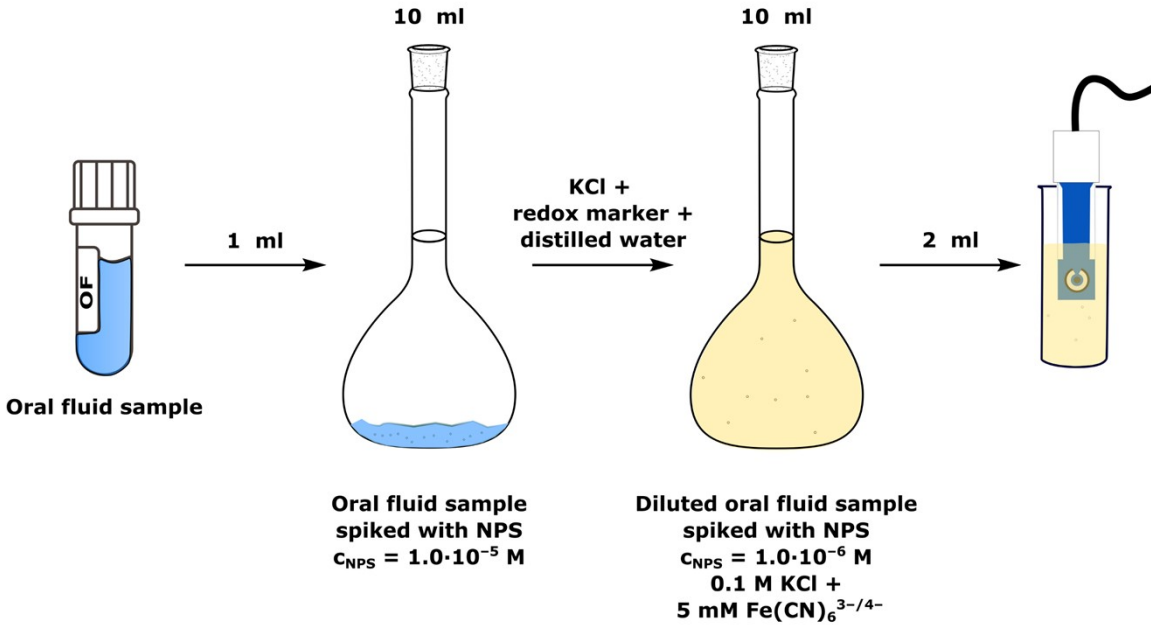
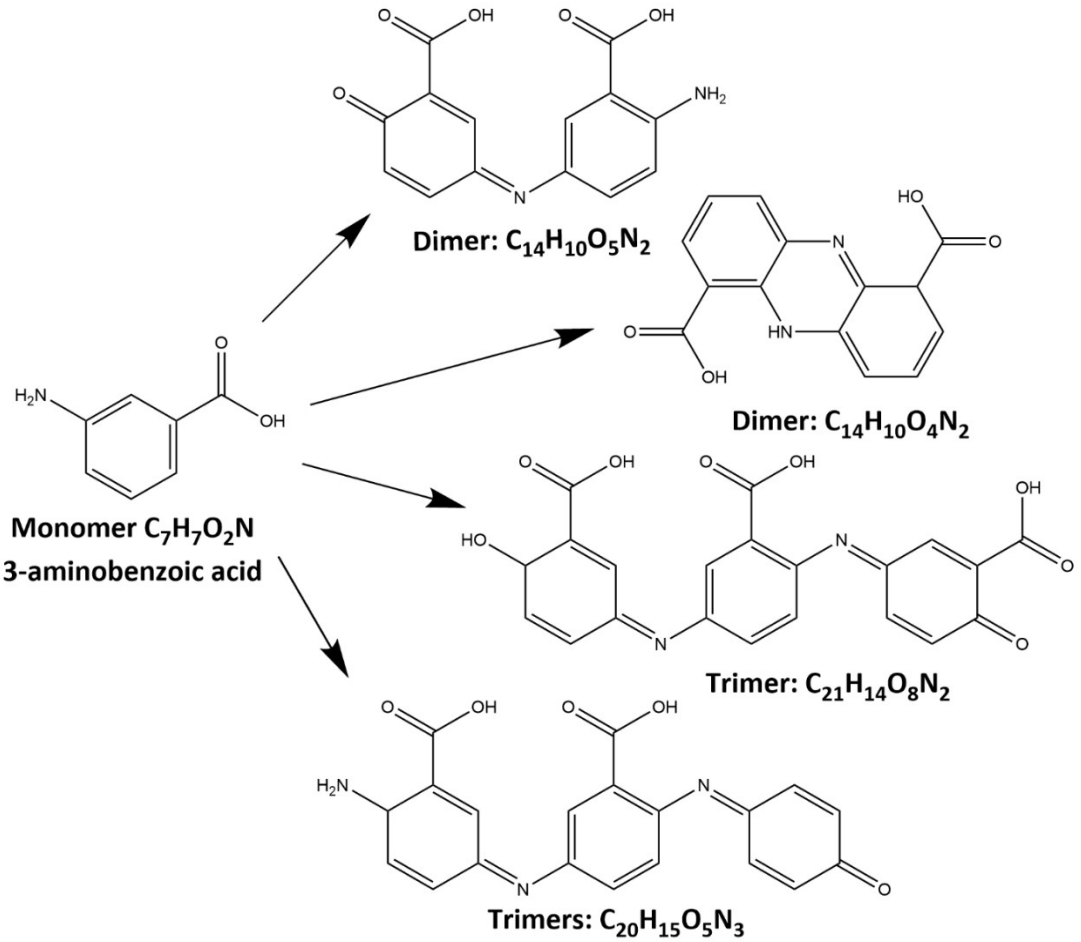
Electronic Supplementary Information

