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Cyclic Voltammetric Analysis of Retinol in Facial Serum

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Abstract: Retinol is an active compound within the retinoid group, derived from vitamin A and characterized by the presence of a cyclohexenyl ring structure. It is commonly incorporated into cosmetic formulations, particularly facial serums. To ensure product safety and efficacy, facial serums containing retinol must comply with established concentration limits to avoid overclaiming. Various analytical methods have been developed and utilized to determine retinol concentration. This research focuses on determining the amount of retinol present in facial serum by employing the cyclic voltammetry technique.. Cyclic voltammetry is an electrochemical method employed to evaluate the activity of specific compounds in solution by measuring the current generated between two electrodes as a function of the applied potential, which is cyclically varied from an initial to a final value and back again. In this study, the analysis was performed using a carbon paste electrode modified with ZnO and TiO_2 nanoparticles in a ratio of 3:2:3:2. The measurement of retinol in facial serum was carried out using a 5000 ppm KCl solution as the supporting electrolyte, phosphate buffer solution at pH 5, a deposition time of 20 seconds, and a scan rate of 0.25 V/s. The retinol concentration in the serum samples was determined based on a standard calibration curve described by the linear equation $y = 0.0000355x + 0.00137$, with a correlation coefficient of $R = 0.99979$, indicating excellent linearity. Based on the calibration curve, the retinol concentrations in the facial serum samples were found to be 0.023% for brand A, 0.021% for brand B, and 0.022% for brand C with a LoD value of 0.001 ppm and a LoQ value of 0.003 ppm. The findings indicate that cyclic voltammetry has the potential to be widely applied in routine quality control within the cosmetic industry, offering an efficient and cost-effective analytical solution to ensure the stability and effectiveness of active ingredients in cosmetic products.

Keywords: Cyclic Voltammetry; Carbon Paste Electrode; Facial Serum; Retinol.

Introduction

Cases of overclaiming retinol content, particularly in facial serums, have recently become a public concern. This issue serves as the basis for the present study, which aims to provide an alternative method for monitoring retinol concentrations in cosmetic products, thereby enhancing consumer awareness regarding the safety of products available on the market. The quantitative analysis of retinol content in cosmetic product formulations is typically conducted using UV-Vis Spectrophotometry [1,2] and High Performance Liquid Chromatography (HPLC) [3, 4]. However, both methods require relatively high costs, complex sample preparation, and longer analysis time [5]. Therefore, it is necessary to develop a method that is more efficient, cost-effective, simple in sample preparation, and possesses high sensitivity and selectivity in detecting analytes, namely the cyclic voltammetry method.

Retinol is an organic compound derived from vitamin A and is widely used today as an anti-ageing agent [6]. Retinol or vitamin A is a compound that contains a cyclohexenyl ring [7]. However, the use of retinol in high doses may lead to adverse effects such as skin irritation, redness, and dryness [8]. Therefore, regulatory limits on retinol usage in cosmetic products have been established. In Indonesia, the National Agency of Drug and Food Control (BPOM) permits up to 1% retinol content, while the Scientific Committee on Consumer Safety (SCCS) recommends a maximum of 0.5% RE (Retinol Equivalents) for body lotions and 0.3% RE for hand creams, facial creams, and other rinse-off products [4].

Retinol analysis was carried out using cyclic voltammetry with a working electrode consisting of a carbon paste electrode (CPE) modified with ZnO and TiO_2 nanoparticles, an Ag/AgCl reference electrode, and a Pt auxiliary electrode. The carbon paste electrode is a mixture composed of graphite powder and paraffin. Graphite-type carbon is conductive, chemically inert, insoluble in water, and possesses good adsorption capacity [9], paraffin is considered a suitable composite component due to its low vapor pressure, chemical inertness, and wide commercial availabilit [10]. The incorporation of nanomaterials as modifiers can enhance the sensitivity, selectivity, electron transfer kinetics, and stability of the working electrode [6,7].

The advantages of the cyclic voltammetry method are that it can analyze analytes at high concentrations, does not cause damage to the analyte, and has stability in oxidizing and reducing conditions within a wide potential range [13]. The oxidation and reduction reactions during the analysis process occur at the working electrode, and the material of the working electrode highly influences the performance of the voltammetric technique. Therefore, the quality of the analysis results is determined by the type of working electrode used [9,10,11].

ZnO and TiO_2 nanoparticles serve as auxiliary adsorbents with superior capability in adsorbing compounds

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due to their large surface area and small particle size [12,13]. Incorporating these two distinct nanoparticles is expected to generate new properties that enhance electron transfer, thereby improving sensitivity, selectivity, and lowering the detection limit. The observations in this study included the determination of deposition time and scan rate using a carbon paste electrode containing a mixture of ZnO and TiO_2 nanoparticles in a 3:2:3:2 (w/w) ratio at pH 5.

