

SUPPLEMENTARY MATERIAL

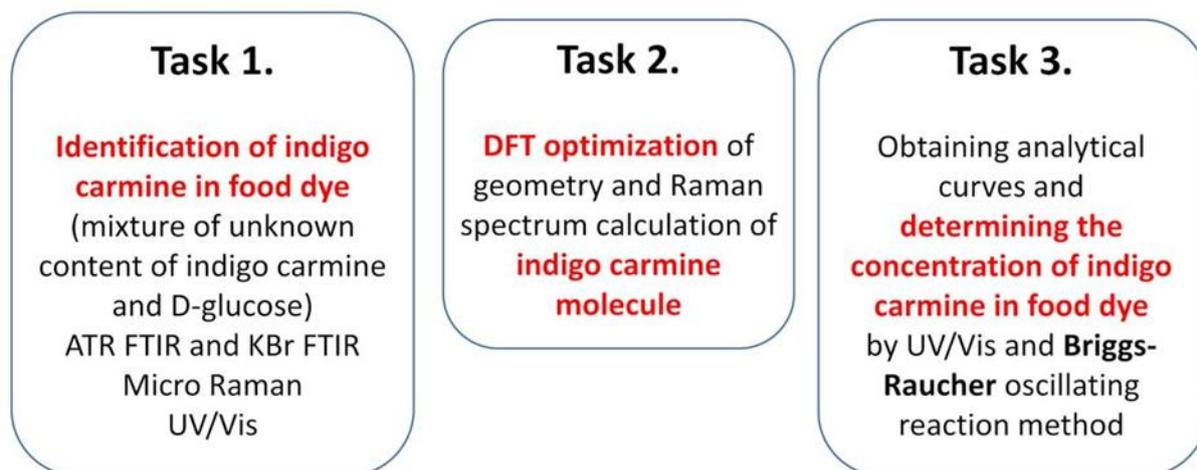


Figure S1. The flow of experimental tasks .

ATR AND KBr FTIR SPECTROSCOPY

ATR was done first as it is the most robust technique. Since it did not yield conclusive results, KBr FTIR, a more sensitive technique, also did not detect indigo carmine. These preliminary results suggested that indigo carmine is present in low concentrations in the food dye. The results obtained for the ATR and KBr measurements of the food dye are presented in Figure S2. a) and Figure S2 b). The vibrations of molecular groups are listed in Table S1.

THE PEAKS OF THE INFRARED SPECTRUM OF D-GLUCOSE (DEXTROSE)

