Supporting Information

Electromembrane extraction using sacrificial electrodes

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Content of SI

1 Equipment and setup of electromembrane extraction system

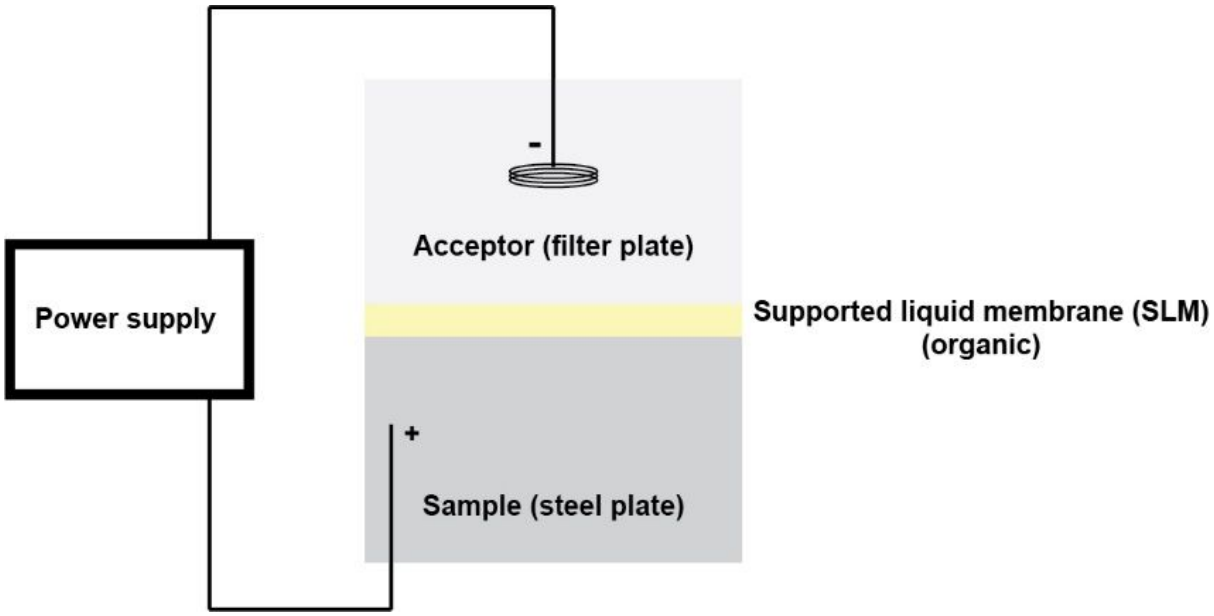


Figure S1. Illustration of the configuration of the EME setup.

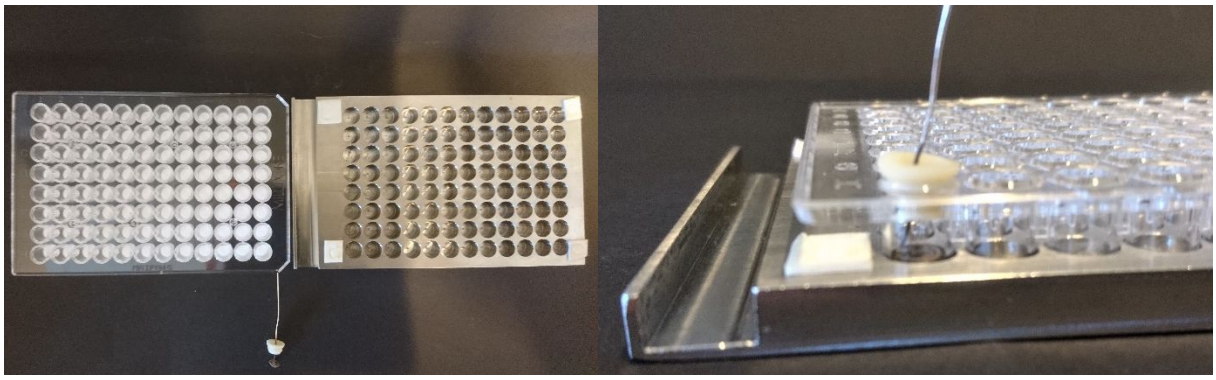


Figure S2. Left) Disassembled EME system with the 96-well steel plate (sample) and the 96-well MultiScreen filter plate (acceptor solution). Right) Assembled system

