A New method for ISE construction for methyl orange dyes and using for indirect determination of Amitriptyline Hydrochloried drug

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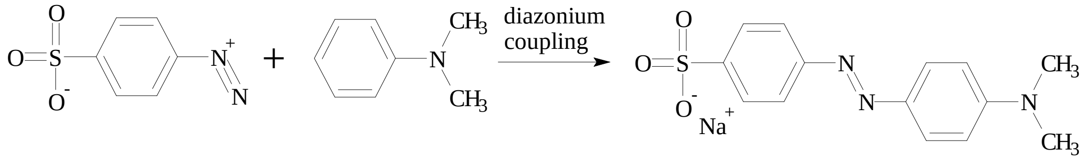
Abstract:

A new method for construction ion-selective electrode (ISE) by heating reaction of methyl orange with ammonium reineckate using PVC as plasticizer for determination methyl orange and determination Amitriptyline Hydrochloried drug by formation ion-pair on electrode surface . The characteristics of the electrode and it response as following : internal solution 10^{-4}M , pH (2.5-5) ,temperature (20-30) and response time 2 sec. Calibration response for methyl orange over the concentration range 10^{-3} -10^{-9} M with R=0.9989 , RSD%=0.1052, D.O.L=0.315X10^{-9} M E_{re}%=(-0.877- -2.76) , Rec%.=(97.230 -101.711) .

Key words: methyl orange, azo compounds, ISE

Introduction:

The practice of using dyes is perhaps the most ancient art of chemistry. Dyeing substances from plant, animal, or mineral sources has been known before written history. The accidental discovery of the purple dye, *mauve,* by W.H. Perkin in 1856 is generally considered to be the birth of the modern chemical industry. Several other synthetic dyes followed. One important group is known as the azo dyes, which are named after their unusual N=N, *azo,* functional group.
Methyl orange, 4-[4-(dimethylamino)phenylazo]benzenesulfonic acid, is an azo dye that forms orange crystals and is commonly used as an acid-base indicator, due to the fact that its anion form is yellow and its acid form is red [1]:



Diazontized sulfanilic acid *N,N-dimethylaniline* *Methyl orange*

The synthesis of methyl orange occurs in two steps.[2]
Step 1: a nitrosonium-ion reacts with the amino group of the sulfanilic acid, attaching a second N-atom at the sulfanilic acid to produce a diazonium salt, the diazotation process.

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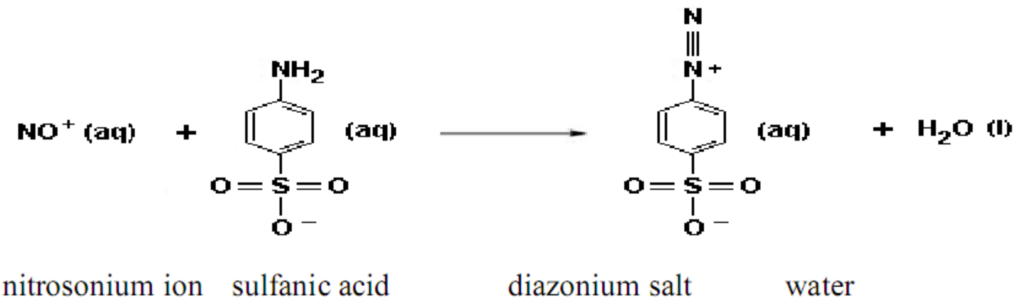
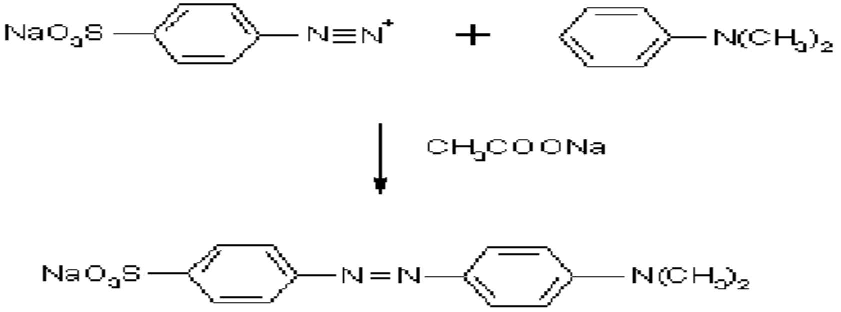


Step 2: the diazonium salt is coupled with N,N-dimethylaniline, in which the coupling takes place in the opposite position from the – $N(CH_3)_2$ group.



