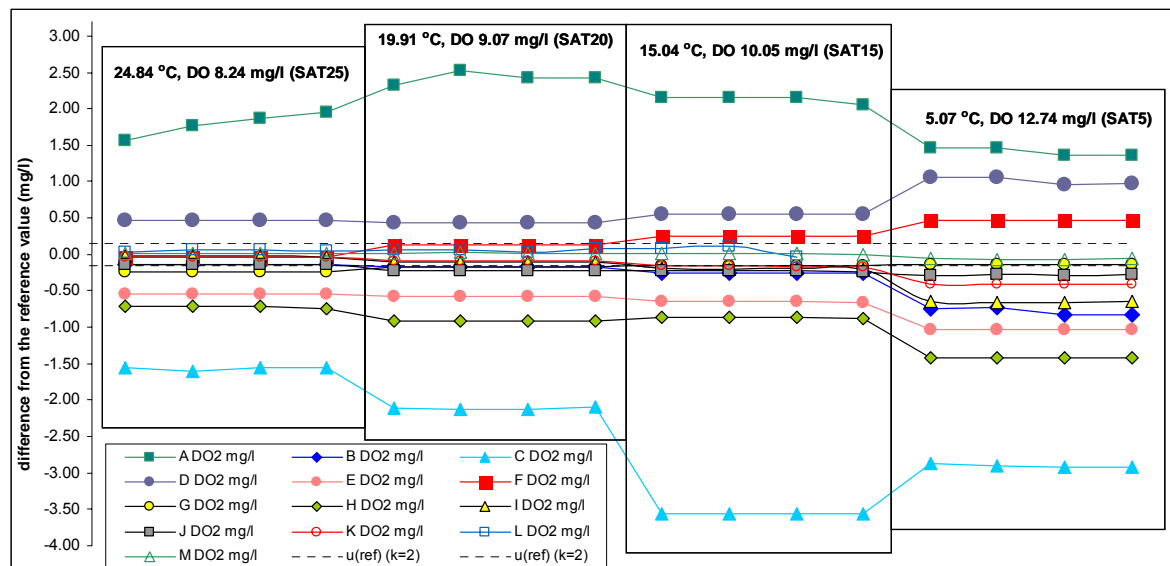
2.5 DO Comparison Measurements Results

The reference DO concentration values at different temperatures are given in Table 2. The participant instruments results are given in Table 3 and differences of the readings of the participant instruments from the reference values are given in Scheme 1. Scheme 2 gives the same information with expanded DO concentration axis. The participant results were recorded in quadruplicate at about 1-3 minute intervals using digital photos. Photographing allows recording the all readings within a very short time and preserving and archiving them for solving possible disputes. Hereinafter the word “participant value” or “participant instruments result” is used with the following meaning: it is the mean of the four readings taken as explained above.

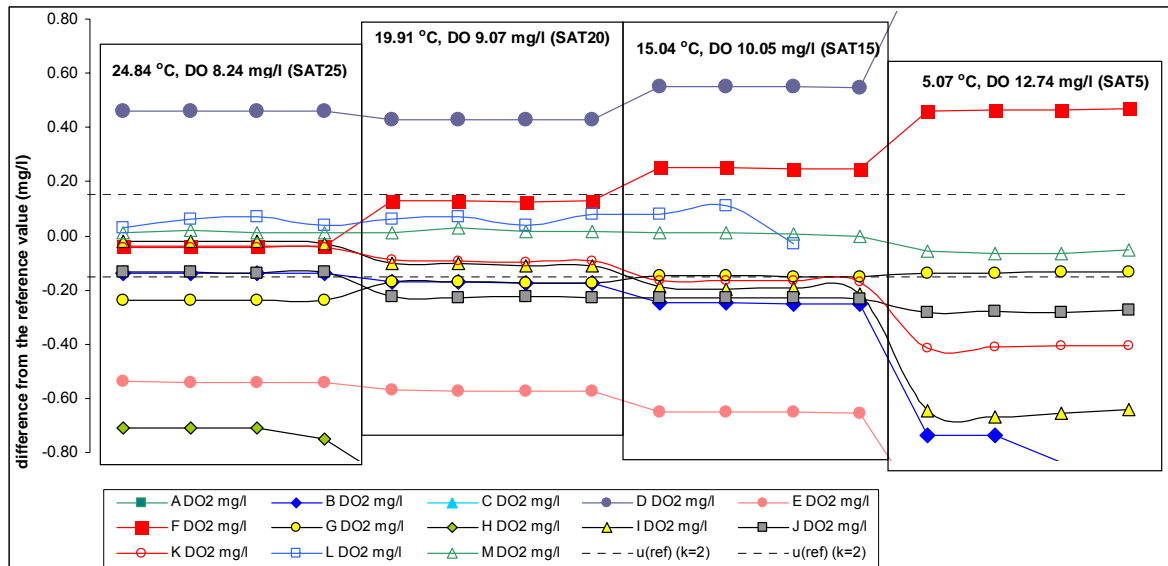
Table 3. DO Readings of Participant Instruments.

Participant	DO concentrations						Temperatures			
	SAT25	SAT20	SAT15	SAT5	TAPW	ZERO	SAT25	SAT20	SAT15	SAT5
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	°C	°C	°C	°C
A	10.03	11.50	12.18	14.15	12.83	3.00	24.90	19.90	14.90	5.10
B	8.10	8.90	9.80	11.95	7.63	0.10	24.80	19.90	15.10	5.68
C	6.67	6.96	6.49	9.83	5.97	0.17	24.90	19.90	15.10	5.20
D	8.70	9.50	10.60	13.75	8.20	0.20	25.00	19.83	14.80	5.00
E	7.70	8.50	9.40	11.70	7.30	0.10	24.80	19.90	15.00	5.40
F	8.20	9.20	10.30	13.20	7.83	0.00	24.90	19.90	15.00	5.30
G	8.00	8.90	9.90	12.60	7.55	0.00	25.00	19.90	14.80	4.98
H	7.52	8.16	9.18	11.31	7.51	0.05	24.90	20.00	15.20	5.30
I	8.22	8.97	9.85	12.08	7.75	0.04	24.90	19.90	15.10	5.10
J	8.11	8.84	9.82	12.46	7.30	0.01	24.85	19.93	15.06	5.08
K	8.20	8.98	9.89	12.33	7.01	0.03	24.83	19.91	15.04	5.07
L	8.29	9.13	10.10				24.70	19.80	15.00	
M	8.25	9.09	10.06	12.68	7.75	0.04	25.00	20.08	15.20	5.20