2 Proof-of-concept extractions

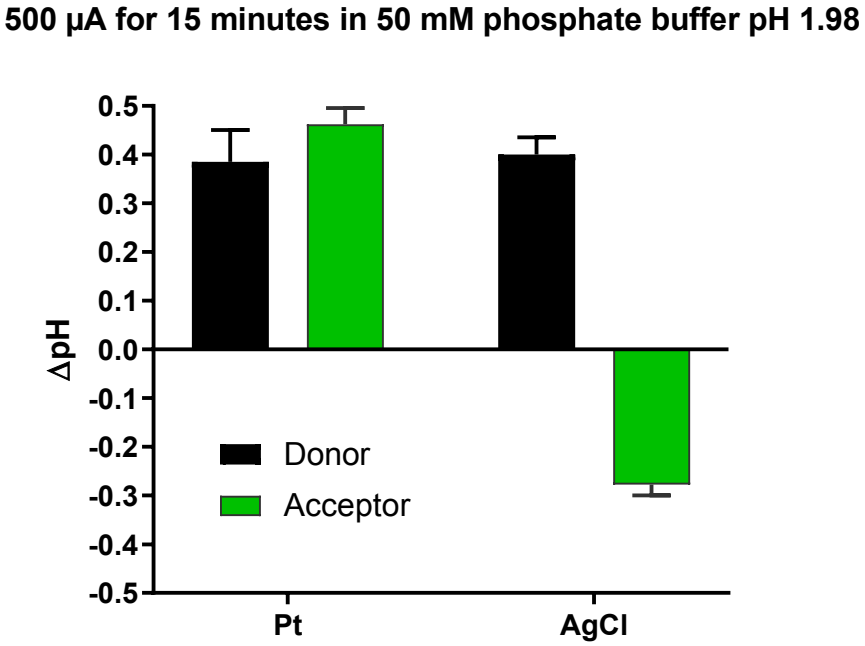


Figure S3. Change in pH-value in the donor and acceptor solution after extractions at 500 µA for 15 minutes from 50 mM phosphate buffer pH 1.98, with platinum (Pt) and silver chloride electrodes (AgCl), respectively. Errorbars represent the standard deviation (n=4).

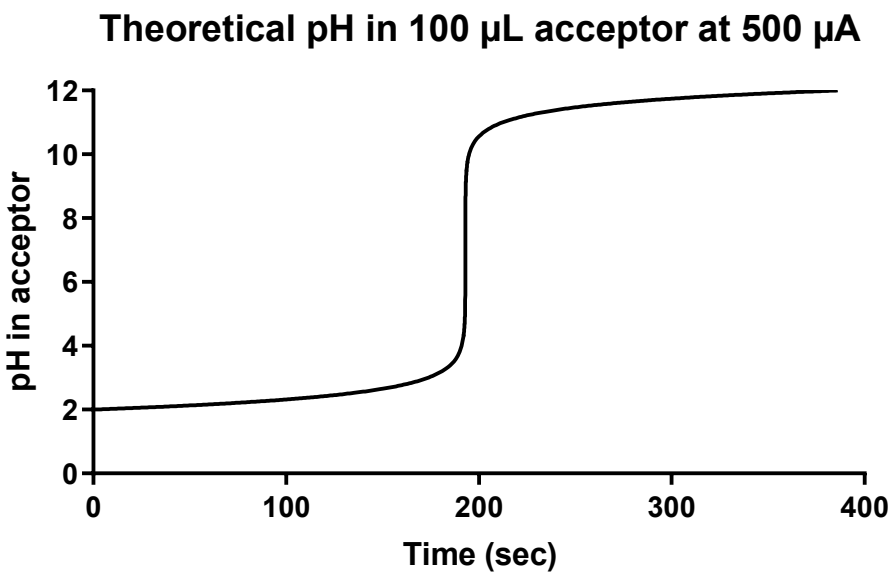


Figure S4. Estimated pH with time in a 100 µL acceptor solution consisting of 10 mM hydrochloric acid (pH 2.0), when applying a constant current of 500 µA.

