Electronic Supporting Information

Anion exchange polymer modified electrodes for detection of Δ9- tetrahydrocannabinol (Δ9-THC): a potential electrochemical sensor for point-of-care and roadside testing.7

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Experimental section

Chemicals and reagents: All chemicals used were of analytical grade and used as received without any further purification. These included sodium chloride (>99.5%, Sigma-Aldrich), Sodium Hydroxide (>97%, Sigma-Aldrich), TRIS buffer solid (>99%, Sigma-Aldrich) methanol (>99.9%, Sigma-Aldrich) and Δ9-tetrahydrocannabinol in methanol (1mg/ml, Sigma-Aldrich, stored at 0°C). All solutions were prepared using 100% ultra-pure steam distilled water from Lucemill Ltd. 2,2",4,4",6,6"-hexamethyl-p-terphenylene-poly [2,2'-(m-mesitylene)-5,5'-bis(N,N'-methylbenzimidazolium)] (HMT-PMBI) was synthesized according to the procedure developed by Holdcroft et al. (Wright et al., 2016; Wright & Holdcroft, 2014). The as-prepared ionomer has a high degree of selectivity over the degree of methylation (dm %). The HMT-PMBI samples in this work are all 92% dm unless stated otherwise. The polymer was received in a membrane form, with iodide (I^-) as the counterion (see Fig 2). In order to avoid potential interferences with the iodine form during the voltammetric studies, the counterion of HMT-PMBI was exchanged with chloride (Cl^-), by soaking the membrane in 1 M NaCl for 24 h, then transferring it into distilled water for 24 h.

Apparatus: Differential pulse voltametric measurements were preformed using a Metrohm Autolab PGSTAT302N controlled by the NOVA 2 software. Silver-Silver Chloride screen printed electrodes were purchased from Metrohm UK Ltd., C11L Screen-Printed Electrode with carbon working, carbon auxiliary electrode and silver/silver chloride reference electrode. The Gii-Sense electrodes were purchased from PalmSense (UK), Gii-Sens Integrated Graphene SPE - Pure 3D Graphene sensing electrode - Graphene CE and WE, Ag/AgCl RE.

General experimental conditions: All experiments were performed at room temperature under ambient conditions. TRIS buffer solution was made using TRIS buffer solid dissolved in distilled water to make a 20mM solution and then pH adjusted to pH 10 using sodium hydroxide and Jenway 3510 pH meter. The Hexamethyl-p-terphenyl poly(benzimidazolium) solid was dissolved in >99.9% methanol to produce a solution of 2% weight by volume of HMT-PMBI, the mixture was sonicated for 15 minutes to ensure dissolution and homogeneousness.

Electrochemical setup: Experiments were carried out using 10ml of solution in a small 10ml glass beaker. The beaker was set up on a magnetic stirrer to stir solutions during preconcentration, the screen-printed electrode was submerged into these solutions for experimentation.

Screen printed Electrode modification: The modified screen-printed electrodes were prepared by drop casting 0.5μL of the methanolic solution of 2% (w/v) HMT-PMBI polymer in the working electrode of Metrohm SPE and 1μL in the working electrode of Gii-Sense SPE. The film deposited on the electrode surface was dried at room temperature for 10 minutes.

Electrochemical measurements: Prior to taking measurements the test solutions were stirred for 30 minutes to preconcentrate THC on the working electrode. Stirring was then shut off and the measurement was performed. The THC current at 0.3 V was used to generate linear fit data. The average current drawn and standard deviation from the triplicate sets of experimental data was plotted with a linear fit. The differential-pulse parameters used were as follows: E Step: 0.01v, E pulse: 0.2v, T pulse: 0.02s, Scan rate: 0.01 v/s.

Ethical Approval: The experiments involving the use of human saliva conducted in this research have been approved by the School of Applied Sciences Research Integrity and Ethics Committee at the University of Huddersfield presenting a reference number SAS-SRIEC-21.09.23-2.

