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Electrochemical impedance spectroscopy measurements for determination of derivatized aldehydes in several matrices

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Abstract

A simple, selective and sensitive electrochemical method is described for the determination of different aldehydes at glassy carbon electrode using electrochemical impedance spectroscopy (EIS). The measurements were performed after their derivatization with 2,4-dinitrophenylhydrazine (DNPH) in acidic medium. The impedance measurements were investigated in the frequency range from 100 mHz to 100 kHz at a potential of 1.0 V versus Ag/AgCl. The Nyquist plots were modeled with a Randle's equivalent circuit. The charge transfer resistance was identified as the dependent parameter on relevant concentration of aldehydes (determined as their hydrazones). Under the optimized conditions, the linearity was established over the concentration range of 1000–0.05 μmol L^{-1}. The limits of detection (LODs) obtained were from 0.097 to 0.0109 μmol L^{-1}. Finally, the

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developed method has been applied to the determination of aldehydes in drinking water, orange juice and apple vinegar samples with relative standard deviations (RSDs) $<$ 3.1% and acceptable recovery rate (around of 80%).

Keyword: Food analysis

1. Introduction

Aldehydes are chemical species widely distributed in nature where their concentrations were determined in many matrices such as atmosphere, [1, 2] water [3, 4, 5], food and beverages [6, 7]. These compounds at a trace amount may contribute to the fresh aroma of various foods, but at higher concentration may facilitate food rancidity and release off-flavor [8]. However, several aldehydes are known to be irritant and carcinogenic. Thus, they are capable of binding to protein and nucleic acids and even impairing their functions [9]. Additionally, they are considered as potential marker for oxidative stress and metabolic status [10], which has been proposed to estimate cancer disease [11] and symptoms of alcohol abuse [12]. Hence, it is critical to establish a method with high selectivity and sensitivity for the determination of aldehydes in various samples.

Electrochemical impedance spectroscopy method (EIS) has been known as one of the most common techniques because it is simple, direct, rapid and has been broadly utilized to quantify organic compounds [13, 14, 15]. Indeed, this sensitive technique is used to monitor the electrical current response of the studied system by applying a periodic small amplitude signal. In faradic impedance, the information obtained from the system response includes capacitance and interfacial charge transfer resistance [16]. These signals can be used to sense different reactions that occur on electrode surface. Consequently, this technique is an efficient tool to investigate the surface processes because of its inherent capability of providing the accurate data [17].

The best way to evaluate correctly the EIS results consists of correlation of the impedance spectra features with underlying microstructural origins of recorded behaviors by means of appropriate and reasonable equivalent circuit [18]. As in EIS determinations, the high polarity and reactivity of aldehydes impose the need for their derivatization prior to their detection, where 2,4-dinitrophenylhydrazine (DNPH) being the most widely used derivatization reagent [19, 20, 21]. In fact, the derivatization technique is known to be based on the reaction of aldehydes with an excess amount of 2,4-dinitrophenylhydrazine (DNPH) in acidic medium [22]. The hydrazones formed are usually determined by high performance liquid chromatography (HPLC) with detection based on UV [23, 24, 25], gas chromatography (CPG) [26], mass spectrometric [27, 28] and electrochemical [29] measurements. However, to the best of our knowledge, no research about aldehydes derivatized with DNPH based on electrochemical impedance spectroscopy had been published.

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In this study, we introduce a novel and simple EIS method for aldehydes determination based on their derivatization with DNPH, profiting of the presence in the derivatizing agent of hydrazine group, which can be easily oxidizable electrochemically. In this work, four aldehydes (acetaldehyde, propionaldehyde, heptanaldehyde and hexanaldehyde) were selected as model compounds. The experimental parameters that may influence the derivatization were studied and optimized. Under the optimal conditions, the analytical methodology was applied for the determination of aldehydes content in water, orange juice and apple cider vinegar samples.

2. Experimental

2.1. Chemicals and reagents

All the chemicals mentioned were of analytical grade and used as received without any further purification. 2,4-dinitrophenylhydrazine, acetaldehyde (17.70 mol L^{-1}, ≥99.0% purity), propionaldehyde (13.41 mol L^{-1}, ≥99.0%), heptanaldehyde (6.79 mol L^{-1}, ≥99.0%), hexanaldehyde (8.61 mol L^{-1}, ≥99.0%), orthophosphoric acid (16.03 mol L^{-1}, 85%, w/v, solution in water) and methanol were purchased from Sigma-Aldrich.