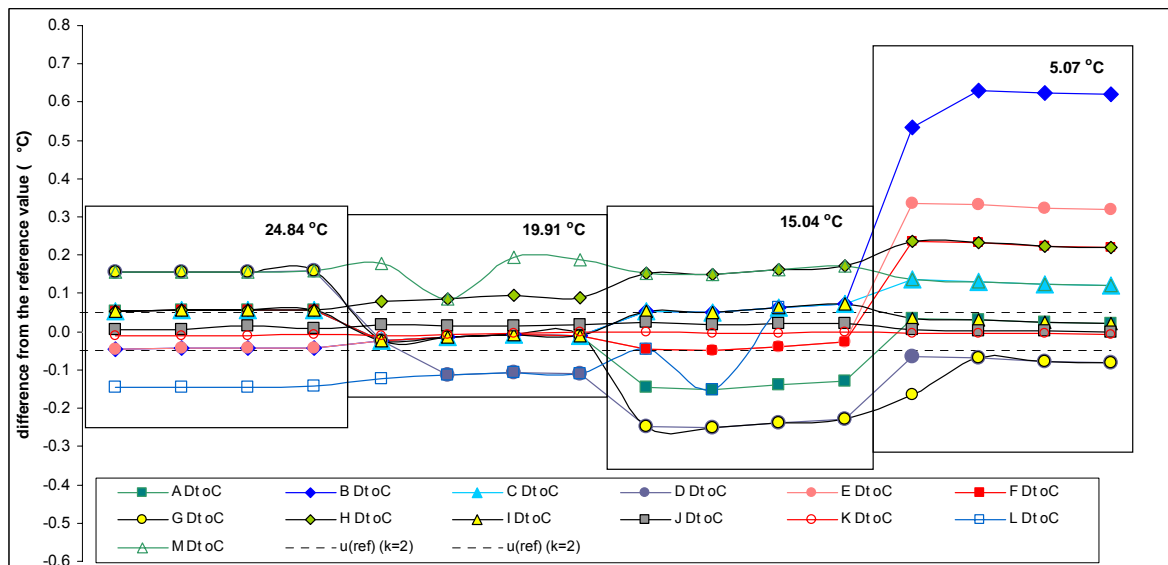
Scheme 1. Differences Between DO Readings of Participant Instruments and the Reference Values (scale: +3.20 .. - 3.80 mg/l).



Scheme 2. Differences Between DO Readings of Participant Instruments and the Reference Values (scale: +0.80 .. - 0.80 mg/l)



Scheme 3. Differences Between Temperature Readings of Participant Instruments and the Reference Values⁶



The mean values and standard deviations of the thirteen participating laboratories and reference values under four different sets of conditions are presented in the following table:

⁶ The estimated uncertainties of the temperature reference values are $\pm 0.05 \text{ }^\circ\text{C}$ ($k = 2$)

Table 4. The Mean Values of the Participating Laboratories and their Absolute and Relative Standard Deviations

Medium ^a	DO concentration			Temperature	
	mean ^b	st dev	% st dev	mean ^b	st dev
	mg/l	mg/l	%	°C	°C
SAT25	8.15	0.75	9	24.88	0.09
SAT20	8.97	0.99	11	19.91	0.07
SAT15	9.81	1.23	13	15.02	0.13
SAT5	12.34	1.14	9	5.20	0.20
TAPW	7.88	1.65	21	19.86	0.08

^a See Table 2 for the acronyms. ^b Mean values of over all participating laboratories.

2.6 Assessing the Agreement between the Participant Values and the Reference Values according to the E_n approach

To assess the agreement between the values of the participants and the reference values uncertainty data of the participant values are needed. The uncertainties of measurement values were estimated by the participants. The expanded uncertainties are presented in the table below:

Table 5. The Self-Declared Expanded Uncertainties^a of the Participant Values.

Participant	DO concentrations						Temperatures			
	SAT25	SAT20	SAT15	SAT5	TAPW	ZERO	SAT25	SAT20	SAT15	SAT5
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	°C	°C	°C	°C
A	0.20	0.20	0.20	0.20	—	—	0.20	0.20	0.20	0.20
B	—	—	—	—	—	—	—	—	—	—
C	—	—	—	—	—	—	—	—	—	—
D	0.20	0.20	0.20	0.20	—	—	0.20	0.20	0.20	0.30
E	—	—	—	—	—	—	—	—	—	—
F	—	—	—	—	—	—	—	—	—	—
G	—	—	—	—	—	—	—	—	—	—
H	—	—	—	—	—	—	—	—	—	—
I	0.13	0.09	0.38	0.32	—	1.00	0.40	0.60	0.30	0.60
J	0.44	0.47	0.52	0.65	0.47	0.26	0.10	0.10	0.10	0.10
K	0.30	0.30	0.30	0.30	0.30	0.30	0.01	0.01	0.01	0.01
L	—	—	—	—	—	—	—	—	—	—
M	0.16	0.16	0.17	0.30	0.16	0.13	0.30	0.30	0.30	0.30

^a All expanded uncertainties are given with a coverage factor 2: $U = k \cdot u_c$ ($k = 2$). Dash means that no uncertainty was reported by the participant.

E_n numbers⁷ were used to assess the agreement between participant values and the reference values. The E_n numbers for DO concentration are found as follows:

$$E_n = \frac{C_{\text{lab}} - C_{\text{ref}}}{\sqrt{U_{\text{lab}}^2 + U_{\text{ref}}^2}} \quad (1)$$

⁷ EN ISO-IEC 17043:2010 *Conformity assessment – General requirements for proficiency testing*, ISO/IEC 2010 (This standard replaces the ISO Guides 43-1 and 43-2).

where C_{lab} is the participant DO value, C_{ref} is the reference value of DO concentration, U_{lab} is the expanded uncertainty of the participant value and U_{ref} is the expanded uncertainty of the reference value.

The E_n scores for temperature:

$$E_n = \frac{t_{lab} - t_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}} \quad (2)$$

where t_{lab} is the participant temperature value, t_{ref} is the reference temperature value, U_{lab} is the expanded uncertainty of the participant value and U_{ref} is the expanded uncertainty of the reference value.

Criteria for laboratory performance based on the E_n numbers⁸:

- a) $|E_n| \leq 1$: **satisfactory** (the result and reference value are accordant);
 b) $|E_n| > 1$: **unsatisfactory** (the result and reference value are not accordant)

The $|E_n|$ numbers of the participants for DO measurement under four sets of conditions (saturation concentration under four temperatures) are given below.

