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New Modified Electrodes of Graphite paste with Nano Silicon dioxide For Determination of Sildenafil citrate Drug

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ABSTRACT

In this research, new graphite paste electrodes modified with silicon dioxide (SiO_2) nano particle are constructed and used for the determination of Viagra drug (Sildenafil citrate, SILC). The electrodes are constructed by preparing ion-pair for (SILC) with phosphotungstic acid (PTA) or phosphomolybdic (PMA) acid using dibutyl phthalate (DBP) as a plasticizer. These electrodes show good sensitivity towards SILC with linear range of (1.0×10^{-7}-1.0×10^{-2}) M, correlation coefficient, (0.9990) and the life time (120) days for both electrodes, limit of detection (5.177×10^{-8} and 5.026×10^{-8}) M, optimum temperature range (23-50 and 23-65)^{o}C , slope (57.33 and 58.01) mV/decade and optimum pH range (2-6 and 2-5), for SILC-PTA and SILC-PMA electrodes respectively. These electrodes were successfully applied for determination of SILC in pure and pharmaceutical preparation form (tablets) with recovery of not less than 98% .

Introduction

Viagra (Sildenafil citrate SILC) is a white to off-white crystalline powder of molecular weight of 666.7 g/mole, and its formula is $C_{28}H_{38}N_6O_{11}S$ and has chemical structure showed in fig(1). SILC is the first drug which approved for the treatment of erectile dysfunction, due to organic causes SILC is an effective and best drug for erectile dysfunction (ED) [1-3] .The studies suggest that Viagra successfully treats erectile dysfunction in men with co morbidities such as hypertension[4], diabetes[5], and depression [6].The side effects of SILC have been reported such as headache, congestion, flushing and dyspepsia [7-9].

Different methods have been reported for the determination of SILC drug in products and biological samples such as high-performance liquid chromatography (HPLC) [10,11], spectrophotometry [12-14], voltammetry[15] atomic absorption[16] and LC-ESI-MS [17,18]. The present work describes preparation, characterization and application of modified graphite paste electrodes for determination of Viagra in pure and pharmaceutical preparations. Performance characteristics of (SILC-PMA) and (SILC-PTA) graphite paste electrodes reveal low detection limit, high sensitivity, good selectivity, fast response time, very long life time and application with accurate determination of Viagra in pharmaceutical preparations.

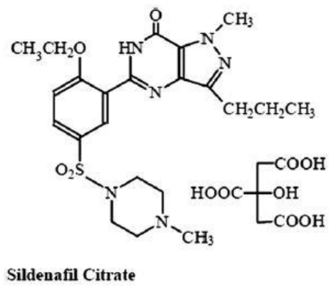

Fig. 1: Chemical Structure of SILC drug

Reagents and materials: All chemicals are of analytical reagent grade. Distilled water was used for the preparation of stock solutions. The following materials: SILC (SDI ,Samara-Iraq) ,Silicon dioxide nano particles (10-30nm) (SS NANO, USA). Dibutyl phthalate (Sigma ,Germany), acetic acid (Merck, Germany), graphite powder (BDH, England) , phosphomolybdic acid (BDH ,England) and phosphotungstic acid (Merck, Germany) were used in this work. A stock solution of 0.01 M of SILC drug is prepared by dissolving 0.6667 g in 5 ml of 1M acetic acid then completed to 100 ml distilled water. Dilute solutions (1×10^{-8} to 1×10^{-3}) M of drug were prepared by appropriate dilution with distilled water. KAMAGRA tablets (50 mg SILC) Ajanta Pharma limited- India , Markafil tablets (100 mg SILC) Marksana pharma ltd- India and Vegamax (100 mg SILC) Macleods pharmaceutical LTD-India are purchased from local pharmacies.

Apparatus

Potentiometric measurements are performed using HANNA instruments301 pH meter, HANNA HI2216 pH meter, Jenway3545 pH meter, calomel electrode No 13-639-52, Fisher Sientific Co. (Germany). For elemental analysis CHN ElementarIsoprime100-Germany was used.