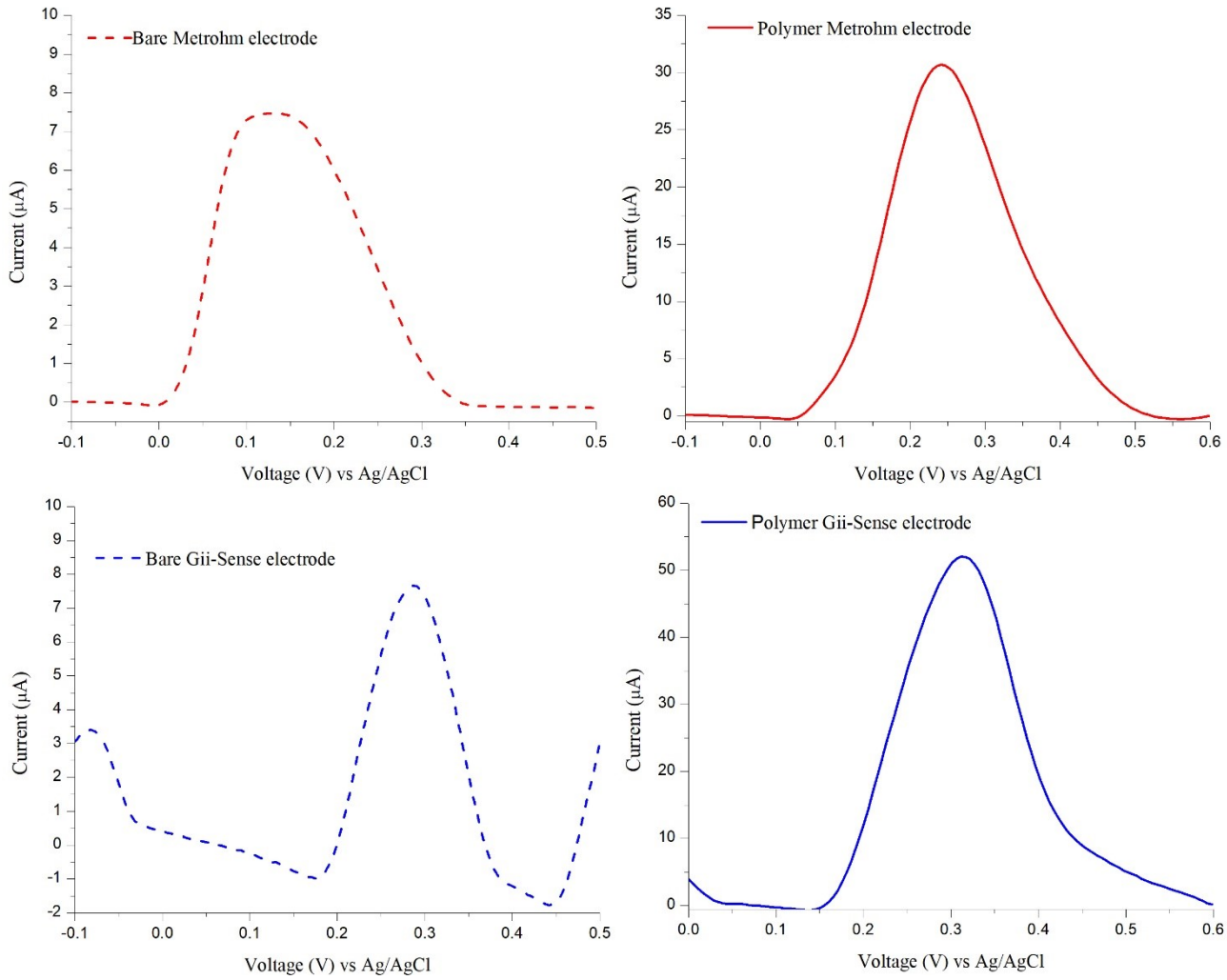

Figure S1. Comparison of Metrohm C11L and Gii-Sense (Carbon WE, Ag/AgCl RE, Carbon CE) screen printed electrodes in the presence of 10µg/ml THC pH 10 TRIS buffer. Doted graphs correspond to unmodified or bare screen printed electrode and the continuous lines to 2% (w/v) HMT-PMBI drop casted screen printed electrode.