Table 6. The $|E_n|$ Numbers of the Participants for DO Measurement^a

Medium	A	B	C	D	E	F	G	H	I	J	K	L	M
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
SAT25	7.1	0.9	10.4	1.8	3.6	0.3	1.6	4.8	0.1	0.3	0.1	0.3	0.1
SAT20	9.7	1.1	14.1	1.7	3.8	0.9	1.1	6.1	0.6	0.5	0.3	0.4	0.1
SAT15	8.5	1.7	23.7	2.2	4.3	1.7	1.0	5.8	0.5	0.4	0.5	0.4	0.0
SAT5	5.7	5.2	19.4	4.1	6.9	3.1	0.9	9.5	1.8	0.4	1.2		0.2
ZERO	20.0	0.7	1.1	1.3	0.7	0.0	0.0	0.3	0.0	0.0	0.1		0.2

^a If participant did not report uncertainty its uncertainty was taken as zero.

The $|E_n|$ numbers of the participants for temperature measurement under four sets of conditions (saturation concentration under four temperatures) are given below:

Table 7. The $|E_n|$ Numbers of the Participants for Temperature Measurement^a

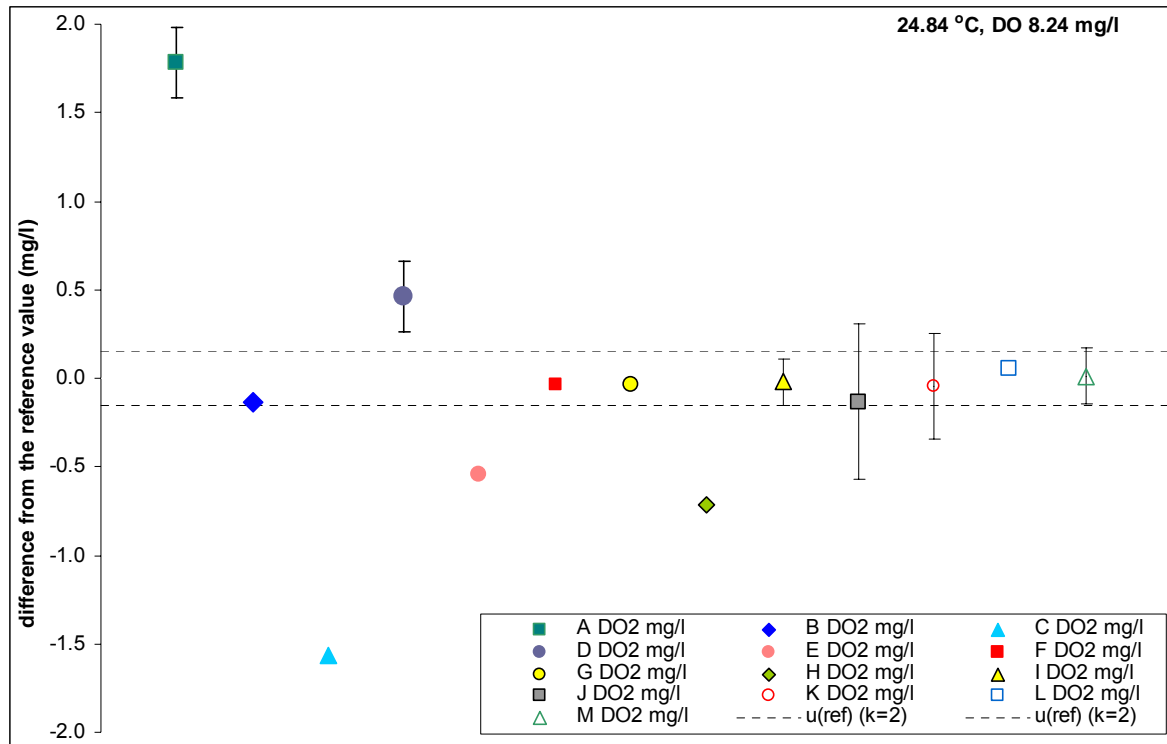
Medium	A	B	C	D	E	F	G	H	I	J	K	L	M
	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C
SAT25	0.3	0.9	1.1	0.8	0.9	1.1	3.1	1.1	0.1	0.1	0.1	2.9	0.5
SAT20	0.1	0.3	0.3	0.4	0.3	0.3	0.3	1.7	0.0	0.2	0.2	2.3	0.5
SAT15	0.7	1.2	1.2	1.2	0.8	0.8	4.8	3.2	0.2	0.2	0.2	0.8	0.5
SAT5	0.1	12.1	2.6	0.2	6.6	4.6	1.9	4.6	0.0	0.0	0.0		0.4

^a If participant did not report uncertainty its uncertainty was taken as zero.

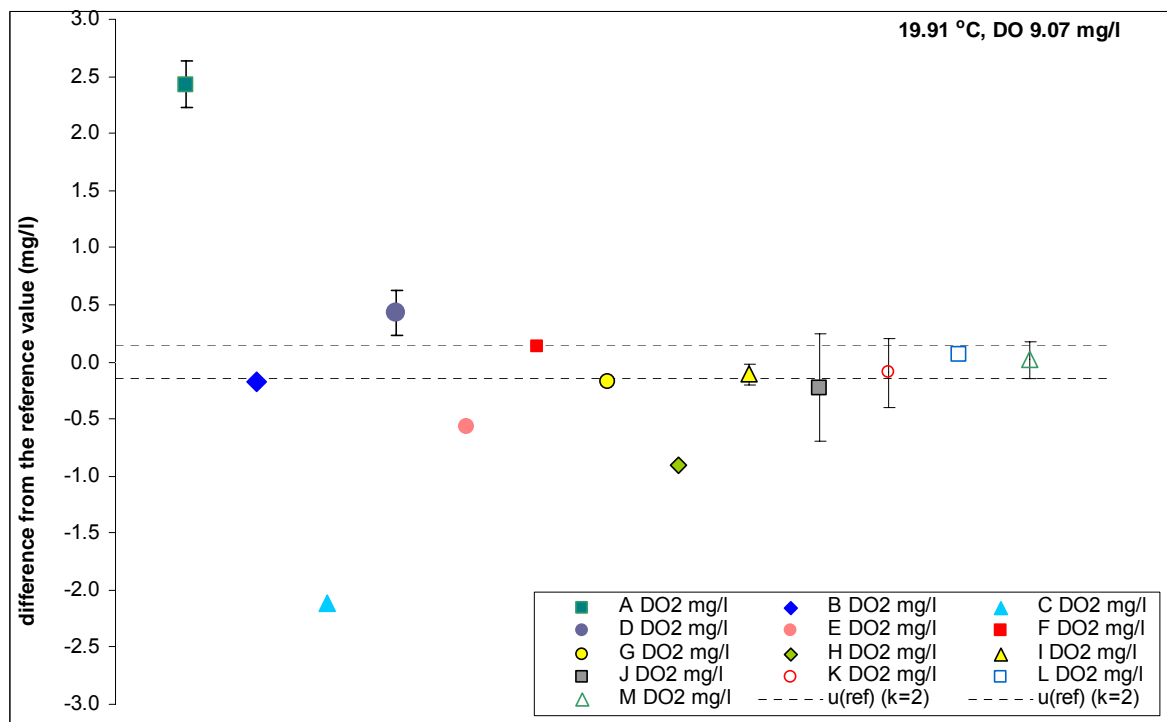
The following Schemes present the differences ($\Delta C = C_{lab} - C_{ref}$) between the participant DO measurement values with their expanded uncertainties and the reference values under the abovementioned sets of experimental conditions.

