

## SPECTROFLUORIMETRIC METHOD FOR IMPURITIES DETECTION IN THE TUNGSTEN TETRAPHENYL-PORPHYRIN

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*Abstract:* An spectrofluorimetric method for the impurities detection in the tungsten tetraphenyl-porphyrin is presented in this paper. The elaborated spectrofluorimetric method for the determination of the TPP impurity from the TPPWCl<sub>4</sub> samples is a sensitive method for small concentration ranges (less than  $1 \times 10^{-6}$  M), where the spectrophotometric absorption method does not lead to reproducible results and has high errors. The method is easy accessible and yields to valuable results in respect at the stability of the complex with tungsten of TPP.

*Key words:* spectrofluorimetry, metallo-porphyrins, small concentration.

### INTRODUCTION

For many years, the metallic complexes of porphyrins have represented the goal of detailed studies for understanding the synthesis possibilities or the biological activities of some natural compounds based on porphyrins [1].

The synthesis of metallo-porphyrins occurs by the substitution of both protons from porphyrinic cavity with a large metal having the dimensions comparable with the capacity of the porphyrinic nucleus. The complexation process yields to a basicity decrease of porphyrin too, so that just the affinity for the ligands electro-donors (halogens, amines, ethers etc) seems justified. Therefore an amplified electro-donating capability of an certain ligand allows for an additional stabilization of the metallo-porphyrin complexes. Besides, the ratio of donor components or possessor of  $\pi$  bonds (double bonds) is affected by the basicity of the porphyrins.

The synthesis of tungsten tetra-phenyl-porphyrine with central ligands chlorine (TPPWCl<sub>4</sub>) is achieved in laboratory by refluxing an WCl<sub>6</sub> solution in CCl<sub>4</sub> in the presence of a stoichiometric amount of tetra-phenyl-porphyrin base free (TPP), for 16 hours at CCl<sub>4</sub> refluxing temperature. Therefore the precursor TPP may be present as an impurity in the synthesized complex amount with tungsten. For the quantitative

determination of the TPP impurities, a sensitive spectral method – spectrofluorimetry - is required [2].

It is applicable in this case because the majority of species present no emission at wavelength less than 700 nm; therefore the spectral interferences are disappearing.

### MATERIALS AND METHOD

For the elaboration of this method, a TPPWCl<sub>4</sub> sample prepared in laboratory and dissolved in CCl<sub>4</sub> was used. The used concentration range is between  $2,5 \times 10^{-5}$  and  $1 \times 10^{-7}$  M. At concentrations less than  $1 \times 10^{-4}$  M the phenomenon called autoextinction, appears.

The measurement is achieved by means of a man-made device for the emission fluorescence installed on a spectrophotometer (SPECORD M 400 Carl Zeiss Jena) with microprocessor.

The zero value of the fluorescence emission is determined by the measurement of the emission of the solvent. This value is subtracted from the value of the fluorescence emission of the solution, for which the presence of TPP,  $T_x$ , is evaluated. According to the magnitude of the difference ( $T_x - T_0$ ), using the graphics subsequently plotted by linear interpolation, the concentration of TPP from the TPPWCl<sub>4</sub> samples (in M) is calculated.

All the measurements and estimations were based on the direct linear proportional dependence between the fluorescence emission and the concentration of the emissive species.

### RESULTS AND DISCUSSION

The concentration measurement for TPP present in the studied sample was achieved by two ways:

- Spectrophotometrically, from the absorption spectrum, for this porphyrin existing the possibility to determine the concentrations from the ratio absorbance/absorption molar coefficient x thickness of layer, according the law Lambert-Beer;
- Spectrofluorimetrically, the identified values ( $T_x - T_0$ ) in the graphic from figures 1, occurring at the concentration values TPP from the analyzed sample.

Table 1- The emission bands of TPP and TPPWCl<sub>4</sub> in the CCl<sub>4</sub> solutions

TPP		TPPWCl <sub>4</sub>	
$\ddot{e}_{exc}$ (nm)	$\ddot{e}_{em}$ (nm)	$\ddot{e}_{exc}$ (nm)	$\ddot{e}_{em}$ (nm)
515	652	752	795
	686		894
	718		960

			1024
			1082

For the beginning, the emission bands of the two porphyrins in  $\text{CCl}_4$ , table 1 were evaluated.

Analyzing this table one may determine that if excited with 515 nm radiation (present in the excitation spectrum of TPP) (with the 652 nm filter adequate to the emission maxim spectra of TPP), one may quantitatively and qualitatively evaluate the presence of this impurity in the  $\text{TPPWCl}_4$  solutions, the latter is not showing the emission in this spectral area.

The linear dependence graphics of the TPP emission intensity dependent on the concentration of TPP is presented in the figure 1. The graphic was drawn with a mathematical processing program elaborated in Turbo Pascal and run by a Phillips computer.

