# Formation – Extraction of Ion Pair Complexes of $[PdI_4]^{-2}$ and $[BiI_4]^{-1}$ with Trifluoperazine Hydrochloride (TFPH) Drug and Determination by Molecular Absorption Spectroscopy

**Ali Ibraheem Khaleel, Suham Tawfiq Amine, Asmaa Ahmed Mohammed**
**Department of Chemistry, College of Education, University of Tikrit- IRAQ**

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**Abstract:-**

This Study includes the determination of (TFPH) drug via the formation of ion association pair with $[pdI_4]^{-2}$ and with $[BiI_4]^{-1}$ in aqueous phase . The analytical results obtained are as follow: the optimum pH is 5 and 4, reaction time is immediate and 5 minutes, mixing time 3 and 4 minutes for the two ion pair respectively. The statistical and other analytical results for the first ion pair in the concentration range (6-40ppm) were as follow: the detection limit is 0.228 ppm, molar absorption coefficient is $2.3635x10^4$ liter $mole^{-1}$ $cm^{-1}$ at 297nm . For $BiI_4$ – TFPH ion pair at 292 nm, the results in the concentration range (0.2-18ppm) were as follow: detection limit is 0.0030 ppm , and molar absorption coefficient is $3.747 \times 10^4$ liter $mole^{-1}$ $cm^{-1}$ . This method was applied to Salabid pharmaceutical preparation with percentage recovery of not less than 98.5%.

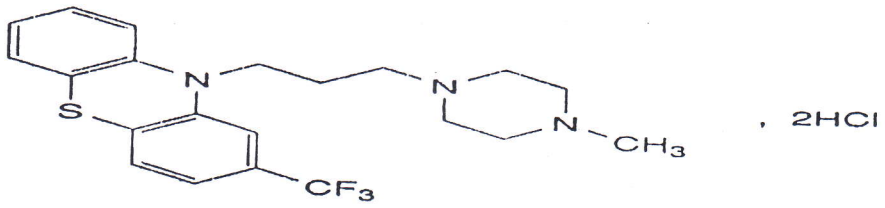
# تكوين و استخلاص المزدوج ألايوني لعقار ثلاثي فلوبيرازين هيدروكلوريد مع المعقدين $[PdI_4]^{-2}$ و $[BiI_4]^{-1}$ و التقدير بمطيافية الامتصاص الجزيئي

**المستخلص:-**

يتضمن البحث تقدير عقار ثلاثي فلوبيرازين هيدروكلورايد (TFPH) بطريقة جديدة باستخدام تقنية الامتصاص الطيفي الجزيئي بتكوين ازواج ترابط ايونية مع معقدي $[PdI_4]^{-2}$ و $[BiI_4]^{-1}$ عند الدالة الحامضية 5 و 4 و بزمن تفاعل لحظي و 5 دقائق و زمن رج 3 و4 دقائق و لكلا زوجي الترابط الايوني على التوالي. ان النتائج الاحصائية و التحليلية للمزدوج الاول لمدى من تراكيز العقار( 6 – 40جزء بالمليون) كانت كالاتي: حد الكشف 0.228 جزء بالمليون و معامل الامتصاص المولاري هو $2.3635x10^4$ لتر مول$^{-1}$ سم$^{-1}$ عند 297 نانوميتر . اما بالنسبة للمزدوج الثاني و عند 292 نانوميتر فالنتائج لمدى من تراكيز العقار (0.2 – 18 جزء بالمليون ) كانت كالاتي: حد الكشف هو 0.0030 جزء بالمليون و معامل الامتصاص المولاري هو $3.747 \times 10^4$ لتر مول$^{-1}$ سم$^{-1}$ . تم تطبيق هذه الطريقة على مستحضر السلابيد بنسبة استردادية مئوية لا تقل عن 98.5%.

**Introduction:-**

Trifluoperazine hydrochloride (TFPH) is of empirical formula ($C_{21}H_{24}F_3N_3S{\cdot}2HCl$) and molecular weight is 480.4[1]. TFPH is used in management of schizophrenia and excessive anxiety [2] and tension associated with neuroses or somatic [3] condition and diverse other methods [4,5]. This important drug has been determined by HPLC [6] and by conjunction between HPLC and NMR [7]. In the field of spectrophotometric methods Wilker [8] used electronic absorption spectroscopy. Ferric ion was used for the determination of TFPH with RSD of not more than 0.8 [9]. Depending on first and second derivatives spectroscopy, TFPH was also determined [10-12]. Kanakpura [13] used chloramine-T for sensitive determination for TFPH. The present paper describes a spectrophotometric method for the determination of (TFPH) in pharmaceutical preparation based on formation of ionic pairs with $[PdI_4]^{-2}$ and $[BiI_4]^{-1}$followed by extraction by 1, 2-dichloroethane.