Oral fluid sample preparation



Scheme S1 Experimental protocol of oral fluid sample preparation for impedance spectroscopy measurements with experimental o-3ABA-modified graphite screen-printed electrodes.

Tentative structures of proposed oligomers 3ABA



Scheme S2 Proposed structures oligomers formed from electrochemically oxidized 3-aminobenzoic acid [34]

[34] T. V. Shishkanova, G. Broncová, Z. Němečková, V. Vrkoslav, V. Král and P. Matějka, J. Electroanal. Chem., 2019, 832, 321-328.

Raman spectroscopy

In the spectrum of aniline hydrochloride (Fig. S2), we observe peak situated at 1634 cm^{-1} (NH_2 deformation vibrations), at 1602 cm^{-1} (the quadrant ring stretching vibrations), at 1203 cm^{-1} (ring–N stretching vibrations), at 1177 cm^{-1} (C–H in-plane bending vibrations), at 1008 cm^{-1} (in-plane aromatic bending vibrations), at 794 cm^{-1} (the quadrant in-plane bending vibrations), at 619 cm^{-1} (C–H quadrant out-of-plane bending vibrations), and at 407 cm^{-1} (out-of-plane deformations of the ring) [S1].

The Raman spectrum of PANI electrochemically deposited on the Au/SPE electrode (Fig. S1) corresponds to the typical spectrum of the protonated emeraldine form of polyaniline described in Encyclopaedia of Polymer Science and Technology and in [S1]. The peak observed at 1602 cm^{-1} is connected with the C=C stretching vibrations in a quinonoid ring. The peak with maximum at approximately 1513 cm^{-1} corresponds to the N–H deformation vibrations associated with the semiquinonoid structures. The band with maximum at 1383 cm^{-1} belongs to the C~$N^{+\bullet}$ vibrations of localized polaronic structures and that at 1335 cm^{-1} to the delocalized polarons. The amount of the localized polarons is higher in comparison to the standard PANI. Quinonoid-ring deformation vibrations correspond to the band situated at 1230 cm^{-1}. The band with maximum at 1176 cm^{-1}

belongs to the C–H in-plane bending vibrations of the semi-quinonoid or benzenoid rings. The band situated at 810 cm^{-1} is linked to the benzene-ring deformations and the band observed at 578 cm^{-1} can be linked to the amine deformation vibrations (in-plane) of the emeraldine salt structure. The out-of-plane deformations of the ring are connected with the bands located at 520 and 430 cm^{-1}.