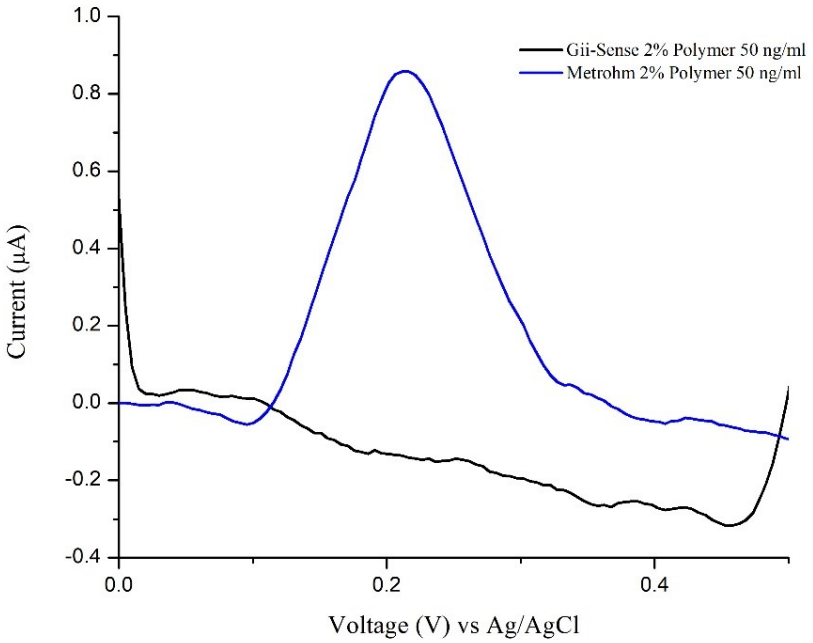

Figure S2. Comparison of Metrohm C11L and Gii-Sense (Carbon WE, Ag/AgCl RE, Carbon CE) 2% (w/v) HMT-PMBI drop casted screen printed electrodes in the presence of 50ng/ml THC pH 10 TRIS buffer.

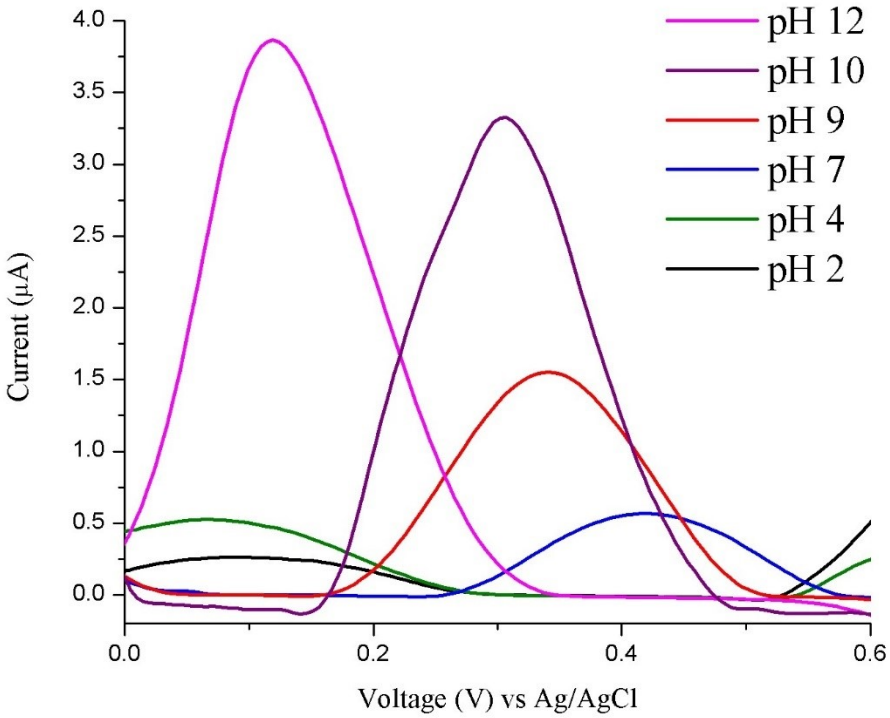

Figure S3. Investigation of pH effect on THC signal using TRIS buffer ranging from pH 2 to 12 with 1μg/ml THC. Metrohm C11L screen printed electrode with 2% (w/v) HMT-PMBI drop casted onto the carbon working electrode.