The standard stock solution of DNPH was prepared by dissolving the required amount in acid water/methanol solution to acquire an initial concentration of 1.0 mmol L^{-1}. Standard stock solutions of aldehyde-2,4-dinitrophenylhydrazone derivatives ranged 0.05–1000 μmol L^{-1} were prepared in acid/water/methanol solution (2:1:7 v:v:v). The chemical formula of the derivatization reaction was shown in Fig. 1. The derivatization of carbonyls with DNPH can be performed under mild reaction conditions (ambient temperature and aqueous solution). The quantitative analysis of aldehydes using DNPH is usually conducted in the acidic medium. The working standard solutions were stored under at 4 °C.

2.2. Apparatus

The measurements were done via an electrochemical impedance analyzer potentiostat (model PGZ 100, Eco Chemie B.V, Utrecht, The Netherlands) with an electrochemical cell involving three electrodes: the counter electrode was a platinum wire and a Ag/AgCl, 3 M KCl electrode was used as the reference and the glassy carbon electrode (1 mm) was used as a working electrode. These measurements are carried out using a computer controlled electrochemical system (Voltalab master 4 software).

The chromatographic systems used is constituted by a Waters 2695 pump, auto sampler and Waters 2998 photodiode array detector (PDA). The Spectra Manager software and Empower Software data registration were used for all absorbance

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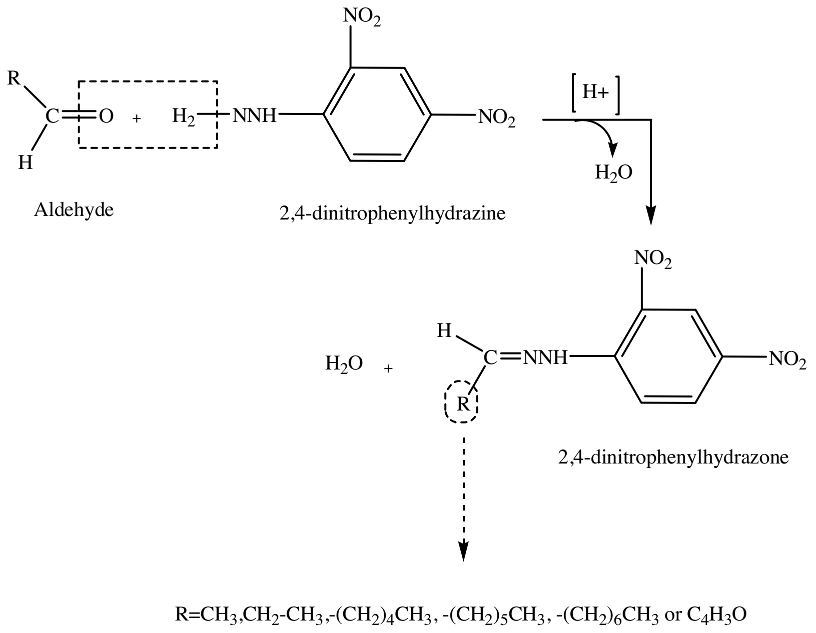

Fig. 1. Derivatization of aldehydes with 2,4-dinitrophenylhydrazine.

measurements. Data acquisition was performed by the Totalchrom Software data registration. The HPLC conditions were as follows: Shim-pack RP-C18 column (250 mm × 4.6 mm, 5 m), injection volume of 10 μL, detection wavelength of 360 nm, velocity of flow of 0.7 mL min^{-1} and column temperature of 30 °C. The methanol-water gradient was set at 0 min, 40% methanol; 17 min, 80% methanol; 18 min, 40% methanol; 20 min, 40% methanol.

2.3. Experimental procedure

Electrochemical measurements of each aldehyde (determined as their hydrazone) were carried out in 30 mL of concentrated hydrochloric acid: water: methanol solution (6:4:20) containing 1.0 mmol L^{-1} of DNPH. The electrochemical impedance spectroscopy was carried out within the frequency from 100 mHz to 100 kHz. The concentration of aldehyde was quantified by an increase of the charge transfer resistance ΔR_{ct} ($\Delta R_{ct} = R_{ct,i} - R_{ct,i0}$),where $R_{ct,i0}$ and $R_{ct,i}$ are the charge transfer resistance values before and after its exposure to DNPH, respectively. All electrochemical experiments were carried out at room temperature (25 ± 1 °C).

The square wave voltammetry (SWV) method was used to evaluate the oxidation potentials of derivatized aldehydes. For this, the 2,4-dinitrophenylhydrazones were synthesized by the reaction of aldehydes with DNPH in acidic medium by following procedure: 400 mg of DNPH was dissolved in phosphoric acid (0.5 mL), followed by a mixture of water (0.7 mL) and methanol (2.5 mL). Then, 1.72 mL

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concentrated aldehyde was added. Accordingly, after stirring the resulting solution (30 min), the precipitated solid was recovered by filtration, washed with ethanol, and dried at room temperature for 24 h.