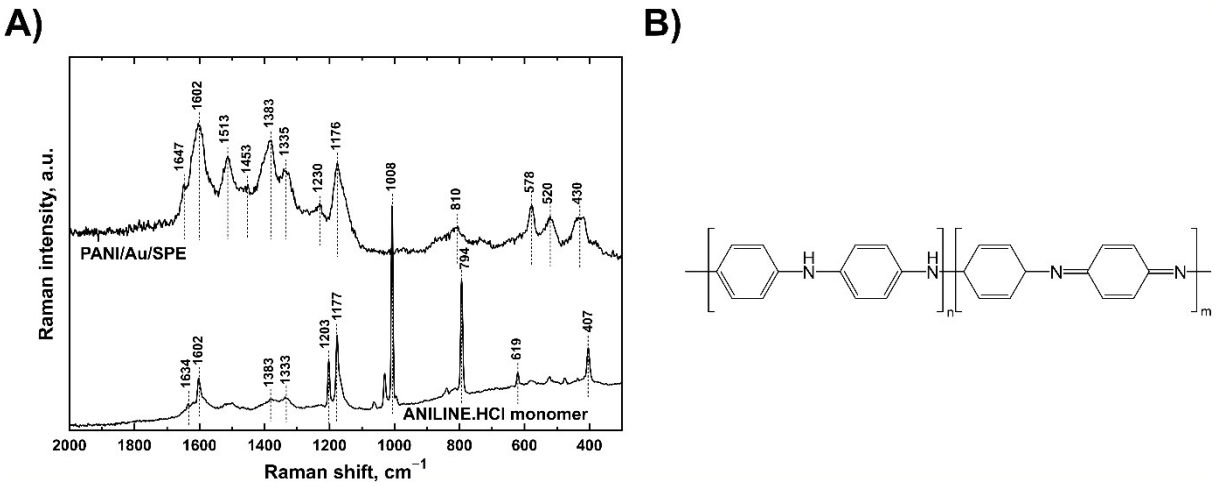


Fig. S1 Dispersive Raman spectra obtained on gold screen-printed electrodes modified with polymerization product of aniline and of the corresponding monomer (A) and the structure of polyaniline.

[S1] J. Stejskal, M. Trchová, P. Bober, P. Humpolíček, V. Kašpárková, I. Sapurina, M. A. Shishov and M. Varga, in *Encyclopedia of Polymer Science and Technology*, 2015, pp. 1-44.