⁸ The E_n number is strongly dependent on the uncertainty of the participant value. Therefore close to zero E_n value does not directly indicate the quality of the participant value but only the agreement between it and the reference value (which, of course, is an important component of the quality of the result).

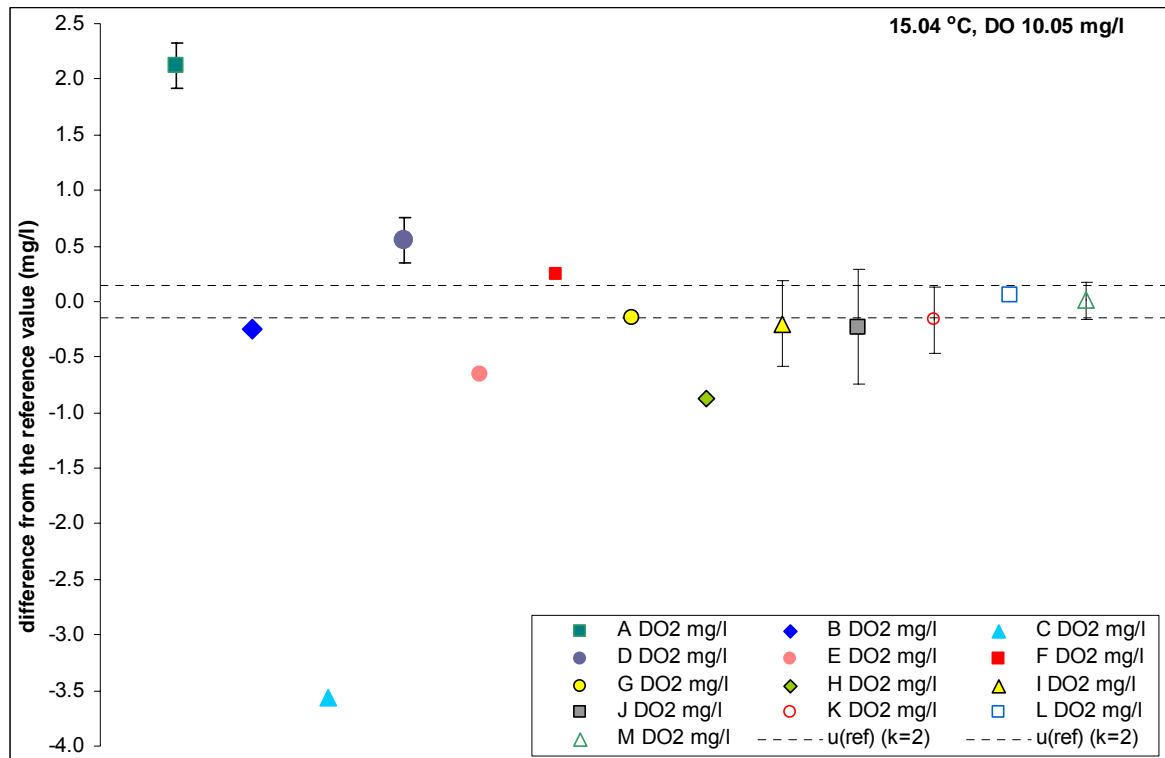
Scheme 4. Differences Between the Participant DO Measurement Values with their Expanded Uncertainties and the Reference Value at Temperature 24.84 °C and DO Concentration 8.24 mg/l.



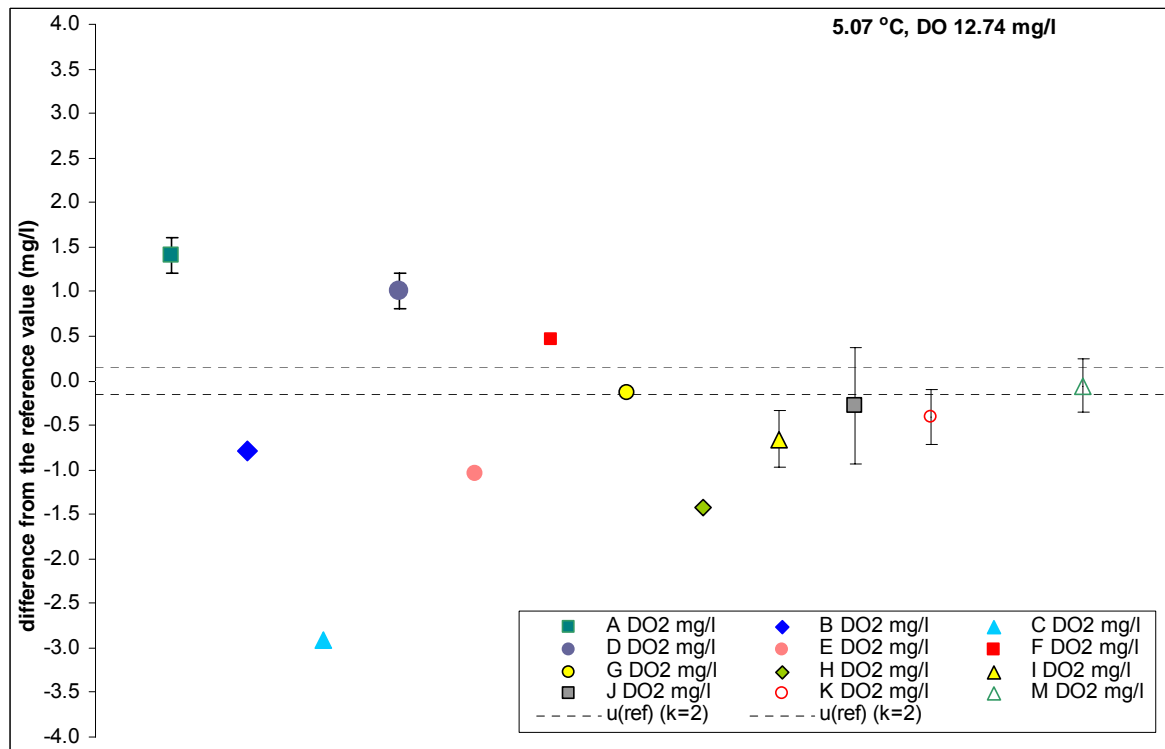
Scheme 5. Differences Between the Participant DO Measurement Values With Their Expanded Uncertainties and the Reference Value at Temperature 19.91 °C and DO Concentration 9.07 mg/l