The performance of the electroanalytical procedure to determine aldehyde was also applied to commercial drinking water and apple cider vinegar samples. Without any pre-treatment of the sample, an accurate volume of each sample was subjected directly for electrochemical measurement of aldehyde as in recommended procedure.

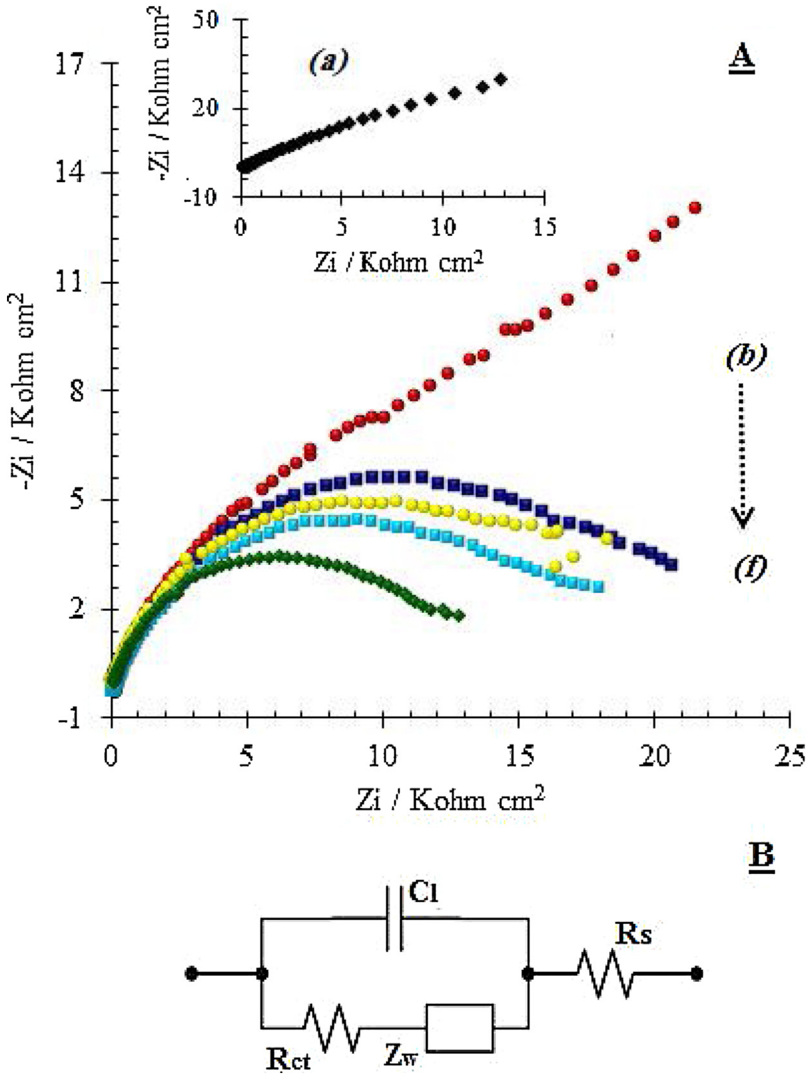

Fig. 2. Nyquist diagrams of different aldehydes derivatized with DNPH in electrolytic solution. (a) Blanc; (b) DNPH; (c) Heptanal; (d) Hexanal; (e) Propanal and (f) Acetaldehyde. [DNPH] = 1.0×10^{-3} mol L^{-1}, [aldehyde] = 9.0×10^{-2} mol L^{-1}.

The impedance spectroscopy was also used to determine concentrations of aldehyde in orange juice, which had been freshly purchased from a Moroccan supermarket. In order to reduce the viscosity of the orange sample and be convenient for experimental operation, the samples were diluted 1:1 with pure water [30].

