Electroanalytical determination of cannabinoids in hashish samples for future implementation in electrochemical sensors

F. Lugli[a], A. Monari[a], R. Barbieri[a] and L. Pigani[a]

[a] Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Modena, Italy

e-mail: **filippo.lugli@unimore.it**

Cannabis sativa L. and its derivatives (such as *hashish*) remain nowadays some of the most used drugs of abuse in Europe [1]. Products with low Δ^9-tetrahydrocannabinol (Δ^9-THC) levels but high cannabidiol (CBD) content have become available on the market, posing new challenges for cannabinoids detection and analyses. Recently, the attention of our research group has been particularly directed toward the development of amperometric sensor systems for the rapid identification of both legal and illegal *Cannabis sativa* L. samples. In this context, a key factor contributing to the success of the sensor system proposed by us [2] was the ability to perform electrochemical measurements using Carbon Black-modified Screen-Printed Electrodes (SPEs-CB) in an electrolyte medium containing boric acid (H_3BO_3), introduced via the Britton-Robinson buffer (BRB) used to maintain a stable pH.

Determination of total cannabinoids concentration in *hashish* samples:

Quantifying the total concentration of cannabinoids in *hashish* extracts provides an indication of the "potency" of the samples in terms of "cannabinoids content". For this reason, this determination was carried out on both legal and illegal *hashish* samples. Ten samples were analyzed electrochemically and the corresponding voltammograms were obtained. The actual concentration of cannabinoids contained in each sample was determined by HPLC analysis. In this first step of the project the considered cannabinoids were Δ^9-THC, Δ^9-tetrahydrocannabinolic acid (THCA), CBD, cannabidiolic acid (CBDA) and cannabinol (CBN). The concentration value of total cannabinoids obtained for each sample was related to the total area of the peaks present in the corresponding voltammogram. In this way, a calibration curve was constructed which made it possible to estimate the total concentration of cannabinoids in unknown samples with a good degree of accuracy.

***Hashish* sample**

Extraction method:
- Sample to solvent ratio 1:100 (w/v);
- EtOH ;
- Dynamic maceration;
- 15 mins (3x).

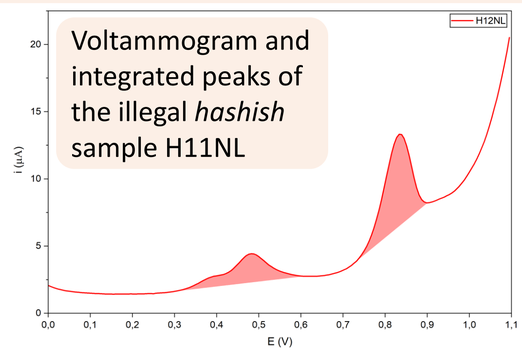
Electrolytic Medium:
- 10% Extract;
- 20% EtOH;
- 70 % BRB;
- solution, pH ~ 7, KCl 0.1 M.

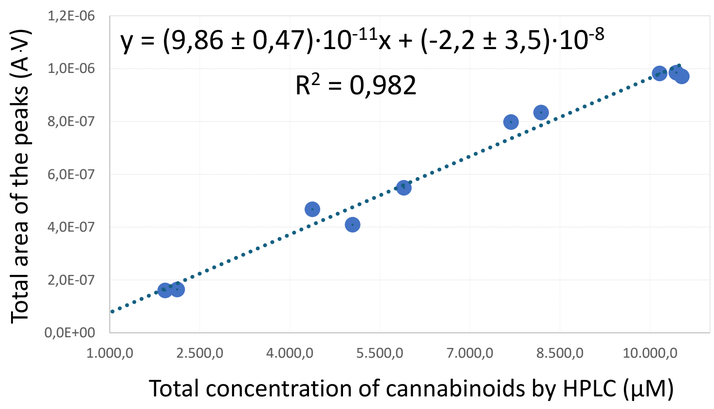
Differential Pulse Voltammetry

Parameters:
PT= 0,1 s
SP= 0,006 V
IT= 0,4 s
PA= 0,05 V

SPE-CB

Voltammogram and integrated peaks of the illegal *hashish* sample H11NL





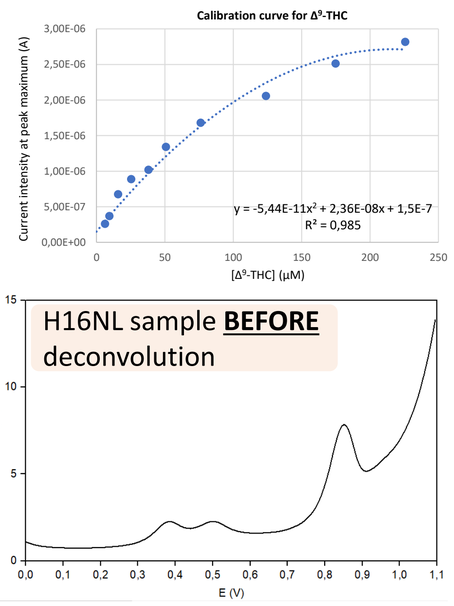
Total cannabinoids content determination in TWO UNKNOWN EXTRACTS