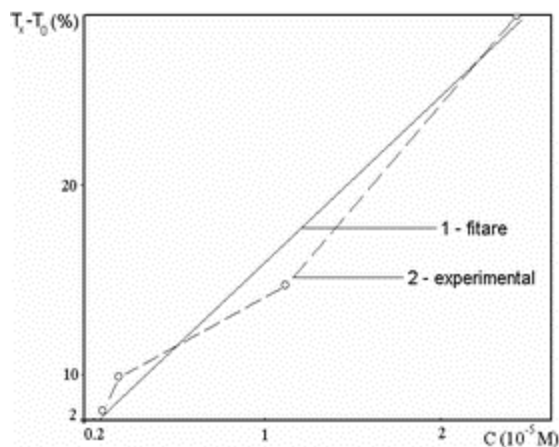


Fig. 1 - The graphical dependence of emission intensity at 675 nm ( $\lambda_{\text{ex}} = 522$  nm) versus the concentration for  $\text{TPP}/\text{CCl}_4$

We achieved the experiments of this method with a  $\text{TPPWCl}_4/\text{CCl}_4$  solution left for a while in the SPECORD M 400 cuvette, monitoring the phenomenon supported by this metallo-porphyrin, knowing that the process of metal removal is not desirable in the study and the applications of this porphyrin [3].

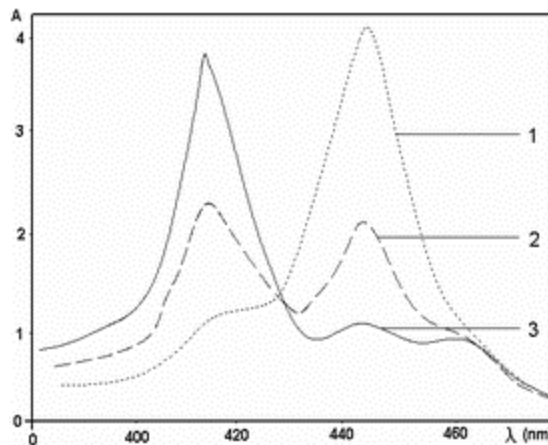


Fig. 2 - The soret band change of TPPWCl<sub>4</sub> during photolysis experiment ( $\Delta t = 2$  minutes,  $t_1 = 0$  min,  $t_2 = 10$  min,  $t_3 = 20$  min)

The variation of the emission spectrum of TPPWCl<sub>4</sub> (figure 2) was also accompanied by the observation of the variation of the absorption spectrum of this porphyrin too (figure 3).

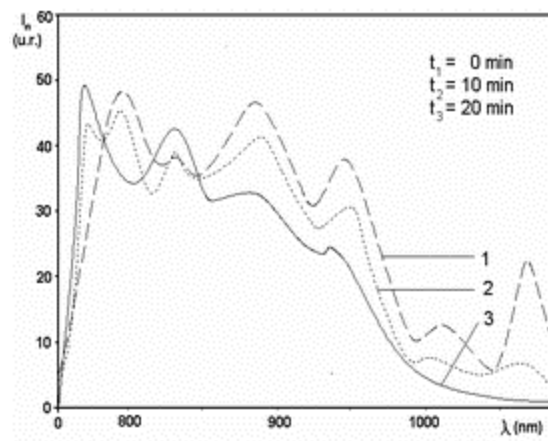


Fig. 3 - The spectral changes of fluorescence band of TPPWCl<sub>4</sub> during the photolysis ( $\Delta t = 2$  minutes)

The concentration values deduced for the TPP impurity in the TPPWCl<sub>4</sub> sample determined in two ways were presented in the table 2. Analyzing the values presented in this table may be detected the good agreement between the two measurement sets, but also the precision of the spectrofluorimetric measurements in the concentration area less than  $1 \times 10^{-6}$  M [4].

Table 2 - The TPP concentrations deduced by the spectral absorption and emission methods

Spectrophotometric absorption method		Spectrofluorimetric method	
Time (hours)	C ( x 10 <sup>-5</sup> M)	Time (hours)	C ( x 10 <sup>-5</sup> M)
0	0.93	0	0.922
1	0.87	1	0.865
2	0.69	2	0.7
3	0.67	3	0.65
4	0.44	4	0.425
5	0.37	5	0.365
6	0.35	6	0.355
7	0.23	7	0.223

The method elaborated in this paper is applicable for accuracy applications in metallo-porphyrins with tungsten, which need the presence of the oxygen and long reaction times.

### CONCLUSIONS

The elaborated spectrofluorimetric method for the determination of the TPP impurity from the TPPWCl<sub>4</sub> samples is a sensitive method for small concentration ranges (less than 1 x 10<sup>-6</sup> M), where the spectrophotometric absorption method does not lead to reproducible results and has high errors.

The method is easy accessible and yields to valuable results in respect at the stability of the complex with tungsten of TPP.

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