Bottom-up evaluation of the uncertainty of a titration with visual end-point detection: Determination of dissolved oxygen by the Winkler Method

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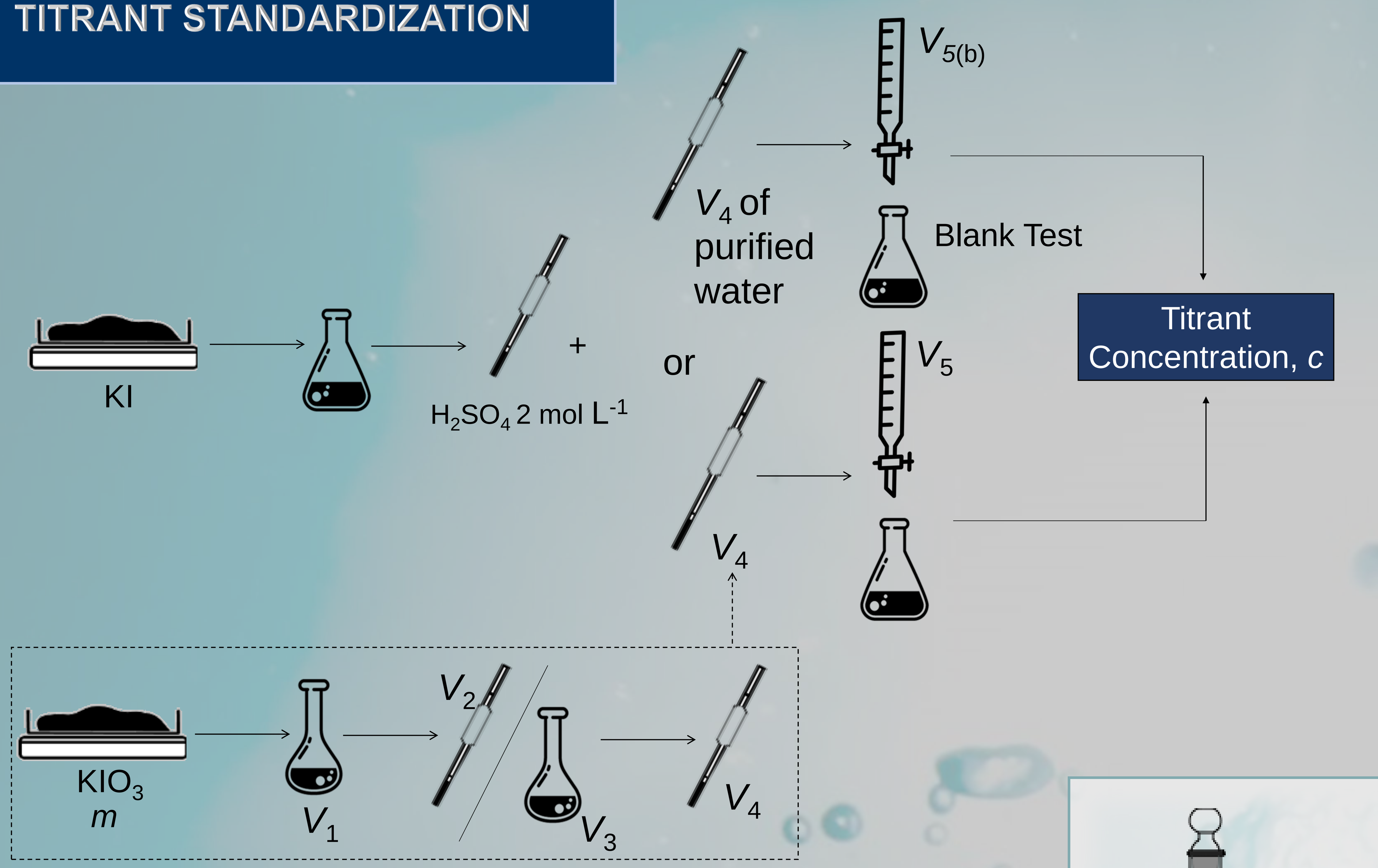
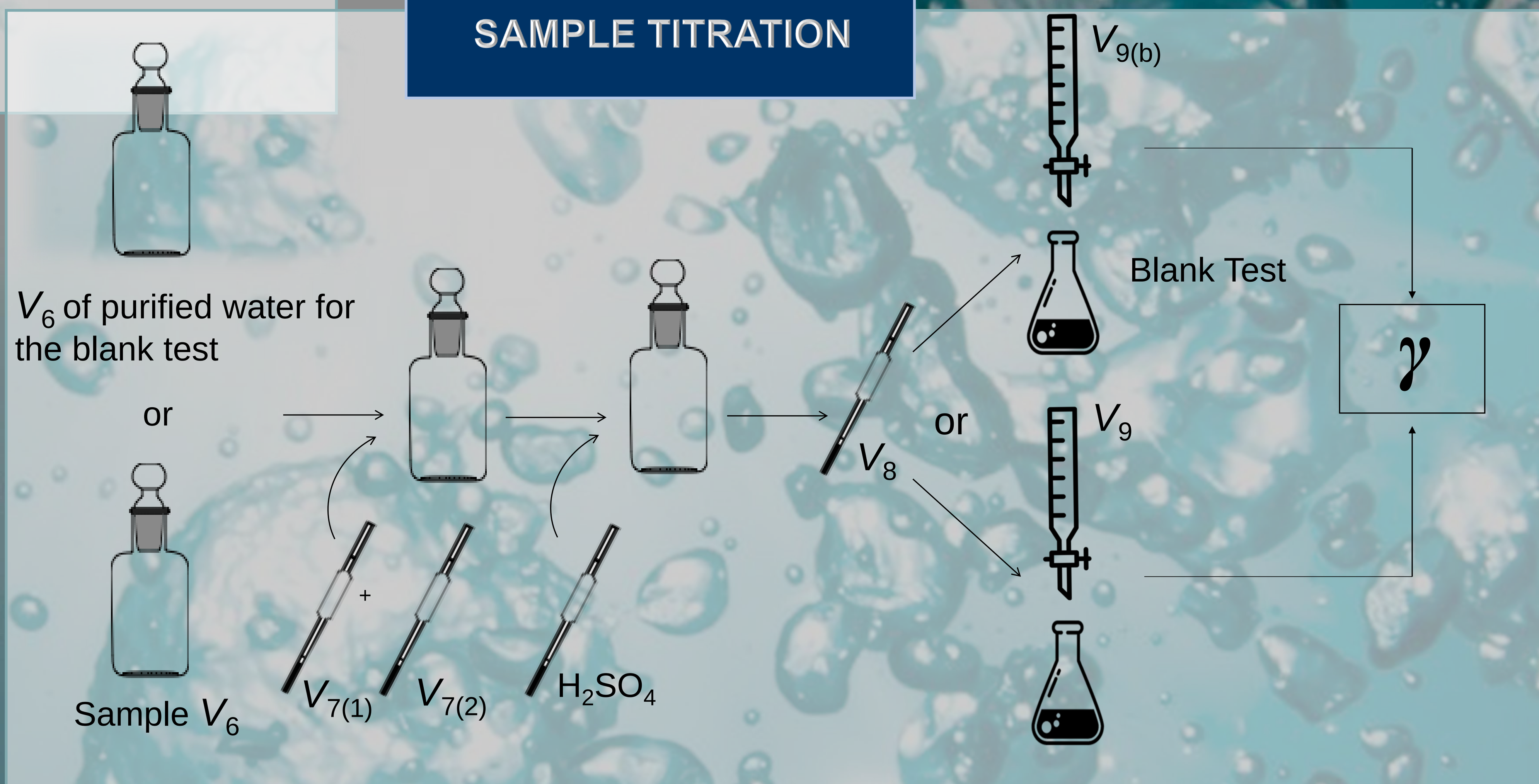
TITRANT STANDARDIZATION



