

Electronic Supporting Information (ESI)

New insights into urea electro-oxidation: complete mass-balances and proof of concept with real-matrix effluent

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ESI 1. Illustration of the EC-cell used in this work.

An illustration and simplified schematic of the electrochemical cell is shown in **Figure ESI 1**. This cell enables continuous collection of the gases produced for analysis in gas chromatography, while allowing sampling of the aqueous phase without breaking the argon atmosphere.

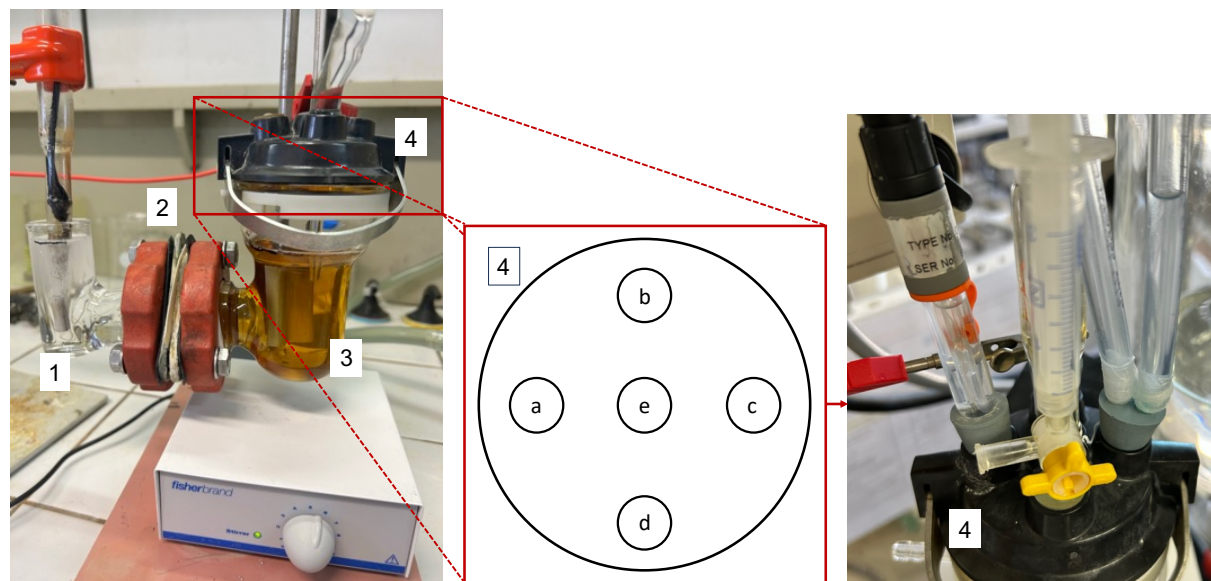


Figure ESI 1. Illustration of the H-type EC cell divided used in this work. *Labels:* 1) cathodic compartment, 2) anionic separator, 3) anodic compartment, 4) sealed-cap keeping the produced gases tight to the external ambient atmosphere. On this cap, various holes allow a) the positioning of the anode, b) the positioning of the reference electrode, c) argon bubbling, d) sampling syringe for the liquid phase and e) sampling of the gas phase to the GC.

ESI 2. Mass spectroscopy procedure for urea determination.

The analytical procedure for the IC determination and TOC analysis were identical to that presented in Hopsort et al¹.

In this work, urea was quantified using an analytical technique involving the coupling of ion chromatography with mass spectroscopy (IC-MS) after diluting all samples by 1000.

a. Chromatographic analysis

The study utilized a Thermo Scientific Dionex™ ICS-5000+ IC-CD system, furnished with a DP analytical pump, an AS-AP auto-sampler, and a DC-5 module containing both Dionex™ CDRS 600 and Dionex™ ADRS 600 suppressors for cation and anion detection, respectively. Additionally, it contained two conductivity detectors (CD). The Dionex™ AXP Auxiliary Pump, working at a flow rate of 0.25 mL.min⁻¹, was employed to maintain neutral pH at the mass spectrometry inlet by linking it to the appropriate suppressor. The cation and anion pathways had full-loop injection volumes of 25 µL and 10 µL, respectively. The IC control and data analysis were handled by Thermo Scientific™ Chromeleon™ Chromatography Data System software (version 7.2.10).

For the segregation of cations, an IonPac CS16-4µm analytical column (2 mm × 250 mm) by Thermo Scientific™ was used. The cationic eluent, methanesulfonic acid (MSA), was produced at a flow rate of 0.16 mL.min⁻¹ using a Thermo Scientific™ Dionex™ EGC 500 MSA Eluent Generator Cartridge. The column was maintained at 40 °C.