Research Methods

Tools and Materials

Beakers, measuring cylinders, voltammetric instrument (797 VA Computrace), analytical balance (Ohaus), copper wire, sandpaper, oven, amber bottles, graphite powder, paraffin, $Na_2HPO_4 \cdot H_2O$, p.a., Chemindo, $NaH_2PO_4 \cdot 2H_2O$, p.a., Chemindo, distilled water, potassium chloride (KCl, p.a., Chemindo), TiO_2 nanoparticles, ZnO nanoparticles, retinol 99% (p.a., JB Chemical), and facial serum product samples.

Preparation of Retinol Standard Solution

A total of 0.01 g of retinol powder (pro analysis grade) was weighed using an analytical balance, then transferred into a 100 mL volumetric flask and diluted with distilled water up to the calibration mark to obtain a 100 ppm retinol standard solution. This stock solution was then further diluted using 25 mL volumetric flasks to prepare standard solutions with concentrations ranging from 10 to 50 ppm.

Preparation of Retinol Sample Solution

Retinol samples were obtained from three commercially available facial serum products. One gram of each serum sample was weighed and dissolved in a 50 mL volumetric flask using distilled water. The solution was then further diluted with distilled water at a ratio of 1:10 to produce the sample solution. The prepared samples were stored in dark bottles to protect them from light exposure.

Working Electrode

Graphite powder, paraffin, TiO_2 nanoparticles, and ZnO nanoparticles previously synthesized using the sol-gel method [18]. The carbon paste electrode was fabricated by mixing graphite, ZnO nanoparticles, TiO_2 nanoparticles, and paraffin in a weight ratio of 3:2:3:2 (w/w) [5]. The mixture was stirred until homogeneous and then packed into an insulating tube or electrode body made from copper wire with a diameter of 4 mm and a length of 15 cm [19]. Prior to its use in retinol analysis, the working electrode was left to rest for 24 hours to ensure proper solidification within the electrode body [20]. The electrode was then characterized by determining the optimal deposition time and scan rate using a standard calibration curve.

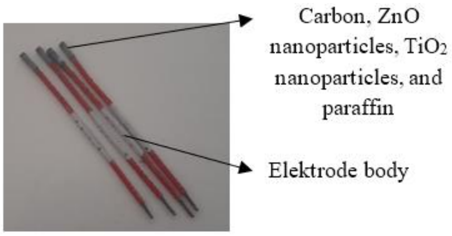

Figure 1. Modified Carbon Paste Electrode

Determination of Optimum Conditions

The optimum deposition time and scan rate were determined using an electrode with a composition ratio of 3:2:3:2 (w/w), at pH 5. The deposition times tested were 20, 40, 60, 80, and 100 seconds, while the scan rates examined were 0.05, 0.1, 0.15, 0.2, and 0.25 V/s. The next step involved adding a mixture of 10 mL of 50 ppm retinol solution, 10 mL of 5000 ppm KCl solution, and 5 mL of phosphate buffer solution at pH 5 into the voltammetry cell. Measurements were conducted over a potential range from -5 V to 4 V.

Determination of Retinol in Facial Serum Samples Using Cyclic Voltammetry

The retinol analysis in the samples was carried out to determine the retinol content in facial serum products. The measurement was performed using the best electrode composition, which was placed into the voltammetry cell containing a mixture of 10 mL of the sample solution, 10 mL of 5000 ppm KCl solution, and 5 mL of phosphate buffer solution at pH 5. The measurement was conducted over a potential range from -5 V to 4 V, using the optimum deposition time and scan rate.

Results and Discussion

Determination of Optimal Deposition Time

Determining deposition time aims to identify the most suitable or optimum duration for the sample to be deposited onto the surface of the working electrode. The deposition time was determined by mixing 10 mL of 50 ppm standard retinol solution with 5 mL of phosphate buffer solution at pH 5 and 10 mL of 5000 ppm KCl solution in the voltammetry cell [21]. The solution was measured using varying deposition times of 20, 40, 60, 80, and 10 s [22]. A voltammogram is obtained as shown in Figure 2.

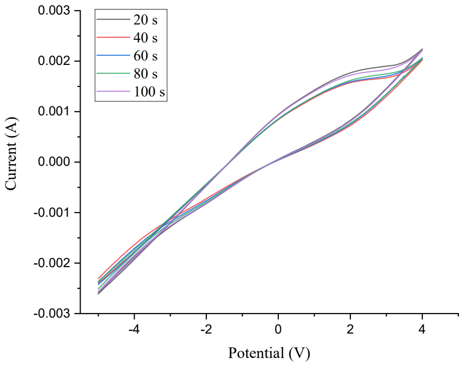

Figure 2. Voltammogram of 50 ppm retinol solution with varying deposition time

Based on Figure 2, the voltammogram of the 50 ppm retinol solution with varying deposition times can be tabulated to show the relationship between deposition time and Ipa (Table 1).