Sample preparation

Four tablets of KAMAGRA 50 mg/tablet (the total tablets weight 0.9746 g) and four tablets of Markafil 100 mg/tablet (the total tablets weight 2.1404 g) are finely powdered and mixed homogeneously, (0.2437) g of KAMAGRA and (0.5351)g of Markafil powder was dissolved in (5) ml acetic acid (1M) then adding amount of distilled water in a 100 mL beaker. The resulting solution was then filtered through Whatman filter paper No. 42 and the volume was completed to the mark with water in a 100-mL volumetric flask to obtain (7.5×10^{-4})M and (1.5×10^{-4})M for KAMAGRA and Markafil respectively. Solutions of concentration range of (1×10^{-7}-1.0×10^{-4} and 1×10^{-7}-1.0×10^{-3}) M for KAMAGRA and Markafil respectively were prepared by appropriate dilution with distilled water. The quantity of SILC was determined by direct and standard-addition methods.

Stock Solutions of Interfering Ions: Solutions of 1.0 $\times10^{-3}$mol L^{-1} for each of HCl, NaOH, NaCl, $BaCl_2$.2H_2O, $CaCl_2$.2H_2O, NH_4Cl, $Fe(NO_3)_3$.9H_2O, Fructose, Cholesterol, Uric acid , Methyl paraben (M.H.B), Propyl paraben (P.H.B), Talc, Mg.stearate and TiO_2 were prepared by dissolving appropriate amount of these materials in distilled water in volumetric flasks of 50ml.

Preparation of ion-pairs

The ion-pairs were prepared by mixing 50 mL of equimolar of 1.0×10^{-2} M SILC to 50 mL of either PTA or PMA, a light orange and yellow precipitate of SILC-PTA and SILC-PMA were formed respectively. The precipitate was filtered through Whatman filter paper (No. 42), and washed with dilute acetic acid (1) M then washed several times with distilled water. The precipitate was left for 2 days to dry at room temperature[19].

Preparation of modified graphite paste electrodes (MGPE)

The sensing electrodes were prepared by mixing accurate weights (0.1) g of appropriate ion pairs with (0.59) g of highly pure graphite powder and plasticizer (0.3) g DBP and (0.01) g Silicon dioxide nano particles in an agate mortar. This mixture paste was carefully packed in plastic tube (3 mm i.d. ,4 length). A shiny and fresh surface was obtained by gently polishing the new graphite paste surface with filter paper [20,21].

Results and Discussion

SILC-PTA and SILC-PMA as an electro active compounds were used to prepare new sensors. Elemental analysis was carried out to confirm the composition of the ion-pair (SILC-PTA) and (SILC-PMA). The obtained results revealed 2:1 [SILC: PMA] and 2:1[SILC-PTA] ion pair as indicated in (table 1).

Table 1: Elemental analysis of the (SILC-PMA) and (SILC-PTA) ion pair

Element analysis	SILC-PTA			SILC-PMA		
	% C	% H	% N	% C	% H	% N
Found	15. 25	1.49	4.15	16.93	1.89	2.86
Calculated	16.94	1.40	3.99	16.99	2.43	2.83
Formula	$[C_{28}H_{38}N_6O_{11}S]_2.[H_3PW_{12}O_{40}]$			$[C_{28}H_{38}N_6O_{11}S]_2[H_3PMo_{12}O_{40})]$. 3 H_2O		

Calibration plot of the fabricated electrodes and limit of detection: The fabricated electrodes (SILC-PTA) and (SILC-PMA) were immersed along with Calomel reference electrode in solutions of SILC in the concentration range of (1×10^{-8}- 1×10^{-2}) M. The E (mV) against –log [SILC] was plotted as shown in (fig 2). Both electrodes show a linear response over the concentration ranges from (1×10^{-7}- 1×10^{-2}) M with near Nernstian slopes of and (57.33 and 58.01) mV /decade for (SILC-PTA) and (SILC-PMA) electrodes respectively. The values of LOD (5.026×10^{-8} and 5.177×10^{-8}) for (SILC-PMA) and (SILC-PTA) electrodes respectively indicate that the sensors under investigation are highly sensitive and can be applied for determination of small amounts of SILC drug.