An IonPac AS11-HC-4µm analytical column (2 mm × 250 mm) by Thermo Scientific™ was utilized for anion segregation. The anionic eluent, KOH, was generated at a flow rate of 0.25 mL.min⁻¹ via a Thermo Scientific™ Dionex™ EGC III 500 KOH Potassium Hydroxide Eluent Generator Cartridge. The column temperature was set at 25 °C. Both eluent concentration profiles can be found in **Figure ESI 2**. The total run duration was 35 minutes.

¹ G. Hopsort, D. P. D. Carmo, L. Latapie, K. Loubière, K. G. Serrano, T. Tzedakis, *Electrochimica Acta*. **2023**, *442*, 141898.
DOI:<https://doi.org/10.1016/j.electacta.2023.141898>.

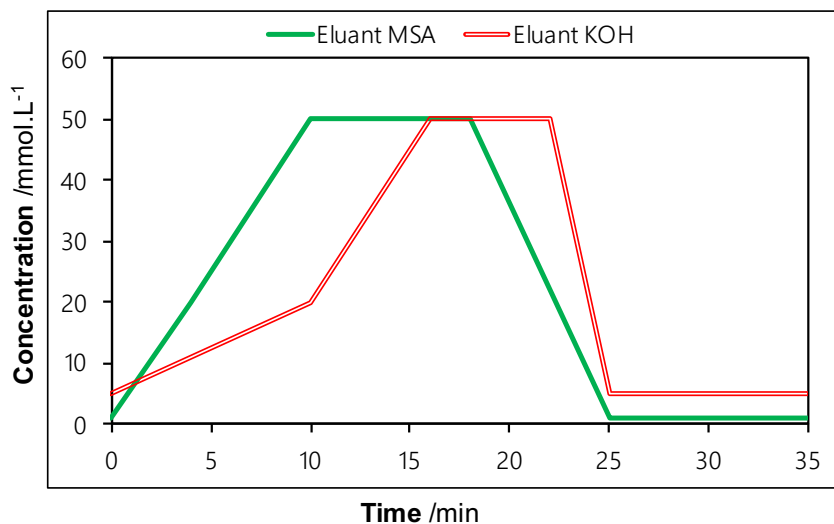


Figure ESI 2. Concentration gradient of anionic (KOH) and cationic (MSA) eluents for an optimal ionic separation.

b. Mass Spectrometric analysis

The IC system was paired with an Orbitrap mass spectroscopy analyzer (Thermo Scientific Q Exactive™ Focus). The Thermo Scientific™ Q Exactive™ Plus software (version 2.11) was utilized for controlling MS, with data processing undertaken by Thermo Scientific™ Chromeleon™ Chromatography Data System software (version 7.2.10) and Thermo Scientific™ Xcalibur™ software.

The mass spectrometry process was carried out using the full-scan method, in both negative (0-35 min, m/z 50-500) and positive modes (0-35 min, m/z 50-500), applying a heated electrospray ionization (ESI) source. For the negative mode, optimal parameters included: a sheath gas flow rate set to 40 a.u., auxiliary gas flow rate at 20 a.u., spray voltage at 3.5 kV, capillary temperature at 300 °C, S-lens RF level at 60, and auxiliary gas heater temperature at 450 °C. For the positive mode, parameters were as follows: sheath gas flow rate at 30 a.u., auxiliary gas flow rate at 10 a.u., spray voltage at 4.5 kV, capillary temperature at 300 °C, S-lens RF level at 60, and auxiliary gas heater temperature at 320 °C.

ESI 3. Ion chromatography analysis.

Figure ESI 3 presents the different cationic (part a) and anionic (part b) chromatograms over time of a potentiostatic electrolysis (0.55 V vs. Hg/HgO) of a human urine solution. This reveals the accumulation of by-products such as formic acid and oxalic acid.