3. Results and discussion

3.1. EIS behavior of 2.4 dinitrophenylhydrazones

The interaction between aldehydes and DNPH at the surface of glassy carbon electrode was investigated by using electrochemical impedance spectroscopy (EIS), which was a useful technique especially for the surface characterization. EIS experiments were carried out at frequency between 100 mHz to 100 kHz and AC amplitude of 5 mV. Fig. 2 shows the impedance diagram of DNPH in the absence (a,b) and the presence of aldehydes (c-f). The Nyquist plots were fitted with R_s(Q [R_{ctw}]), where R_s refers to the electrolyte resistance, R_{ct} is the charge transfer resistance, Q is the constant phase element, and w is the Warburg impedance coupled to R_{ct}, which is related to Nernstian diffusion. In this circuit, the charge transfer resistance is the circuit element that has a simple physical meaning describing how fast the rate of charge transfer occurs during the oxidation of DNP hydrazones. In particular, the charge transfer resistance (R_{ct}) of the DNPH is remarkably decreased in the presence of the considered aldehydes. This is because the DNPH combined with aldehydes leads to the formation of stable 2,4-

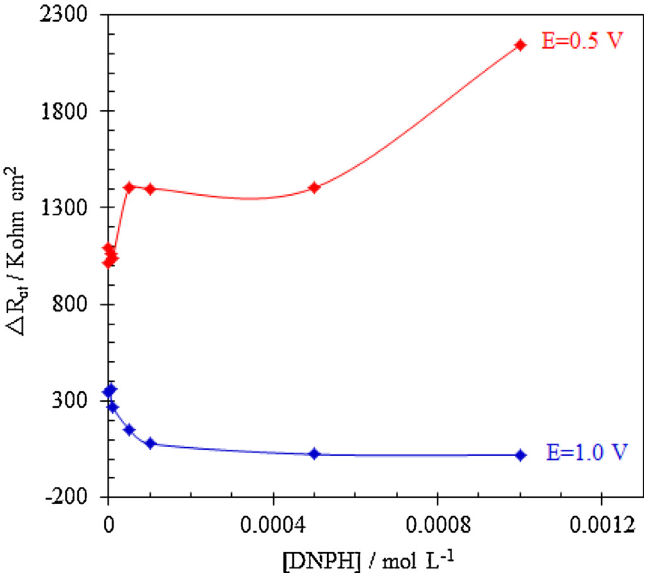

Fig. 3. Variation of the charge transfer of derivatives vs. DNPH concentrations of the Nyquist diagram recorded at E = 0.5 V vs. Ag/AgCl and E = 1.0 V vs. Ag/AgCl (Heptanal as example). [DNPH] = 1.0×10^{-3} mol L^{-1}, [Heptanal] = 9.0×10^{-2} mol L^{-1}.

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dinitrophenylhydrazone (DNP-hydrazone). The rate of charge transfer occurs during the oxidation of the aldehydes was decreased by the addition of DNPH. In fact, a decrease of charge transfer resistance is caused by the formation of hydrazones resulting from specific interaction of DNPH and aldehyde. This parameter could be severely modified at potentials where the oxidation of hydrazones formed occurs.

3.2. Reactivity of DNPH and aldehydes

The reactivity of DNPH and aldehyde can be studied by following either the consumption of DNPH (potential 0.5 V) and/or the formation of the hydrazone (potential 1.0 V). Fig. 3 shows the results obtained for detection of aldehyde using DNPH derivatization at the two detection potential values. These potentials values were chosen based on the different considerations. The first was in line with the E, i.e., +0.5 V vs. Ag/AgCl for hydrazine oxidation, and the second one had to be higher even under hydrazone evolution process to assure a faster oxidation rate (+1.0 V vs. Ag/AgCl). The R_{ct} value increased obviously with the increasing concentration of DNPH albeit at 0.5 V. However, if the potential is altered to +1.0 V, the ΔRct value decrease with the concentration of derivatizing reagent, resulting in complexes formation of aldehyde-2,4-dinitrophenylhydrazone.

In this context, the EIS measurements were performed in the potential range from 0.1 V to 1.5 V. Fig. 4 gives the Nyquist plots of electrochemical impedance spectra of aldehydes in solution containing 1.0 mmol L^{-1} of DNPH. The impedance spectra for potentials below 0.9 V vs. Ag/AgCl exhibited a quarter circle portions, corresponding to a large charge transfer resistance. Above this threshold, the spectra became a well-defined capacitive depressed semicircle with increasing potential. Eventually, at applied potentials as high as 1.0 V vs. Ag/AgCl, a slightly decrease in the impedance can be observed. Moreover, the R_{ct} value did not undergo any change at applied potentials as high as 1.5 V vs. Ag/AgCl. Consequently, the optimized potential was deduced as 1.0 V for further work.

The results obtained are confirmed with square wave voltammetry (SWV) method. Fig. 5 shows the voltammograms of different aldehydes as their hydrazone form using GCE electrode. Therefore, the oxidation of aldehydes was obtained approximately at 1.21 V, 1.06 V, 1.05 V and 1.15 V potentials for acetaldehyde, propanal, hexanal and heptanal respectively. This confirms the choice of 1.0 V as the optimal potential. Therefore, the electrochemical oxidation of hydrazones from aldehydes at GCE generates the corresponding diazonium.