Methyl orange

Used as an indicator in 0.1% aqueous solution (pH: 3.1 red, 4.4 yellow) for the titration of mineral acids, (not organic acids) and strong bases. Used in dyeing and printing textiles, as a dyestuff. Molecular formal $C_{14}H_{14}N_3O_3SNa$, $(CH_3)_2NC_6H_4N=NC_6H_4SO_3Na$, IUPAC name Sodium 4-[(4-dimethylamino)phenyldiazenyl]benzenesulfonate; other name "benezenesulphonic acid, p-((p-(dimethylamino) phenyl) azo)-, sodium salt"; 4-[4-(Dimethylamino) phenylazo] benzenesulfonic acid ,sodium salt ;Soduim 4-[(dimethylamino) phenylazo] benzenesulfonate, Molar mass 327.33g\mol ,Density 1.28g.cm^{-3} .[3]

Different methods have been reported for use methyl orange of determination such as A novel bipolar stationary phase (HCPS-MO)was prepared by impregnation of hypercrosslinked polystyrene (HCPS)with methyl orange and its ion-exchange properties were studied it is capable to separate both cations and anions[4].The reaction of the some drugs :benzydamine HCl , levamisole HCl and mebeverine HCl with methyl orange to formed yellow ion-pair complexes were extracted with dichloromethane[5].The corrosion inhibition efficiency of methyl orange in controlling corrosion of carbon steel immersed in well water has been evaluated by weight loss method both in absence and presence of zinc ion[6]. Ion-pair formation of terbinafine with methyl orange extracted with chloroform and the absorbance measured at 422nm[7].Advanced treatment of wastewater with methyl orange and heavy metals on TiO_2 ,fly ash and their mixtures [8].Silca gel supported titanium dioxide photocatalyst for methyl orange photoreduction [9].Extractive spectrophotometric determination of some αAdrenergic –antagonists in pure forms and in pharmaceutical formulations based on the formation of yellow colored chloroform ion-pair complexes between the basic nitrogen of the drugs and dyes such methyl orange[10]. A thorough literature survey has revealed that no method determination of methyl orange therefore, the aim of this work was to develop ion selective electrode for determination methyl orange directly and determination amitriptylin.HCl drug by formation ion-pair on electrode surface .

Material and Methods :

Apparatus: pH meter Jenway 3310,calomel electrode , Sartorius balance , Magnetic stirrer with hot plate, ultrasonic path ,microwave ,gallenhamp England for m.p.

Solution:

All materials used ,solids and liquids are pure and the water used for preparing the solution is distilled water .High-molecular-weight poly (vinyl chloride)(PVC),di-n-butyl phthalate (DBPH),ammonium reineckate (A.R) ,methyl orange (M.O)were obtained from Fluka , Amitriptylin.HCl standard was obtained from the State Company of Drug Industries and Medical Appliances ,Samara ,Iraq ,Amitriptyline .HCl tablets (25mg Amitriptyline .HCl);Actavis,Barnstaple,EX32 8NS,UK.The stock solution of 1000 µg/ml Amitriptyline .HCl was prepared by dissolving an appropriate amount of Amitriptyline .HCl in 100ml of distilled water.A standard solutions (10-100 µg/ml)were prepared by diluting the appropriate amount in distilled water.

Sample preparation:

A homogenized powder was prepared from ten accurately weighed Amitriptyline .HCl tablets (0.10339gm). An appropriate amount of this powder was dissolved in distilled water in a100ml Erlenmeyer flask. Dissolution of the drug was assisted by means of a magnetic and by an ultrasonic bath .the mixture was then filtered and made up to the mark with water in 100ml volumetric flask to obtaine solution (250 µg/ml).