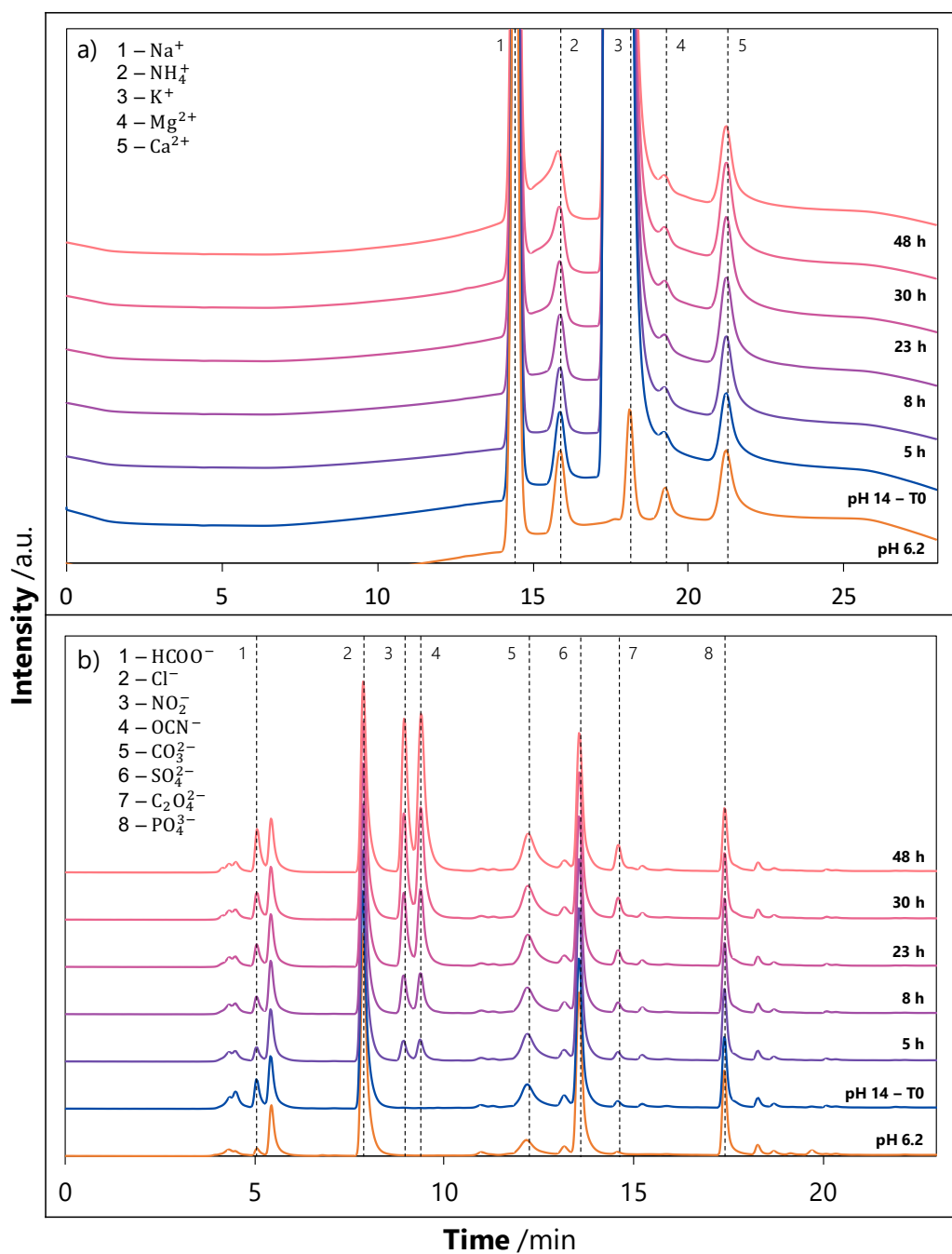


Figure ESI 3. Typical a) cationic and b) anionic chromatograms obtained during IC analysis during potentiostatic electrolysis (0.55 V vs. Hg/HgO) of urine solution in alkaline medium at pH 14.

ESI 4. Calibration curves of formic and oxalic acids for IC analysis.

The calibration curves obtained by ion chromatography for formic and oxalic acids are shown in the **Figure ESI 4**. They enable to quantify their quantity present in urine during electrolysis. The linear relationship between the molar concentrations and the peak area signals obtained in IC are presented in **Eqs. ESI (1)-ESI (2)**.

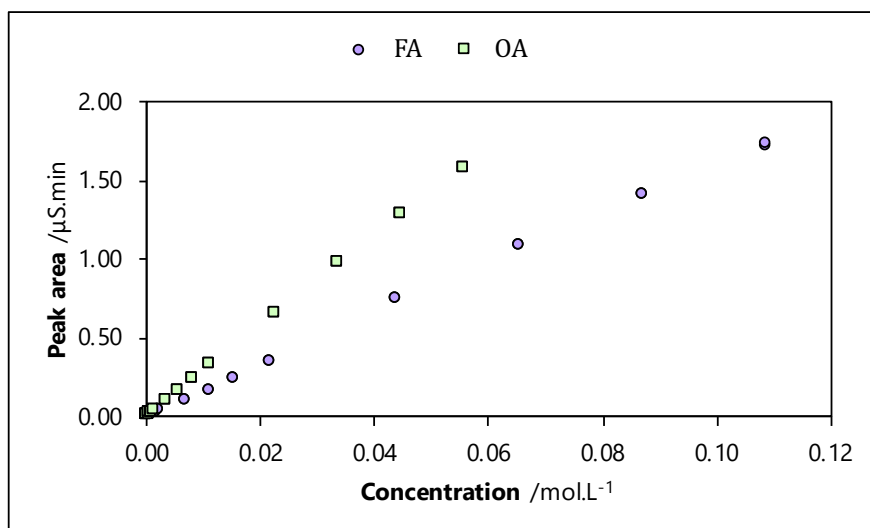


Figure ESI 4. Calibration curves of formic and oxalic acids obtained by IC analysis.

$$A_{\text{FA}} = 16.06 \times [\text{FA}]_{\text{mol}\cdot\text{L}^{-1}} \text{ with } T_r = 4.5 \text{ min and } R^2 = 0.999 \quad \text{ESI (1)}$$

$$A_{\text{OA}} = 28.69 \times [\text{OA}]_{\text{mol}\cdot\text{L}^{-1}} \text{ with } T_r = 25.2 \text{ min and } R^2 = 0.999 \quad \text{ESI (2)}$$

ESI 5. Gas chromatography analysis.