Scheme 6. Differences Between the Participant DO Measurement Values With Their Expanded Uncertainties and the Reference Value at Temperature 15.04 °C and DO Concentration 10.05 mg/l

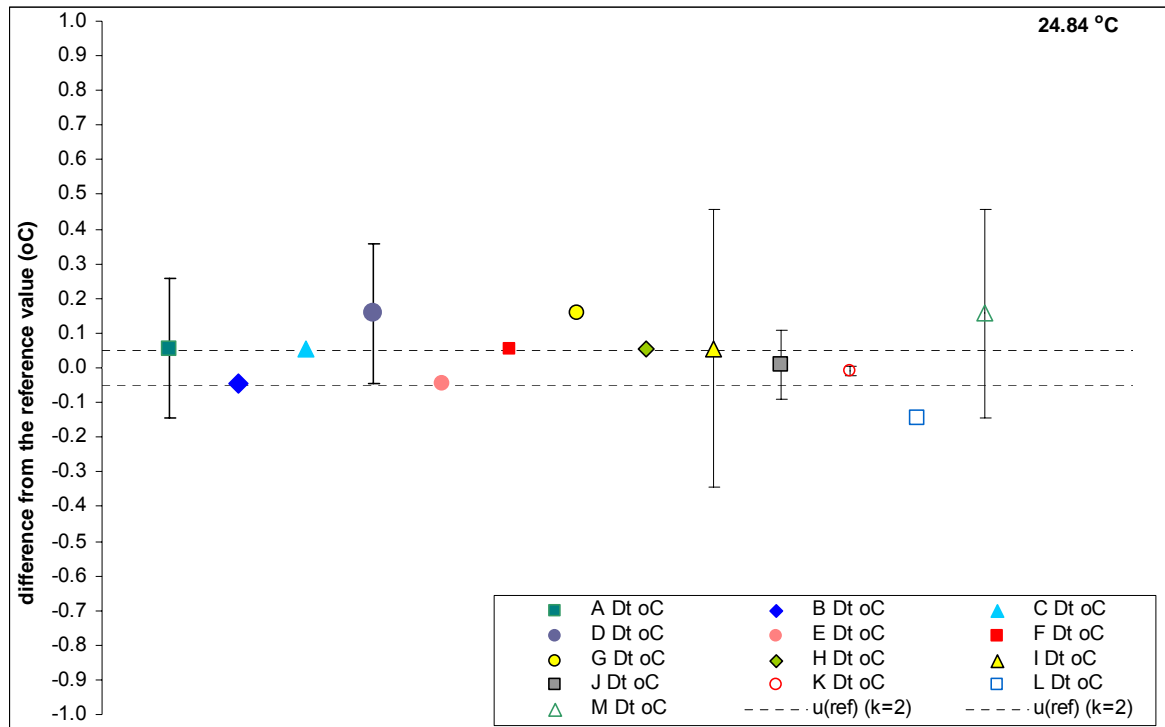


Scheme 7. Differences Between the Participant DO Measurement Values With Their Expanded Uncertainties and the Reference Value at Temperature 5.07 °C and DO Concentration 12.74 mg/l

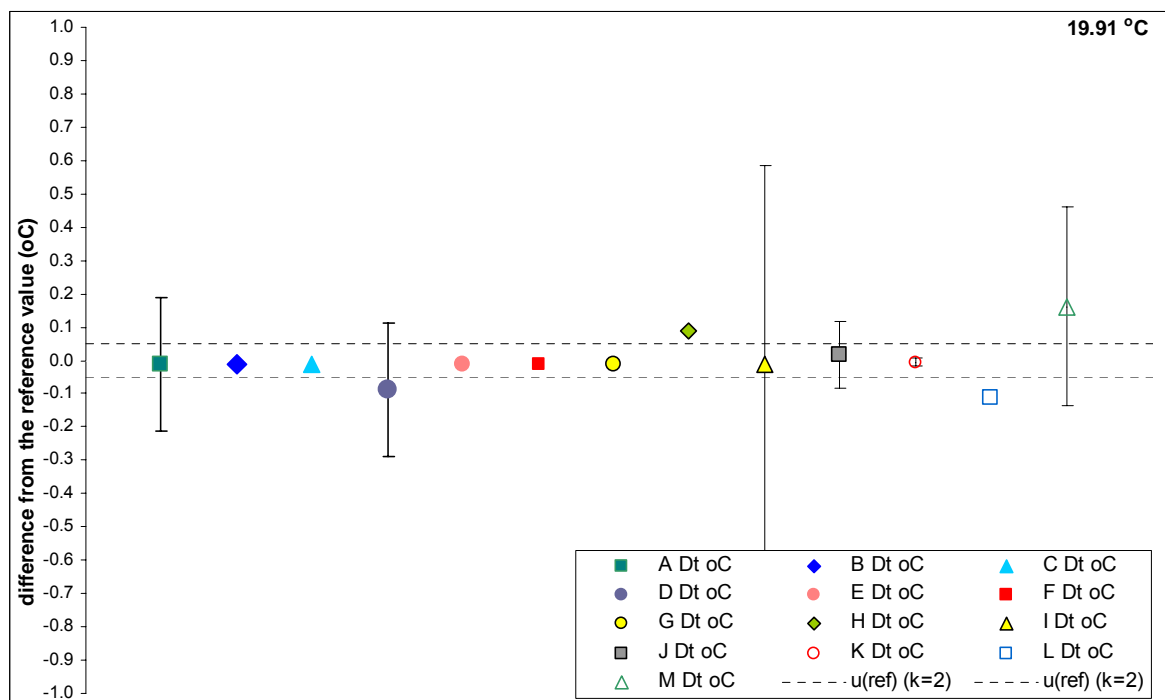


The following Schemes present the differences ($\Delta t = t_{\text{lab}} - t_{\text{ref}}$) between the participant temperature measurement values with their expanded uncertainties and the reference values under different sets of experimental conditions.