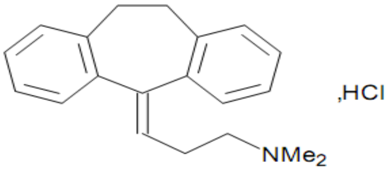


Fig.1 chemical structure of Amitriptyline .HCl

Preparation of complex:

New method developed formation complex between methyl orange (M.O)m.p=>300 and ammonium reineckate (A.R) m.p= 270 consist mix equal moles each one after scrunch each other alone by agate mortar and mixed and then put in microwave instrument for 30min produce red-brown precipitation m.p =221 .

Preparation of membrane [11]:

1- 45 mg of high relative molecular weight PVC dissolved in the mixture of (10ml THF+10ml acetone) .

2-Add 1mg from new complex above to the mixture and mix well by ultrasonic bath

3-Add 0.43ml of dibutyl phthalate plasticizer to the mixture and mix it well by using ultrasonic bath

4- This solution was poured into glass Petri dish (5cm dimeter),and was allowed to evaporate during 72hr. at room temperature .The thickness of membrane obtained was about 0.3mm.

5-The membrane produce in Petri dish taken by tong and put in plastic clear bag .

-Membranes were cut out and glued to the polished end of PVC tubes by means of a PVC-THF solution. The electrode bodies consisted of a glass tube to which the PVC tube was attached at one end and filled with an internal solution (1X10^{-2}M of methyl orange).The membrane was conditioned by immersing in a same solution for 3h before measurements.

General procedure:

The electrode was calibrated by transferring 20ml aliquots of (1X10^{-6}_1X10^{-3}M) aqueous solution of methyl orange (M.O) to 50mL beakers followed by immersing the M.O electrode together with a calomel reference electrode in the solution .The potential reading were recorded ,and the e.m.f. were plotted as a function of the logarithm of the M.O concentration .The calibration graph was used for subsequent determination of unknown M.O concentrations.

Results and Discussion:

Effect of the internal solution

The influence of the concentration of the internal filling solution (IFS) on the potential response of the M.O selective membrane electrode was studied .The M.O concentration was changed from(1X10^{-6} to 1X10^{-2})M. It was found that the variation in the concentration of the internal solution caused a difference in the potential response and the slope as shown in Table 1.The exact reason for this behavior is not known ,but is believed to be due to liquid junction effect .

Table1.Effect of the internal filling solution (IFS) on the response of a M.O electrode

Conc.of IFS/M	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
Slope/mVdecade^{-1}	18.7	16.5	18.8	14.9	3.8
Correlation coefficient	0.9914	0.9984	0.9979	0.9869	0.9944

A 1X10^{-4}M IFS gives a better slope (18.8mVdecade^{-1}) which is near to the Nernst behavior .Therefore, a concentration of 1X10^{-4} M ,was selected as the internal filling solution .

The effect of pH

The effect of the pH of the test solution on the electrode potential was also studied .The variation in the potential with pH changes was followed by the addition of small ,volumes of HCl and NaOH 0.1M to the test solution (1X10^{-3}_1X10^{-6}) M of M.O For each pH value ,the potential was recorded ,and thus potential pH curves for all conc.M.O were constructed the results are shown in Fig.2

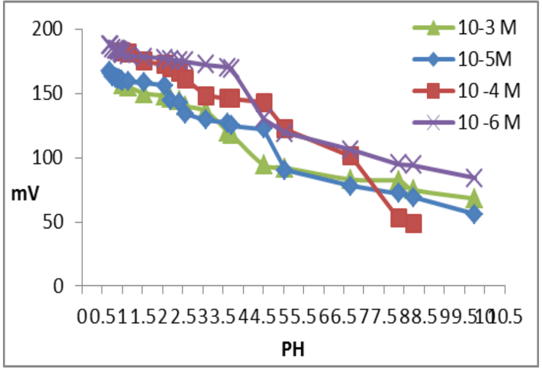


Fig.2 Effect of the pH on the response of the M.O electrode

The potentials were found to be dependent of the pH from(2.5-5) and in this range the electrode can be used for M.O determination .The decrease in mV reading at pH >3.5 may be due to the interference of hydronuim ion and the penetration of H_3O^+ into the membrane surface or a gradual increase of the protonated species [12,13].At higher pH values pH<6 free base precipitated in the test solution and consequently the concentration of the unprotonated species gradually increased .As a result lower e.m.f reading were recorded .The decrease in the potential readings at pH>6 on the other hand can be probably attributed to the penetration of OH^-ion into the gel layer of the membrane [13].