Figure ESI 5 shows a typical chromatogram obtained after injection of mixed standard gases by gas chromatographic analysis.

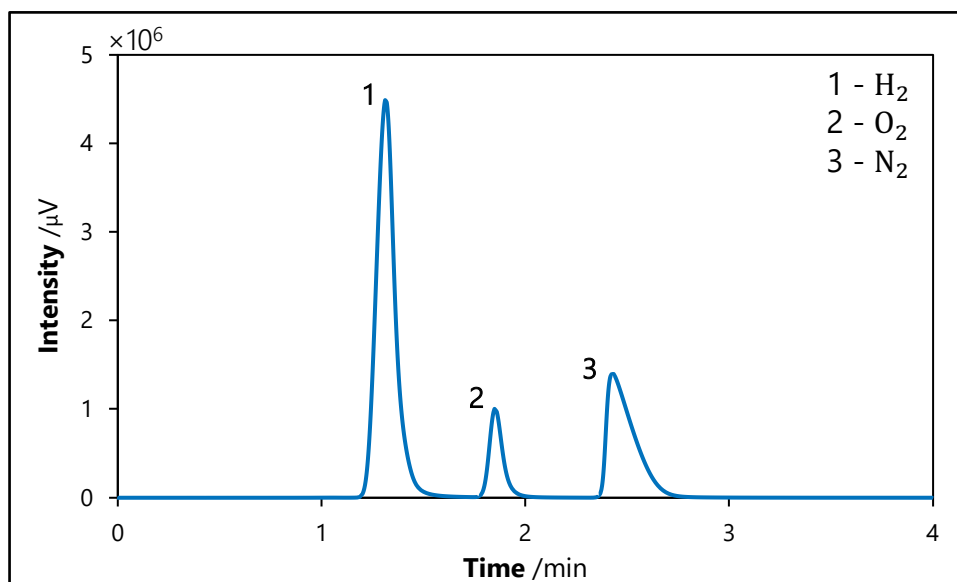


Figure ESI 5. Typical chromatogram obtained during GC analysis of mixed gases which can be obtained during potentiostatic electrolysis (0.55 V vs. Hg/HgO) of urine solution in alkaline medium at pH 14 (anodically and cathodically).

ESI 6. Calibration curves of nitrogen, oxygen and hydrogen in GC analysis.

The calibration curves for the three gases (N_2 , O_2 and H_2) obtained by gas chromatography are presented graphically in **Figure ESI 6**, and the linear relationships between the measured signal and the injected concentration are summarized in **Eqs. ESI (3)-ESI (5)**.

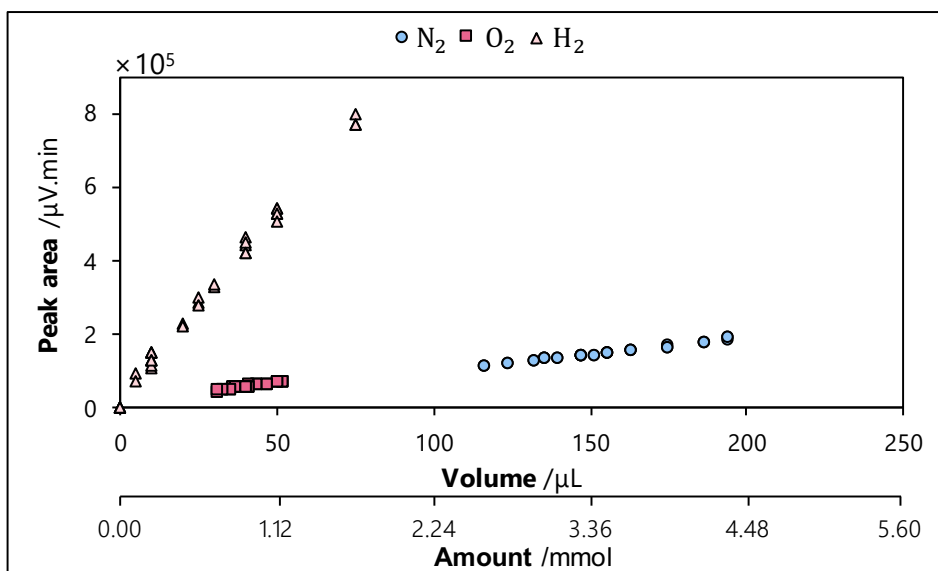


Figure ESI 6. Calibration curves of nitrogen, oxygen and hydrogen obtained by GC analysis.

$$A_{N_2} = 879.0 \times V_{N_2} \text{ with } T_r = 2.4 \text{ min and } R^2 = 0.998 \quad \text{ESI (3)}$$

$$A_{O_2} = 1241.1 \times V_{O_2} \text{ with } T_r = 1.8 \text{ min and } R^2 = 0.997 \quad \text{ESI (4)}$$

$$A_{H_2} = 9849.2 \times V_{H_2} \text{ with } T_r = 1.2 \text{ min and } R^2 = 0.991 \quad \text{ESI (5)}$$

where A_i is the peak area obtained by GC analysis ($\mu V \cdot \text{min}$), T_r is the retention time (min) in the GC and V_i is the injected volume at atmospheric pressure of the compound i (μL).