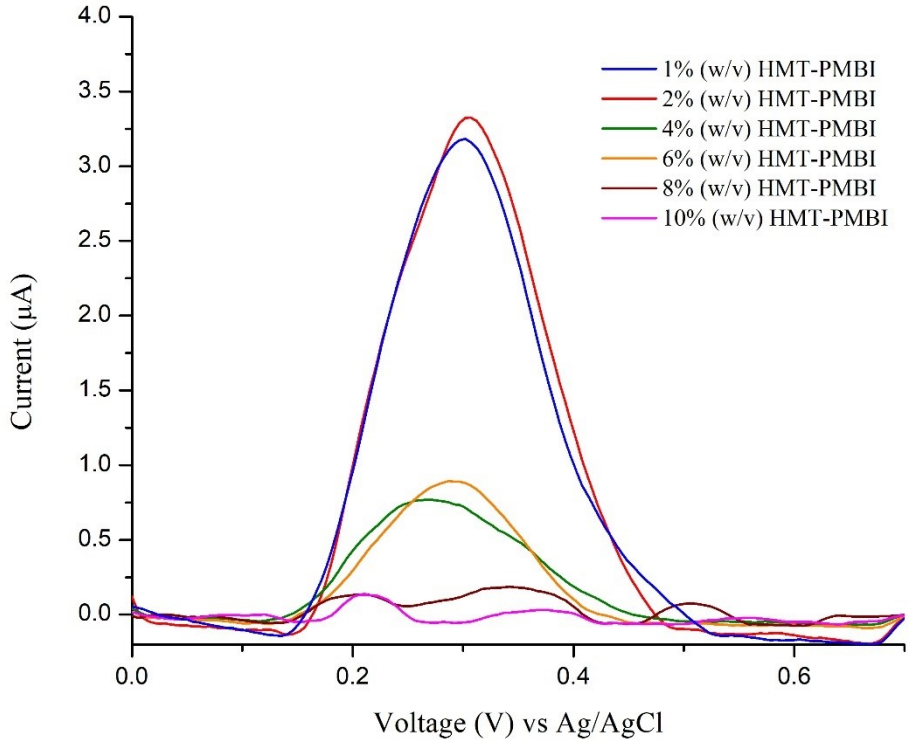

Figure S4. Effect of increasing the concentration of HMT-PMBI drop casted into the screen printed electrode. Metrohm C11L screen printed electrode with 2% (w/v) HMT-PMBI was drop casted (0.5µL) onto the carbon working electrode. All the electrochemical analysis was performed by Differential Pulse Voltammetry E Step: 0.01v, E pulse: 0.2v, T pulse: 0.02s, Scan rate: 0.01 v/s. The concentration of THC employed was 1000ng/mL in TRIS buffer pH 10.

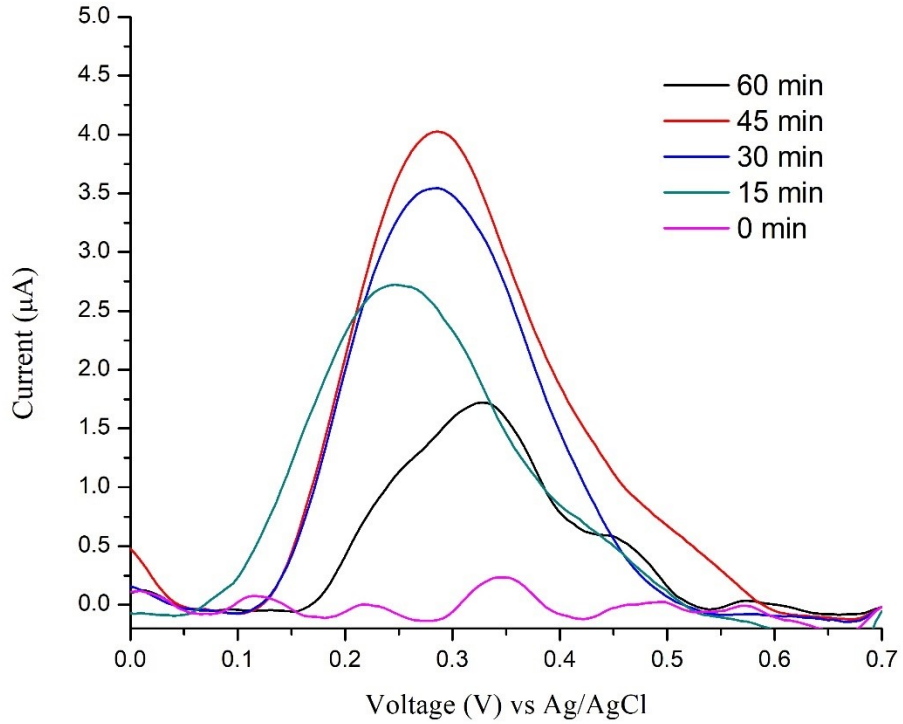

Figure S5. Comparison of how preconcentration time effects THC absorption onto the screen printed electrode. Metrohm C11L screen printed electrode with 2% (w/v) HMT-PMBI was drop casted (0.5µL) onto the carbon working electrode. All the electrochemical analysis was performed by Differential Pulse Voltammetry E Step: 0.01v, E pulse: 0.2v, T pulse: 0.02s, Scan rate: 0.01 v/s. The concentration of THC employed was 1000ng/mL in TRIS buffer pH 10.