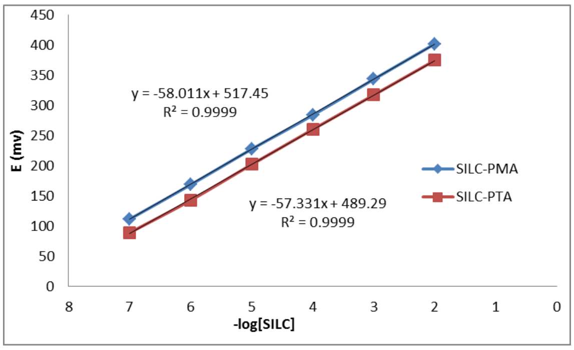

Fig. 2: Standard curve of SILC using new SILC-PTA and SILC-PMA electrodes

Effect of pH: The effect of pH on the performance of the two electrodes was investigated using concentration of (1.0×10^{-3})M of SILC drug at different pH values (1-9). The pH value was adjusted by addition of small volumes of HCl and/or NaOH solution (0.1-1 M of each). The potential at each pH value was recorded. It is obvious (fig 3) that the pH range is from (2-5) for (SILC-PMA) and (2-6) for (SILC-PTA) the potential is independent on pH . However the potential decreases gradually at pH values higher than 5 for (SILC-PMA) and higher than 6 for (SILC-PTA). It is worth noting that at more than pH 7 a white precipitate of drug is formed and that may be the cause of potential decrease. At pH values lower than 2 the potential readings decrease which can be related to interference of hydronium ion [22,23].

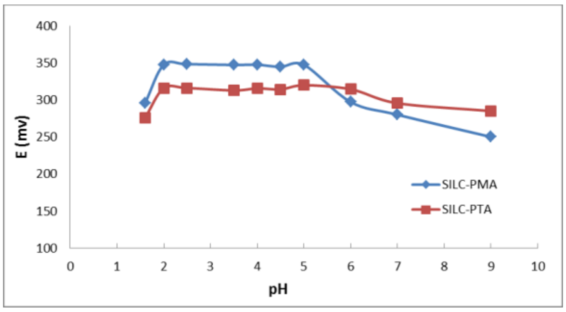

Figure (3): Effect of pH on the response of SILC-PTA and SILC-PMA electrodes using SILC solution (1×10^{-3})M

Effect of temperature

The change of potential is measured by changing the temperature of the drug solution from (23-65) °C for concentration of 10^{-3} M. The relationship between the temperature and the measured potential is plotted. The results in (Fig 4) showed that the appropriate working temperature is (23-65)°C for (SILC-PMA) and (23-50)°C for (SILC-PTA).

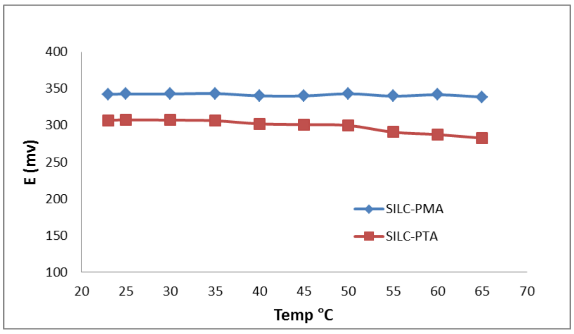

Fig. 4: Effect of temperature on the response of SILC-PMA and SILC-PTA electrodes

Selectivity of the studied sensors

The selectivity coefficients (log K) of the studied sensors were determined applying separate solution method (SSM) [24, 25]. In SSM, the potential of cell comprising the new constructed electrode and a reference electrode is measured in two separate solutions, where (SILC) and (interfering ion) are at the same activity. Selectivity coefficients were calculated using Nicolsky equation [25] : **log K = (Ej – Ei)/S** where Ei is the potential measured in (1×10^{-3}) mol/L SILC ,Ej the potential measured in 1×10^{-3} mol/L of the interfering ion or compound , S is the slope of the calibration plot. The K value represents the difference in potential in the presence of interfering ion (j) and when (j) is not present. When the value is less than 1 this indicates that the electrode shows low response to the interfering ions. The results of selectivity are shown on table (2). The K values shows a very high selectivity of the electrodes towards the SILC

Table 2: K value of both SILC-PMA and SILC-PTA electrodes

Interfering ion or compound	K	
	SILC-PTA	SILC-PMA
Na^{+1}	2.67×10^{-3}	9.80×10^{-2}
H^{+1}	1.30×10^{-2}	9.38×10^{-2}
$NH4^{+1}$	5.07×10^{-2}	9.57×10^{-2}
Ba^{+2}	4.25×10^{-2}	9.31×10^{-2}
Ca^{+2}	3.23×10^{-2}	8.01×10^{-2}
Fe^{+3}	3.80×10^{-2}	9.20×10^{-2}
Cl^{-1}	3.03×10^{-2}	7.91×10^{-2}
Fructose	2.98×10^{-2}	8.23×10^{-2}
Cholesterol	3.17×10^{-2}	9.42×10^{-2}
Uric acid	3.01×10^{-2}	8.23×10^{-2}
Mg .stearate	3.88×10^{-2}	7.69×10^{-2}
M.H.B	3.53×10^{-2}	8.01×10^{-2}
P.H.M	3.83×10^{-2}	8.74×10^{-2}
Talc	3.74×10^{-2}	7.72×10^{-2}
Ti^{+4}	4.46×10^{-2}	1.186×10^{-1}