ESI 7. Raw data of molar amount of reactants and adducts during urea electrolysis.

The **Table ESI 1** shows the raw data obtained when determining the quantities of reagents and products during the chronoamperometric electrolysis of a 50 hours urea solution.

Table ESI 1. Molar quantities of reagents and products during electrolysis of synthetic urea solution

Time (h)	Charge (C)	CO(NH ₂) ₂	OCN ⁻	CO ₃ ²⁻	NO ₂ ⁻	NH ₄ ⁺	N ₂	Sum
		(mol)						
0	0	1.97×10 ⁻²	/	6.00×10 ⁻⁴	/	/	/	2.03×10 ⁻²
2	1080	1.70×10 ⁻²	9.89×10 ⁻⁴	1.80×10 ⁻³	5.44×10 ⁻⁴	2.30×10 ⁻³	1.56×10 ⁻³	2.42×10 ⁻²
9	2500	1.32×10 ⁻²	2.47×10 ⁻³	4.20×10 ⁻³	1.63×10 ⁻³	6.89×10 ⁻³	2.23×10 ⁻³	3.06×10 ⁻²
18	3500	9.75×10 ⁻³	3.95×10 ⁻³	6.60×10 ⁻³	2.12×10 ⁻³	1.15×10 ⁻²	2.59×10 ⁻³	3.65×10 ⁻²
28	4200	7.22×10 ⁻³	5.44×10 ⁻³	7.20×10 ⁻³	2.61×10 ⁻³	1.38×10 ⁻²	2.81×10 ⁻³	3.91×10 ⁻²
43	5000	4.77×10 ⁻³	6.43×10 ⁻³	9.00×10 ⁻³	2.88×10 ⁻³	1.61×10 ⁻²	4.02×10 ⁻³	4.32×10 ⁻²
50	5400	3.96×10 ⁻³	6.92×10 ⁻³	9.60×10 ⁻³	3.16×10 ⁻³	1.70×10 ⁻²	4.46×10 ⁻³	4.51×10 ⁻²

ESI 8. Carbon balance of urea during chronoamperometric electrolysis of a synthetic urea solution.

The carbon balance during urea electrolysis is shown in **Figure ESI 7**.

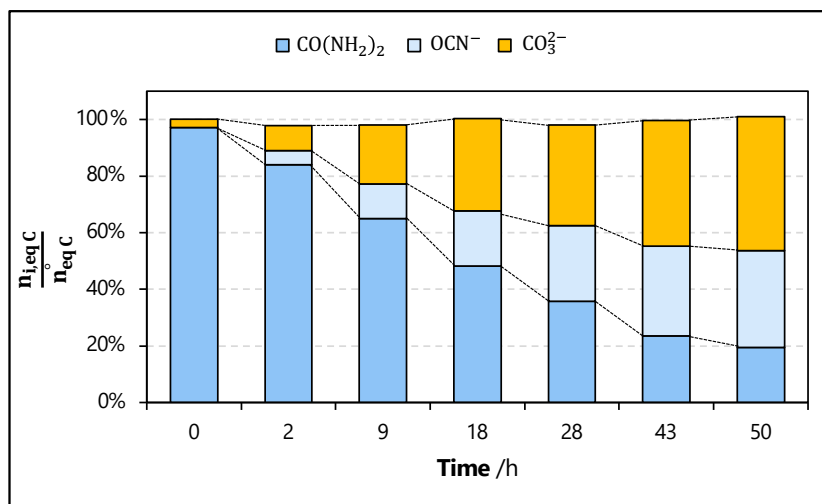


Figure ESI 7. Typical results obtained from chronoamperometry electrolysis of a synthetic urea (0.33 mol.L⁻¹) solution in alkaline medium (1 mol.L⁻¹ KOH): carbon mass balance.

ESI 9. Characterization of the precipitate caused by alkalinization of urine.

Alkalinization of human urine to pH 14 causes precipitation of compounds initially present in the solution. Visual observation and light microscope images of the precipitate are shown in **Figure ESI 8**.

