Determination of Oxygen according to Winkler

Description

Dissolved oxygen is an important parameter for the quality of water or a water bodies. Dissolved oxygen can be determined using various methods, e.g. measurement using an oxygen electrode or titration according to Winkler. The Winkle titration is still the reference method and can be found in various standards such as DIN EN 25813 or ISO 5813.
Winkler titration is based on iodometric titration with sodium thiosulphate.
As the oxygen content of a sample can change rapidly (O_2 - absorption from the air, O_2 - consumption by biological or chemical processes), the sample must be protected from air by using special sample bottles (Winkler bottle). The oxygen in the sample is fixed by reaction with $Mn(OH)_2$. After acidification and addition of potassium iodide, the resulting iodine is titrated.

The content of Oxygen (DO) is calculated in mg/L.

$$O_2 + 4\ Mn(OH)_2 + 2\ H_2O \rightarrow 4\ Mn(OH)_3$$
$$2\ Mn(OH)_3 + 2\ KI + 6\ H^+ \rightarrow 2\ Mn^{2+} + I_2 + 6\ H_2O$$
$$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + 2\ S_4O_6^{2-}$$

Instruments

Titrator	TL 5000, TL 7000 or higher
Exchangeable head	WA 10
Electrode	Pt 62, Pt 62 RG
Cable	L 1 A
Stirrer	TM 235
Lab accessory	Glass beaker 150 mL
	Magnetic stirrer bar 30 mm

Reagents

1	Sodium thiosulfate 0.01 mol/L
2	Sulfuric acid (H_2SO_4) 96%
3	Sodium Hydroxide
4	Manganese(II)sulfate monohydrate
5	Potassium iodide
6	Sodium azide
7	Distilled Water
All reagents should be of analytical grade or better.	

Titration procedure

Reagents

Sodium thiosulfate 0.01 mol/L

$Na_2S_2O_3$ 0.01 mol/L is available as a ready-to-use solution.
The titer determination is done as described in the application note "Titer determination of Sodium thiosulfate".

Sulfuric acid 1:1

50 mL H_2SO_4 96% are added to 50 mL dist. Water.

Alkaline Iodide-solution

35g of solid Sodium hydroxide and 30g of Potassium iodide are dissolved in approx. 50mL of water.
Approx. 1g sodium azide is dissolved in a little water and added to the NaOH / KI solution. The solution is then made up to 100ml.
The sodium azide can be omitted if the sample does not contain nitrite.

Manganese(II)sulfate-solution

38g $MnSO_4$ x H_2O are dissolved in a little water and made up to 100mL. If the solution is cloudy, a few drops of sulphuric acid can be added. If necessary, the solution must be filtered.

Cleaning and storage of the electrode

The electrode is cleaned with distilled water. Pt 62 RG can be stored in dist. Water. Pt 62 is stored in KCl solution 3 mol/l.

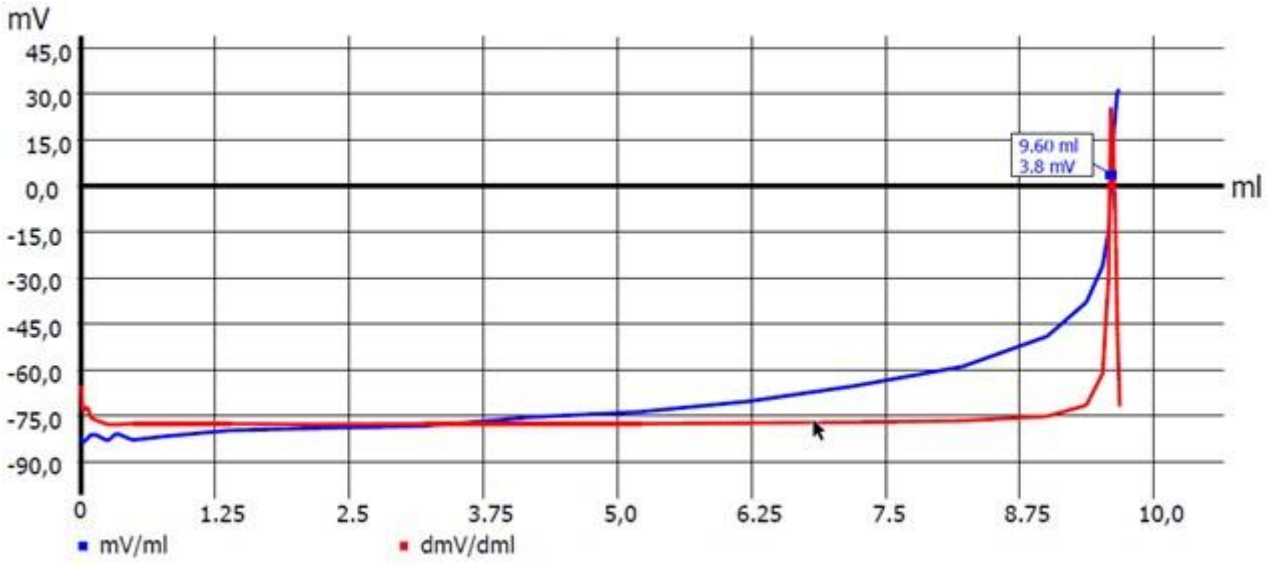
Sample preparation

To fix the oxygen, 1 mL of $MnSO_4$ - solution and 2 mL of alkaline iodide solution are added to the sample immediately after sampling, the sample bottle is closed and shaken briefly. A brown precipitate forms.

For titration, 1.5 mL of Sulfuric acid 1:1 is added to the sample. The sample is then titrated with 0.01 mol/L thiosulphate to an equivalence point.

Titration parameter

Sample titration



A Pt 62 RG with glass reference was used for this titration. If electrodes with a different reference system are used, the curve is falling.

Default method	Iodometry (back)		
Method type	Automatic titration		
Modus	Dynamic		
Measured value	mV		
Measuring speed / drift	normal	Minimum holding time	3 s
		Maximum holding time	15 s
		Measuring time	3 s
		Drift	10 mV/min
Initial waiting time	0 s		
Dynamic	average	Max step size	1.0 mL
		Slope max ml	10
		Min. step size	0.02 mL
		Slope min. ml	120
Damping	none	Titration direction	decrease
Pretitration	off	Delay time	0 s
End value	off		
EQ	On (1)	Slope value	300
Max. titration volume	50 ml		
Dosing speed	100%	Filling speed	30 s

Calculation:

O_2 – content in mg/L:

$$O_2[mg/L] = \frac{(EQ1 - B) * T * M * F1}{W * F2}$$

EQ 1		Consumption of the titrant on the first EQ [mL]
B		Blank
T	WA	Actual concentration of the titrant [mol/L]
M	31,998	Molecular weight of O_2 [g/mol]
V		Sample amount [mL]
F1	1000	Conversion factor
F2	4	Conversion factor

Xylem Analytics Germany Sales GmbH & Co. KG,
SI Analytics
Erich-Dombrowski-Straße 4 • 55127 Mainz, Germany

Tel+ 49 6131 894-5111
TechInfo.xags@xylem.com
xylemanalytics.com

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Let's Solve Water