**Experimental:-**

*Apparatus:* Shimadzu UV-visible spectrophotometer UV-1650 PC was used to measure the absorbance using 1cm quartz cells. The following apparatus were also used: Jenway pH meter 3310, Heidolph MR3001 magnetic stirrer, Jenway Hot plate 1001, sartorius balance, and Isuzu hot air rapid drying oven.

***Solutions***: All chemicals used were of analytical grade.

1- *Standard Palladium Solution (1mg/ml)*: 0.100g of Pd powder (Fluka) was dissolved in aqua regia, evaporated to dryness, and then 3ml of concentrated HCl was added and the resulting solution was evaporated to half volume and then diluted with distilled water to the mark in a volumetric flask of 100ml.

2- *Standard Bismuth Solution*: 2.32gm of Bi $(NO_3)_3.5H2O$ (Fluka) was dissolved in 15 ml of distilled water and 1ml of concentrated nitric acid was added and then diluted by distilled water to a volume of 20 ml.

3- *Reagents*: The following solutions: 40% and 50% KI(BDH), 1% ascorbic acid (BDH), 0.1M HCl (Reidel-dehen), and 0.1M NaOH (Fluka) were prepared by appropriate dissolution and dilution .

4- *Inorganic Ion-pair Complexes*:

A- *$[PdI_4]^{-2}$ Solution (100 ppm)*: To 2.5ml of Pd solution, 5ml of HCl (1:1), 5ml of 40% KI and 0.1ml of 1% ascorbic acid solution were added the resulting solution was diluted with distilled water in 25ml volumetric flask.

B- *$[BiI_4]^{-1}$ Solution (450 ppm)*: To 1ml of bismuth solution, 12.5ml of 50% KI and 97.5 ml of distilled water were added.

5- *Procedure for determination of (TFPH) in pharmaceutical preparation :*

Ten tablets of salabid ( average weight of one tablet is 0.2197g) were carefully crushed , and then 0.2298 gm of the resulted powder was dissolved in 30ml of 0.1 M HCl and diluted to the mark with the same solution in a volumetric flask of 50ml .

6.25ml were transferred into a volumetric flask of 25 ml and diluted to the mark with solution of 0.1 M HCl . From this solution the desired volume was transferred into 5ml volumetric flask onto which the optimum volume of either $[PdI_4]^{-2}$ or *$[BiI_4]^{-1}$ was* added and extraction was carried out by 4mlof1.2-di chloroethane and the absorbance was recorded.

**Results and Discussion:-**

***Recommended procedure:***

5ml of the aqueous phase containing (TFPH) was extracted )into 4ml of 1,2 dichloroethane with reaction time of less them 5 minutes and optimum condition of : pH 5 and 4, mixing time of 3 and 4 minutes for the determination with $[PdI_4]^{-2}$ and $[BiI_4]^{-1}$ respectively at wavelength of 297nm for the former and 292nm for the latter .

1- ***Complexes Spectra***: using distilled water as a reference, solution of $[PdI_4]^{-2}$ exhibits two maximum absorptions (Fig .1) at 322 and 408nm, while solution of $[BiI_4]^{-1}$shows two peaks at 337nm and 462nm (Fig. 2).