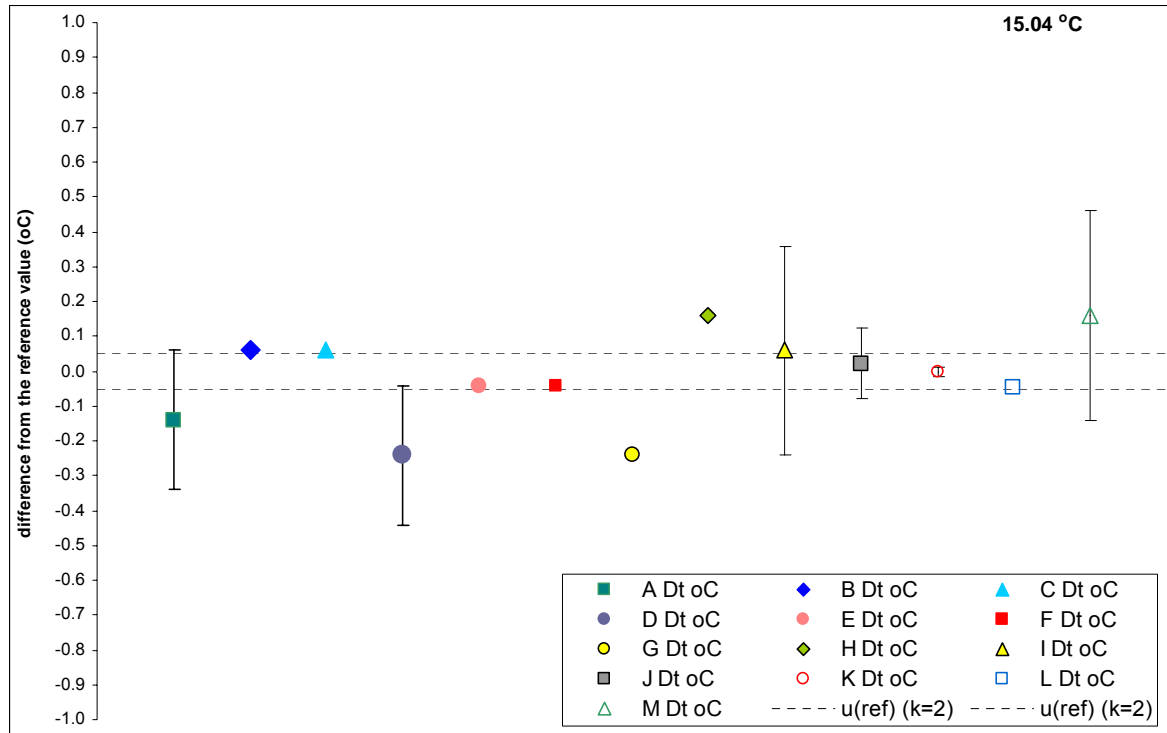
Scheme 8. Differences Between the Participant Temperature Measurement Values With Their Expanded Uncertainties and the Reference Value at temperature 24.84 °C



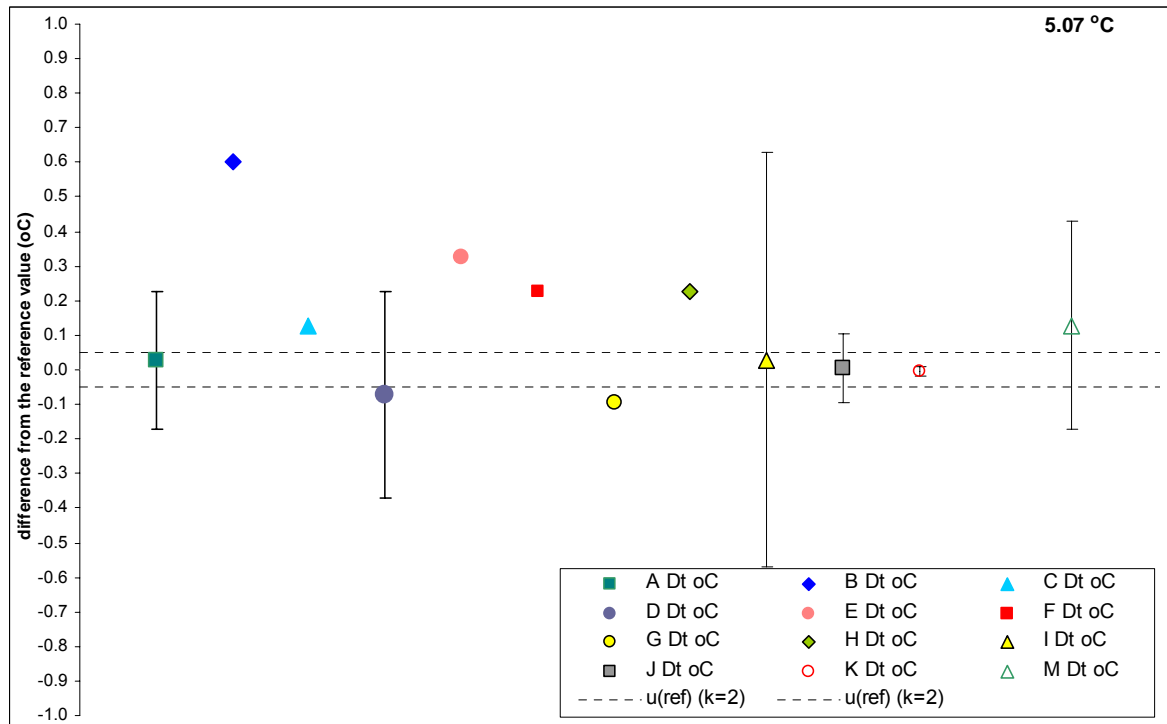
Scheme 9. Differences Between the Participant Temperature Measurement Values With Their Expanded Uncertainties and the Reference Value at Temperature 19.91 °C



Scheme 10. Differences Between the Participant Temperature Measurement Values With Their Expanded Uncertainties and the Reference Value at Temperature 15.04 °C



Scheme 11. Differences Between the Participant Temperature Measurement Values With Their Expanded Uncertainties and the Reference Value at Temperature 5.07 °C



2.7 Assessing the Agreement between the Participant Values and the Consensus Values according to the z-score approach

Participant result were also evaluated according to the z-score approach^{9,10}. The z-score for a participant value is calculated according to the following equation:

$$z = \frac{x - x_c}{s} \quad (3)$$

where x is the participant's value, x_c is the consensus value and s is the target standard deviation. The consensus values and target standard deviations for the respective measurement conditions were found using the Algorithm A as described in the ISO 13528:2005 standard.¹⁰ This algorithm gives the so-called robust estimates of the consensus value and standard deviation of participants. Absolute (i.e. unsigned) values of z-scores ($|z|$ values) are used for assessing the acceptability of the DO and temperature results as described in Table 8.

Table 8. Criteria for laboratory performance based on the z-Scores Assessment.

$ z $ Value	Acceptability of the Result	Required Action
$ z \leq 2$	Acceptable result	No action is required
$2 < z < 3$	Doubtful result	Preventive action is required
$ z \geq 3$	Unacceptable result	Corrective action is required

The $|z|$ scores of the participants for DO measurement under six sets of conditions for DO and four for Temperature measurement are presented in Table 9 and Table 10, respectively.

Table 9. The $|z|$ values of the Participants for DO Measurement.

