

## Detection of Phosphine Derivates Using Metalloporphyrins

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300223-Timisoara, Romania**Abstract**

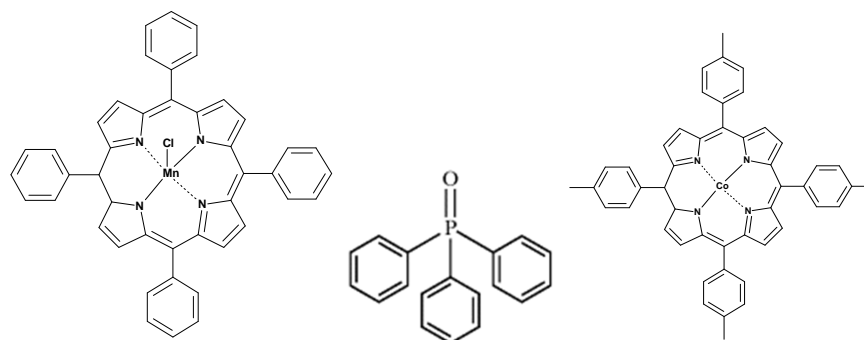
Starting from the knowledge that phosphine derivatives exhibit medium/high toxicity, in this study we focused on the behavior of Co(II)-5,10,15,20-tetratolyl-porphyrin (CoTTP) and Mn(III)-5,10,15,20-tetraphenyl-porphyrin chloride (MnTPPCL) as active UV-vis chromophores for the detection of triphenylphosphine oxide (LC50=12.2µg/mL, LC90=29.5µg/mL). The increase of triphenylphosphine oxide concentration generates the hypochromic effect on the Soret bands of the two metalloporphyrins. A comparison regarding the efficiency of the two metalloporphyrins in detecting phosphine derivatives was done.

Keywords: Co(II)-tetratolylporphyrin, Mn(III)-tetraphenylporphyrin, UV-vis, phosphine derivatives-detection, AFM.

**Introduction**

Due to  $d\pi$ - $\pi$  bonding that diminishes the electron density on oxygen, tertiary phosphine oxides are weak bases. Triphenylphosphine oxide (Ph<sub>3</sub>PO) is a widely used reagent material for synthesis of organophosphorus compounds and as catalyst, cocatalyst, Lewis base and monodentate neutral oxygen donor ligand. It is already known that Mn and Mg have a strong affinity to PO group in Ph<sub>3</sub>PO [1] and the coordination chemistry of P=O ligands and their coordination capabilities were largely studied [2].

Complexes of lanthanide nitrates with phosphine oxides have been investigated since the 1960s [3]. Due to its versatile ligand properties triphenylphosphine oxide was used in synthesis of TiO<sub>2</sub>-hybrids incorporating Eu<sup>3+</sup> in order to improve Eu<sup>3+</sup> luminescence [4] or in the polymeric composites for the detection of dopamine [5]. The detection of Ph<sub>3</sub>PO was reported by <sup>31</sup>P-NMR in complexes to silanes, siloxanes and stannanes [6] but in this study, related to our previous research [7] we proposed a facile and non-toxic detection, using a Mn-porphyrin, namely: Mn(III)-5,10,15,20-tetraphenyl-21H,23H porphyrin chloride (structure in Figure 1).



**Figure 1.** Structures of Mn(III)-5,10,15,20-tetraphenyl-porphyrin chloride (MnTPPCL), triphenylphosphine oxide and Co(II)-5,10,15,20-tetratolyl-porphyrin (CoTTP).

**2. Experimental****2.1. Reagents**

All reagents used in this work were *purum analiticum*, provided by Merck, Fluka and Sigma-Aldrich. The porphyrin bases, were synthesized according to our previous report [8]. The

manganese and cobalt complexes were prepared [9] using large excess of salts (mole ratio 1/20 porphyrin/salts). Stock solutions of metalloporphyrins  $0.5 \times 10^{-5}$  M and  $2 \times 10^{-4}$  M solution of triphenylphosphine oxide, all dissolved in toluene have been prepared for UV-vis experiments.