Life time and response time

For the determination of the storage stability for (SILC-PTA) and (SILC-PMA) electrodes, the potentiometric measurements were carried out at optimum conditions of (pH and Temperature) for several times every week. The performance of the electrodes have been tested by peotentiometric calibration of SILC standard solutions on different days. The results remark that (SILC-PTA) and (SILC-PMA)electrodes can be used for 4 month without significant change in the value of potential. The IUPAC definition of response time is the time required to reach the steady state with potential change of ± 1 mv from the moment of contact of the (SILC-PTA) and (SILC-PMA) electrodes and the calomel electrode of the drug solution. The fast response time is an important and influential factor in electrode measurements [26,27]. The lowest response time of the new graphite paste for the (SILC-PMA) electrode was 10 second for concentration 10^{-7}M and 28 second for concentration 10^{-2}M and the lowest response time for new graphite paste of the (SILC-PTA) electrode was 18 second for concentration 10^{-7} M and 40 second for concentration 10^{-2} M as shown in (Fig. 5).

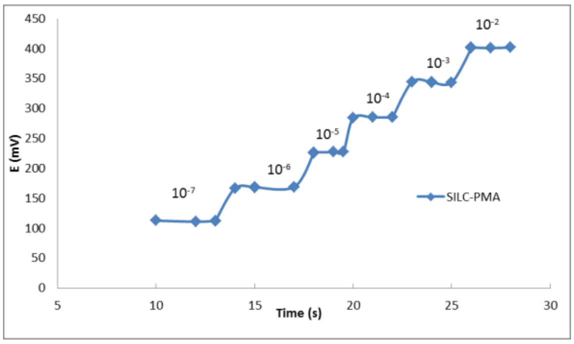

Fig. 5: Response time of SILC-PMA for concentration (10^{-7}- 10^{-2})M

Precision and Accuracy: To evaluate the accuracy and precision of the proposed method, pure and pharmaceutical drug solutions at two different levels (within the working limits) are analyzed, each solution was repeated for (6 or 5) times. Precision and accuracy are based on the calculated percent relative standard deviation (RSD%) and percent relative error (RE %). The value or RE% is not more than (-1.87) and value or RSD% is not more than 0.508. The results (table 3) show that these methods have reasonable precision and accuracy.

Analytical Applications: Viagra was determined using a standard addition method for pharmaceutical preparations and direct calibration method for both pure and pharmaceutical forms. The observed results were calculated as the recoveries% using the prepared electrodes (SILC-PTA) and (SILC-PMA). The percentage recoveries for determination of SILC pure drug solutions are (99.85 and 98.41) for (SILC-PMA and SILC-PTA) electrodes respectively. The percentage recoveries for determination of SILC tablets (Markafil 100 mg tablet) by calibration curve (direct method) are (99.54 and 98.13) and for (Kamagra 50 mg tablet) are (98.25 and 98.61) for (SILC-PMA and SILC-PTA) electrodes respectively. The percentage recoveries for determination of SILC tablets (Markafil 100 mg tablet) by standard addition are (98.21 and 99.30) and for (Kamagra 50 mg tablet) are (99.60 and 99.73) for (SILC-PMA and SILC-PTA) electrodes respectively in (table 3).

Table 3: Statistical treatment of data for determination of SILC in pure and pharmaceutical preparations using new (SILC-PTA) and (SILC-PMA) electrodes