	A	B	C	D	E	F	G	H	I	J	K	L	M
Medium	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
SAT25	4.3	0.0	3.2	1.3	0.9	0.2	0.3	1.3	0.2	0.0	0.2	0.4	0.3
SAT20	5.1	0.0	3.9	1.1	0.8	0.5	0.0	1.5	0.1	0.2	0.1	0.4	0.3
SAT15	4.1	0.2	6.1	1.3	0.9	0.7	0.0	1.3	0.1	0.1	0.0	0.4	0.3
SAT5	1.4	0.2	1.7	1.2	0.4	0.7	0.3	0.7	0.1	0.2	0.1		0.4
TAPW	8.2	0.2	2.3	1.1	0.3	0.5	0.1	0.0	0.4	0.3	0.7		0.4
ZERO	34.3	0.3	1.1	1.5	0.3	0.8	0.8	0.3	0.4	0.8	0.5		0.4

⁹ EN ISO-IEC 17043:2010 *Conformity assessment – General requirements for proficiency testing*, ISO/IEC 2010 (This standard replaces the ISO Guides 43-1 and 43-2).

¹⁰ ISO 13528:2005. *Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons*, ISO, 2005.

Table 10. The $|z|$ values of the Participants for Temperature Measurement.^a

Medium	A	B	C	D	E	F	G	H	I	J	K	L	M
	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C	°C
SAT25	0.1	1.0	0.1	1.2	1.0	0.1	1.2	0.1	0.1	0.4	0.6	2.1	1.2
SAT20	0.2	0.2	0.2	1.3	0.2	0.2	0.2	1.3	0.2	0.3	0.1	1.6	2.4
SAT15	0.9	0.5	0.5	1.6	0.2	0.2	1.6	1.2	0.5	0.3	0.1	0.2	1.2
SAT5	0.3	2.7	0.2	0.8	1.3	0.7	0.9	0.7	0.3	0.4	0.5		0.2

^a At 20 °C (SAT20) more than 50% of the results were the same. In such cases the Algorithm A breaks down and cannot be used. Instead the arithmetic mean and standard deviation were used as consensus value and target standard deviation, respectively.

2.8 DO measurements in an oxygen-free solution

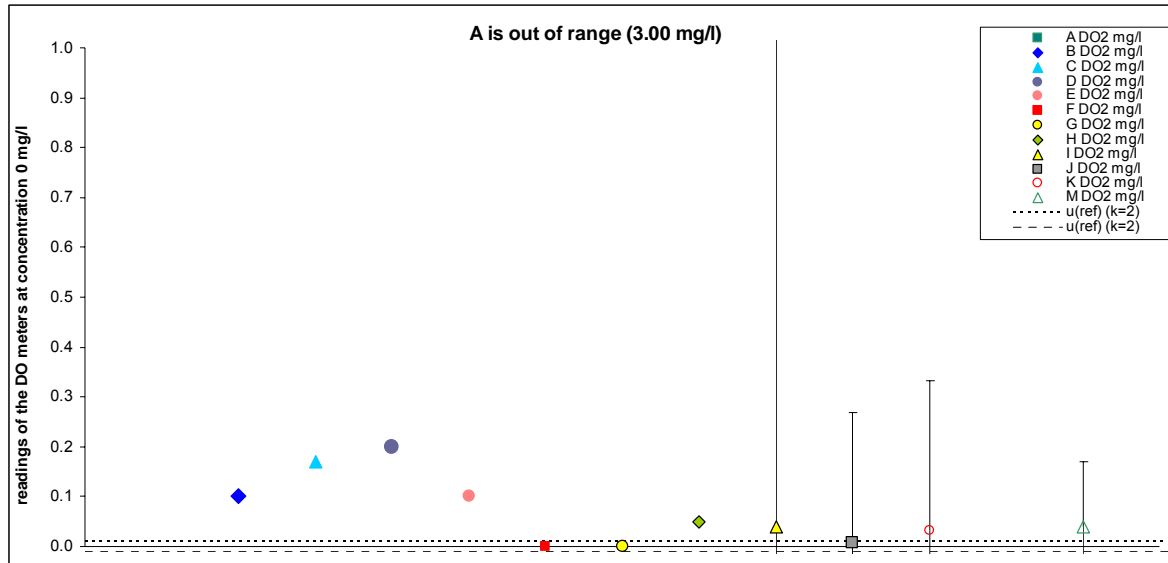
The oxygen-free solution was prepared according to the standard ISO 5814:1990⁴ by adding saturated sodium sulfite containing catalytic amount of cobalt chloride solution to the water. This measurement is first of all meant for checking the zero values of the participant instruments. Ideally the so called the “zero value” in zero-oxygen medium should be zero. There are no predefined criteria available for evaluation the closeness to zero. Therefore we use criteria based on our earlier experience presented in Table 11.

Table 11. Criteria for laboratory performance in the zero value assessment.

Value, x^a	Acceptability of the Result	Required Action
$ x \leq 0.1$	Acceptable result	No action is required
$0.1 < x < 0.3$	Doubtful result	Sensor is end of life
$ x \geq 0.3$	Unacceptable result	Sensor should be replaced

^a The reading was recorded after 8 minutes.

The zero values of the participants are presented in Scheme 12 and Table 12.

Scheme 12. Readings of Participant Instruments at DO Concentration 0 mg/l.^a

^a The reading was recorded after 8 minutes. The value of participant A is too high to be displayed on the scheme.

Table 12. Readings of Participant Instruments at DO Concentration 0 mg/l.^a

	A	B	C	D	E	F	G	H	I	J	K	L	M
Medium	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
ZERO	3.00	0.10	0.17	0.20	0.10	0.00	0.00	0.05	0.04	0.01	0.03		0.04

^a The reading was recorded after 8 minutes.

Besides the reading itself, also the response time gives useful information. Short response time means that the sensor has been designed well and is in good working order. Long response time means that the sensor is ill-designed or, in the case of amperometric sensors, the internal electrolyte needs to be replaced. Response time is usually evaluated using the so-called response factor $R_{\%}$, which is defined as the percentage of reading change (from the final reading change) that occurs during a given time when the medium where the sensor is immersed changes to another:

$$R_{\%} = \frac{C_0 - C_t}{C_0} \cdot 100\% \quad (4)$$

where C_0 is the initial reading in tapwater medium, C_t is the reading after 3 minutes from adding the concentrated Na_2SO_3 solution.

In our case the sensor was initially immersed in tap water with DO concentration around 8 mg l⁻¹ and then the DO concentration was brought to zero. The readings were taken after 3 minutes. The criteria used for assessment of the response time are presented in Table 12.

Table 13. Criteria for laboratory performance based on Response factor Assessment.

R% (3 minutes)	Acceptability of the Result
≥99	Good
≥98	Acceptable
≥97	Doubtful
≥96	Too inert
<96	Unacceptable

The reading changes are presented in Scheme 13.

