Supplementary Material

Voltammetric pH determination and water quality screening – a novel method based on iridium dioxide electrodes

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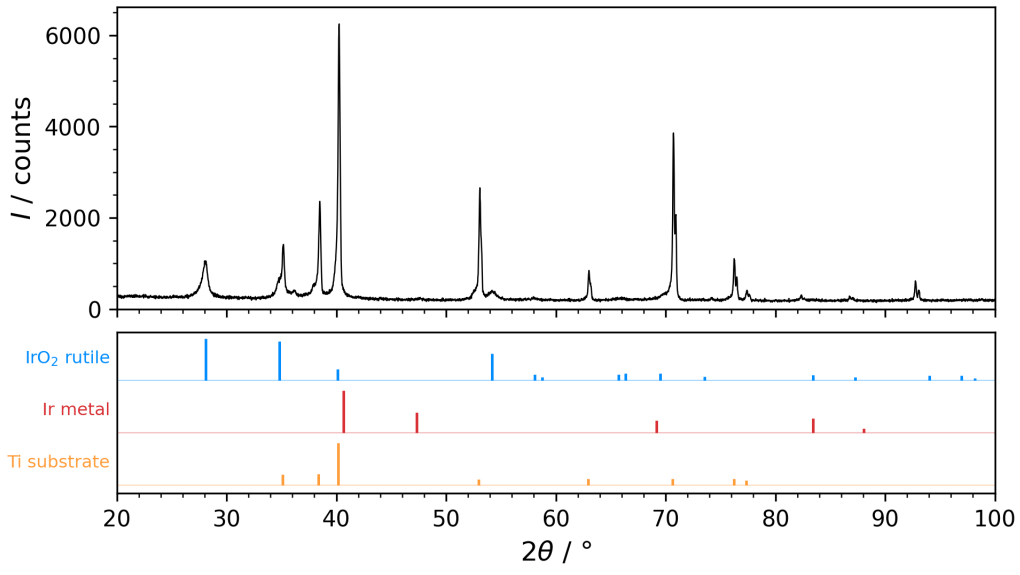
4. Numerical evaluation of cyclic voltammograms

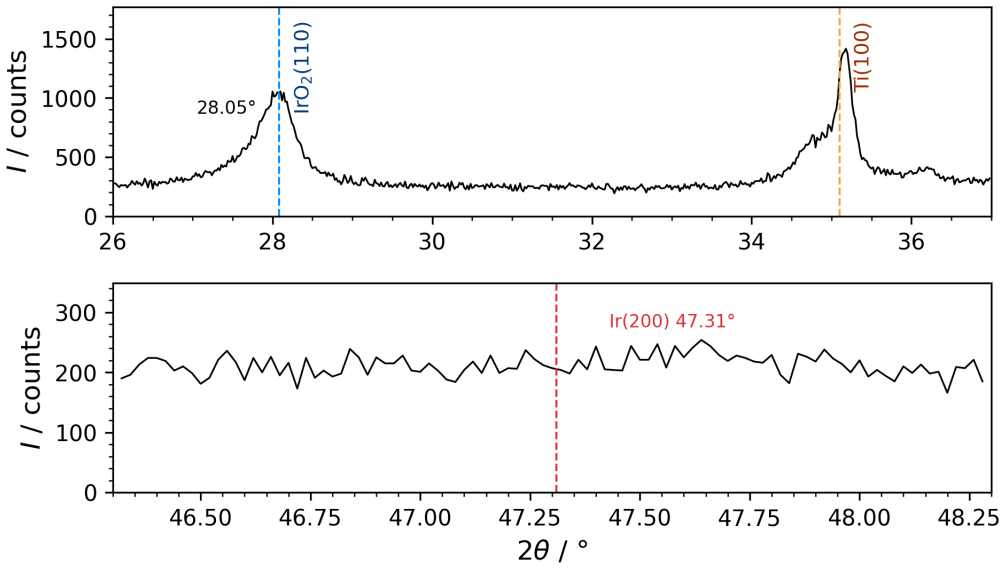
4.1 Experimental setup for pH titration and statistical analysis

Electrode preparation. As a substrate for the IrO_2 working electrode (area: 1 cm²), a titanium foil (0.05 mm × 300 mm, ASTM B265 Ti Gr. 1, Ankuro Int. GmbH) abraded to create a rough surface, subsequently cleaned with distilled water and acetone, dried, and cut into a 4 cm × 4 cm piece. This was placed into a device equipped with a PTFE gasket, which confined the liquid volume to the intended area of 3.5 cm × 3.5 cm. Using a pipette, 0.5 mL of the precursor solution (125 mg of $IrCl_3 \cdot xH_2O$ from Alfa Aesar in 5 mL of 1 mol L^{-1} HCl and 20 ml of acetone) was added dropwise into the device. The solvent was subsequently evaporated slowly in a drying oven at 60 °C over a period of 30 minutes. The titanium sheet, coated with $IrCl_3$, was removed from the mould and heated in a furnace at a heating rate of 4 K/min to 500 °C, followed by a 10-minute isothermal step in ambient atmosphere. A 1 cm² piece was cut from the coated foil, crimped onto a cable, and bonded into a glass shaft using epoxy resin (Epoxonic EX 2986). The uncoated back side of the electrode was also electrically insulated with epoxy resin.