Table 1. Variation of deposition time and anodic peak current

Deposition time (s)	Ipa (A)
20	0.00223
40	0.00202
60	0.00206
80	0.00205
100	0.00212

Based on Table 1, it can be seen that the highest Ipa is 0.00223 A at a deposition time of 20 s. This indicates that, at that specific time, the electrode surface exhibits the most optimal electrochemical activity, as the formed active layer is still relatively thin, allowing efficient electron transfer and ion diffusion processes. An optimum deposition time enhances the preconcentration process, which in turn supports the stability of the species formed on the electrode surface.

Determination of Optimal Scan Rate

The scan rate affects the flux rate of the sample in forming the diffusion layer on the electrode surface, where the rate of diffusion layer formation during the process is proportional to the concentration [23]. The scan rate was determined by mixing 10 mL of 50 ppm standard retinol solution with 5 mL of phosphate buffer solution at pH 5 and 10 mL of 5000 ppm KCl solution in the voltammetry cell. The solution was measured using varying scan rate of 0,05, 0,01, 0,15, 0,2, 0,25 V/s [5]. A voltammogram is obtained as shown in the following figure 3:

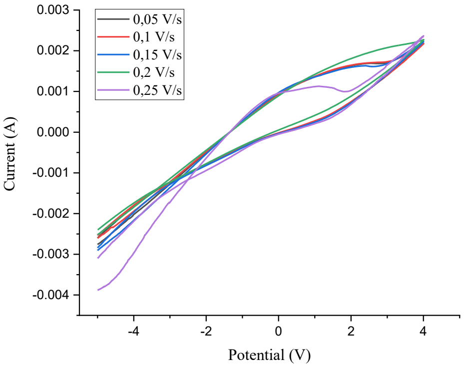

Figure 3. Voltammogram of 50 ppm retinol solution with varying scan rate

Based on Figure 3, the voltammogram of the 50 ppm retinol solution with varying deposition times can be tabulated to show the relationship between deposition time and Ipa (Table 2).

Table 2. Variation of scan rate and anodic peak current

Scan rate (V/s)	Ipa (A)
0.05	0.00217
0.1	0.00221
0.15	0.00222
0.2	0.00226
0.25	0.00236

Based on Table 2, it can be seen that the highest Ipa is 0.00236 A at a scan rate of 0,25 V/s. Based on the curve showing the relationship between scan rate and the resulting Ipa, a consistent increase in the curve indicates that the higher the scan rate, the faster the oxidation reaction of retinol occurs and the thinner the diffusion layer formed on the electrode surface. This leads to a more rapid electron transfer, resulting in a higher peak current. The higher the scan rate, the greater the current response generated [24].

Preparation of the Standard Curve

After obtaining the optimal parameters, measurements were carried out on several concentrations of standard retinol solution (10, 20, 30, 40, and 50 ppm) [24]. Each standard retinol solution in the voltammetry chamber contained 10 mL of standard retinol, 5 mL of phosphate buffer solution at pH 5 and 10 mL of 5000 ppm KCl solution. The deposition time was set to 20 s and the scan rate to 0.25 V/s. The resulting voltammogram is shown in Figure 4.

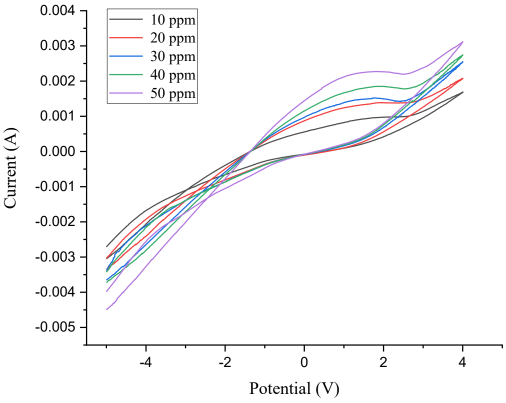

Figure 4. Voltammogram of the retinol standard solution

The concentration is directly proportional to the observed peak current, as evidenced by the lowest peak current at a concentration of 10 ppm and the highest at 50 ppm. The relationship between concentration and peak current indicates that higher concentrations result in greater current responses. This is due to the greater accumulation of retinol on the surface of the working electrode at higher concentrations, leading to a higher generated current. Based on this voltammogram, a table was then created to show the relationship between concentration and anodic peak current (Table 3).

Table 3. Ipa of retinol standard solution

Standard concentration (ppm)	Ipa (A)
10	0.00173
20	0.00207
30	0.00244
40	0.00278
50	0.00315

The Ipa results of the standard retinol solution were analyzed using OriginPro 2018 software to generate a calibration curve [25], as presented in Figure 5.