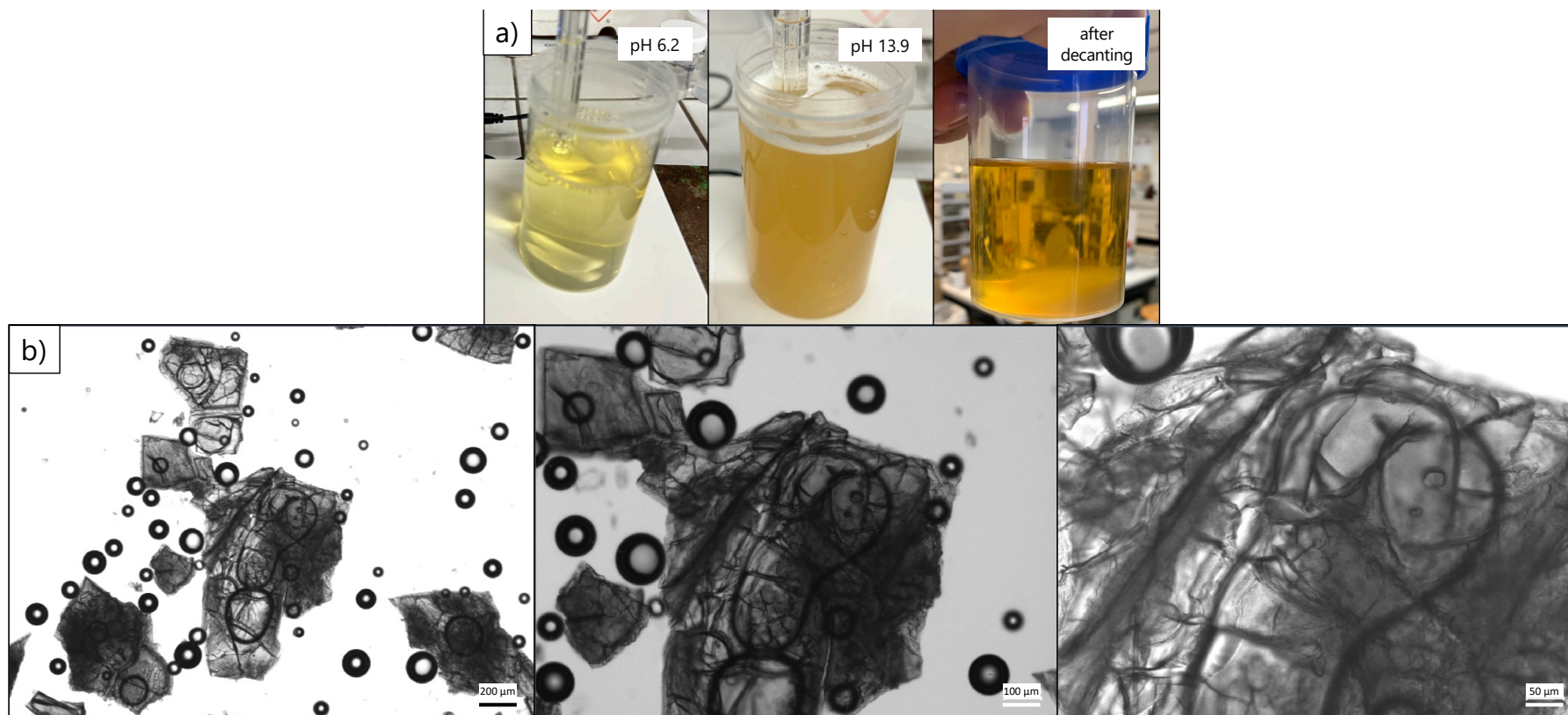


Figure ESI 8. a) Observation of a precipitate in a human urine sample (pH 6.2) formed after adding KOH pellets to reach pH 14 and b) optical microscope image of the crystals obtained.

An elementary analysis of the precipitate was performed using an ICP-OES determination. A HORIBA Ultima 2 was used for the analysis with a nitrogen purging.

The sample was nebulized into Ar plasma, specifically Ultra High Purity 4.5 Grade argon with 99.999% purity, via a concentric pneumatic nebulizer paired with a cyclonic spray chamber. The operating guidelines recommended by the manufacturer were strictly adhered to: an auxiliary gas flow of 0.2 L per minute (except for alkali compounds, Na and K, where 0.5 L per minute is used), a nebulizer gas flow of 0.6 L per minute, and a radiofrequency power of 1.2 kW. Special care was taken in choosing wavelength to reduce disruption. For S: 181.978 nm, P: 213.618 nm, Mg: 285.213 nm, Ca: 396.847 nm, Na: 589.592 nm and K: 769.896 nm were used. Calibration curves are given in **Figure ESI 9** and results obtained from the precipitate analysis is presented in **Table ESI 2**.