X-ray diffraction pattern of IrO_2/Ti electrode, measured using a Rigaku MiniFlex 600 (XRD).



(a)



(b)

Figure S1: **(a)** XRD spectra of the IrO_2-coating at the titanium electrode. Bottom row: reference diffraction patterns for IrO_2, metallic iridium and titanium. **(b)** Detailed view for IrO_2(110), Ti(100) and Ir(200) pattern lines.

Test cell. The electrochemical cell included the IrO2/Ti electrode, an Ag|AgCl|3M KCl reference electrode (Metrohm 6.0726.100) and a platinum sheet counter electrode (2.5 cm × 2.0 cm). The fixed distances were 1 cm between working electrode to reference electrode, and 1 cm between reference electrode to counter electrode throughout the entire experiment. The electrolyte solution was contained in a double-walled, temperature-controlled beaker with a capacity of approximately 150 mL. During all measurements, the solution was maintained at a temperature of 25 °C using a Julabo 200F thermostat.

Experimental setup and measurement procedure. For the automated execution of tests, a test bench was designed with a Raspberry Pi serving as the central control unit (Figure S2). The procedure during the titration was as follows:

1. Determination of the upper and lower switching potentials for cyclic voltammetry by incrementally increasing or decreasing the potential (for the upper and lower limits, respectively) in 50 mV steps, until the onset of oxygen or hydrogen evolution. This is indicated by a sharp rise in the measured current, which was detected using a threshold value applied to the first derivative of the current-potential curve.
2. Execution of cyclic voltammetric measurements within the limits established in step 1, at potential scan rates of v = 0.1, 0.2, 0.3, 0.5, and 1.0 V s^{-1} (each over 6 cycles), using an EC301 potentiostat (Stanford Research Systems). The first cycle in each set was discarded.
3. If the final volume has not yet been reached: addition of 1 M NaOH in a predefined volume increment using a Titronic 97/20 (Schott) titrator equipped with a 20 mL burette. The device was modified with two relays to enable remote control via the Raspberry Pi. Volume data were retrieved via an RS232 interface. A magnetic stirrer ensured continuous mixing during the addition of the NaOH. Once the target volume was reached, the stirring process was stopped. A 30-second equilibration phase allowed the liquid to come to rest.
4. Return to step 1 until the measurement program in Figure S3 is completed.

Reproducibility. Example evaluation of 5 cycles at an IrO_2|Ti electrode see Figure S4 and Table S1.

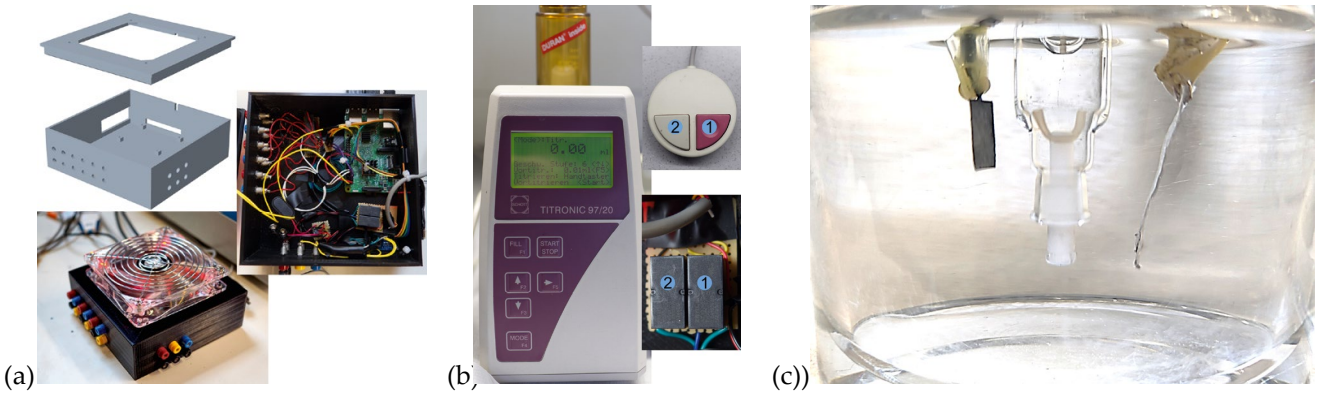


Figure S2. **(a)** Central processing unit of the electrode test bench: housing, internal components, and external view. **(b)** Automatic burette with printed-circuit relay configuration for dispensing and filling. **(c)** Three-electrode arrangement in a double-walled glass vessel. From left to right: WE (IrO_2|Ti electrode), RE (Ag|AgCl|3M KCl), CE (Pt-sheet).