## 2.2. Apparatus

UV-visible spectra were registered on JASCO UV- V-650 visible spectrometer using 1 cm pass cells. Atomic force microscopy (AFM) investigations were performed on Nanosurf@EasyScan 2 Advanced Research AFM. AFM images were obtained in contact mode.

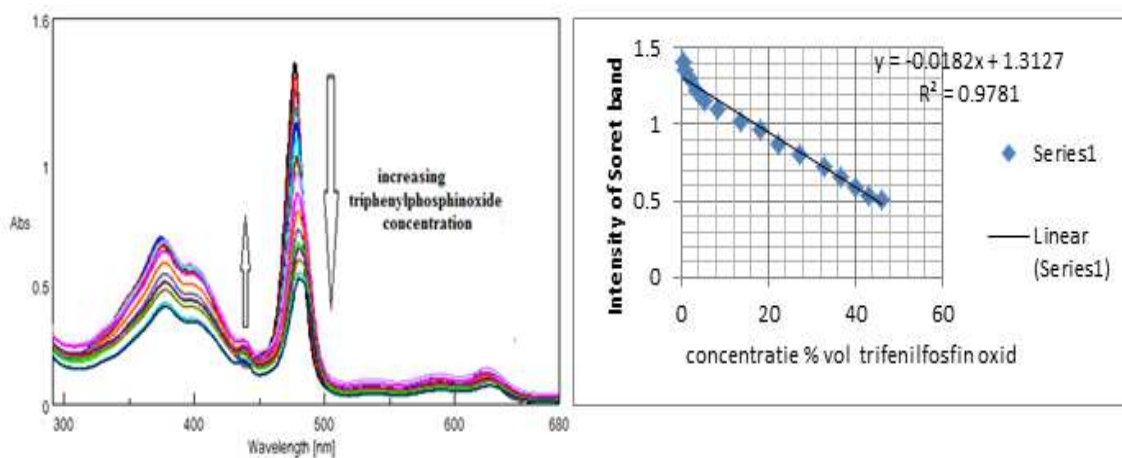
## Results and discussion

Complete considerations regarding the UV-vis hyper spectra of Mn-metalloporphyrin were presented in the reported paper [8].

The UV-vis spectrum of triphenylphosphine oxide in toluene has the absorption maximum at 283 nm and do not influence these determinations.

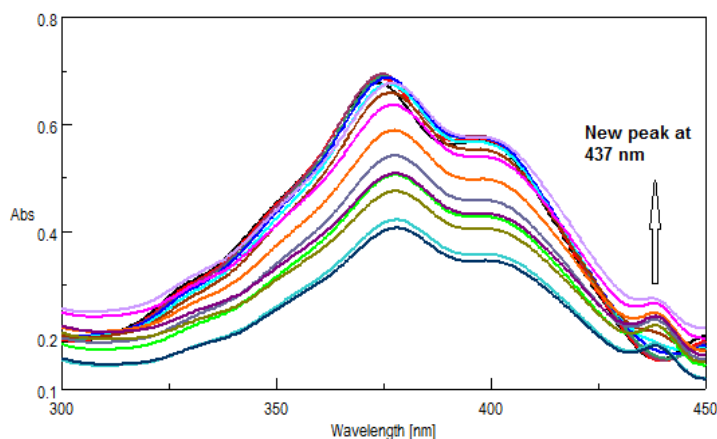
For the UV-vis detection of triphenylphosphine oxide a spectrophotometric titration was performed by adding 100  $\mu$ L triphenylphosphine oxide in toluene to each metalloporphyrin solution dissolved in toluene.

By increasing concentration of triphenylphosphine oxide we noticed a continuous decrease in intensity of the Soret bands of both metalloporphyrins, as shown in Figures 2, 3 and 4. The dependence between the intensity of absorption measured at Soret band and the concentration of triphenylphosphine oxide is linear, characterized by a very good correlation coefficient of 0.978.