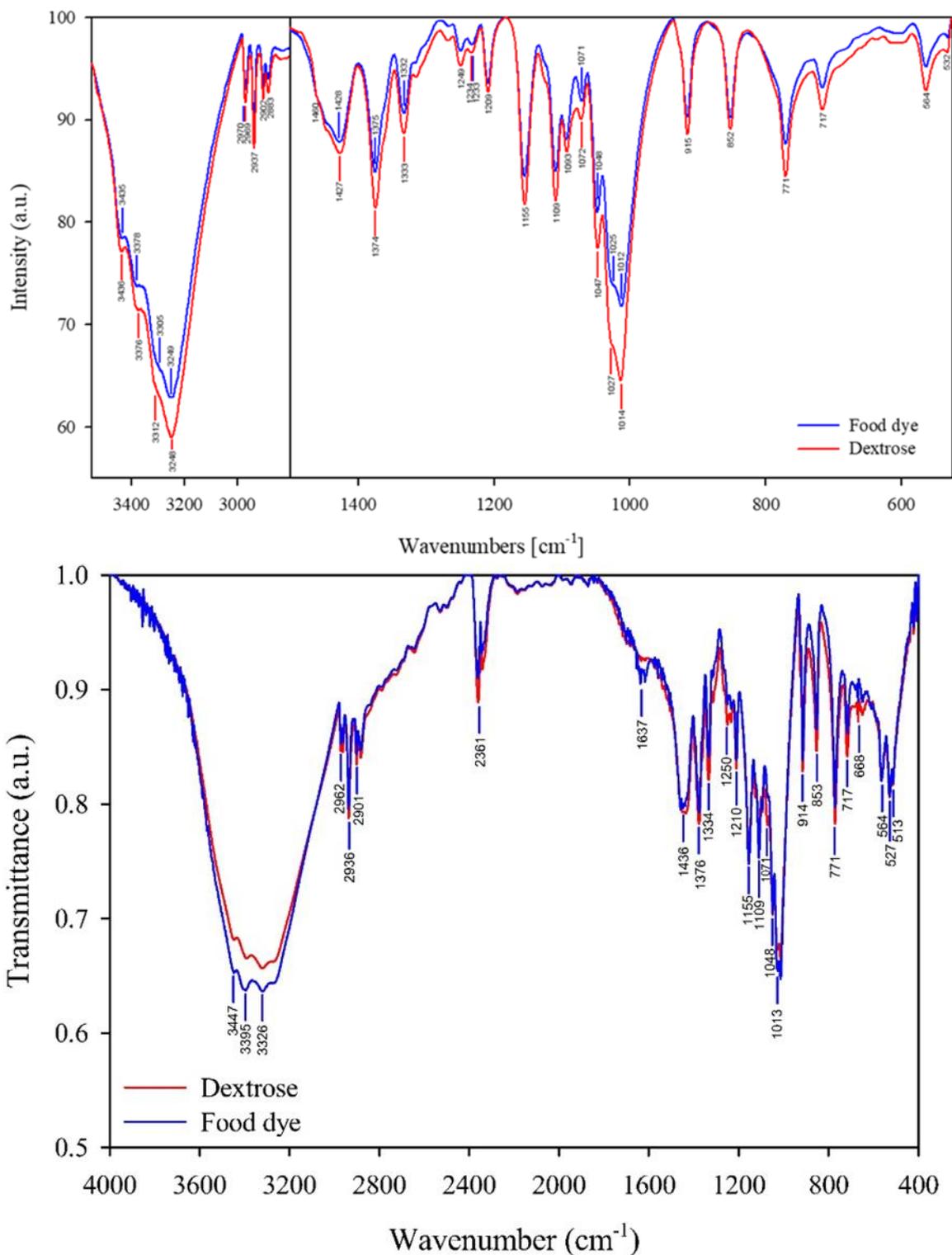


Figure S2. a) The ATR FTIR spectra of the food dye and of D-glucose (dextrose)

Figure S2. b) The KBr-pellet IR spectrum of food dye and D-glucose

The high amount of dextrose in food dye implicates the overlapping spectra of dextrose and food dye that may be observed from Figure S2 a) and b). Due to the overlapping spectra of dextrose and food dye, there is no specific peak indicating the confirmation of indigo carmine that may be observed. Thereby, only a small amount of indigo carmine is shown to be in this food dye which is composed of indigo carmine and dextrose. For this reason, we find that indigo carmine cannot be detected by such bulk sample techniques as ATR and KBr.

The following table lays out the assignment of dextrose peaks in both the FTIR spectra.

Table S1: The assignment of the dextrose peaks of the infrared spectrum

IR	D-glucose[S1]			ATR	KBr
	α -D	β -D-M	Assignment		
3410	3418	3146	ν OH	3248	3326,3347,3395
3393	3408	3123	ν OH	2970	2962
2944	2963	3099	ν_s CH of C ₂	2937	2936
2913	2939	3085	ν_{as} CH of C ₁	2902	2901
1460	1441	1465	δ CH ₂ + δ OHC+ δ CCH	1427	1436
1382	1352	1390	δ OCHC+ δ COH+ δ CCH	1374	1376
1340	1333	1320	δ CCH+ δ OHC	1333	1334
1224	1218	1278	δ CH+ δ OH in plane	1249	1250
1203	1220	1232	δ CH+ δ OH in plane	1209	1210
1149	1137	1205	ν CO + ν CC	1155	1155
1111	1116	1162	ν CO	1109	1109
1050	1058	1088	ν CO + ν CC	1072	1071
1025	1026	1066	ν CO	1047	1048
995	944	1032	ν CO + ν CC	1014	1013
915	900	993	ν CO + ν CC+ ν_{as} ring of pyranose	915	914
837	834	909	δ CH	852	853
776	762	815	δ CCO+ δ CCH	771	771
622	619	694	CH ₂	717	717