The effect of temperature

The effect of different temperature on range solutions ($1X10^{-3}$ -$1X10^{-6}$ M) were studied for to selected the best temperatures range among (5-40C^0). The rustle are shown in Fig.3

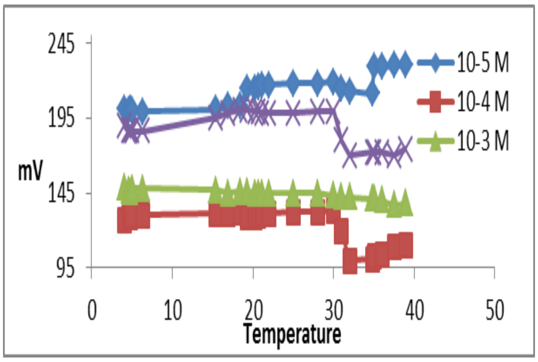


Fig.3 Effect of the Temperature on the response of the M.O electrode

It was found the best range (20-30 C^0) therefore, working at room temperature.

The effect of response time

The effect of response time on range solutions ($1X10^{-3}$ -$1X10^{-6}$ M) was studied by observed stability of response after immersion studied electrode (M.O) with calomel electrode in solutions ,It was found only 2sec. enough for response of all concentrations , Fig.4 illustrate this

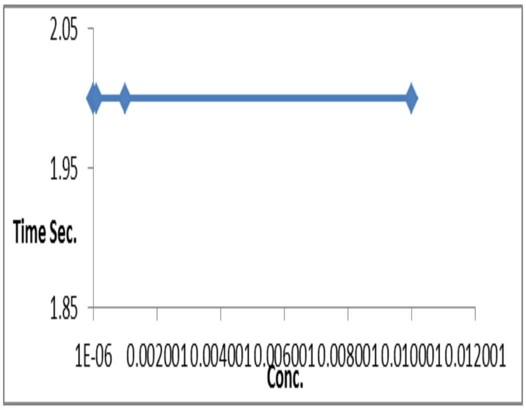


Fig.4 Effect of the response time on the response of the M.O membrane electrode

Calibration graph

Using the optimized membrane conditions described above, the potentiometric response of the electrode was studied based on the M.O concentration in the range of ($1X10^{-3}$_$1X10^{-9}$M) , in series of 50 mL beakers , It was found increase the mV value with decrease conc. solution of M.O ,The exact reason for this behavior may be retune to increase of attraction with increase the conc..The results given inFig.5 and Table 2.show the characteristics performance of the M.O membrane electrode .

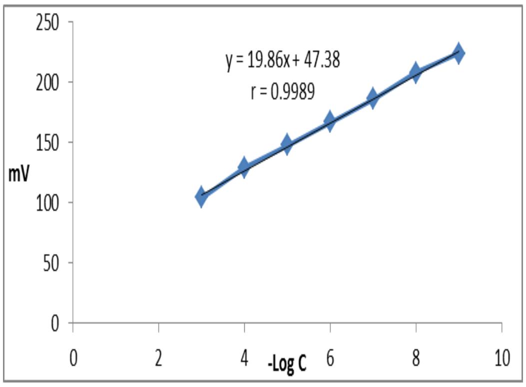


Fig.5 Calibration graph of the M.O membrane electrode

Table 2. Response characteristics of M.O membrane electrode

Slope(mVdecade^{-1})	Intercept (mV)	*Correlation coefficient r	LOD (M)
19.86	47.38	0.9989	$0.315X10^{-9}$