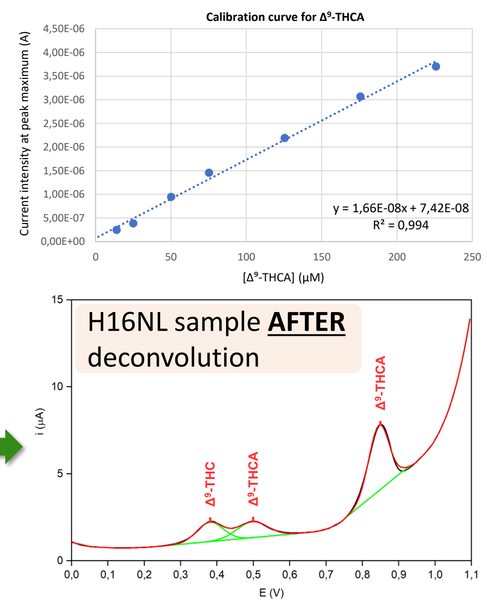
Sample name	$[CANN.TOT]_{HPLC}$ (µM)	$[CANN.TOT]_{EXP}$ (µM)	Recovery factor
H11NL	10012	9650	0,96
H7NL	7048	7362	1,04

Determination of Δ^9-THC and Δ^9-THCA concentrations in *hashish* samples using a deconvolution method:

The next step of the project was to find a way to individually quantify Δ^9-THC and Δ^9-THCA in illegal *hashish* samples. Δ^9-THC is the primary psychoactive cannabinoid in *Cannabis sativa* L. and its derivatives, so accurate measurement is essential to assess the legality of *hashish* samples. Because Δ^9-THCA is the acidic precursor of Δ^9-THC and fully converts into Δ^9-THC during decarboxylation, it must also be quantified. The quantification of Δ^9-THC and Δ^9-THCA was carried out using the current intensity (i) relative to the maximum of the registered voltammetric peaks, interpolating the values obtained in two calibration curves constructed respectively using standard solutions of Δ^9-THC and Δ^9-THCA at different concentrations. Due to the high overlap between the voltammetric peaks of the two cannabinoids, it was necessary to use an appropriate deconvolution method in order to obtain high-accuracy quantification. The deconvolution of the voltammetric peaks relating to Δ^9-THC and Δ^9-THCA was carried out using the deconvolution software included in the Origin 2025 program.

Sample name	$\%\Delta^9\text{-THC}_{HPLC}$ ($\%^w/_w$)	$\%\Delta^9\text{-THCA}_{HPLC}$ ($\%^w/_w$)	$\%\Delta^9\text{-THC}_{EXP}$ ($\%^w/_w$)	$\%\Delta^9\text{-THCA}_{EXP}$ ($\%^w/_w$)	Recovery factor (Δ^9-THC)	Recovery factor (Δ^9-THCA)
H3NL	2,07	9,03	2,36	10,55	1,14	1,17
H6NL	6,90	10,25	7,09	11,36	1,03	1,11
H7NL	5,93	15,21	6,54	19,77	1,10	1,30
H9NL	7,10	26,71	6,21	23,99	0,88	0,90
H11NL	7,05	27,46	6,16	25,00	0,87	0,91
H12NL	5,62	21,50	6,05	23,31	1,08	1,08
H13NL	8,22	27,74	7,46	27,32	0,91	0,99
H14NL	6,80	29,22	6,10	28,76	0,90	0,98
H15NL	7,83	26,05	8,59	30,76	1,10	1,18
H17NL	7,71	25,74	6,31	23,66	0,82	0,92





Conclusions:

The results obtained have shown that the electrochemical analysis method we have developed [2] allows us to quantify the total cannabinoids content in all *hashish* samples (legal or illegal) and to individually quantify the Δ^9-THC and Δ^9-THCA content in the illegal ones. Furthermore, a multivariate method for the deconvolution of voltammetric peaks of the cannabinoids present in *hashish* extracts is currently under development. The design features of the SPEs used make them particularly suitable for application in sensor systems that allow rapid, simple, and *in situ* analysis of Cannabis sativa L. samples. The research group has already demonstrated the effectiveness of the analysis method on *marijuana* matrices [2] and a prototype of a device for the on-field analysis of *marijuana* samples is in the final stages of development. The goal of this work was therefore to transfer all the knowledge and results obtained on *marijuana* samples, to the *hashish* matrix as well.

References:

[1] https://www.euda.europa.eu/publications/european-drug-report/2025/cannabis_en

[2] A. Monari *et al.*, "Electrochemical sensors for fast classification of different *Cannabis sativa* L. samples according to total Δ^9-tetrahydrocannabinol content," Talanta, vol. 282, p. 126958, Jan. 2025, doi: 10.1016/J.TALANTA.2024.126958.