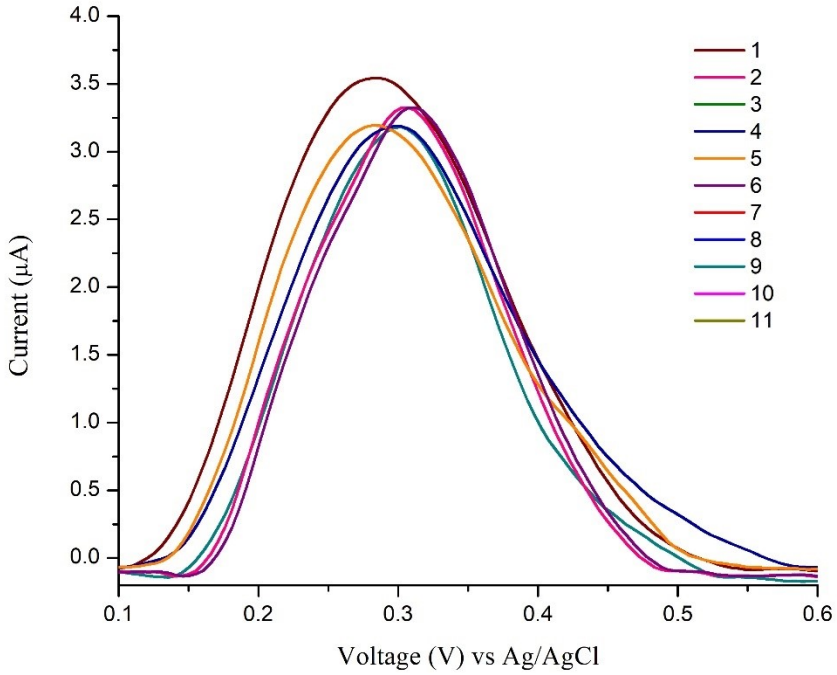

Figure S6. Repeatability study of 11 different Metrohm C11L screen printed electrode with 2% (w/v) HMT-PMBI was drop casted (0.5μL) onto the carbon working electrode. All the electrochemical analysis was perfomed by Differential Pulse Voltammetry E Step: 0.01v, E pulse: 0.2v, T pulse: 0.02s, Scan rate: 0.01 v/s. The concentration of THC employed was 1000ng/mL in TRIS buffer pH 1, 40 min preconcentrating time.

Table S1. Recent electrochemical sensor for the detection of THC.

Method	LOD (ng/mL)	Linear range (ng/mL)	Portable	Drawback	Reference
SENS carbon electrode	40.8	314 - 3140	Yes	Poor detection limit considering the typical saliva threshold of 25 ng/mL	(Williams, White, Hunt, & Meyerhoff, 2023)
CuPc/SPGE[a]	1.370	10 - 1500	Yes	High sensor cost involving the use of TX-100, hexadecyltrimethylammonium bromide and Copper phthalocyanine.	(Pholsiri, Khamcharoen, Vimolmangkang, Siangproh, & Chailapakul, 2023)
EMMA-Sense[b]	1.5	Log c: 0.3-31.4	Yes	High SPE cost using gold counter electrode, low stability of 3 days.	(Kékedy-Nagy, Perry, Little, Llorens, & Shih, 2023)
MWCNT/Carbon electrode	157.2	314 - 1887	No	Use of non-environmentally friendly chemicals such as MWCNT, not portable process as it requires centrifugation.	(Mishra et al., 2020)
Au-PET[c]	0.1	0.1-100	No	High-cost sensor and non-portable system.	(Stevenson et al., 2019)
m-Zensor electrodes	1.6	2 - 25	No	The pretreatment/electrodeposition step makes the SPCEs air sensitive, reducing their shelf life to 24h or requiring N_2 or vacuum storage.	(Ortega, Ahmed, Tuteja, Srinivasan, & Rajabzadeh, 2022)
Mediator-SPE	NR*	25-50	Yes	Complicated sensor fabrication and very small concentration range.	(Wanklyn et al., 2016)
HMT-PMBI/SPE	5.28	10-1000	Yes	40 minute preconcentration time	This work

[a] copper-phthalocyanine-modified screen-printed graphene electrodes; [b]electrochemical multiplatform microfluidics aptamer-based sensor; [c] gold on polyethylene terephthalate biosensor; [d] N-(4-amino-3-methoxyphenyl)-methanesulfonamide mediated detection; * Not Reported

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