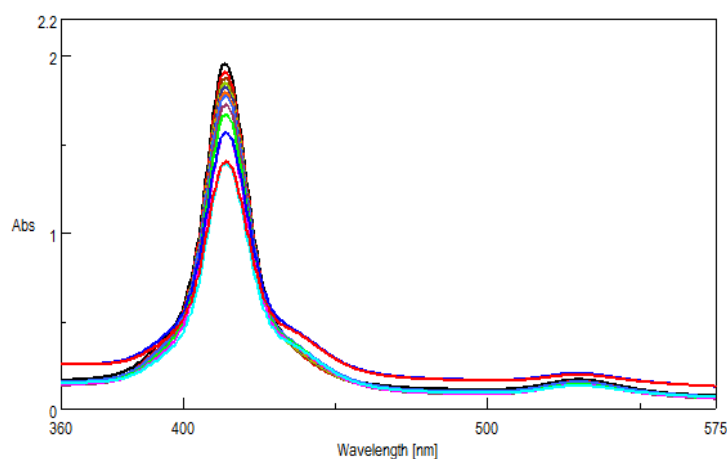


**Figure 2.** UV-vis spectra showing the linear dependence of triphenylphosphine oxide increasing concentration and MnTPPCl, in toluene.

Besides, a novel peak is formed at 437 nm, as a proof of the new complex formation, its intensity increasing as the phosphine derivative content is increasing. Figure 4 displays the effect of increasing the concentration of triphenylphosphine oxide on UV-vis spectrum of CoTTP. The same phenomenon is produced, the Soret band intensity is decreasing by increasing the concentration of the triphenylphosphine oxide, but the dependence is not a regular one.



**Figure 3.** UV-vis spectra revealing a novel peak generated by the complex formation between triphenylphosphine oxide and MnTPPCl, in toluene.



**Figure 4.** The influence of increasing triphenylphosphine oxide concentration on UV-vis spectra of CoTTP.

The explanation of the lower quality detection provided by Co-porphyrin can be that triphenylphosphine oxide is relatively basic and is a better ligand for hard or intermediate metal centers, as manganese case is.

### Conclusions

The metalloporphyrins are a class molecules with excellent sensing properties. With the increase of amount of the phosphine oxide, a continuous decrease regarding the intensity of the Soret bands of the two metalloporphyrins tested for detection qualities was put into evidence. A novel peak in the UV-vis spectrum at 437 nm proved the complex formation between the Mn-porphyrin and the phosphorus derivative. This Mn-metalloporphyrin offers a good base to develop a novel sensor for small amounts of toxic  $\text{Ph}_3\text{PO}$ .

### Acknowledgements:

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## References

- [1] G. Ciani, M. Manassero, M. Sansoni, J. Inorg. Nucl. Chem. 34(5) (1972) 1760–1762.
- [2] T.S. Lobana, N. Bala, Transit. Metal Chem. 19 (1) (1994) 115-116.
- [3] S. Xu, M. Liu, H.-L. Han, (...), Y.-Y. Chen, J.-Y. Yao, Polyhedron 85 (2015) 69-75.
- [4] Y. Lv, J. Zhang, W. Cao, Y. Fu, X. Wu, J. Alloy Compd. 462 (1-2) (2008) 153-156.
- [5] S. Köytepe, A. Paşahan, E. Ekinçi, B. Alici, T. Seçkin, J. Polym. Res. 15 (3) (2008) 249-257.
- [6] M. Zeldin, P. Mehta, W. Vernon, Inorg. Chem. 18 (2) (1979) 463–466.
- [7] A. Palade, A. Lascu, I. Creanga, G. Fagadar-Cosma, M. Birdeanu, E. Fagadar-Cosma, DJNB 10 (3) (2015) 729 – 735.
- [8] E. Fagadar-Cosma, C. Enache, I. Armeanu, D. Dascalu, G. Fagadar-Cosma, M. Vasile, I. Grozescu, Mat. Res. Bull. 44 (2009) 426-431.
- [9] E. Fagadar-Cosma, M. Mirica, I. Balcu, C. Bucovicean, C. Cretu, I. Armeanu, G. Fagadar-Cosma, Molecules 14(4) (2009) 1370-1388.