Sample	SILC-PMA			SILC-PTA		
Pure drug	Taken [SILC] M	Found	% Recovery	Taken [SILC] M	Found	%Recovery
	Direct calibration method					
	1.0×10^{-2} 1.0×10^{-3} 1.0×10^{-4} 1.0×10^{-5} 1.0×10^{-6} 1.0×10^{-7}	9.928×10^{-3} 9.854×10^{-4} 9.976×10^{-5} 9.980×10^{-6} 9.984×10^{-7} 1.0188×10^{-7}	99.28 98.54 99.76 99.80 99.84 101.88	1.0×10^{-2} 1.0×10^{-3} 1.0×10^{-4} 1.0×10^{-5} 1.0×10^{-6} 1.0×10^{-7}	9.983×10^{-3} 9.986×10^{-3} 9.888×10^{-5} 9.820×10^{-6} 9.754×10^{-7} 9.726×10^{-8}	99.83 98.76 98.88 98.20 97.54 97.26
Mean±SD% n Variance RE% RSD%	99.85 ± 0.302 6 0.091 -0.15 0.302			98.41 ± 0.296 6 0.087 -1.59 0.300		
Markafil (100 mg)	1.5×10^{-3} 1.0×10^{-3} 1.0×10^{-4} 1.0×10^{-5} 1.0×10^{-6} 1.0×10^{-7}	1.489×10^{-3} 1.0115×10^{-3} 9.835×10^{-5} 1.0112×10^{-5} 9.893×10^{-7} 9.791×10^{-8}	99.26 101.15 98.35 101.12 98.93 97.91	1.5×10^{-3} 1.0×10^{-3} 1.0×10^{-4} 1.0×10^{-5} 1.0×10^{-6} 1.0×10^{-7}	1.482×10^{-3} 9.865×10^{-4} 9.871×10^{-5} 9.834×10^{-6} 9.748×10^{-7} 9.683×10^{-8}	98.80 98.65 98.71 98.34 97.48 96.83
Mean±SD% n Variance RE% RSD%	99.45 ± 0.506 6 0.256 -0.55 0.508			98.13 ± 0.292 6 0.085 -1.87 0.297		
Kamagra (50 mg)	7.5×10^{-4} 1.0×10^{-4} 1.0×10^{-5} 1.0×10^{-6} 1.0×10^{-7}	7.472×10^{-4} 9.876×10^{-5} 9.814×10^{-6} 9.779×10^{-7} 9.698×10^{-8}	99.62 98.76 98.14 97.79 96.98	7.5×10^{-4} 1.0×10^{-4} 1.0×10^{-5} 1.0×10^{-6} 1.0×10^{-7}	7.49×10^{-4} 9.886×10^{-5} 9.853×10^{-6} 9.792×10^{-7} 9.790×10^{-8}	99.86 98.86 98.53 97.92 97.90
Mean±SD% n Variance RE% RSD %	98.25 ± 0.373 6 0.139 -1.75 0.379			98.61 ± 0.298 6 0.088 -1.39 0.302		
Standard addition method						
Markafil (100 mg)	1.0×10^{-4}	9.821×10^{-5}	98.21	1.0×10^{-4}	9.930×10^{-5}	99.30
%RE	-1.79			-0.7		
Kamagra (50 mg)	7.5×10^{-4}	7.47×10^{-4}	99.60	7.5×10^{-4}	7.48×10^{-4}	99.73
%RE	-0.4			-0.27		
Robustness Ruggedness	98.69± 0.24 98.20±0.09			97.30± 1.14 98.76±0.154		

Content Uniformity Assay Test:
To study the content uniformity assay for pharmaceutical preparations of SILC drug, four individual tablets of Vegamax (100mg) were placed in separate 100-mL beakers and dissolved in 100 mL distilled water to obtain (1.5×10^{-3}) M , the potential of each solution was recorded using the new graphite paste electrodes (SILC-PMA and SILC-PTA). The mean potential was used to evaluate the content uniformity applying straight line of calibration graph. The results are shown in table(4)

Table 4: The results of Content uniformity Assay

Parameter	Vegamax (100mg)	
	SILC-PTA	SILC-PMA
Taken Conc.	1.5×10^{-3}	
Found Conc.*	1.482×10^{-3}	1.489×10^{-3}
%Recovery ± SD	98.78 ± 0.11 •	99.26 ± 0.11
Variance	0.013	0.013
%RSD	0.116	0.114
% RE	-1.22	-0.73

*mean of 4 determinations

Comparison with previous reported electrodes

The modified electrode was prepared by adding nano-silicon oxide and compared with other electrodes prepared from the same drug. It was found to be more sensitive, their life time is longer than the other electrodes and has a lower detection limit. The performance characteristics of the proposed electrodes and those previously reported electrodes are compiled in table (5) for comparison.