KBr, a more sensitive technique compared to ATR, yielded almost entirely similar peak positions in the IR spectra. Only the bands corresponding to stretching OH vibrations are not in the same positions, as well as for the vibrations of δ CH₂+ δ OHC+ δ CCH [S1]. The peak positioned at 564 cm⁻¹ is of CCO, OCO and CCH, while the peak positioned at 527 cm⁻¹ is of τ CO, OCO, CO, τ CCO vibrations. The peak positioned at 513 cm⁻¹ is of τ CO and

C₄C₅O₅[S2] . The peak that appears at 1637 cm⁻¹ is absorbed water in the material. The peaks positioned at 2343 cm⁻¹, 2361 cm⁻¹ and 668 cm⁻¹ belong to the uncorrected CO₂.

RAMAN SPECTROSCOPY

Table S2. The lengths and angles between the atoms in the indigo carmine molecule

Bound	Bound length/Å	Bond	Angle/ °	Bond	Angle/ °
O ₂₇ =S ₂₅	1.49635	O ₂₇ =S ₂₅ =O ₂₆	111.06899	H ₃₀ -C ₁₀ -C ₇	120.77773
S ₂₅ =O ₂₆	1.49873	O ₂₆ =S ₂₅ =O ₂₈	110.21532	C ₁₀ -C ₇ -C ₆	120.67618
S ₂₅ =O ₂₈	1.49802	O ₂₇ =S ₂₅ =O ₂₈	111.10462	C ₁₀ -C ₁₁ -S ₁₄	118.57470
S ₂₅ -C ₂₂	1.79833	O ₂₅ -C ₂₂ -C ₂₁	118.57478	C ₁₂ -C ₁₁ -S ₁₄	119.89087
C ₂₂ -C ₂₁	1.39590	C ₂₂ -C ₂₁ -H ₃₄	121.40348	C ₁₁ -S ₁₄ =O ₁₅	108.03586
C ₂₁ -H ₃₄	1.08608	H ₃₄ -C ₂₁ -C ₂₀	120.77773	O ₁₅ =S ₁₄ =O ₁₇	110.21540
C ₂₁ -C ₂₀	1.39306	C ₂₁ -C ₂₀ -C ₁₉	120.67618	O ₁₇ =S ₁₄ =O ₁₆	111.07746
C ₂₀ -C ₁₉	1.41859	C ₂₀ -C ₁₉ -C ₂₄	121.36016	O ₁₅ =S ₁₄ =O ₁₆	111.09590
C ₁₉ -C ₂₄	1.39516	C ₁₉ -C ₂₄ -H ₃₆	121.57856	O ₂₆ =S ₂₅ -C ₂₂	108.00656
C ₂₄ -H ₃₆	1.08559	H ₃₆ -C ₂₄ -C ₂₃	120.82717	O ₂₇ =S ₂₅ -C ₂₂	108.25944
C ₂₃ -C ₂₄	1.39787	C ₂₄ -C ₂₃ -H ₃₅	120.45778	C ₂₂ -C ₂₁ -C ₂₀	117.81876
C ₂₃ -H ₃₅	1.08497	H ₃₅ -C ₂₃ -C ₂₂	118.52595	C ₁₉ -C ₂₄ -C ₂₃	117.59427