The calibration curve of the standard retinol solution obtained has a linear regression equation of $y = 0{,}0000355x + 0{,}00137$ with a linear regression coefficient $R = 0{,}99979$. This linear equation is used to determine the unknown concentration of retinol in facial serum samples using the cyclic voltammetry method.

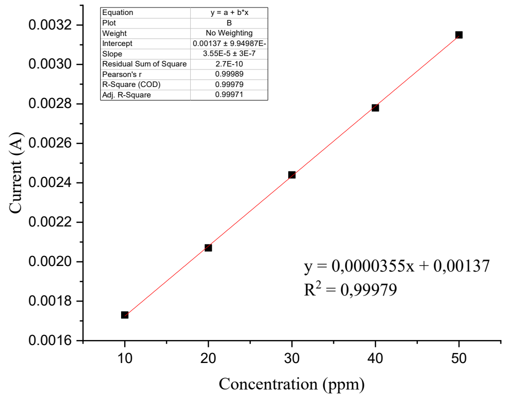

Figure 5. The calibration curve of retinol standard solution

Determination of Retinol Content in Facial Serum Samples

Using the same procedure as the standard retinol treatment, 10 mL of facial serum solution from various brands containing retinol was mixed with 5 mL of phosphate buffer solution at pH 5 and 10 mL of 5000 ppm KCl solution. The deposition time was set to 20 s and the scan rate to 0.25 V/s. The retinol samples in facial serum from various brands were measured using cyclic voltammetry, resulting in the voltammogram shown in Figure 6.

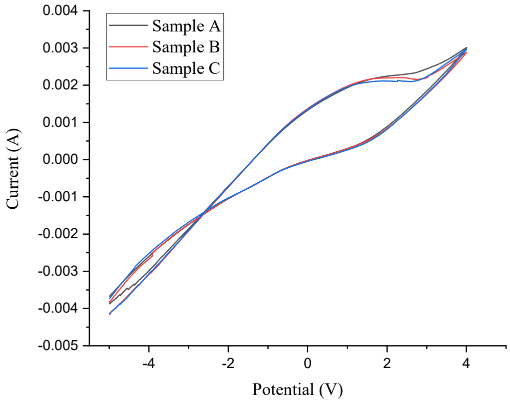

Figure 6. Voltamogram of facial serum samples from various brands containing retinol

The concentration of retinol in the sample can be determined by substituting the peak current (Ipa) obtained from the cyclic voltammetry measurement into the linear equation of the standard curve, which is y = 0,0000355x + 0,00137. Based on the voltammogram in Figure 6, a table was created to show the relationship between retinol-containing serum brands and their anodic peak current (Table 4).

Table 4. Various brands of facial serum containing retinol and their corresponding anodic peak current

Sample	Ipa (A)
A	0.00301
B	0.00288
C	0.00296

Based on the linear regression equation of the standard retinol solution, the retinol content in facial serums from various brands was determined as follows: Brand A = 46,22 ppm (0,023%), Brand B = 42,58 ppm (0,021%), and Brand C = 45,00 ppm (0,022%). All three samples meet the recommended dosage requirements, as each has a retinol concentration below 1% [26]. The calculated values of LoD (Limit of Detection) and LoQ (Limit of Quantification) using the cyclic voltammetry method were 0.001 ppm and 0.003 ppm, respectively. The results obtained in this study are superior compared to those reported by Putri [5], which had a LoD of 0.342 ppm and a LoQ of 1.038 ppm. Moreover, the analysis results of retinol content in facial serum samples demonstrate that the carbon paste electrode modified with nano ZnO and nano TiO_2 is effective and reliable for retinol detection.

Conclusion

A study was conducted to analyze the retinol content in facial serums from various brands containing retinol using cyclic voltammetry. The measurements were performed using a modified carbon paste electrode incorporating ZnO and TiO_2 nanoparticles the setup consisted of a working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode. The optimal conditions were a deposition time of 20 s, a scan rate of 0.25 V/s, and a pH of 5. The determination of retinol content in the facial serum samples was carried out using the linear regression curve of the standard retinol solution. The results showed that Brand A contained 46.22 ppm (0.023%), Brand B contained 42.58 ppm (0.021%), and Brand C contained 45.00 ppm (0.022%) of retinol with a LoD value of 0.001 ppm and a LoQ value of 0.003 ppm. The cyclic voltammetry method has the potential to be scaled up for broader commercial testing systems and applied to various other cosmetic products containing electroactive compounds, thereby supporting rapid, efficient, and sustainable quality control.

Author's Contribution

Ananta Adita Eka Putra: contributed to this research as the primary researcher and author of the entire study, with the aim of producing research that is beneficial to a wide audience. Pirim Setiarso: contributed to this research as the academic supervisor by providing guidance and suggestions throughout the study.

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