3.3. Optimization of reaction conditions

In order to obtain the highest derivatization efficiency for aldehydes considered, the derivatization conditions were investigated using EIS method at room

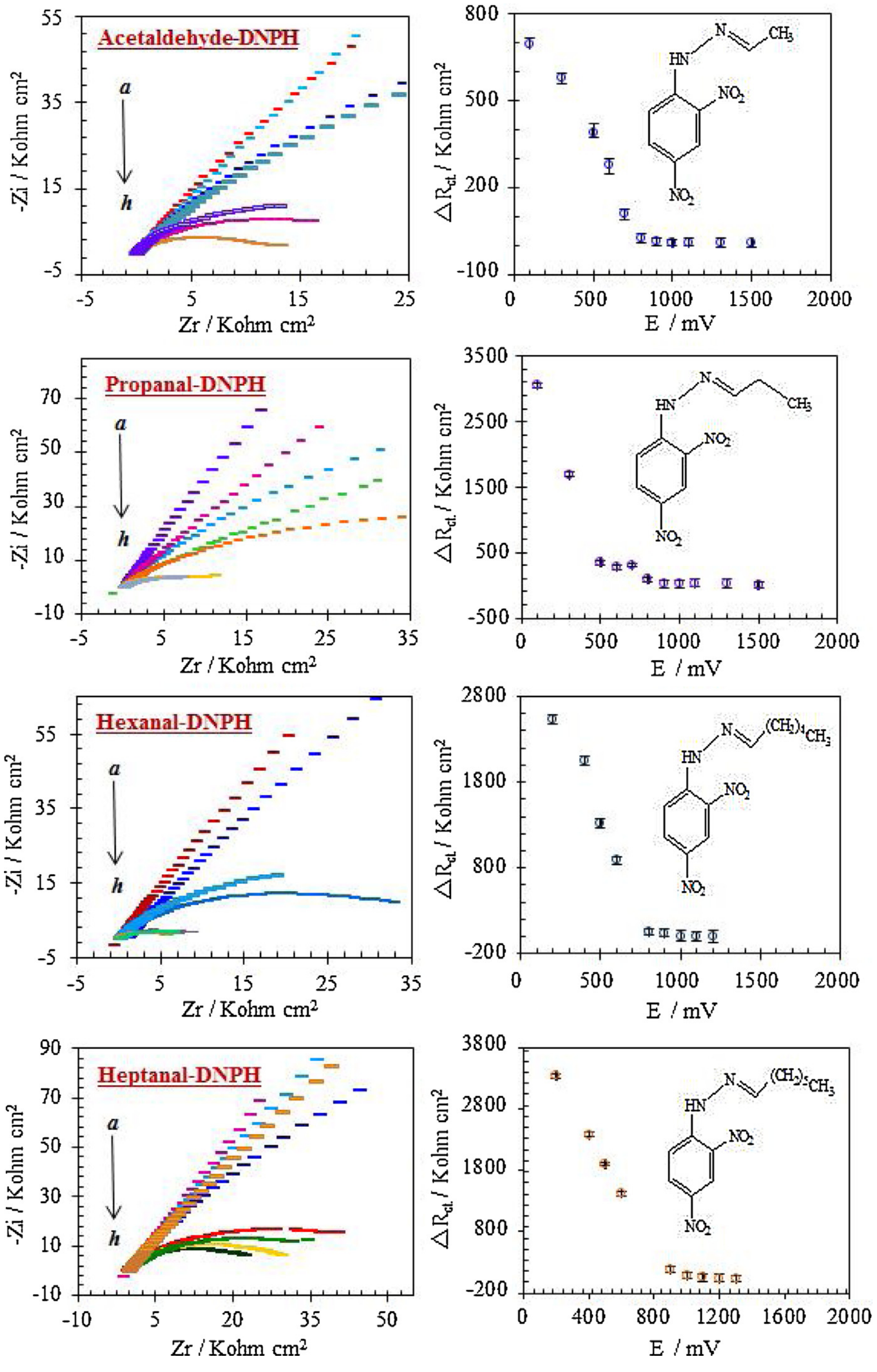

Fig. 4. Effect of applied potential on the Nyquist diagram of derivatized aldehydes. a) 0.1; b) 0.3; c) 0.5; d) 0.7; e) 0.9; f) 1; g) 1.3; h) 1.5 V. [DNPH] = 1.0×10^{-3} mol L^{-1}, [Aldehyde] = 9.0×10^{-2} mol L^{-1}.