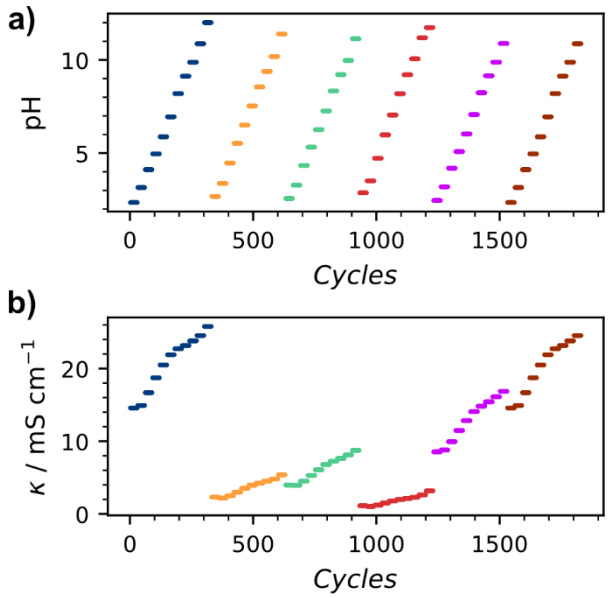


Figure S3. Range of measurement parameters: **(a)** variation of the pH value in the buffer solution, **(b)** measured conductivity over 1830 single voltammetric charge-discharge cycles.

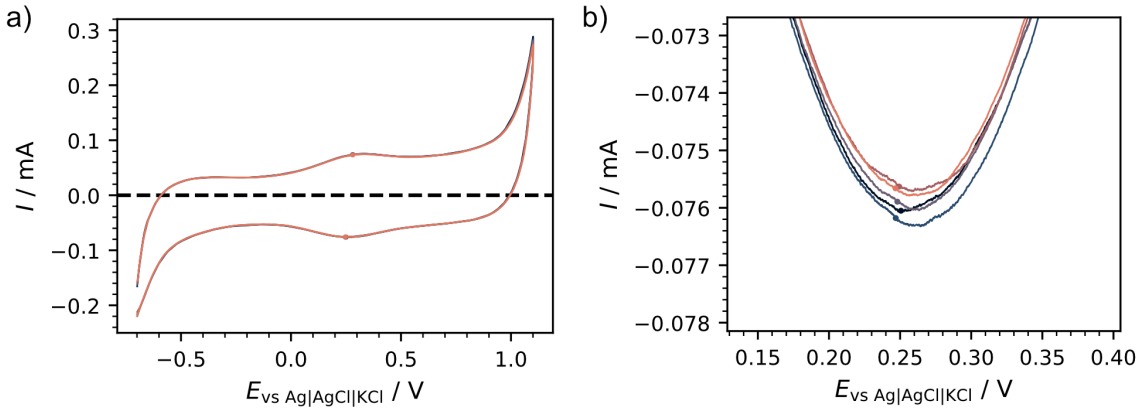


Figure S4: **(a)** Overlapping cyclic voltammograms from five consecutive measurements at an IrO_2|Ti electrode in the test solution (scan rate 100 mV/s; pH 6.95; conductivity 21.9 mS/cm; cycles 152–156). **(b)** Magnified view of the reduction peak. The curves were smoothed using a Savitzky-Golay filter.

Table S1: Evaluation of the five cyclic voltammograms in Figure S4.

Cycle	$E_{p,ox}$ / V	$E_{p,red}$ / V	$E_{1/2}$ / V
2	0.2806	0.2506	0.2656
3	0.2794	0.2469	0.2631
4	0.2814	0.2480	0.2647
5	0.2803	0.2494	0.2648
6	0.2808	0.2468	0.2638
Mean	0.2805	0.24834	**0.2644**
Standard deviation s			0.00097
measurement uncertainty, including Student factor (t = 1.142): $u = \frac{t \cdot s}{\sqrt{5}}$			± 0.0005
for a 95% confidence interval (t = 2.776)			**± 0.0012**

5. Practical voltammetric pH determination: Additional examples

5.2 *Proof of linearity*

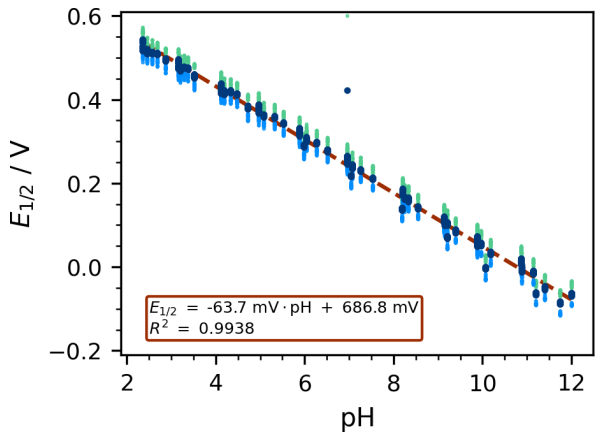


Figure S5. Corrected half-wave potentials of the Ir(III)/Ir(IV) redox peak at different scan rates versus solution pH us-ing equation (12). Green: oxidation peak potential, Blue: reduction peak potential. Dark red: Linear least squares fit.