*n=7

Table 3. Accuray ,Precision

Conc. M	Experimental value	Calculated value	E_{re}%	Rec%
$1X10^{-9}$	224.135	226.12	-0.877	99.122
$1X10^{-8}$	207.764	206.26	0.729	100.729
$1X10^{-7}$	186.231	186.400	0.09	99.909
$1X10^{-6}$	166.879	166.54	0.203	100.203
$1X10^{-5}$	147.987	146.68	0.891	100.891
$1X10^{-4}$	128.99	126.82	1.7110	101.7110
$1X10^{-3}$	103.998	106.96	-2.76	97.230

Table 4. r,r^2 ,RSD% , t Measured ,t table

r	r^2	RSD%	t. Measured	t .table
0.9989	0.9978	0.1052	50.7	2,447

Selectivity of electrode

Measured selectivity for electrode of M.O by mixed solutions method after application the optimum condition on the solution of 10^{-4}M methyl orange and added different concentration of foreign ions and measured the potential first without foreign ions and second with foreign ions in 20ml observed the electrode studies was high selectivity against the methyl orange solution compared with foreign ions depends on value of the selectivity coefficients were determined by the following equation [14-15] :

$$K_{I,j}^{pot} = \frac{Cimin\ .P}{Cj\ max\ X100} \text{......(1)}$$

Where

$C_i$min= the minimum conc.for studied ion

$C_j$max= the maximum conc.for foreign ion

P=relative error

The foreign ions were (K^+ ,Na^+,Li^+,Ba^{2+},Cu^{2+},Cd^{2+},Pd^{2+},Al^{3+} ,Cr^{3+}, Cl^-,Br^-,NO_3^-,SO_4^{2-},CO_3^{2-},PO_4^{3-}) ,Table 5. illustrate this

Table 5. Potentiometric selectivity coefficients of some foreign ions on the M.O electrode

Foreign ions/Conc.M	the selectivity coefficients		
	10^{-3}	10^{-4}	10^{-5}
K^+	0.002	0.007	0.00013
Na^+	-0.0198	-0.022	-0.0176
Li^+	0.00142	0.00142	0.00143
Ba^{2+}	0.0015	0.00952	0.0174
Cu^{2+}	0.0063	0.0054	0.014
Cd^{2+}	0.0025	0.0025	-0.0032
Pd^{2+}	-0.00489	-0.00337	0.00335
Al^{3+}	-0.00735	-0.00735	-0.00735
Cr^{3+}	0.0015	0.00301	0.00687
Cl^-	-0.0049	-0.008	-0.016
Br^-	0.00081	0.00081	0.0016
NO_3^-	0.0141	0.0075	0.0075
SO_4^{2-}	0.0024	0.00082	-0.00082
CO_3^{2-}	-0.025	-0.0178	-0.00982
PO_4^{3-}	0.0113	0.0176	0.0176

Analytical application

1-The M.O membrane electrode was used for the determination in experimental solution of M.O by using standard-addition method ,it was used 10 ml of 10^{-4} M M.O solution and added (0.1-3)ml of 10^{-3}M to obtained the graph Fig .6 illustrate this

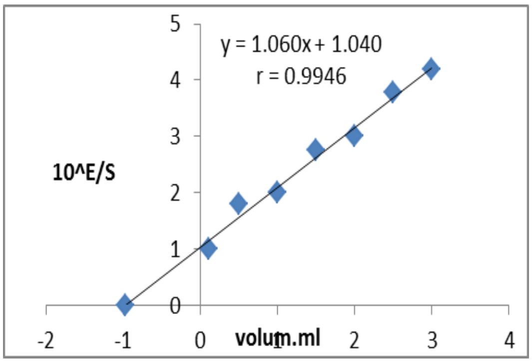


Fig.6 Calibration graph of the standard-addition method

The change in the potential reading was record after each addition and was used to calculate the concentration of M.O by the following equation:

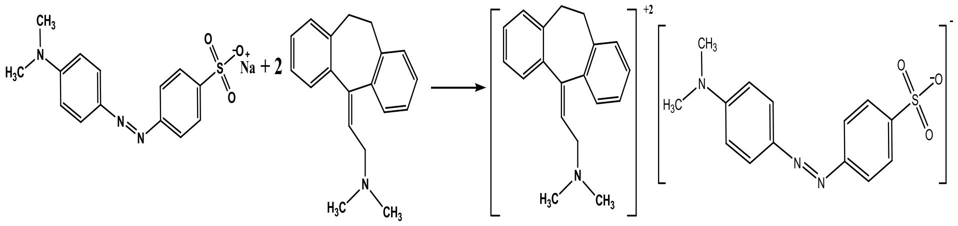
$C .V=V_e X$

Where C and V are the concentration and volume of an unknown sample respectively V_e and X are the concentration and volume of standard solution .Results of the standard –addition method are given in Table 6.