3 Design of experiments methodology and results

The DOE method for optimization of electroplating strategy was designed and analyzed in the software MODDE Pro 12.1. The experimental run order, coded parameter values and actual values are given in Table S1.

Table S1. DOE run order and design.

Exp No	Run Order	KCl concentration	Current	Time	KCl conc (M)	Current (mA/cm)	Time (min)
		Coded values			Actual parameter value		
17	1	0	0	0	1.875	1.200	8.0
19	2	0	0	0	1.875	1.200	8.0
11	3	0	-1.4712	0	1.875	0.023	8.0
14	4	0	0	1.47119	1.875	1.200	15.4
16	5	0	0	0	1.875	1.200	8.0
10	6	1.47119	0	0	3.530	1.200	8.0
7	7	-1	1	1	0.750	2.000	13.0
3	8	-1	1	-1	0.750	2.000	3.0
8	9	1	1	1	3.000	2.000	13.0
12	10	0	1.47119	0	1.875	2.377	8.0
2	11	1	-1	-1	3.000	0.400	3.0
4	12	1	1	-1	3.000	2.000	3.0
13	13	0	0	-1.4712	1.875	1.200	0.6
6	14	1	-1	1	3.000	0.400	13.0
15	15	0	0	0	1.875	1.200	8.0
18	16	0	0	0	1.875	1.200	8.0
5	17	-1	-1	1	0.750	0.400	13.0
1	18	-1	-1	-1	0.750	0.400	3.0
9	19	-1.47119	0	0	0.220	1.200	8
20	20	0	0	0	1.875	1.200	8.0

Table S2. p-values of the factors in the model following analysis of variance (ANOVA). Only factors with $p<0.05$ are included.

Factor	p-value
KCl	0.004
Time	<0.0001
Current	<0.0001
$Current^2$	0.006
Time*Current	0.0001