C ₂₃ -C ₂₂	1.40501	C ₂₃ -C ₂₂ -C ₂₁	121.53435	C ₂₄ -C ₂₃ -C ₂₂	121.01627
C ₂₀ -C ₂	1.47023	C ₂₀ -C ₂ =O ₁	130.53313	C ₂₀ -C ₂ -C ₃	104.04648
C ₂ =O ₁	1.23341	O ₁ -C ₂ -C ₃	125.42037	C ₁₉ -C ₂₀ -C ₂	107.69036
C ₂ -C ₃	1.49639	C ₂ -C ₃ -N ₁₈	108.40419	C ₆ -N ₅ -C ₄	110.27459
C ₃ -N ₁₈	1.37710	C ₃ -N ₁₈ -H ₃₃	122.17508	N ₅ -C ₄ -C ₈	108.40419
N ₁₈ -H ₃₃	1.01219	C ₃ -N ₁₈ -C ₁₉	110.27459	C ₁₁ -S ₁₄ =O ₁₆	108.25949
N ₁₈ -C ₁₉	1.38540	N ₁₈ -C ₁₉ -C ₂₀	109.58438	S ₂₅ -C ₂₂ =C ₂₃	119.09087
C ₃ =C ₄	1.36648	C ₂ -C ₃ =C ₄	126.37752	C ₂₁ -C ₂₀ -C ₂	131.63345
C ₄ -N ₅	1.37710	N ₁₈ -C ₃ =C ₄	125.21829	C ₂₄ -C ₁₉ -N ₁₈	129.05546
N ₅ -H ₂₉	1.01134	C ₃ =C ₄ -N ₅	125.21829	C ₁₃ -C ₆ -C ₇	121.36016
N ₅ -C ₆	1.38540	C ₃ =C ₄ -C ₈	126.37752	C ₂₂ -S ₂₅ -O ₂₆	108.00656
C ₆ -C ₇	1.41859	C ₄ -C ₈ =O ₉	125.42038	C ₂₂ -S ₂₅ -O ₂₇	108.25944
C ₇ -C ₈	1.47023	C ₄ -C ₈ -C ₇	104.04648	C ₂₂ -S ₂₅ -O ₂₈	108.06455
C ₈ -O ₉	1.23341	O ₉ =C ₈ -C ₇	130.53314	C ₁₁ -S ₁₄ -O ₁₆	108.25944
C ₈ -C ₄	1.49639	C ₈ -C ₇ -C ₆	107.69036	C ₁₁ -S ₁₄ -O ₁₅	108.03586
C ₆ -C ₁₃	1.39516	C ₇ -C ₆ -N ₅	109.58438	C ₁₁ -S ₁₄ -O ₁₇	108.03539

C ₁₃ -H ₃₂	1.08559	C ₆ -N ₅ -H ₂₉	127.58039
C ₁₃ -C ₁₂	1.39787	H ₂₉ -N ₅ -C ₄	122.14502
C ₁₂ -H ₃₁	1.08497	N ₅ -C ₆ -C ₁₃	129.05546
C ₁₂ -H ₁₁	1.40501	C ₆ -C ₁₃ -H ₃₂	121.57856
C ₁₁ -C ₉	1.39590	H ₃₂ -C ₁₃ -C ₁₂	120.82717
C ₁₀ -H ₃₀	1.08608	C ₆ -C ₁₃ -C ₁₂	117.59427
C ₁₀ -C ₇	1.39306	C ₁₃ -C ₁₂ -H ₃₁	120.45778
C ₇ -C ₆	1.41859	H ₃₁ -C ₁₂ -C ₁₁	118.52595
C ₁₁ -S ₁₄	1.79833	C ₁₃ -C ₁₂ -C ₁₁	121.01627
S ₁₄ =O ₁₆	1.49634	C ₁₂ -C ₁₁ -C ₁₀	121.53435
S ₁₄ =O ₁₇	1.49817	C ₁₁ -C ₁₀ -H ₃₀	121.40348
S ₁₄ =O ₁₅	1.49856	C ₁₁ -C ₁₀ -C ₇	117.81876