Analytical applicability of o-3ABA modified electrodes: Analytical parameters

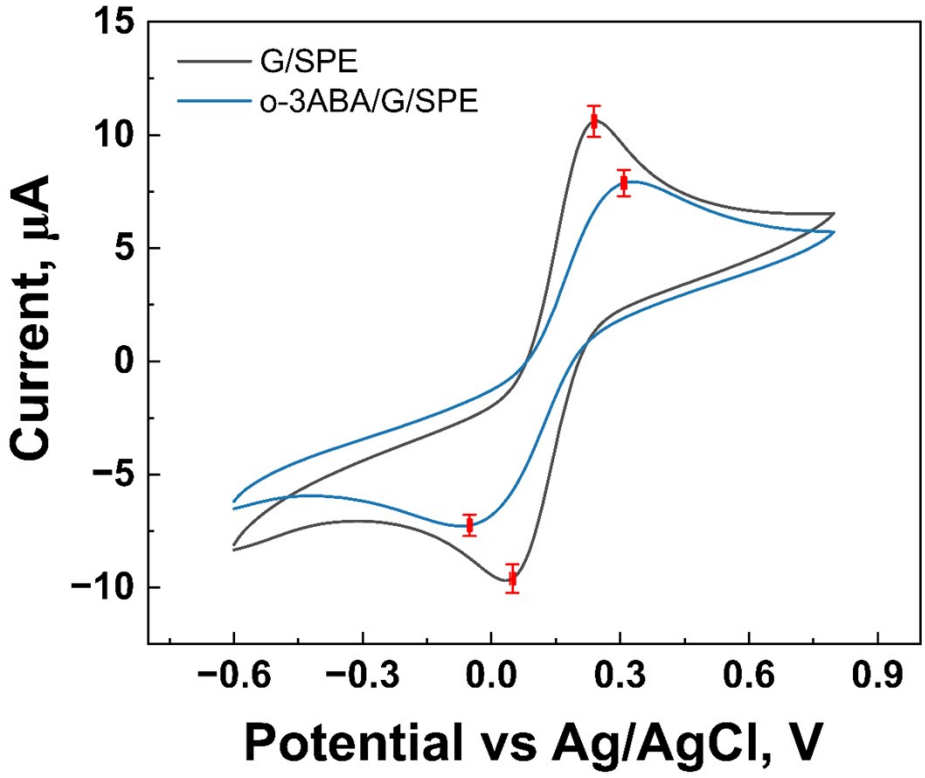


Fig. S2 Testing and comparing repeatability of electrochemical signal obtained before and after modification of graphite screen-printed electrode with 3-aminobenzoic acid oligomers (n=5). Experimental conditions: 5 mM $Fe(CN)_6^{3-/4-}$ solution containing 0.1 M KCl

Table S1 Parameters of cyclic voltammograms obtained during measurement with unmodified and o-3ABA-modified electrodes (n=5).

	Before modification		**After modification**	
	Anodic peak	Cathodic peak	Anodic peak	Cathodic peak
Potential, mV	236.5 ± 4.5	42.9 ± 5.5	302.5 ± 5.5	–32.9 ± 4.5
Current, µA	10.83 ± 0.69	–10.13 ± 0.63	7.07 ± 0.58	–6.79 ±0.47

Table S2 Reproducibility of electrochemical signal obtained for o-3ABA-modified electrodes (n=3) in model samples

Concentration (µM)	log (c_{NPS})	2-aminoindane		butylone	
		CPE (nF)	RSD (%)	CPE (nF)	RSD (%)
1.00	–6.00	868.11 ± 119.51	13.77	644.67 ± 88.13	13.67
3.00	–5.52	731.59 ± 84.40	11.54	632.87 ± 70.04	11.07
5.00	–5.30	699.50 ± 72.62	10.38	617.53 ± 53.37	8.64

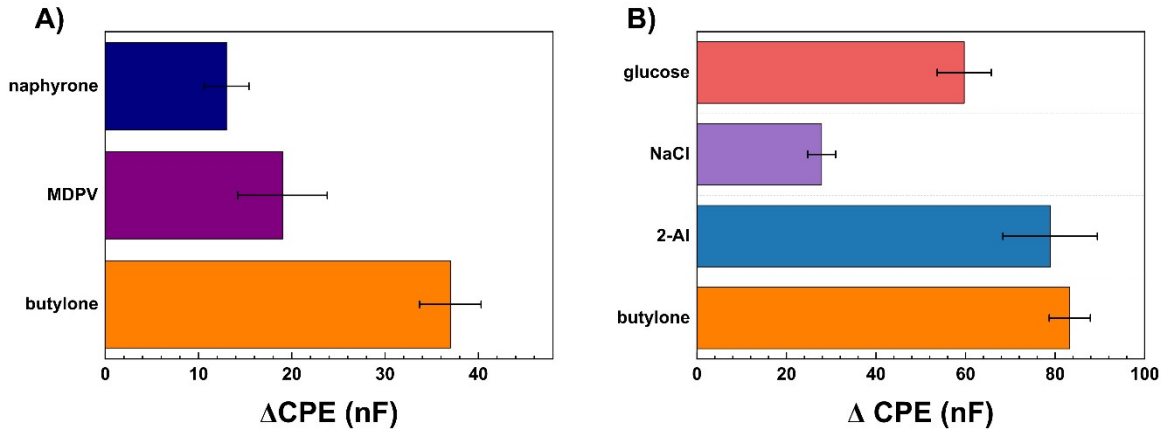


Fig. S3 Influence of synthetic cathinones (A) and substances present in oral fluid samples (B) on the electrochemical signal of o-3ABA/G/SPE.