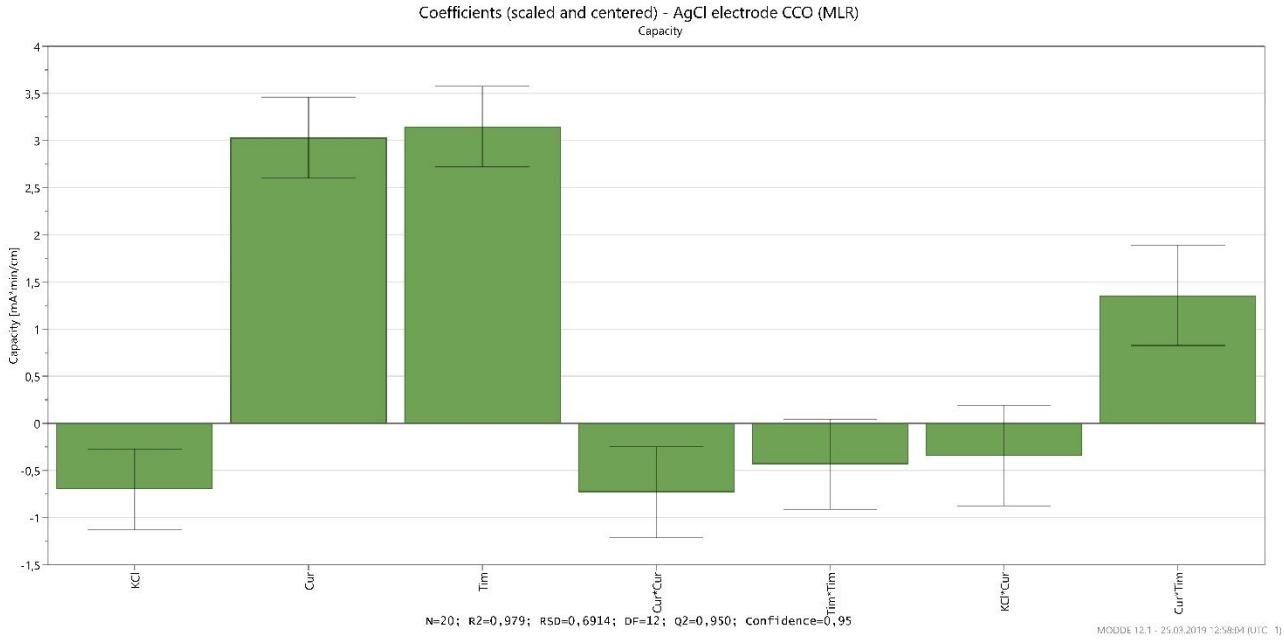


Figure S5. Coefficients plot of the model.

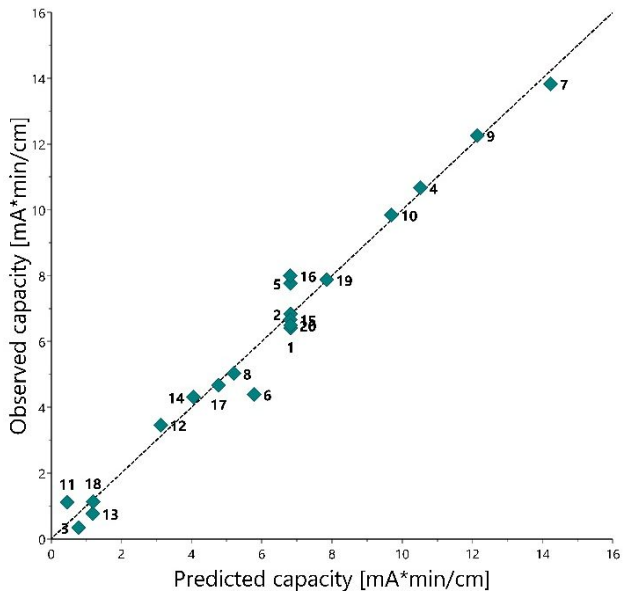


Figure S6. Observed vs predicted values of the redox capacity according to the fitted model. The numbers indicate the run order of the experiments.