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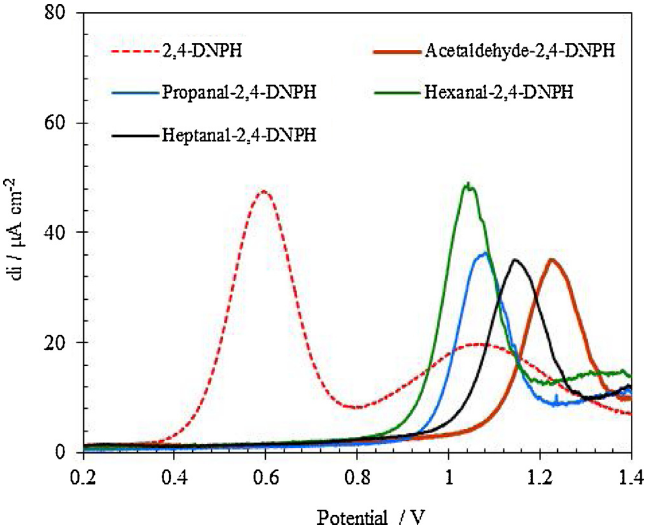

Fig. 5. Square wave voltammograms obtained for oxidation of 1.0 mmol L^{-1} DNPH and 1.0 mmol L^{-1} 2.4 dinitrophenylhydrazones on GCE in electrolytic solution. Pulse: 50 mV, Amplitude: 1 mV and Duration: 1s.

temperature. The derivatization parameters affecting the whole sensing process, including DNPH concentration and derivatization time were optimized.

3.3.1. *Effect of DNPH concentration*

The concentration of derivatizing reagent (DNPH) plays a vital role in the derivatization of aldehydes. Sufficient reagent was necessary to ensure the complete derivatization and obtain accurate quantitative analysis. In this study, the effect of DNPH concentrations on the derivatization yields were investigated using EIS method (Fig. 6A). The results indicate that the ΔR_{ct} values decreased rapidly as the concentration of DNPH increased from 1 to 1000 µmol L^{-1}. In order to

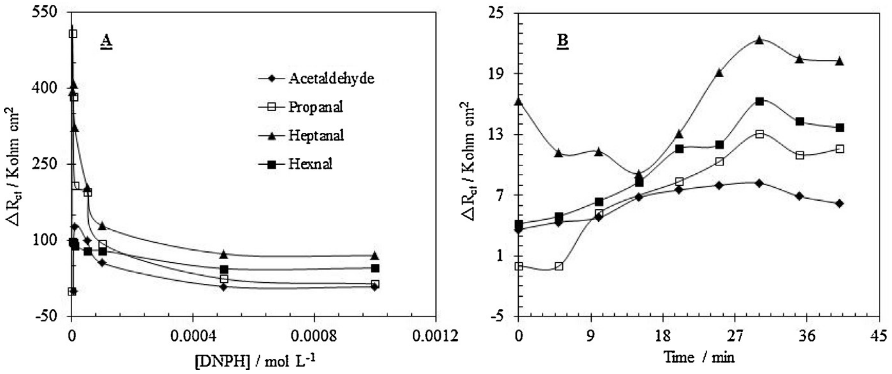

Fig. 6. Selection of the experimental conditions. Effects of DNPH concentration (A) and derivatization time (B) on the charge transfer of derivatives. Concentration of standard aldehydes solution: 9.0×10^{-2} mol L^{-1}.

obtain a low detection limit, a concentration of 1000 μmol L^{-1} DNPH was chosen in subsequent experiments.

3.3.2. *Effect of derivatization time*

The derivatization time could affect significantly the derivatization efficiency. For this, the effect of the derivatization time was tested from 0 to 40 min prior to EIS measurement (Fig. 6B). Long time could accelerate the derivatization reaction. However, when the reaction time was longer than 30 min, the ΔR_{ct} value had no obvious change. This indicated that the derivatization reaction has completed. Therefore, 30 min was chosen as the reaction time.