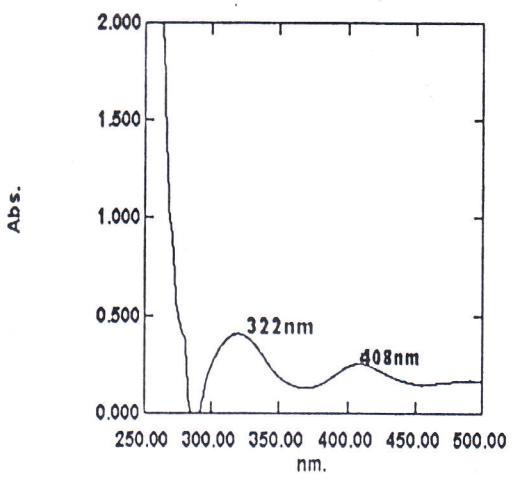



Fig (1):- Absorption spectrum of $[PdI_4]^{-2}$ complex

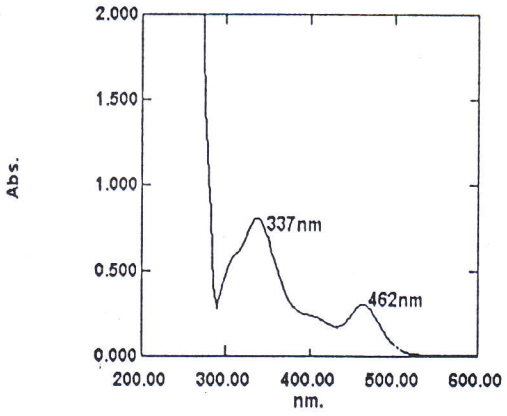



Fig (2):- Absorption spectrum of $[BiI_4]^{-1}$complex

2- ***Drug Spectra***: One ml of TFPH (100ppm) was transferred into 10ml volumetric flask and diluted to the mark with 0.1M HCl .This solution shows two maximum absorption at 280 and 308nm (Fig.3).

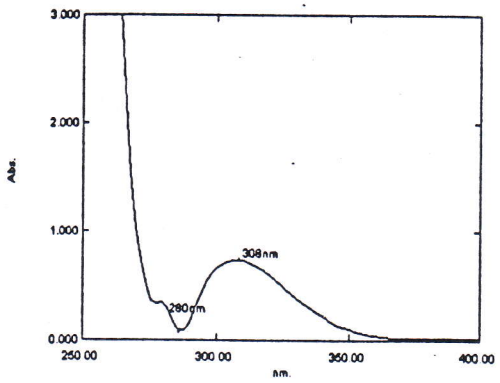



Fig (3):- Absorption spectrum of TFPH drug

3- ***Ion – Pair Association Spectra***: Solution of faint brown color (Fig. 4) or orange color (Fig. 5) were obtained on mixing 0.5ml of 100ppm drug with 0.5ml of either $[PdI_4]^{-2}$ or $[BiI_4]^{-1}$ respectively. After extraction of ion pair into 1,2-dichloroethane, the first solution absorbs at 297nm and 363nm and the second absorbs at 292nm and 358 nm.

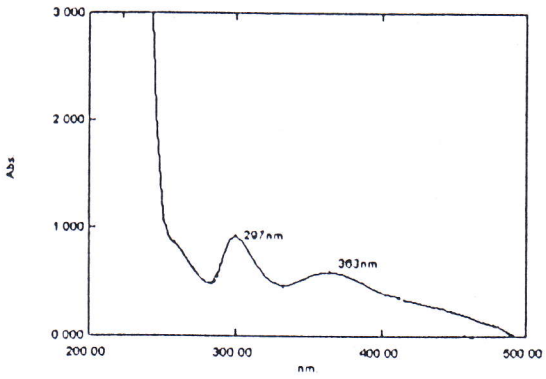



Fig (4):- Absorption spectrum of ion pair of $[PdI_4]^{-2}$ with TFPH drug

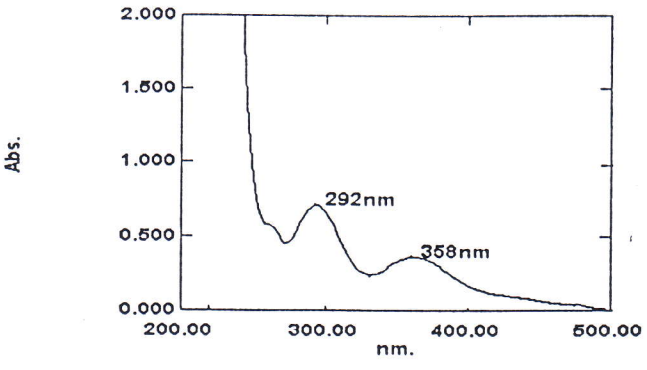



Fig (5):- Absorption spectrum of ion pair of $[BiI_4]^{-1}$ with TFPH drug

Since the wavelengths of 297 and 292 nm for ion pairs of $[PdI_4]^{-2}$ and $[BiI_4]^{-1}$ respectively with TFPH are of higher value of molar absorption coefficient than at 363 and 358 nm, thus these wavelengths were chosen to construct the calibration curves . Figures (6-11) show results of the optimum conditions, and summary of the results are shown on table (1).