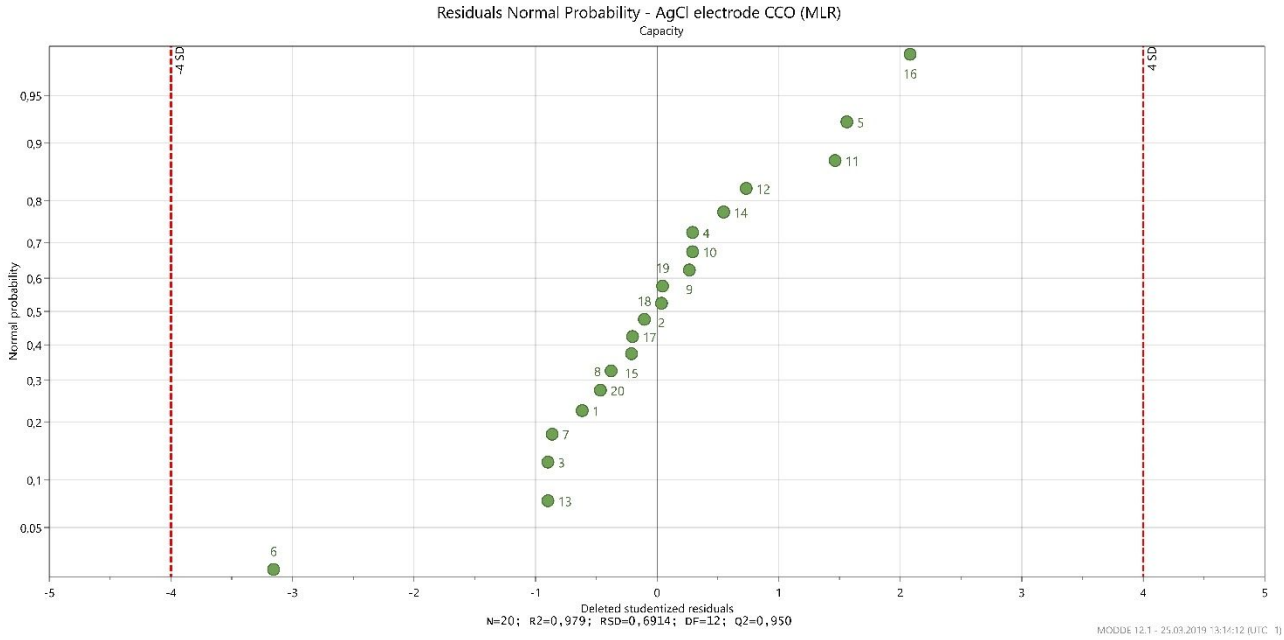
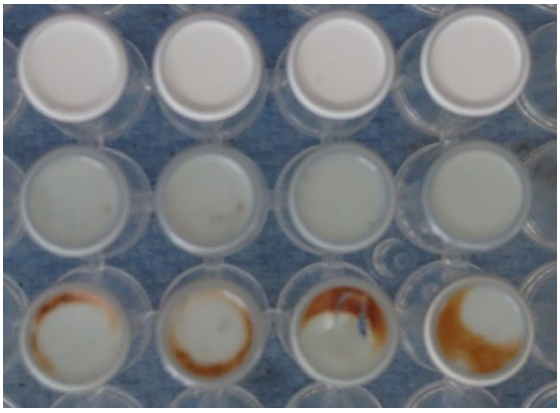


Figure S7. Normal probability plot of the model.

4 Real extraction results



Unused PVDF filter membrane

NPOE SLM after 15 minutes at 500 µA with AgCl electrode

NPOE SLM after 15 minutes at 500 µA with platinum electrode

Figure S8. Difference in appearance of NPOE SLMs after 500 µA extraction current for 15 minutes with either AgCl acceptor electrodes or platinum electrodes.