Table 6. M.O analyzed by using standard –addition method for the proposed electrode

Taken /M	Found/M	RE%	Rec%
1X10^{-4}	9.8X10^{-5}	-2	98.0

2- The electrode was used for determination of Amitriptyline .HCl drug by formation ion-pair on electrode surface in pharmaceutical preparations after construction calibration graph of standard solution from drug in the range of (10-100 µg/ml) the result given in Fig.7 and table 7 by using direct method the suggest reaction as fallowing:



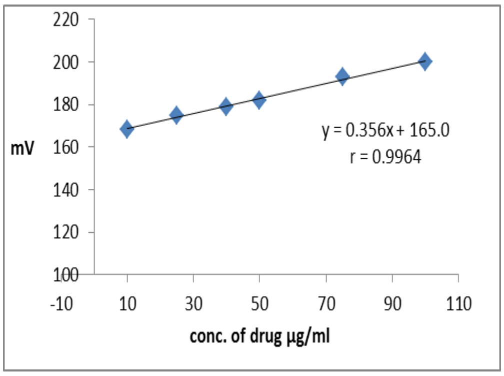


Fig.7 Calibration graph of the Amitriptyline .HCl drug

Table 7. Amitriptyline .HCl drug analyzed by using direct method for the proposed electrode

Taken.µg/ml	Found.µg/ml	RE%	Rec%
50	50.56	1.12	101.12

Conclusions

Ion selective electrode for determination methyl orange directly and determination amitriptylin.HCl drug by formation ion-pair on electrode surface was developed .Sensor based on M.O-AR .The application of the electrode to the determination of M.O and amitriptylin. HCl drug in pharmaceutical preparation is characterized by a high degree of precision and accuracy. The use of the proposed electrode offer an advantages of fast response ,elimination of any sample pretreatment or separation steps and the direct determination of sample in turbid or colored solution .