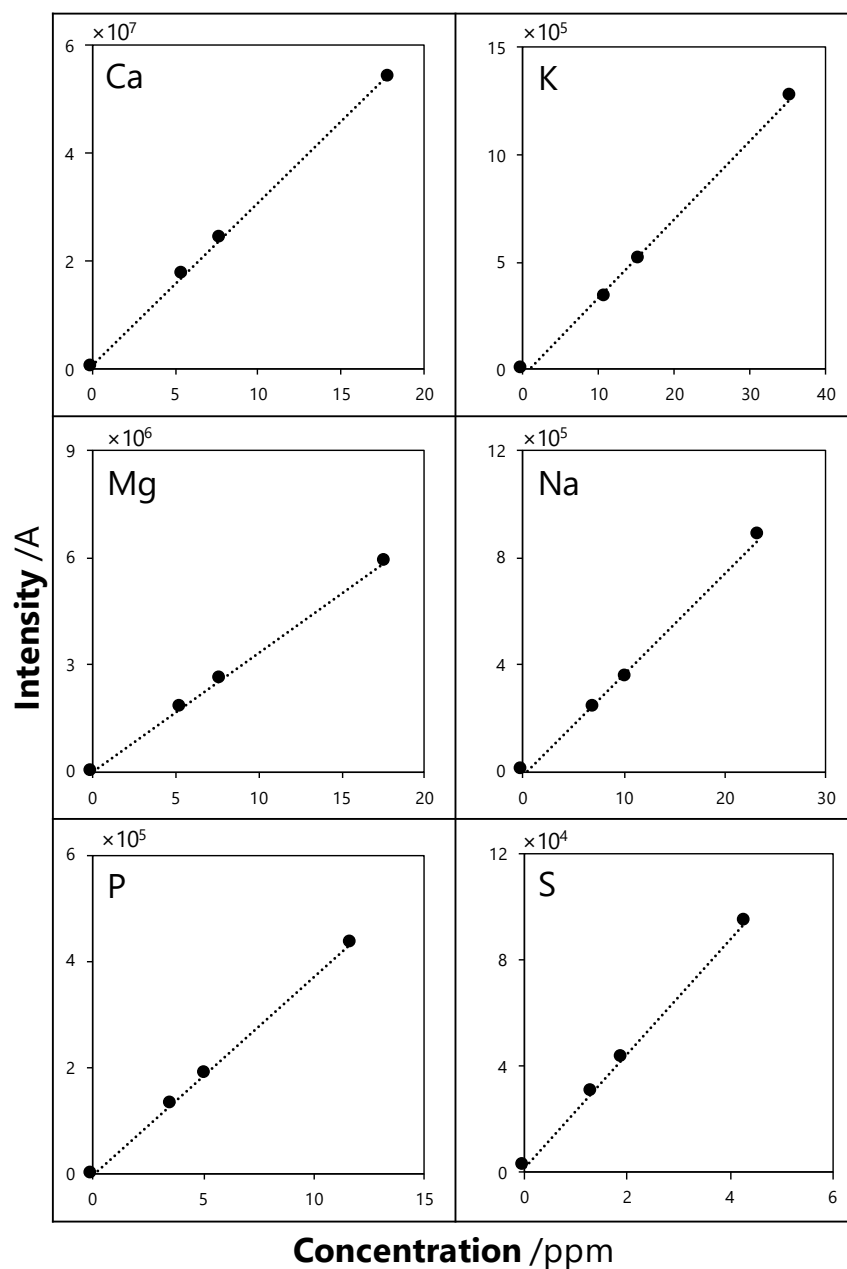


Figure ESI 9. ICP calibration curves.

Peak area = $3.02 \times 10^6 \times [\text{Ca}] + 6.29 \times 10^5$ with $R^2 = 0.999$ **ESI (6)**

Peak area = $3.67 \times 10^4 \times [\text{K}] - 3.10 \times 10^4$ with $R^2 = 0.997$ **ESI (7)**

Peak area = $3.32 \times 10^5 \times [\text{Mg}] + 1.28 \times 10^4$ with $R^2 = 0.999$ **ESI (8)**

Peak area = $3.80 \times 10^4 \times [\text{Na}] - 1.69 \times 10^4$ with $R^2 = 0.997$ **ESI (9)**

Peak area = $3.71 \times 10^4 \times [\text{P}] - 5.92 \times 10^2$ with $R^2 = 0.999$ **ESI (10)**

Peak area = $2.14 \times 10^4 \times [\text{S}] + 2.07 \times 10^3$ with $R^2 = 0.999$ **ESI (11)**

Table ESI 2. Elementary composition of the precipitate obtained by ICP analysis.

Elementary analyte	Ca	Mg	K	Na	P	S
Weight fraction (%)	7.3	16.0	5.3	1.0	3.8	0.1

ESI 10. Raw data of molar amount of reactants and adducts during urine electrolysis.

The **Table ESI 3** shows the raw data obtained when determining the quantities of reagents and products during the chronoamperometric electrolysis of a 48 hours human urine solution.