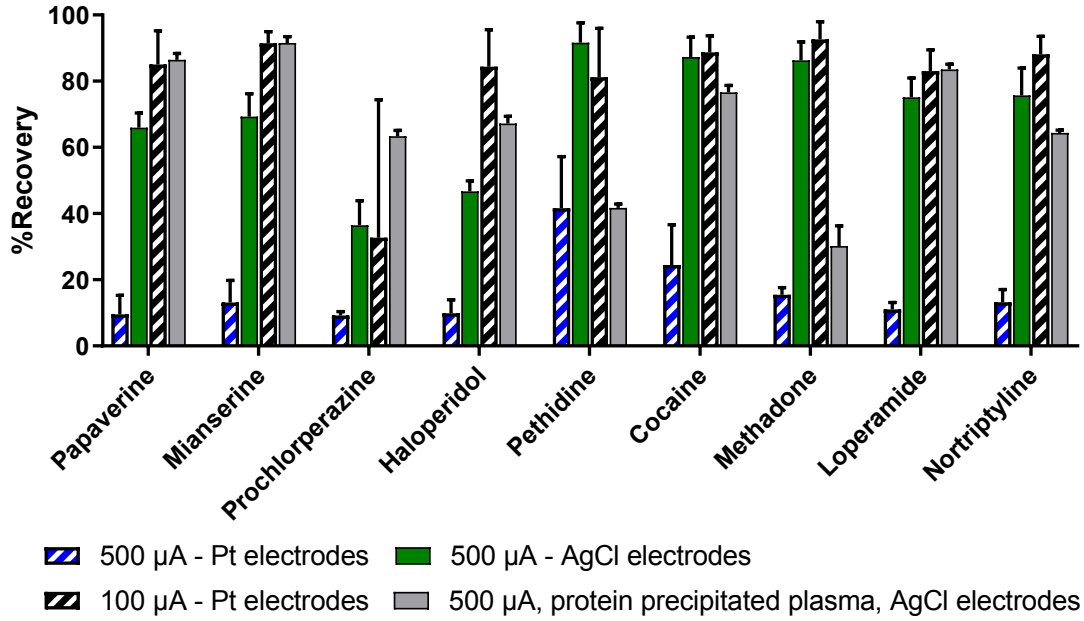


Figure S9. Extraction recoveries from 10 µg mL^{-1} of nine non-polar bases for different EME system configurations. Both sample and acceptor solutions were in 10 mM HCl, except for the protein precipitated plasma sample. Blue striped) 500 µA current with platinum electrodes from standard solution. Green) 500 µA current with AgCl electrodes from standard solution. Black striped) 100 µA current with platinum electrodes from standard solution. Grey) 500 µA current with AgCl electrodes from spiked protein precipitated plasma. The bases are listed by increasing pKa values. Error bars represent the standard deviation (n=6).

5 µ-EME experiments

Inhibition of pH change with the sacrificial electrode was also demonstrated with µ-EME. The experiment was a replication of a previously report on pH changes from electrolysis.[11] 0.5 µL 1-pentanol was sandwiched between the anolyte (MQ water) and the catholyte (1 mM phenolphthalein in MQ water) (1.5 µL of both). As seen from Fig. S9, the solution surrounding the cathode developed a pink color associated with pH increase, when a normal silver electrode was used. This was even after very small exposure to current (0.07 mC). Contrarily, with a sacrificial electrode as the cathode, no pH change was observed even after 1.3 mC (> 18-fold higher exposure).

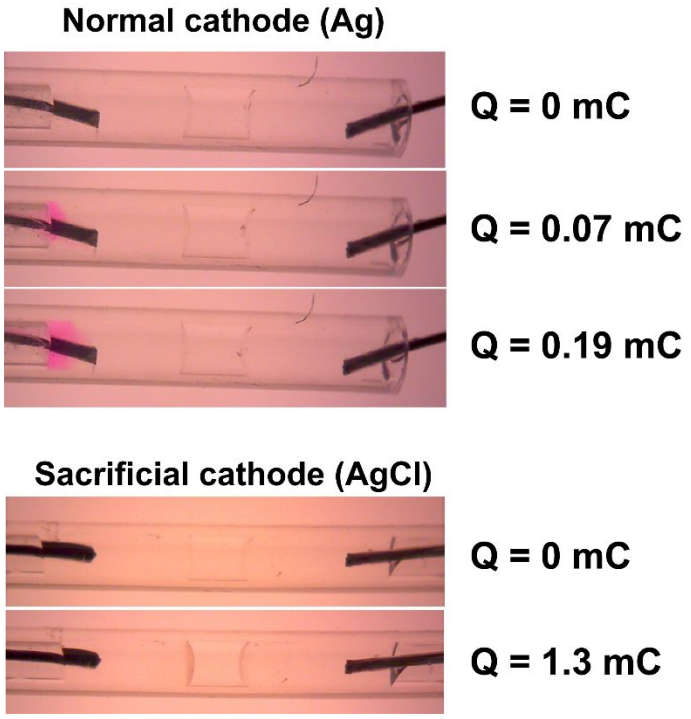


Figure S10. μ-EME setup. The cathode was located to the left and the anode to the right. For all experiments, the anode was of silver (Ag). The amount of current each system had been exposed to for individual photographs is given next to the photo (mC). The upper photographs show the development of color of phenolphthalein as the pH increases at the cathode with a normal silver electrode. The lower photographs show no pH increase when a sacrificial electrode was used. Voltage: 150 V.