3.4. Effect of aldehyde concentration

The quantitative methods were established under the optimized conditions with electrochemical impedance spectroscopy detection. Fig. 7 shows the Nyquist diagrams at different aldehydes concentrations after addition of 1000 mmol L^{-1} of DNPH in electrolytic solution. It is found that the diameter of the Nyquist circle decreases when increasing the aldehydes concentration. This decrease is directly related to both the concentration of DNPH and the formation of new formed

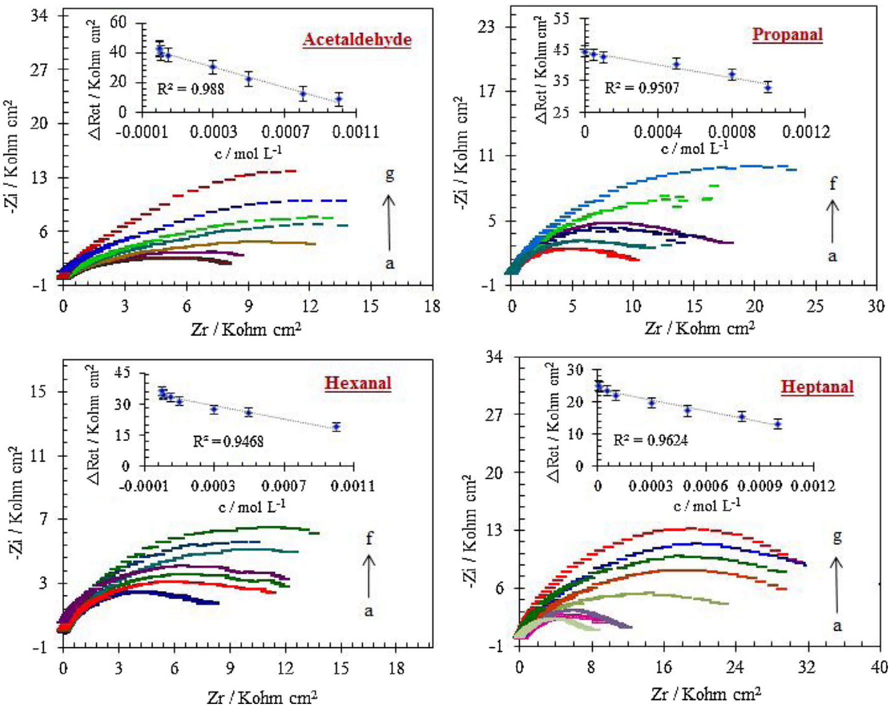

Fig. 7. The Nyquist spectra of different concentrations of aldehydes at GCE using EIS method. a) 1000; b) 800; c) 100; d) 10; e) 5; f) 0.5; g) 0.05 μmol L^{-1}.

Table 1. Calibration data and analytical results for the determination of aldehydes by EIS.

Compounds	Linear range (μmol L^{-1})	LOD (μmol L^{-1})	LOQ (μmol L^{-1})	Slope (Kohm cm^2 μmol L^{-1})	RSD (%)
Acetaldehyde	1000-0.05	0.0109	0.036	3200.82	2.47
Propanal	1000-0.5	0.047	0.15	680.86	3.5
Hexanal	1000-0.5	0.06	0.2	533.06	3.2
Heptanal	1000-0.05	0.97	76.15	31.711	2.62

product at the working electrode. The percentage of formation (R (%)) of aldehyde-2,4-DNPH was evaluated according to the equation:

$$R\ (\%) = (R_0 - R_1)/R_0 \times 100$$

Where R_0 and R_1 are the resistance of charge transfer recorded before and after reaction, respectively.

The calibration curves were obtained by plotting the relative resistance versus aldehyde concentration. The calibration plots obtained for the four aldehydes derivatives are in the ranges of 1000–0.5 μmol L^{-1} (for propanal and hexanal) and 1000–0.05 μmol L^{-1} (for acetaldehyde and heptanal). The correlation coefficient (R^2) shows superior values higher than 0.99. The limit of detection and limits of quantification (LOQs) are estimated from the equations:

$$LOD = 3\ Sb/m$$
$$LOQ = 10\ Sb/m$$

In the above equations, Sb the standard deviation of the blank solution (Sb = 3.1 Kohm cm^2) and m denotes the slope of the linear range of the respective calibration plot. Limits of detection (LODs) and limits of quantification (LOQs) of the method

Table 2. Comparison of different methods for the determination of aldehydes in various samples.

Methods	Linear aliphatic aldehydes	Limit of detection μmol L^{-1}	[Refs]
HPLC –UV/vis	Formaldehyde-pentanal	0.12 – 1.67	[31]
Extraction/evaporation-HPLC-UV/vis	Formaldehyde and acetaldehyde	0.150 – 0.16	[32]
PMME-HPLC-UV/vis	Formaldehyde, acetaldehyde, and butanal	0.014 – 0.019	[25]
CE-ED	Acetaldehyde, propionaldehyde, butyraldehyde and hexylaldehyde	4 – 13	[33]
EIS	Acetaldehyde, propanal, hexanal and heptanal	0.097 – 0.0109	Present work

HPLC-UV/vis: High Performance Liquid Chromatography (HPLC) with detection based on UV.