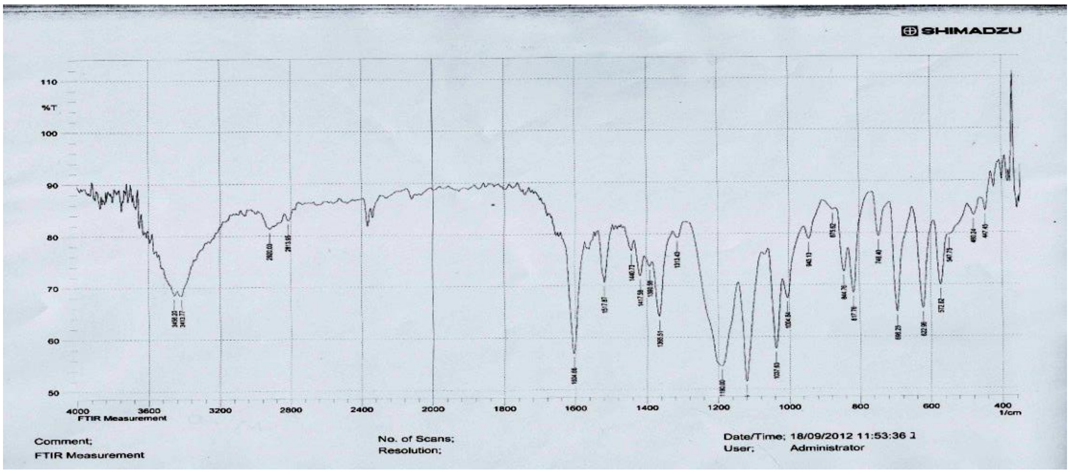


Fig.8 The IR spectrum of Methyl orange

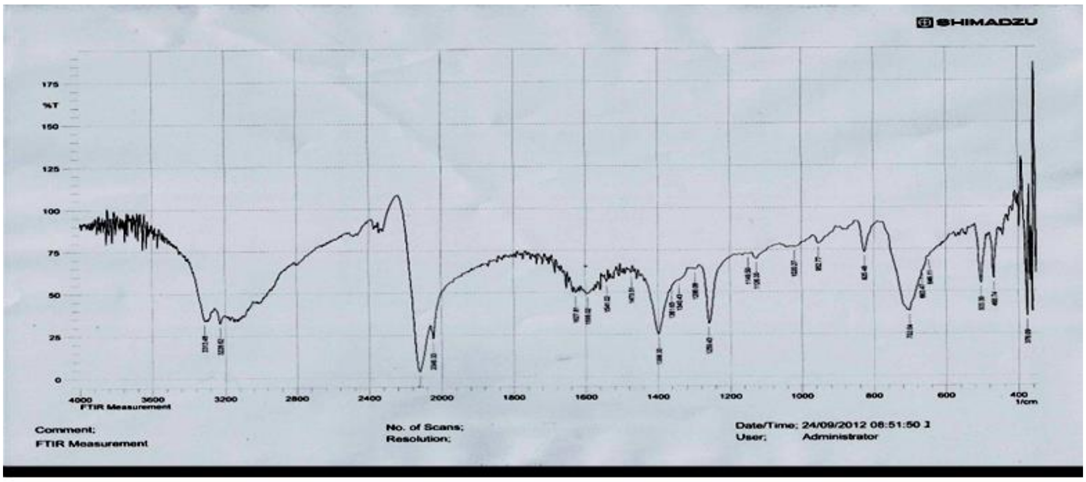


Fig.9 The IR spectrum of Ammonium reineckate

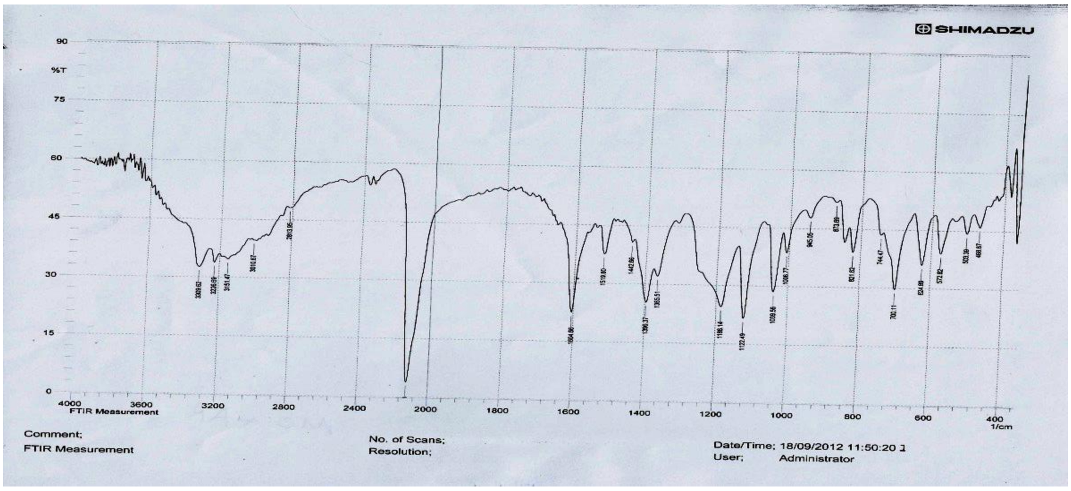


Fig.10The IR spectrum of Ammonium reineckate + Methyl orange

References:

1- Labhsetwar ,K. 1988.Synthesis of Methyl Orange and Its Application to Textiles Organic Chemistry With Vernier Software & Technology .Wiley and Sons ,2nd Ed., New Jersey pp 378.

2- Pungor , E. 2012. STUDENT WORK BOOK Methyl Orange – online synthesis –Department of Research and Theory in Education VU University Amsterdam The Netherlands ,1st Ed., Amsterdam pp 218.