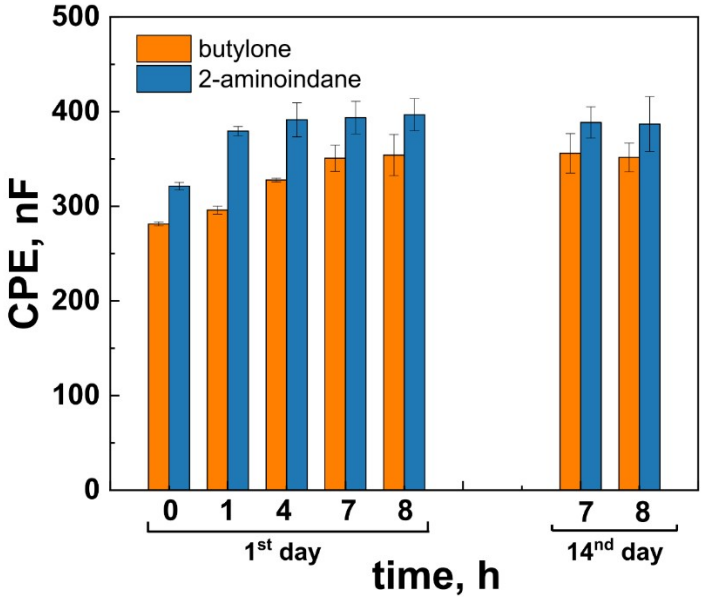


Fig. S4 Inter-day stability of the o-3ABA modified G/SPE electrodes with 1 mM concentration of the analyte (n=3).

Analytical applicability of o-3ABA modified electrodes: Analysis of model and oral fluid samples

Determination of NPS in model samples and oral fluid

Table S3 The experimental data obtained with the determination of chosen new psychoactive substances (c = $1.0 \cdot 10^{-6}$ M) in model samples and oral fluid

Concentration (μM)	log (c_{NPS})	Model sample		Oral fluid sample	
		2-aminoindane	butylone	2-aminoindane	butylone
		CPE (nF)		CPE (nF)	
1.00	–6.00	801.6	581.8	678.9	878.2
2.00	–5.70	770.7	559.1	640.7	863.6
3.00	–5.52	756.9	545.0	622.6	848.9
4.00	–5.40	736.5	530.0	601.6	842.1
5.00	–5.30	726.4	522.6	596.4	837.0
6.00	–5.22	719.7	521.6	588.6	833.9

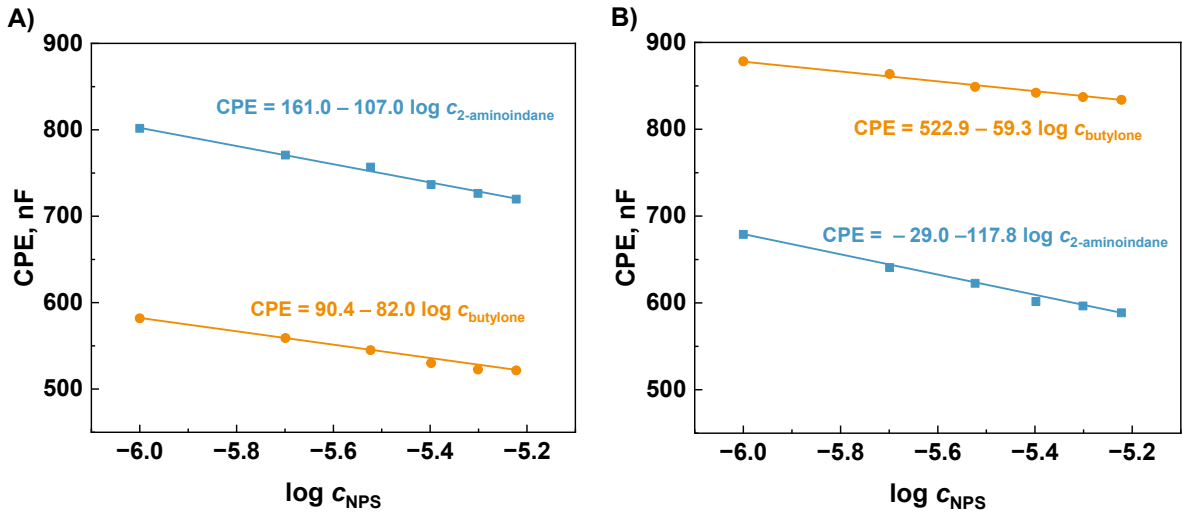


Fig. S5 The concentration dependences obtained with the determination of chosen new psychoactive substances in model samples (A) and oral fluid (B)