Table S3. The theoretical and experimental values of the vibration bands obtained in this current research compared to the literature [25 from manuscript]

This research		Literature[25]				
B97D		B3PW91			B3LYP	
Exp.	cc-pVTZ	Exp.	LANL2D Z	6- 311++G* *	LANL2 DZ	6- 311++G* *
1240	1235	1240	1239	1243	1265	1244
1296	1293	1290	1288	1280	1288	1296
1346	1348	1344	1357	1345	1343	1352
1576	1588	1576	1511	1509	1621	1616
1626	1625	1623	1640	1632	1635	1634
1697	1703	1698	1687	1701	1669	1681

Video1.mp4 to video4.mp4 record the molecule's vibration for the bands as indicated by the arrows in Figure S3.

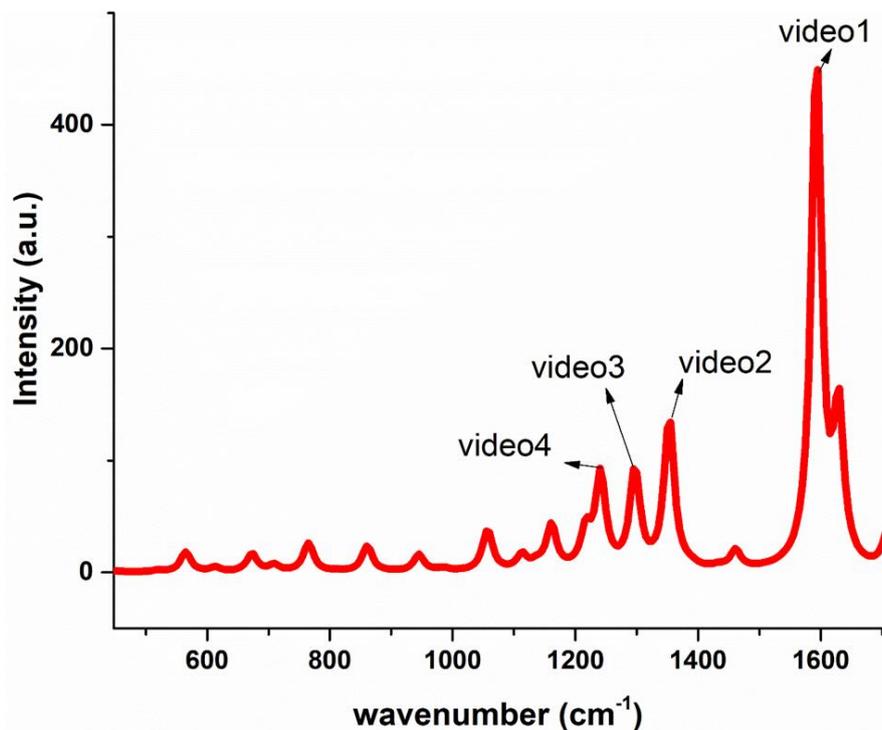


Figure S3. The multimedia (video1.mp4 to video4.mp4) of complex vibrations of the indigo carmine functional groups obtained for the most intensive peaks

The Gaussian output log file (4447431_opt_raman_Na.log) may be used to read the Raman vibrations of indigo carmine in Facio software.

UV/VIS METHOD

According to the UV/Vis spectra obtained for an aqueous solutions of indigo carmine, an analytical curve was plotted, as presented in Figure S4. The absorbance of the measured aqueous solution of the mixture of indigo carmine and dextrose has been marked in the UV Vis analytical curve. The points chosen to create the analytical curve are marked in orange.