3 - Aburuz , S. 2008 . Material safety data sheet methyl orange .Wiley and Sons , Chichester , 1st Ed.,Austin pp 17.

4- Maria , G. Lubov,V. and pavel N. 2001 . Ion-exchange properties of hypercrosslinked polystyrene impregnated with methyl orange. J.Chromatography A. 920:79-85.

5-El-Didamony, M. 2008. Spectrophotometric determination of benzydamine HCl, levamisole HCl and mebeverine HCl through ion-pair complex formation with methyl orange, Spectrochimica Acta. Part A (69) : 770-775.

6- Sathiyabama, J. , Arockia ,J. and John , A. 2008.Methyl orange as corrosion inhibitor for carbon steel in well water, Ind.J..of Che. Technology. 15:462-466.

7- Marinela , M. Crina, C. 2008. Spectrophotomrtric determination of terbinafine through ion-pair complex formation with methyl orange ,Farmacia. 4: 393-401.

8- Maria, V. Radu, C. Luminita, A.and Anca ,D. 2009. Advanced treatment of wastewater with methyl orange and heavy metals on TiO2, fly ash and their mixtures, Cat. Toda. :137-142.

9- Joshi, M., Mangrulkar, A., Labhsetwar, K. and Parwate, D. 2012. Silica gel supported Titanium dioxide photocatalyst for methyl orange Photoreduction, Int. j. of Kno. Eng.3 (1):137-139.

10- Ragaa, R. , Nahla , S. Ayman ,A,and Walid ,A , 2012. Extractive spectrophotometric determination of some α-Antagonists in pure forms and in pharmaceutical formations , Che.Ind & Che.Eng. 18 (2) : 179-191.

11- Katsu, T. Ido, K. Moriya, A. Nakae, Y. and Sakata , I ., 2000.Valproate-selective membrane electrode based on gallium(III) tetraphenylporphyrin, Electroanalysis. 12 (16): 1282-1285.

12- Stefan , R. Aboul-Enejn, H.and Baiulescu , G. 1996 .Ion-selective electrodes in analytical chemistry, Sens.Actuators B (37) 141-143.

13- Arvand , M. Vejdani, M.and Moghimi , M. 2008 .Construction and performance characterization of ion selective electrode for potentiometric determination of atenolol in pharmaceutical preparations , Desalination 255: 176-184.

14- Buck R. and Lindner, E. 1994 .Recommendations for nomenclature of ion-selective electrodes, Pure Appl. Chem. 66 (12): 2527-2536.

15- Umezawa, Y. Umezawa, K.and Sato, H., 1995. Selectivity coefficients for ion-selective electrodes: Recommended methods for reporting K values, Pure Appl. Chem., 67 (3) : 507-518.

طريقة جديدة لبناء قطب انتقائي غشائي ايوني لتقدير صبغة المثيل البرتقالي واستخدامه في تقدير عقار هيدروكلوريد الامبتربتيلين بصورة غير مباشرة

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الخلاصة:

طريقة جديدة لبناء قطب غشاء ايوني جديد يعتمد على تفاعل حراري بين صبغة المثيل البرتقالي والمادة الفعالة امونيوم رنيكات باستخدام متعدد الفنيل كلورايد الملدن لتقدير صبغة المثيل البرتقالي ، حيث تم دراسة افضل محلول مليء داخلي وكان 10^{-4} مولاري وبدالة حامضية تتراوح بين (2.5-5) عند درجة حرارة بمدى (20-30) وزمن استجابة لايتجاوز 2 ثانية ، وبعد بناء منحني المعايرة لوحظ أن مدى التراكيز التي اعطت استجابة تتراوح بين (10^{-3} – 10^{-9}) مولاري وبمعامل ارتباط =0.9989 ، الانحراف القياسي النسبي = 0.1052 ، وحد كشف = $0.315X10^{-9}$ وتراوح الخطأ النسبي المئوي (-0.877-¯2.76) وكانت الاستردادية المئوية (97.230-101.711) مما يدلل على ان الطريقة المقترحة دقيقة وحساسة .