Table 5: Comparison of the new MGPE with those previously reported in literature

Parameter	**SILC-PTA**	**SILC-PMA**	**SILC-PMA**	**SILC-TPB***	**SILC-PTA**
Slope, mV/decade	57.33	58.01	55.50	55.40	36.90
Linear Conc. Range, M	1×10^{-8} -1×10^{-2}	1×10^{-8}-1×10^{-2}	1×10^{-5}-1×10^{-2}	1×10^{-2}-1×10^{-7}	1×10^{-5}-1×10^{-2}
Working pH	2-6	2-5	3-6	3-5	----
limit of detection, M	5.177×10^{-8}	5.026×10^{-8}	5.0×10^{-5}	9.0×10^{-8}	----
Life time ,day	120	120	30	30	----
Electrode type	MGPE	MGPE	liquid membrane electrode	Carbon Paste Electrodes	Carbon Paste Electrodes
Ref. no.	present study	present study	[28]	[20]	[29]

TPB* was sodium tetra phenyl borate.

Robustness and Ruggedness

The robustness method of the (SILC-PMA) and (SILC-PTA) was examined by changing the aqueous solution to acetate buffer pH (3.4). The ruggedness was checked by using another model of pH-meter (HANNA, HI 2216). The results of this investigation are shown in table(3) and figure (6 and 7).

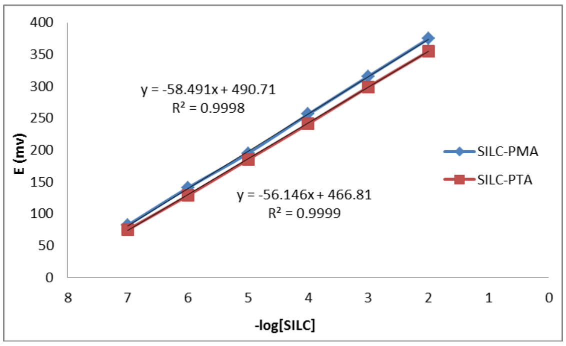

Fig. 6: The effect of acetate buffer pH (3.4) (robustness) on response of the SILC-PTA and SILC-PMA electrodes.

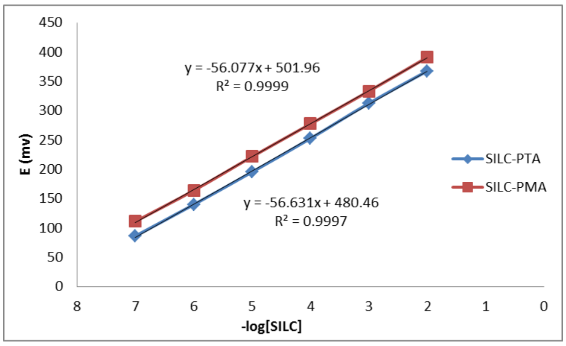

Fig. 7: Test of ruggedness of SILC-PTA and SILC-PMA electrodes by using another model of pH-meter (HANNA HI 2216)

Conclusion

The proposed method introduced an ion selective electrodes for the determination of SILC based on graphite powder and DBP as a plasticizer and using PTA or PMA as active materials. These electrodes showed a successful application with low limit of detection and good recovery. The electrodes also showed long life time, fast response time, good selectivity and reasonable working concentration ranges.

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أقطاب محورة جديدة من عجينة الكرافيت مع ثاني أوكسيد السيليكون النانوي لتقدير عقار سترات السيلدينافيل

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الملخص

في هذا البحث تم بناء قطبين جديدين من عجينة الكرافيت المحور بإضافة ثاني أوكسيد السليكون النانوي واستخدم لتقدير عقار السيلدينافيل. تم تصنيع هذه الأقطاب بتحضير مزدوج أيوني للعقار مع حامض الفوسفوتنكستك أو حامض الموليبديك واستخدام ثنائي بيوتيل الفثاليت كملدن. هذه الأقطاب أعطت حساسية جيدة لعقار الفياكرا بمدى خطي ($10^{-7}-10^{-2}$) مولاري ومعامل ارتباط 0.9990 وعمر زمني 120 يوم لكلا القطبين. أن حد الكشف كان (5.177×10^{-8} و 5.026×10^{-8}) مولاري ومدى درجة الحرارة المثلى (23–50 و23–60) درجة مئوية وميل (57.55 و58.01) mV/decade ومدى الدالة الحامضية (2–6 و2–5) لكل من قطب العقار مع حامض الفوسفوتنكستك وحامض الموليبديك على التوالي. تم استخدام هذه الأقطاب بنجاح لتقدير العقار بشكله النقي وفي الحبوب باسترجاعية لاتقل عن 98%.