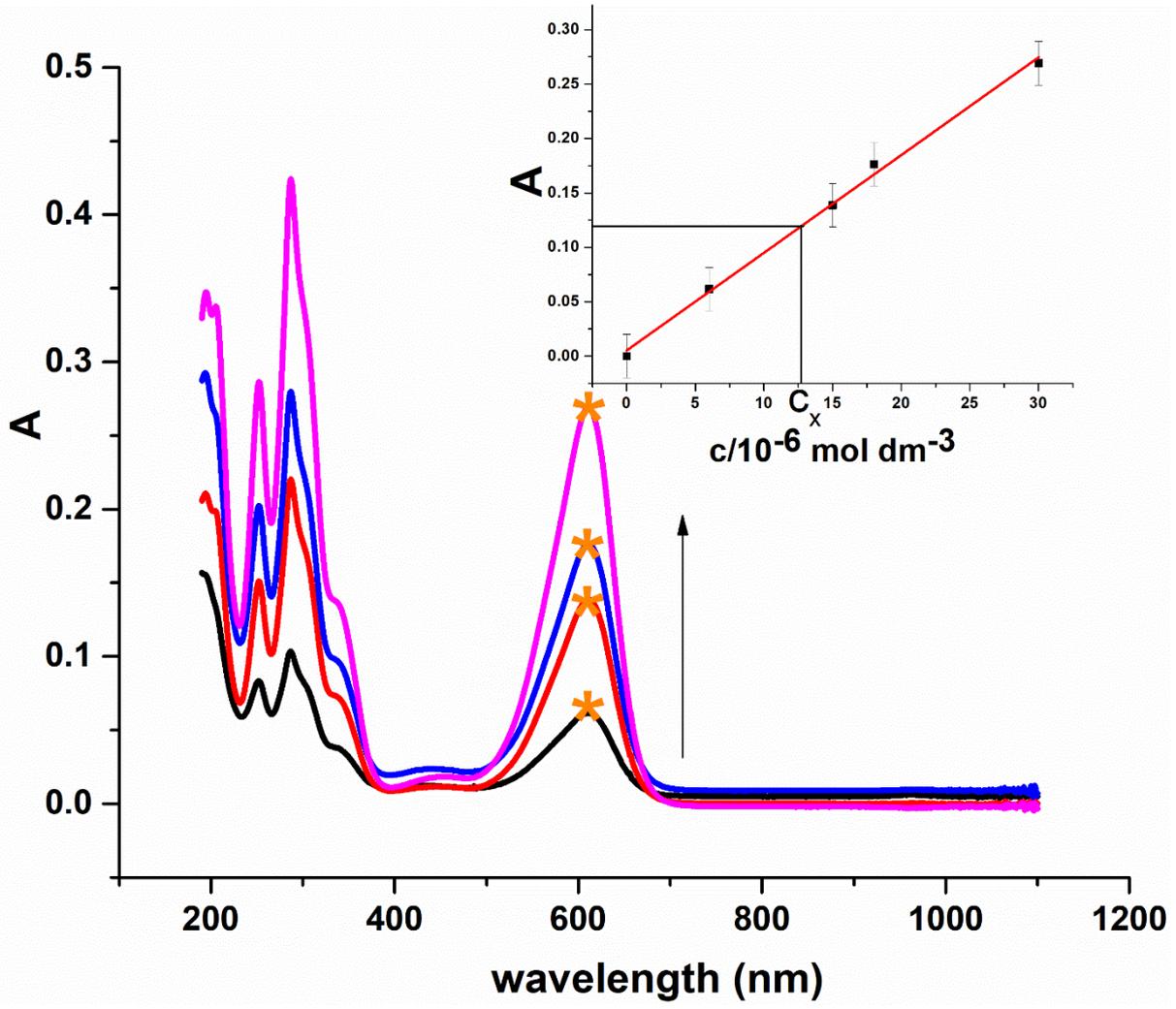


Figure S4. The indigo carmine standard concentrations' UV/Vis spectrum of $3.00 \times 10^{-5} \text{ mol dm}^{-3}$; $1.80 \times 10^{-5} \text{ mol dm}^{-3}$; $1.50 \times 10^{-5} \text{ mol dm}^{-3}$ and $0.60 \times 10^{-5} \text{ mol dm}^{-3}$ (the arrow indicating the rise of concentration). Insert: UV/Vis calibration curve (the dependence of A at $\lambda_{\text{max}} = 611 \text{ nm}$ as a function of the concentrations).