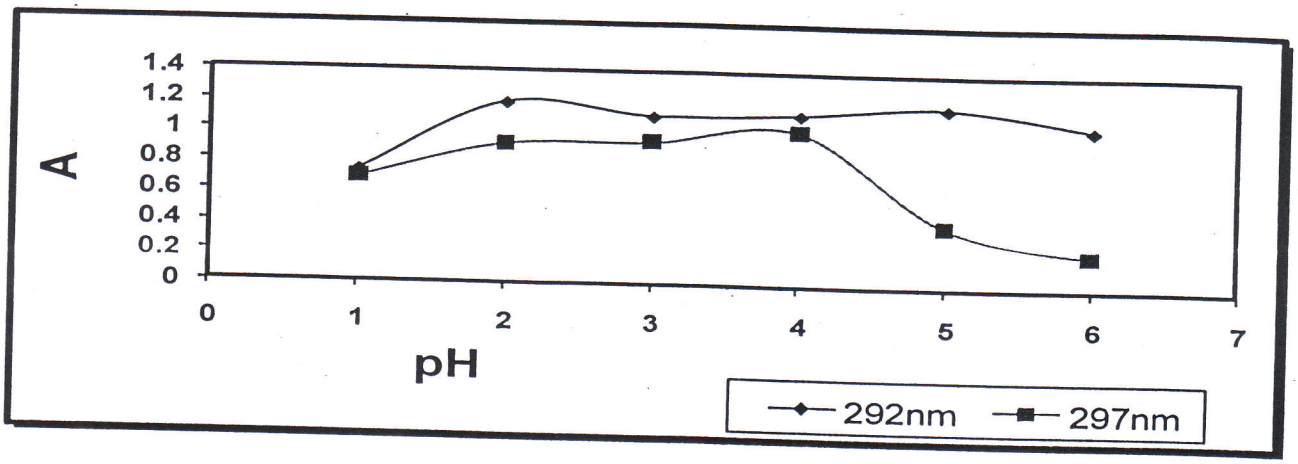



Fig (6):- Effect of pH on the absorption of ion pair of TFPH with $[PdI_4]^{-2}$ and $[BiI_4]^{-1}$