Table ESI 3. Molar quantities of reagents and products during electrolysis of human urine.

pH	Time (h)	Charge (C)	CO(NH ₂) ₂	OCN ⁻	NO ₂ ⁻	NH ₄ ⁺	N ₂	FA	OA	Sum
			(mol)							
6.2	0	/	1.49×10 ⁻²	/	/	1.07×10 ⁻³	/	/	4.22×10 ⁻⁵	1.60×10 ⁻²
14	0	/	1.40×10 ⁻²	/	/	1.52×10 ⁻³	/	9.56×10 ⁻⁵	5.11×10 ⁻⁵	1.57×10 ⁻²
	5	740	1.40×10 ⁻²	2.21×10 ⁻⁴	3.59×10 ⁻⁴	1.33×10 ⁻³	1.56×10 ⁻³	7.04×10 ⁻⁴	2.71×10 ⁻⁴	1.85×10 ⁻²
	8	1230	1.39×10 ⁻²	6.48×10 ⁻⁴	7.02×10 ⁻⁴	1.25×10 ⁻³	2.23×10 ⁻³	8.96×10 ⁻⁴	3.42×10 ⁻⁴	2.00×10 ⁻²
	23	2628	1.30×10 ⁻²	1.39×10 ⁻³	1.33×10 ⁻³	9.33×10 ⁻⁴	2.59×10 ⁻³	1.89×10 ⁻³	6.20×10 ⁻⁴	2.18×10 ⁻²
	30	3256	1.18×10 ⁻²	1.75×10 ⁻³	1.58×10 ⁻³	9.00×10 ⁻⁴	2.81×10 ⁻³	2.21×10 ⁻³	8.33×10 ⁻⁴	2.19×10 ⁻²
	48	4508	1.12×10 ⁻²	2.48×10 ⁻³	2.18×10 ⁻³	8.50×10 ⁻⁴	4.02×10 ⁻³	3.20×10 ⁻³	1.06×10 ⁻³	2.49×10 ⁻²

ESI 11. Distribution of the identified carbonaceous species compared to the measured TOC.

Table ESI 4 and **Figure ESI 10** show the distribution of the identified carbonaceous species compared with the measured TOC. The identified carbonaceous molecules (urea, cyanate, FA, OA) represent only 43% of the total TOC before alkalization of urine. This confirms that urine contains significant quantities (57%) of other carbon-containing molecules (such as creatinine, urobilin, etc), not quantified in this study.

Table ESI 4. Carbonaceous species concentrations during electrolysis.

pH	Time (h)	Charge (C)	TOC	CO(NH ₂) ₂	OCN ⁻	FA	OA	Sum
			(g _{eqC} .L ⁻¹)					
6.2	0	/	7.12	2.99	/	/	0.02	3.00
14	0	/	6.61	2.80	/	0.02	0.02	2.84
	5	740	6.15	2.81	0.04	0.14	0.11	3.10
	8	1230	5.78	2.79	0.13	0.18	0.14	3.23
	23	2628	6.00	2.60	0.28	0.38	0.25	3.50
	30	3256	5.50	2.37	0.35	0.44	0.33	3.49
	48	4508	5.39	2.23	0.50	0.64	0.42	3.79

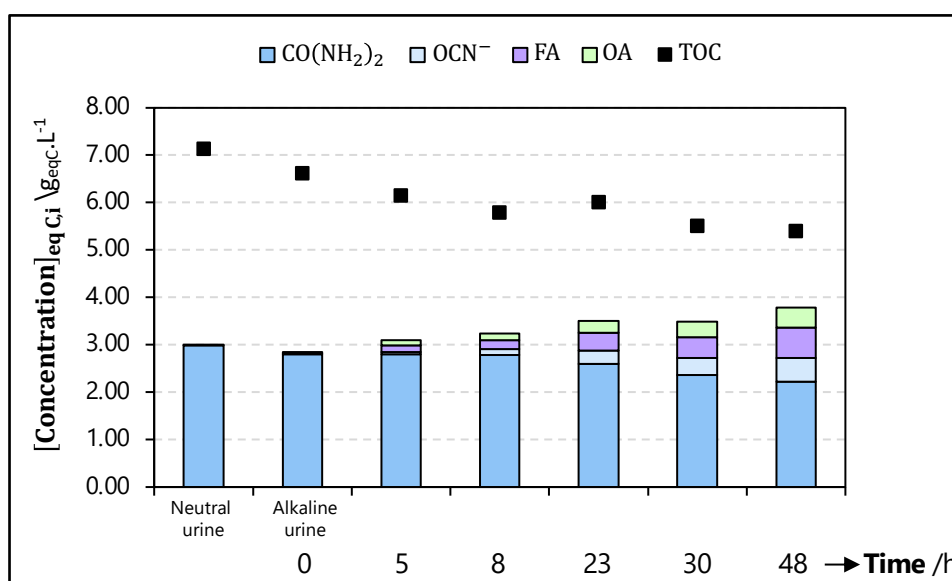


Figure ESI 10. Histogram of concentrations of *identified* carbon species and TOC measured during electrolysis of a urine solution.