Although the D-glucose yields no UV/Vis spectrum, the indigo carmine does, as presented in Figure S5.

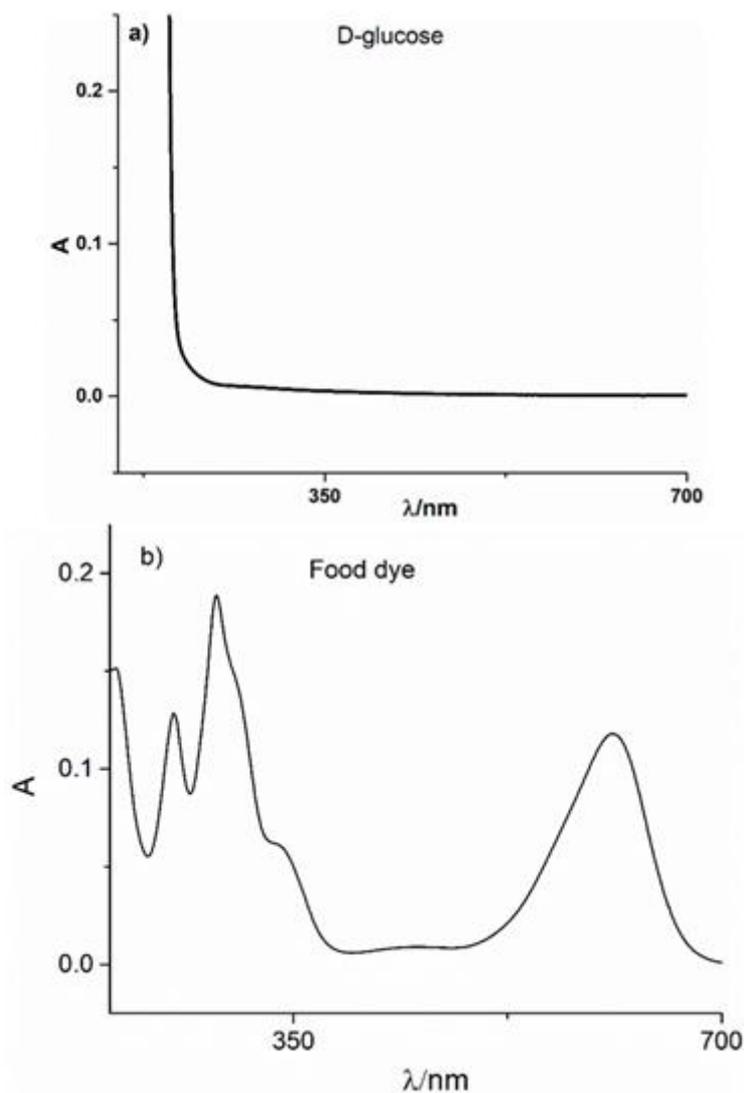


Figure S5. The UV/VIS spectrum of D-glucose **a)** food dye (mixture of indigo carmine and D-glucose) **b).**

THE BRIGGS-RAUSCHER METHOD

The recorded Pt-potential vs. time series (or oscillogram) of the BR reaction free of analyte is shown at **Figure S6 a) in three oscillograms** . The influence of D-glucose (added at 30 s from the beginning of the BR reaction) to the oscillating BR reaction, as well as the basic BR oscillogram, are presented in **Figure S6 b)**.