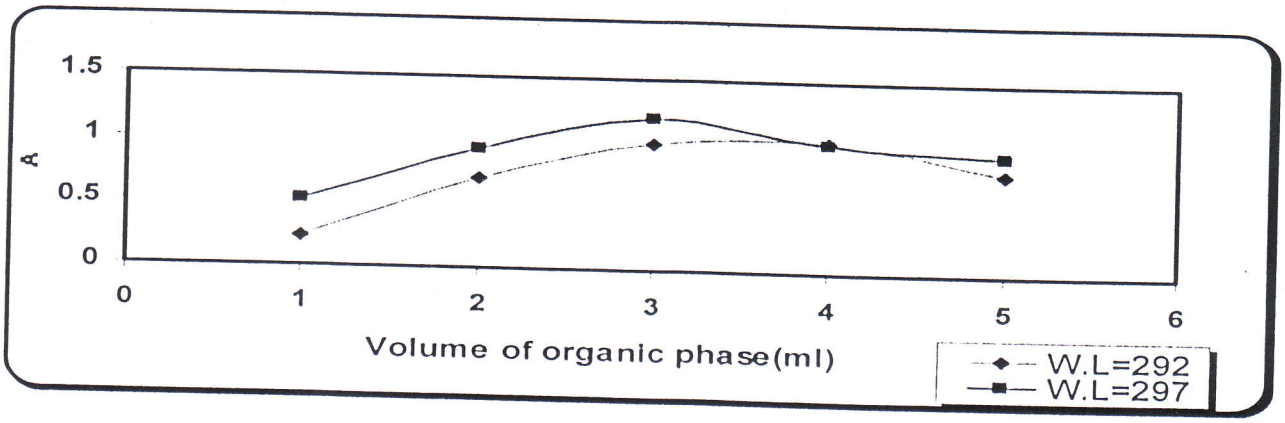



Fig (7):- Effect of organic phase volume on the extraction of ion pairs

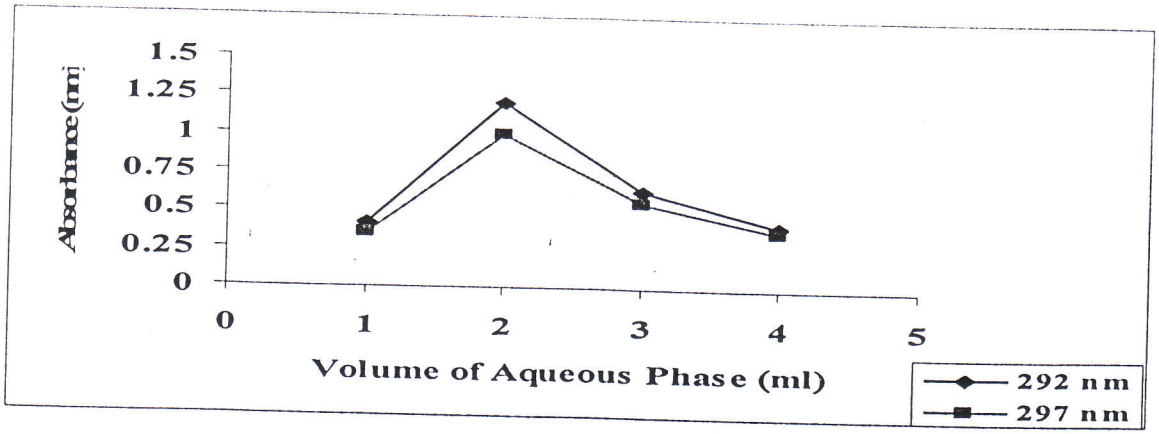



Fig (8):- Effect of aqueous phase volume on the extraction of ion pairs

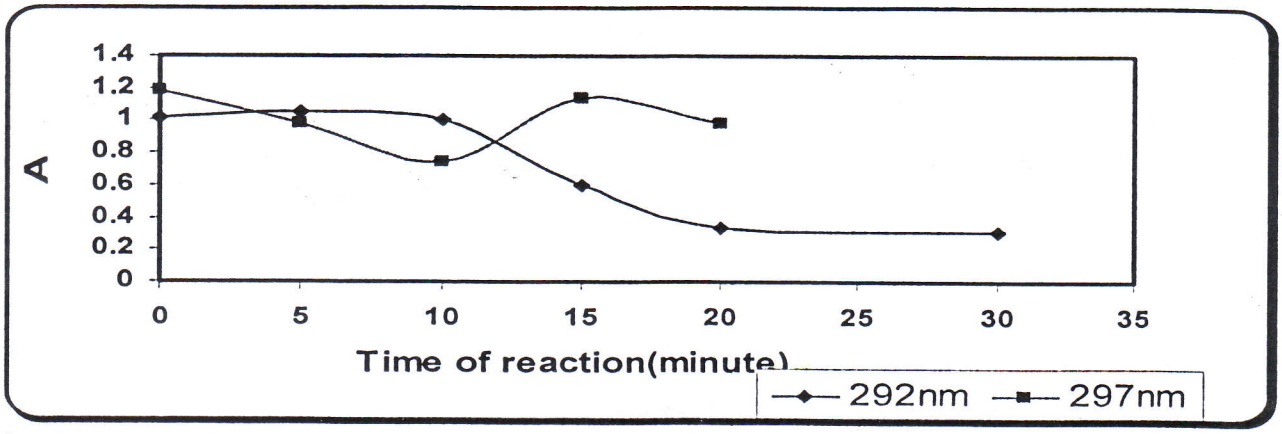



Fig (9):- Effect of reaction time on the formation of ion pairs

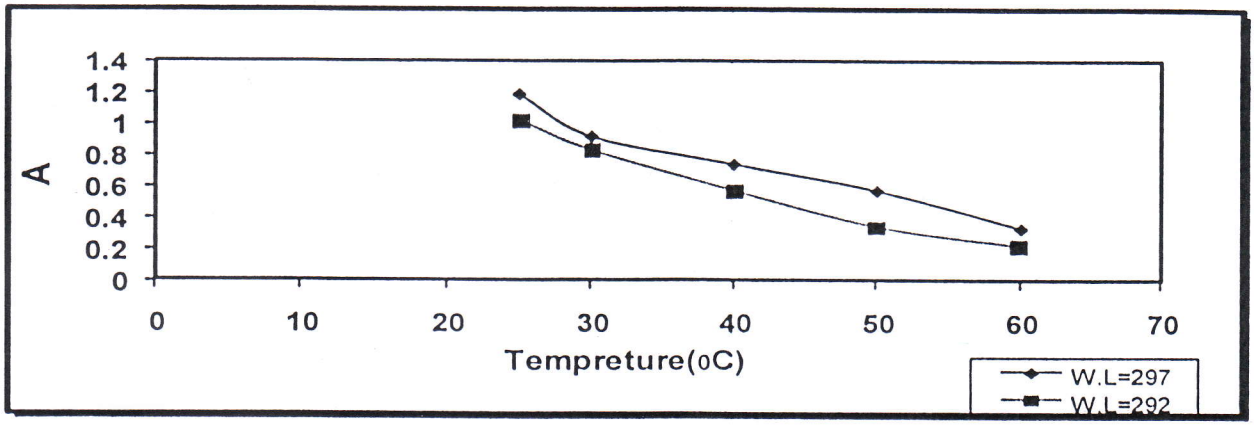



Fig (10):- Effect of temperature on the formation of ion pairs

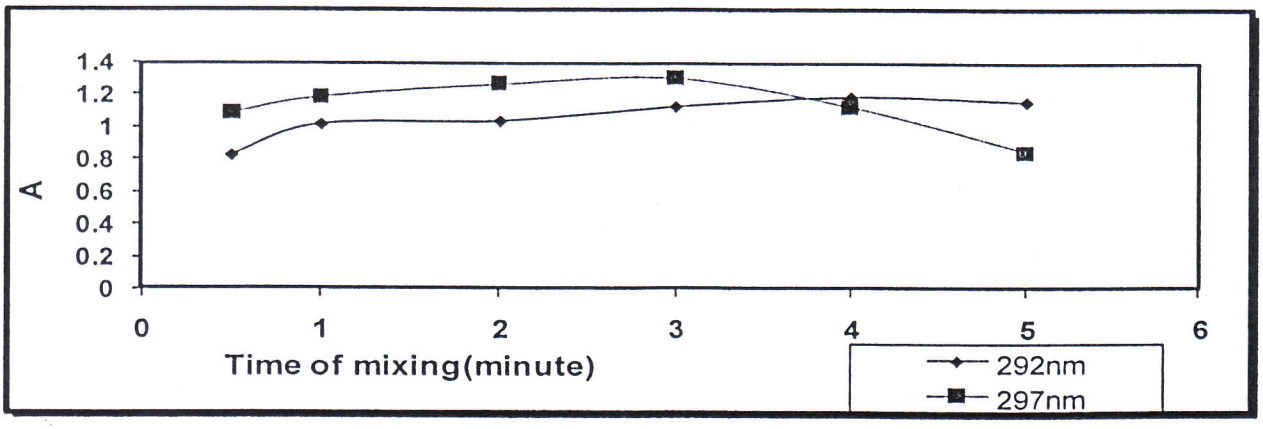



Fig (11):- Effect of mixing time on the formation of ion pairs

**Table (1):-** Summary of optimum conditions for the formation - extraction of ion pairs at 25°C.

| Ion- Pairs | Optimum Conditions | | | |
|---|---|---|---|---|
| | pH | Time of Reaction | Ratio of Phases | Time of Mixing |
| TFPH+$[PdI_4]^{-2}$ | 5 | Immediate | 4org. / 5aq. | 3 min |
| TFPH+$[BiI_4]^{-1}$ | 4 | 5 min. | 4org. / 5aq. | 4 min |

At the optimum conditions, the calibration graphs were constructed (Fig. 12 and Figure. 13). The linear range for TFPH - $PdI_4$ is (6 – 40 ppm) and for TFPH-$BiI_4$ is (0.2 – 18 ppm). The important statistical and analytical results are summarized in table (2).