5.3 pH-determination in real samples – calibration

Table S2. **Calibration measurement** using two buffer solutions for pH 3 and pH 10, each **at a low and high conductivity**. The Ir(III/IV) peak potentials and currents are average values of 10 voltammetry cycles. Conductivity calibration: RA=0.8333 cm· ϱ + 44.9 Ωcm² (R²: 0.9729). Linear pH calibration: $E_{1/2}$ = –69.9 mV·pH + 706.8 mV (R²: 0.9977).

Buffer solution		Reference values (glass electrode)			Cyclic voltammetry				Evaluation of cyclic voltammetry	
Calibration sample: pH, conductivity	v V s^{-1}	**pH**	κ mS cm^{-1}	**ϱ** Ω cm	$E_{p,Ox}$ V	$I_{P,Ox}$ mA	$E_{p,Red}$ V	$I_{P,Red}$ mA	R / Ω (Eq. 14)	$E_{1/2}$ / V
pH 3, low	1	3.03	1.2	843	1.0776	1.616	-0.1025	-1.447	366.7	–
pH 3, high	1	3.03	16.0	63	0.6257	2.028	0.4257	-1.661	38.8	–
pH 10, low	1	9.54	2.2	453	0.4671	1.550	-0.3506	-1.388	258.9	–
pH 10, high.	1	9.50	24.8	40	0.1506	2.382	-0.0434	-1.875	32.2	–
pH 3, low .	0.1	3.03	1.2	843	0.6160	0.260	0.4051	-0.189	–	0.498
pH 3, high	0.1	3.03	16.0	63	0.4963	0.233	0.4894	-0.182	–	0.492
pH 10, low.	0.1	9.54	2.2	453	0.1501	0.260	-0.0227	-0.188	–	0.054
pH 10, high.	0.1	9.50	24.8	40	0.0419	0.288	0.0152	-0.209	–	0.027

Table S3 **Voltammetric pH measurement of beverage samples**. Peak potentials and currents are average of five voltammetry cycles. **Calibration based on four buffer solutions**: $\mathrm{pH} = (706.8 - E/\mathrm{mV})/69.9$,
and for resistivity $\rho = (RA/\Omega\mathrm{cm}^2 - 44.9)/0.8333$.
Reference values were determined using a glass electrode and a commercial conductivity meter.

		Reference values		Data of voltammetric pH measurement								
Sample	v V/s	pH	ϱ kΩ cm	$E_{p,Ox}$ V	$I_{P,Ox}$ mA	$E_{p,Red}$ V	$I_{P,Red}$ mA	R_e Ω	RA Ω cm²	$E_{1/2}$ (V)	pH	ϱ kΩ cm
Apple juice	1	3.25	0.43	0.7824	1.210	0.2130	-1.050	226.7	437.8	0.4622	3.50	0.47
	0.1			0.5241	0.167	0.4105	-0.122					
Apple spritzer	1	3.87	0.53	0.7851	1.112	0.1493	-0.953	280.3	541.5	0.4322	3.93	0.60
	0.1			0.4890	0.155	0.3864	-0.116					
Coke	1	2.56	0.80	1.0766	1.583	0.0244	-1.413	332.2	641.7	0.5225	2.63	0.72
	0.1			0.6464	0.252	0.4229	-0.179					
Mineral water	1	6.85	1.73	0.7779	0.865	-0.4588	-0.755	728.6	1407.2	0.2523	6.50	1.64
	0.1			0.5586	0.154	-0.0231	-0.112					
Lemonade	1	3.55	1.16	0.9685	0.998	0.0057	-0.876	483.5	934.0	0.4520	3.64	1.07
	0.1			0.5599	0.159	0.3656	-0.115					
Coffee	1	5.45	0.78	0.7324	1.053	-0.0266	-0.711	397.8	768.4	0.3410	5.23	0.87
	0.1			0.4515	0.179	0.2613	-0.101					
Mate iced tea	1	3.13	1.55	1.0713	0.961	0.0189	-0.817	559.8	1081.3	0.4702	3.38	1.24
	0.1			0.6349	0.170	0.3398	-0.109					