Scheme 13. Dynamics of Changes in the Readings of Participant Instruments (TAPW → ZERO)

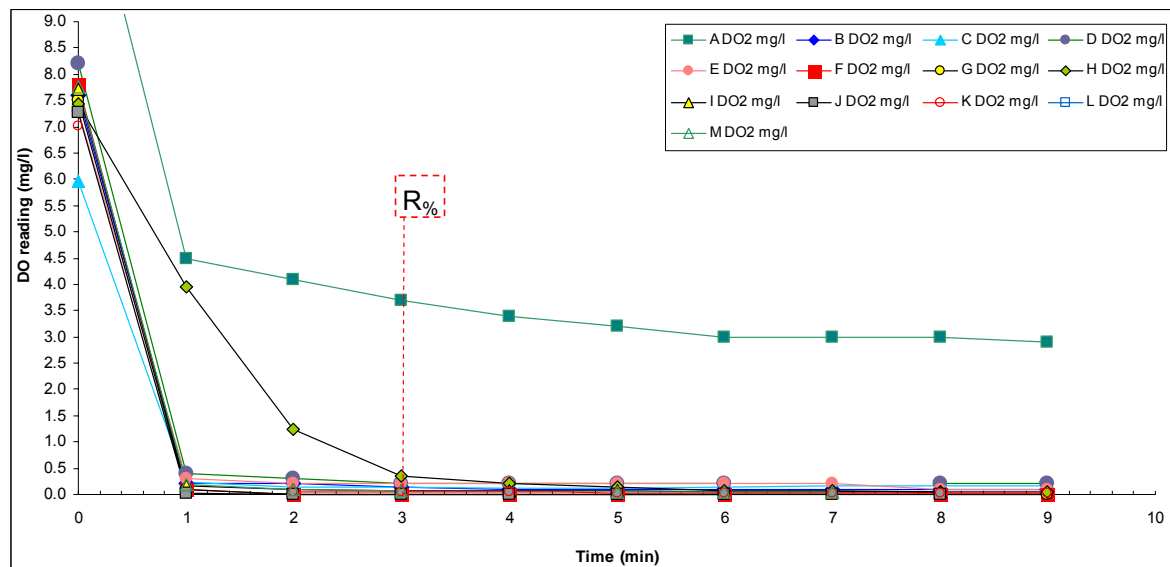


Table 14. The R% values of the Participants

Participant	R%
A	70.6
B	98.0
C	97.8
D	97.6
E	97.3
F	100.0
G	100.0
H	95.3
I	99.0
J	99.9
K	99.5
L	-
M	99.1

3. Conclusions and Recommendations

DO measurements are usually deemed easy measurements by routine laboratories. In reality, the physical and chemical processes underlying the measurements are complex and these measurements are not at all as robust as often considered. The results of this intercomparison fully support this statement: out of altogether 63 measurement results obtained by the participants 33, which is 52%, were unacceptable according to the E_n numbers. According to the z-score approach, the picture is better, but still 11% of the results are unacceptable.

Assessment of participant performance was carried out in four ways: according to E_n and z-scores, the zero value and the response factor approach ($R_{\%}$). The E_n approach needs both an independent reference value and uncertainty estimates from the participants. If a participant has not presented uncertainties or these are too optimistic then the absolute values of the E_n scores are automatically inflated and may be above 1 even if the difference of the result from the reference value is not large. The z-score approach uses statistical criteria only and with the small number of laboratories it is usually very mild. The last two ways are specifically meant to assess whether the sensor is in good working order. The following table summarizes the findings of the organizers as recommendations for the laboratories.

Table 15. Comments and Recommendations of the Organizer to the Participants.

Participant	Sensor type	Organizer comment
A	amperometric	The sensor most probably is at the end of its lifetime (very high zero current and slow response). As a minimum, the electrolyte and membrane (or the whole sensing element) should be replaced. Then new calibration should be performed. Introducing a control chart for monitoring the instrument would be highly advisable.
B	amperometric	There is possibly a problem with the temperature measurement and/or compensation in the instrument. Uncertainty evaluation is needed.
C	amperometric	It is possible that the sensor is at the end of its lifetime (high zero current). The electrolyte and membrane (or the whole sensing element) should be replaced. More frequent calibration is needed. Uncertainty evaluation is needed. Introducing a control chart for monitoring the instrument would be highly advisable.
D	amperometric	It is possible that the sensor is at the end of its lifetime (high zero current). The electrolyte and membrane (or the whole sensing element) should be replaced. New calibration would be advisable. Introducing a control chart for monitoring the instrument would be highly advisable.
E	amperometric	More frequent calibration is needed. Uncertainty evaluation is needed. Introducing a control chart for monitoring the instrument would be highly advisable.
F	amperometric	There is possibly a problem with the temperature compensation in the instrument. Uncertainty evaluation is needed. Introducing a control chart for monitoring the instrument would be highly advisable.
G	amperometric	More frequent calibration is needed. Uncertainty evaluation is needed. Introducing a control chart for monitoring the instrument would be highly advisable.
H	amperometric	It is possible that the sensor is at the end of its lifetime (slow response). Calibration is needed. Uncertainty evaluation is needed. Introducing a control chart for monitoring the instrument would be highly advisable.
I	amperometric	There is possibly a problem with the temperature compensation in the instrument. Introducing a control chart for monitoring the instrument would be highly advisable.
J	optical	-
K	optical	-
L	optical	Participated in too few measurements to give an overall assessment. Uncertainty evaluation is needed.
M	optical	-

The elapsed time from the last calibration was very different from participant to participant ranging from few days to over one year. Calibration frequency around once a year is

unacceptably low, because the properties of the sensor drift. This is also seen from the results of this intercomparison. At the same time calibration is very easy as the reference medium used for calibration of the commercial DO sensors is usually air. All commercial oxygen sensors are equipped with manuals that among other things describe how to carry out calibration. Another useful means for improving the quality of the measurement results is to maintain a control chart. Control chart of dissolved oxygen concentration measurement can be set up in two ways: either by measuring oxygen in moist air (saturated with water) or in water saturated with air. Ideally, data point for the control chart should be recorded on every day when the measurements are done. This enables seeing trends in the sensor behavior and taking action before things go out of hand. Guidelines for setting up a control chart can be obtained from the documentation of the instruments and from the authors of this report.

Several of the participants did not report uncertainties for their results, even though most of them are accredited according to the ISO/IEC 17025,¹¹ which states that competent laboratories have to evaluate their measurement uncertainties.

It remains first of all to the laboratories themselves to find out what their problems in particular cases are. However, the organizers hope that the present intercomparison helped to find the right direction.

¹¹ ISO/IEC 17025:2005 *General requirements for the competence of testing and calibration laboratories*. ISO, 2005.

4. Acknowledgments

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5. Annex 1

The Experimental Setup for DO Intercomparison