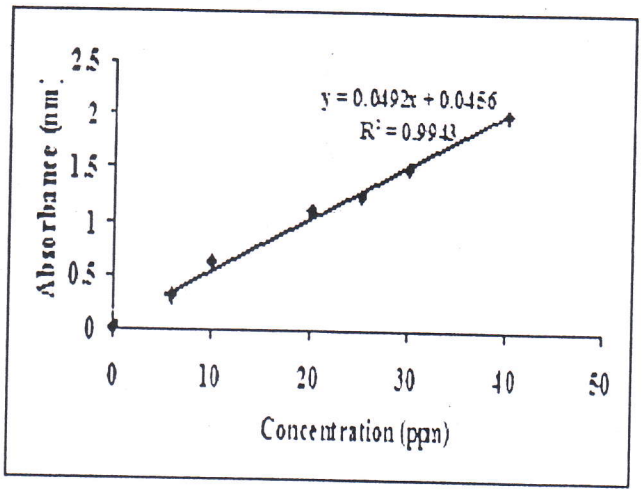



Fig (12):- Calibration curve at 297 nm for TFPH – $PdI_4$ ion pair

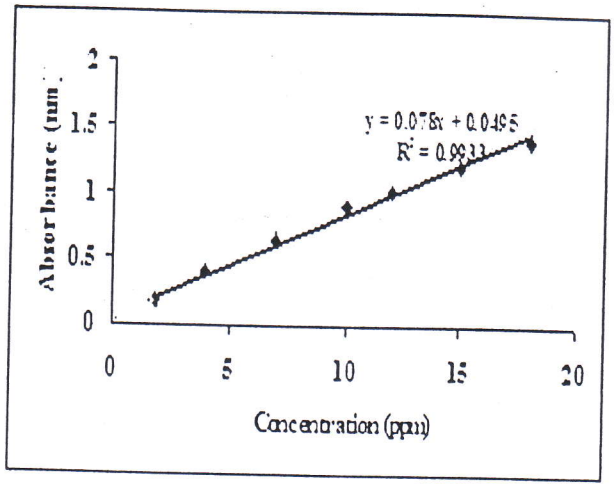



Fig (13):- Calibration curve at 292 nm for TFPH – $BiI_4$ ion pair

Table (2):- Accuracy and precision of the developed method.

| $\lambda_{max}$ (nm) | Linear range (ppm) | RSD % | Detection limit (ppm) | Relative error ($E_{rel}$ %) | *Rec. % | ε (L / mol. Cm) | Sandell's index (µg / $cm^2$) |
|---|---|---|---|---|---|---|---|
| 297 with $[PdI_4]^{-2}$ | 6 - 40 | 0.566 | 0.228 | 1.25 | 101 | $2.3635 \times 10^4$ | 0.0218 |
| 292 with $[BiI_4]^{-1}$ | 0.2 – 18 | 0.346 | 0.0030 | 3 | 103 | $3.747 \times 10^4$ | 0.0176 |

*average of five determinations.

The stability of extracted species was studied at these wavelengths (table 3). It can be concluded that the value of absorption decreases with time for both ion pairs. This can be attributed to the nature of electrostatic attraction between $[PdI_4]^{-2}$ or $[BiI_4]^{-1}$ with TFPH [14]

***Analytical application:-***

This method was applied to the Salabid pharmaceutical preparation with percentage recovery of not less than 98.5 %( table 4).

**Conclusions:-**

A simple and sensitive spectrophotometric method has been developed for the determination of Trifluoperazine Hydrochloride (TFPH) drug by formation – extraction of its ion pairs with either $[PdI_4]^{-2}$ or $[BiI_4]^{-1}$. Good precision and accuracy were obtained when this method was applied to Salabid pharmaceutical preparation.

**Table (3):-** The stability of extracted ion pairs of $[PdI_4]^{-2}$ and $[BiI_4]^{-1}$ at 297 and 292 nm.

| $\lambda_{max}$ (nm) | Absorption | | | | (%) Recovery after 72 hours |
|---|---|---|---|---|---|
| | At preparation | After one hour | After 24 hours | After 72 hours | |
| 297 With $[PdI_4]^{-2}$ | 1.310 | 1.300 | 1.270 | 1.242 | 95.00 |
| 292 With $[BiI_4]^{-1}$ | 1.193 | 1.181 | 1.162 | 1.030 | 86.00 |

**Table (4):-**Application of the developed method for the determination of Salabid tablets (SDI/ IRAQ).

| $\lambda_{max}$,nm | Concentration (ppm) | | Rec.% | Erel. % |
|---|---|---|---|---|
| | Prepared | measured | | |
| 297 with $[PdI_4]^{-2}$ | 8 | 7.90 | 98.75 | - 1.25 |
| 292 with $[BiI_4]^{-1}$ | 3 | 3.08 | 102.7 | 2.66 |

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