Introduction

Dissolved oxygen concentration in water is a crucial parameter to assess the condition or evolution of aquatic ecosystem health. This determination can be performed using an electrochemical sensor or the reference Winkler method that allows a more reliable measurement of this parameter. The comparison of dissolved oxygen values determined on two occasions or two samples requires calculating the measurement uncertainty. This uncertainty is also relevant to understand if the determination has adequately low uncertainty.

SAMPLE TITRATION



Input quantities and the respective partial derivatives

x_i	$\frac{\partial\gamma}{\partial x_i}$	x_i	$\frac{\partial\gamma}{\partial x_i}$
P	$\frac{\gamma}{P}$	f_1	$\frac{\gamma}{(V_5 - V_{5(b)} + f_1)}$
m	$\frac{\gamma}{m}$	V_6	$\frac{\left(\frac{A}{V_6}\cdot B\right)-\left(\frac{B}{V_6-V_7}\cdot A\right)}{B^2}$
M(KIO_3)	$\frac{A}{B\cdot M(KIO_3)}$	$V_{7(1)}$	$\frac{\gamma}{(V_6-V_7)}$
V_1	$\frac{A}{B\cdot V_1}$	$V_{7(2)}$	$\frac{\gamma}{(V_6-V_7)}$
V_2	$\frac{\gamma}{V_2}$	V_8	$\frac{A}{B\cdot V_8}$
V_3	$\frac{A}{B\cdot V_3}$	V_9	$\frac{\gamma}{(V_9-V_{9(b)}+f_2)}$
V_4	$\frac{\gamma}{V_4}$	$V_{9(b)}$	$-\frac{\gamma}{(V_9-V_{9(b)}+f_2)}$
V_5	$\frac{\gamma}{(V_5-V_{5(b)}+f_1)}$	f_2	$\frac{\gamma}{(V_9-V_{9(b)}+f_2)}$
$V_{5(b)}$	$-\frac{\gamma}{(V_5-V_{5(b)}+f_1)}$	*M* (O_2)	$\frac{\gamma}{M(O_2)}$

$$A = P\cdot m\cdot V_2\cdot V_4\cdot 6\cdot(V_9 - V_{9(b)} + f_2)\cdot V_6\cdot M(O_2)$$

$$B = (KIO_3)\cdot V_1\cdot V_3\cdot(V_5 - V_{5(b)} + f_1)\cdot V_8\cdot(V_6 - V_7)\cdot 4$$

The visual end-point detection's uncertainty, $u(f_2)$, was estimated by the difference between observed measurement precision and combined models of all precision components except the end-point detection [1-3]

$$\gamma = \frac{c\cdot(V_9 - V_{9(b)} + f_2)\cdot V_6\cdot M(O_2)\cdot 10^6}{V_8\cdot(V_6 - V_7)\cdot 4}$$

$$f_2 = \frac{\gamma_{Ref}\cdot(V_6 - V_7)\cdot V_8\cdot 4}{C\cdot V_6\cdot M(O_2)\cdot 10^6} - V_9 + V_{9(b)}$$

$$s(f_2) = \sqrt{s_\gamma^2 - \left[\left(\frac{\partial\gamma}{\partial V_8}\cdot s_{V_8}\right)^2 + \left(\frac{\partial\gamma}{\partial V_9}\cdot s_{V_9}\right)^2\right]}\Big/\left(\frac{\partial\gamma}{\partial f_2}\right)$$

$$u(f_2) = \sqrt{\left[\sum\left(\frac{\partial f_2}{\partial x_i}\right)^2\cdot u(x_i)^2\right] + s^2(f_2)}$$

NEW

A user-friendly MS-Excel spreadsheet that allows applying the developed uncertainty evaluation procedure was developed.

Results and discussion

- The determination of dissolved oxygen from analytical portions not lower than 50 mL is fit for environmental monitoring
- It allows measurements between 0.3 mg L-1 and 14.6 mg L-1 with an expanded uncertainty between 0.36 mg L-1 and 0.74 mg L-1 (confidence level=95%)
- This uncertainty allows differentiating dissolved oxygen values between 0.51 mg L-1 and 1.0 mg L-1 with less than a 5% probability of being wrongly assumed a relevant difference [1]
- The described uncertainty evaluation strategy can also be used in other titrimetric determinations [1]

References

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