PMME–HPLC-UV/vis: Polymer Monolith Microextraction with in situ derivatization coupled to HPLC.

CE-ED: Microchip Electrophoresis with Electrochemical Detection.

EIS: Electrochemical Impedance Spectroscopy method.

Table 3. Statistical results for the analysis of aldehydes in real samples using EIS method and HPLC(sample 1: drinking water; sample 2: orange juice and sample 3: apple cider vinegar)..

Aldehyde	**GCE**						**HPLC**					
	Sample 1		**Sample 2**		**Sample 3**		**Sample 1**		**Sample 2**		**Sample 3**	
	Recovery rate (%)	**RSD (%)**	**Recovery rate (%)**	**RSD (%)**	**Recovery rate (%)**	**RSD (%)**	**Recovery rate (%)**	**RSD (%)**	**Recovery rate (%)**	**RSD (%)**	**Recovery rate (%)**	**RSD (%)**
Acetaldehyde	108.14	3.04	122	2.35	155.21	2.03	104.45	4.6	135.99	4.3	158.4	3.4
Propanal	80.61	3.6	89	1.91	57.22	2.64	89.61	7.3	92.1	4.6	69.4	6.1
Hexanal	77.03	2.52	87.03	1.03	73.47	1.63	98.41	4.4	88.9	3.1	80.4	4.8
Heptanal	87.55	1.53	97.16	1.21	87.31	2.02	96.37	3.6	106	5.7	93.3	4.4

RSD: Relative standard deviation.

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were in the range of 0.097–0.0109 μmol L^{-1} and 0.15–76.15 μmol L^{-1}, respectively. All statistical results are recorded in Table 1. Moreover, the repeatability of the proposed method was investigated by successive measurements (n = 6) in solution containing appropriate amount of aldehyde (for each aldehyde). The results obtained are evaluated in term of relative standard deviations (RSDs) where the maximum value reached is 3.5%.

3.5. Comparison with other methods

Some other methods reported in literature were compared with the proposed method, and the results are summarized in Table 2 [25, 31, 32, 33]. Of these reported methods, no EIS study is done for examination of quantification of aldehydes using 2,4-dinitrophenylhydrazine derivatization. For sensing of aldehydes, this method provided lower detection limits than other reported methods. The proposed method is also cost-effective, very fast, sensitive, easy in handling and able to perform the analysis in real samples, such as beverages and water samples.

3.6. Analysis of real samples

It is important to notice that there are few studies focused on the quantitative analysis of aldehydes by using DNPH as derivatization reagent, mainly in air samples [34, 35, 27] and hardly ever in water samples [36, 37]. Concretely in water samples, Richardson et al. [38, 39] have reported a qualitative method for analyzing and identifying highly polar aldehydes and ketones in ozonated drinking waters, where they are presented as disinfection by-products (DBPs). On the other hand, the interest in the analysis of carbonyl compounds in food and beverages samples as pollutants has increased significantly in recent years [30, 40, 41]. Indeed, all the samples including the drinking water, orange juice and apple cider vinegar were analyzed using the EIS proposed method. Then, the results were compared to those obtained using the HPLC method (Table 3). Indeed, the method presents approximately comparable results to those obtained by HPLC method, where the recovery rates reached are around of 80%. Therefore, the obtained results are satisfactory indicating that the proposed method can be used efficiently for the determination of aldehydes in samples analysis.

4. Conclusion

A rapid and sensitive method has been developed for the direct determination of several aldehydes based on their derivatization with DNPH prior to EIS analysis. The complex formed can facilitate the electron-transfer to the electrode and leads to decreasing R_{ct}. The reactivity study of DNPH and aldehyde reveals that 1.0 V was the optimized potential to assure the oxidation of 2.4-dinitrophenylhydrazones.

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Under optimized conditions, the derivatized aldehydes analysis present limits of detection in order of 0.01 μmol L^{-1}. Moreover, the analytical results show that, under the optimized working conditions, the present method can be widely applied to determine of aldehydes in drinking water, orange juice and apple cider vinegar samples with acceptable recovery rates.

Declarations

Author contribution statement

Wafaa Boumya: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Fethallah Laghrib: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Sara Lahrich: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Abdelfattah Farahi: Conceived and designed the experiments; Analyzed and interpreted the data.

Mounia Achak: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Mina Bakasse: Contributed reagents, materials, analysis tools or data.

M. Abderrahim El Mhammedi: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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