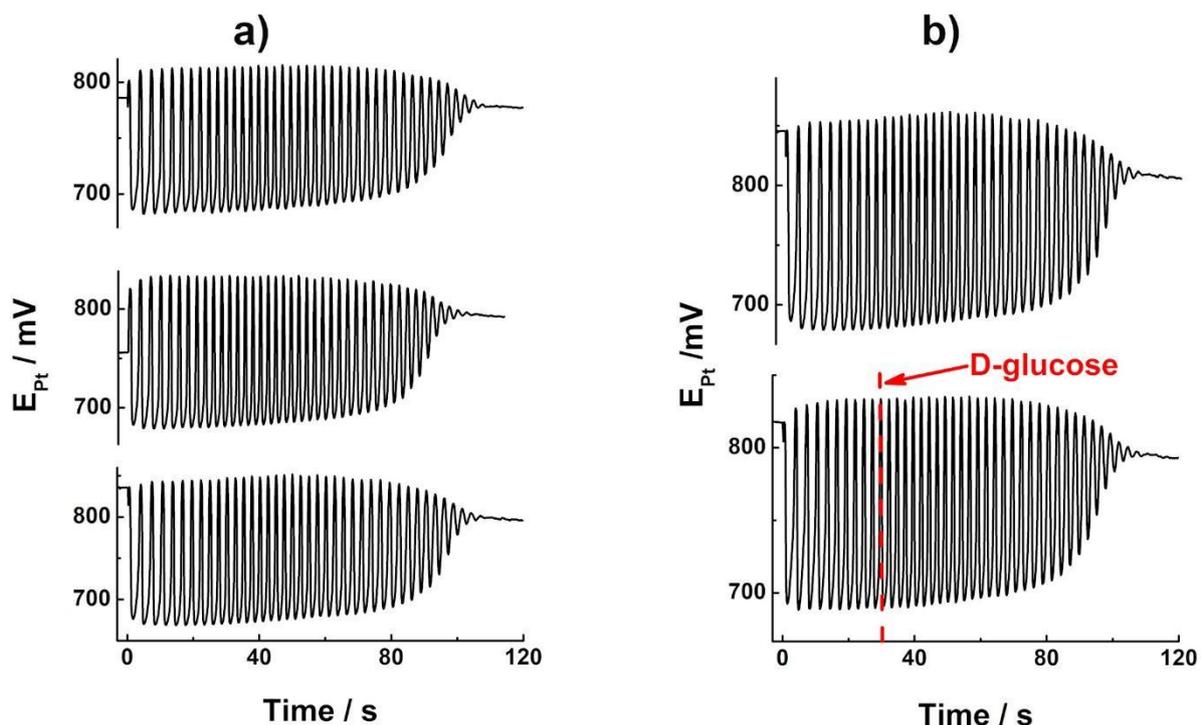


Figure S6. The Basic BR oscillogram in three oscillograms a) and the influence of D-glucose (100 μ l, 0.1 mol/dm³) to BR oscillogram b). The initial reactant concentrations in the system were $[\text{CH}_2(\text{COOH})_2]_0 = 0.0789 \text{ mol dm}^{-3}$, $[\text{MnSO}_4]_0 = 0.00752 \text{ mol dm}^{-3}$, $[\text{HClO}_4]_0 = 0.03 \text{ mol dm}^{-3}$, $[\text{KIO}_3]_0 = 0.0752 \text{ mol dm}^{-3}$ and $[\text{H}_2\text{O}_2]_0 = 1.176 \text{ mol dm}^{-3}$.

S REFERENCES:

[S1] Analysis of the structure and vibrational spectra of glucose and fructose M.Ibrahim, M. Alaam, H. El-Haes, A. F. Jalbout, A. de Leon, Analysis of the structure and vibrational spectra of glucose and fructose, *Eclat. Quim.* 31(3) (2006) 15-21.

<https://doi.org/10.1590/S0100-46702006000300002>

[S2] M.V.Korolevich, R.G.Zhbankov, V.V.Sivchik, Calculation of absorption band frequencies and intensities in the IR spectrum of α -d-glucose in a cluster, *J. Mol. Struct.*, 220 (1990) 301-313. [https://doi.org/10.1016/0022-2860\(90\)80120-9](https://doi.org/10.1016/0022-2860(90)80120-9)